Predicting the Yield Stress of Polymer Glasses Directly from Processing Conditions: Application to Miscible Systems

A previously developed model which predicts the yield stress of a polymer glass directly from processing conditions is applied to a system of miscible polymers. The selected system consists of a blend of polycarbonate with polyester and three blend compositions of increasing weight percentages polyester are investigated with respect to their aging kinetics. Based on these kinetics, the yield stress as it results form the thermal history experienced during processing is predicted and found to be in good agreement with experimental results. The parameters governing the evolution of the yield stress are shown to follow the rule of mixtures, enabling the prediction of the yield stress of any blend composition.

1 Introduction

It is well-known that the mechanical properties of a polymer glass are strongly influenced by its thermal history. This is clearly demonstrated by the result of annealing treatments, which not only lead to an increase in yield stress, but also in a substantial increase of the failure time under static and dynamic loading conditions (Klompen et al., 2005a; Janssen et al., 2008b; Narisawa et al., 1978; Crissman and Mckenna, 1987, 1990). It is much less known that similar results can also be achieved by manipulation of the thermal history experienced during the material during processing. By variation of the mold temperature during injection molding of polycarbonate, the product lifetime could be be increased by several decades (Engels et al., 2006a). The yield stress and the lifetime under static loading conditions are intimately related and shown to be governed by the same kinetics (Bauwens-Crowet et al., 1974; Nanzi, 1994). Hence knowledge of the exact value of the yield stress enables direct prediction of the materials performance in long-term loading (Klompen et al., 2005a; Janssen et al., 2008a).

It was demonstrated by Govaert et al. (2005) that the methodology developed by Klompen et al. (2005b) to capture the evolution of the yield stress of a polymer glass during annealing below the glass transition temperature, T_g, i.e. physical aging (Hutchinsen, 1995), can also be applied to relate the yield stress of a polymer product to its processing conditions. To achieve this, the kinetics which govern the evolution of yield stress below T_g are applied to the thermal history the material experiences during processing. This approach proved to give accurate results for polycarbonate over a large range of mold temperatures and facilitated the prediction of product performance without a single (product-related) mechanical test (Engels et al., 2006a).

In the present study we wish to extend this approach to other polymer systems. Since previous studies were focussed on polycarbonate, a logical choice is to investigate blends based on this material. Since the current approach is limited to homogeneous, isotropic material behavior, we limit ourselves to miscible polymer blends where no heterogeneity due to phase separation occurs.

Mixing of polymers is a way of creating materials with optimum, or better properties, the rational being simple: the blend combines the properties of its constituents resulting in a material with intermediate properties, e.g. in the case of poly(styrene)/poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPE) (van Melick et al., 2003), which forms a homogeneous blend, the ductility of PPE is combined with the processability of PS. For the polymer blend a commercially available miscible blend of polycarbonate with a polyester is chosen: Xylex™Resin (Xylex, 2008) produced by Sabic Innovative Plastics (Bergen op Zoom, The Netherlands). Polycarbonate is mostly mixed with polyester to achieve a lower susceptibility to stress cracking on contact with fuels and chemicals and for an overall better processability, i.e. lower melt viscosity and lower processing temperatures (Utracki, 2002). Since the exact composition of Xylex is protected by the manufacturer, the material will be referred to as PX in this paper.

First the aging kinetics of the PX, pure PC and an 50/50 weight percentage blend of PX with PC (which will be called PC/PX-50/50) will be determined. Next, yield stresses will be predicted based on the thermal history experienced during processing.
2 Development of Properties

2.1 Yield Stress Evolution

The basis of the modeling approach is a 3D constitutive framework which accurately describes and predicts the large strain deformation behavior of polymer glasses (Klompen et al., 2005b). This framework incorporates a methodology to capture the aging kinetics of polymer glasses, and these aging kinetics were in a later study used to predict the yield stress as it follows from processing conditions (Govaert et al., 2005). Aging not only affects the yield stress, but also has a pronounced effect on other polymer properties, e.g. enthalpy, volume, creep compliance and stress-relaxation modulus (Hodge et al., 1993; Hutchinson, 1995; Struik, 1978; Scherer, 1986). However, it is generally accepted that the time scales on which aging affects these different properties are not identical and also not correlated in a simple manner (Hutchinson, 1995; Scherer, 1986).

This study focusses on the evolution of the uni-axial yield stress with physical aging which, for an experiment performed at a constant rate of strain and at a constant reference temperature, $T_{ref}$, is given by (Klompen et al., 2005b):

$$\sigma_y(t) = \sigma_{y,0} + c \cdot \log\left(\frac{t_{eff}(t, T(t)) + t_a}{t_0}\right),$$

where $\sigma_{y,0}$ and $c$ are two constants (intersection of the curve with the vertical axis at $t = 1$ s, and slope of the linear relation of state with the logarithm of time, respectively). It has to be noted that the value of $\sigma_{y,0}$ depends on the strain rate chosen, which will be used later in this paper. $t_0$ is the initial age of the material, $t_0 = 1$ s and $t_{eff}$ is the effective aging time which depends on the thermal history, $T(t)$, and is defined as:

$$t_{eff}(t, T(t)) = \int_0^t a_t^{-1}(T(t')) \, dt'.$$

The effective aging time is thus the elapsed time accelerated by temperature which captures the thermal history of the material. This acceleration is governed by an Arrhenius dependency:

$$a_T(T(t)) = \exp\left(\frac{\Delta U_a}{R} \left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right),$$

where $\Delta U_a$ is the activation energy of aging, $R$ the universal gas constant and $T_{ref}$ the reference temperature, i.e. the temperature where the expression governing the evolution of the yield stress, represented by Eq. 1, is valid.

Fig. 1 shows a schematic representation of the evolution of the yield stress (Eq. 1) with time and its division in two regions, that is, a processing related and service related region. The initial height of the yield stress is directly determined by the processing conditions, but with service life (aging) the yield stress increases and follows, independent of its initial properties, the same evolution with time. The length of the processing related region can be defined as the initial age, $t_a$, of the material, i.e. the time at which the yield stress starts to increase (Klompen et al., 2005b).

2.2 Predicting Properties from Processing

The prediction of the evolution of yield stress during processing is based on the assumption that the physical processes involved are identical to those governing the increase in yield stress during annealing. The process starts during the cooling process at the moment that the temperature passes through the glass transition temperature. From that moment on there will be a build-up of effective aging time, $t_{eff}$, with thermal history. In essence the end-level of $t_{eff}$ is equal to the parameter $t_a$, the initial age of the material.

To predict the end-level of $t_{eff}$ after cooling, the evolution of the effective time stated in Eq. 2 is applied. As the build-up of the effective time can only occur in the glassy state, below the glass transition temperature $T_g$, the evolution equation is, to a first approximation, specified as (Govaert et al., 2005):

$$T > T_g: \quad t_{eff,c} = 0 \quad \text{and} \quad t_{eff,c} = 0,$$

$$T \leq T_g: \quad t_{eff,c} = \int_0^T a_t^{-1}(T_c(t')) \, dt',$$

where $T_c(t)$ is the thermal history the material experiences during processing, and $t_{eff,c}$ is the effective aging time which accumulates during cooling. The resulting yield stress is subsequently determined by introduction of $t_{eff,c}$ into Eq. 1:

$$\sigma_y(t) = \sigma_{y,0} + c \cdot \log\left(\frac{t_{eff}(t, T(t))}{t_0}\right).$$

The thermal history during processing is determined by means of numerical simulation of the injection molding process using a commercial injection molding simulation package (MoldFlow MPI). The product used in this study is a flat rectangular plate, therefore allowing the use of a 2.5D approach in which the velocity and temperature fields are computed 3D, but for the pressure a 2D-approximation is used. Of course any other finite element approach/package can be used.

$T_g$ is effectively used as an input parameter and determined from the maximum of the loss angle of a Dynamic Mechanical Thermal Analysis (DMTA) experiment. This is a very limited interpretation of the complex phenomenon known as the glass transition (McKenna, 1989). However, in another study on the yield stress evolution during processing (Engels et al., 2006b), using the framework of structural relaxation (Tool, 1946; Narayanaswamy, 1971; Moynihan et al., 1976), incorporating a physically more accurate description of the glass transition, the same accuracy of the yield stress predictions as achieved in the more simple approach used here (Govaert et al., 2005) were found.
3 Experimental

3.1 Materials

The materials used in this study were kindly provided by Sabic Innovative Plastics (Bergen op Zoom). Polycarbonates used are the Lexan 161R (adopted from (Klompen et al., 2005b) and Lexan 141R grades, with number-averaged and weight-averaged molecular weights of 9.2 and 25.8 kg/mol and 11.6 and 27.9 kg/mol respectively. The yield stress and its evolution for a polymer glass are independent of molecular weight: yielding is governed by processes which occur on a scale of segmental chain mobility and are not be influenced by molecular weight, as long as a critical minimal weight is not surpassed (Klompen et al., 2005b). The difference in molecular weights for the polycarbonate will therefore not lead to differences in experimental results. Xylex (PX) behaves under normal processing conditions as a homogeneous blend (transparent material, one T_g) of polycarbonate with polyester. In this study the X8300 grade is used. The polycarbonate used in this material is the 141R grade. A 50/50 weight percentage mixture of PC with PX was compounded on a TA Instruments Q800 in film tension mode on a 25 mm twin-screw corotating extruder. The 50/50 weight percentage blend of the two materials will be called PC/PX-50/50.

3.2 Injection Molding

Samples used to determine aging kinetics were standard ISO 527 tensile bars that were injection molded conform ISO 294. Next to standard tensile bars, rectangular plates with dimensions 70 × 70 × 1 mm³ were injection molded, see Fig. 2. These samples are used for the prediction of properties from processing history. The mold (Axxicon Mould Technology) has a V-shaped runner of 4 mm thickness and an entrance of 70 × 1 mm² which results in a uniform filling of the mold cavity, as proven by several short shot experiments. Processing parameters are summarized in Table 1. A packing pressure of 500 bar is used for all samples to minimize shrinkage. Variation of the packing pressure from 25 bar to 900 bar proved to have no effect on the measured properties of the plates. To investigate the influence of the temperature history, the mold temperature is varied in steps of 10°C between the values given in Table 1. From the injection molded plates, rectangular bars of 70 × 10 mm² are cut parallel and perpendicular to flow direction. Gauge sections of 33 × 5 mm² are then machined into these bars, see Fig. 2 (right).

3.3 Annealing Treatments

Annealing treatments are performed in air circulated ovens at various temperatures (as indicated in the respective figures). Equilibration of the samples to the annealing temperature was found to be approximately 15 min. After the required annealing period samples were removed from the hot air ovens and allowed to cool to room temperature prior to testing.

3.4 Mechanical Testing

All tensile testing was performed under a constant linear strain rate on a Zwick Z010 tensile tester. The tensile tests to determine the aging kinetics are performed at a strain rate of 10⁻² s⁻¹. The tensile tests to validate the predicted properties following from processing history are done at a strain rate of 10⁻³ s⁻¹. All tensile tests were performed at room temperature (22°C) and yield stresses given are engineering stresses.

3.5 Thermal Testing

Dynamical Mechanical Thermal Analysis (DMTA) was performed on a TA Instruments Q800 in film tension mode on
samples $20 \times 5 \times 1$ mm$^3$ at 1 Hz from $-120$ to $220$ °C at a heating rate of 3 °C/min.

Differential Scanning Calorimetry (DSC) curves were measured using a Mettler Toledo DSC823e equipped with a FRSS sensor. The machine was calibrated with the melting peaks of indium, lead, tin, zinc, benzophenone and benzoic acid. Scans were performed from 20 to 280 °C at a heating rate of 10 °C/min. Standard 40 μl aluminium crucibles are used and samples weigh approximately 20 mg. Nitrogen is used as a purge gas.

4 Results

Figs. 3, 4 and 5 (left-hand side) present the results of the annealing experiments for PX; the PC/PX-50/50 blend and the pure PC. The PX and the PC/PX-50/50 materials are annealed at 35, 50, 57, 65, 80 and 85 °C. The results for the PC are taken from Klompen et al., (2005b); samples were annealed at 80, 100, 120 and 130 °C. For PX at the high annealing temperatures, i.e. 80 and 85 °C, the yield stress is reaching a limiting equilibrium value (bauwens-Crowet and Bauwens, 1982; G’Sell and McKenna, 1992; Engels et al., 2006b), see Fig. 3 (left). Also it is apparent that aging sets in on shorter time scales for PX then for PC/PX-50/50 and PC. At 35 °C the PC/PX-50/50 blend shows almost no increase in yield stress with aging time, whereas a clear increase is already visible for PX. Moreover, at 80 °C the yield stress only starts to increase for PC, whereas the PX grade is already reaching its limiting equilibrium value. These differences in increase in yield stress with time and temperature can be explained by the differences in $T_g$. Values of the $T_g$’s determined by DSC and DMTA are listed in Table 2, experimental curves are shown in Figs. 7 and 8. The closer the annealing temperature is to the $T_g$ of the material, the sooner aging can be expected to set in.

<table>
<thead>
<tr>
<th>Material</th>
<th>DSC °C</th>
<th>DMTA °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PX</td>
<td>90</td>
<td>105</td>
</tr>
<tr>
<td>PC/PX-50/50</td>
<td>116</td>
<td>132</td>
</tr>
<tr>
<td>PC</td>
<td>143</td>
<td>155</td>
</tr>
</tbody>
</table>

Table 2. Glass transition temperatures

Fig. 3. PX: annealing results (left; lines are drawn as guides to the eye); master curve constructed thereof (right)

Fig. 4. PC/PX-50/50: annealing results (left; lines are drawn as guides to the eye); master curve constructed thereof (right)

Fig. 5. PC: annealing results (left; lines are drawn as guides to the eye); master curve constructed thereof (right)
From the results of the annealing experiments, master curves can be constructed using time-temperature superposition (TTS). The shift factors needed to construct the master curves of PX and PC/PX-50/50 were assumed to follow the proposed Arrhenius dependence (Eq. 3). For the pure polycarbonate the results of Klompen et al. (2005b) are adopted. The resulting master curves are presented in Figs. 3, 4 and 5 (right-hand side). The activation energies used to construct these master curves are given in Table 3. As reference temperatures the lowest annealing temperature applied is used. The activation energies are determined in an iterative way on the annealing data together with the results of the yield stresses versus mold temperatures. The annealing data themselves do not give an unique optimum fit for the activation energy. However, the activation energy chosen determines the parameters needed to describe the kinetics of aging, i.e. $\sigma_{y,0}$ and $c$ (Eq. 1), and thus influences the prediction of the yield stress as it follows from processing conditions. The experimental sets together (annealing and processing), do render an unique solution for each material leading to the values of the activation energies as listed in Table 3. Surprisingly, the determined activation energies follow the rule of mixtures.

The master curves for all three materials are shown together in Fig. 6, where they are shifted to room temperature (here taken to be 22 °C). Also the descriptions of the master curves by means of Equation 1 are added. The parameters used are listed in Table 3. The slopes are fitted to the final evolution with time. The intersects, $\sigma_{y,0}$, of PX and PC are fitted to experimental data, whereas the value for the PC/PX-50/50 blend was determined based on the assumption of a linear dependence with blend composition, i.e. the rule of mixtures. Clearly this assumption holds very well. The final slopes of the master curves seem, however, to be independent of the blend composition. Furthermore, the curves by means of Eq. 1 give a somewhat too sharp transition from non-aging to aging in the region were aging first sets in. This is, however, a minor discrepancy. The initial ages of the different materials do not scale linearly with blend composition. This can be rationalized since the mold temperatures used to make the tensile bars were the same, thus giving each material a different offset with respect to its $T_g$ and therefore very different thermal histories.

The unique set of parameters is obtained by an iterative process for which a value of $T_g$ is needed to mark the onset of property development. Analogous to Govaert et al. (2005), these were determined from DMTA experiments, see 7 (left). All three materials shows a single, sharp $T_g$, indicating that we are dealing with materials that are miscible on a molecular scale. Remarkably, however, for the initially miscible PX we see that the modulus increases at high temperatures, indicative for crystallization induced phase separation. A further indication for crystallization was the observation that the DMTA samples turned from transparent to opaque after testing. DSC experiments were performed for confirmation, and a similar phenomenon is visible (see Fig. 8). Well above the $T_g$ of polycarbonate, crystallization sets in as witnessed by the exotherm and subsequent endotherm.

Therefore, in the extreme case of prolonged heating above $T_g$, the miscibility of the system seems limited. Similar observations on other polyester/polycarbonate systems are reported in literature (Utracki, 2002; Marchese et al., 2004; Samios and Kalfoglou, 2000; Yavari et al., 2005). Note that the samples which were manufactured in the light of this study, by standard injection molding, were always completely transparent, having only a single $T_g$. The conclusion, that, when processed on a normal processing time scale, the resulting system is miscible on a molecular scale.
The yield stress of a polymer glass, i.e. polycarbonate, can be accurately predicted based on the processing conditions used, following a modeling approach using an effective time. Here this approach is validated for a miscible blend of polycarbonate with a polyester and good agreement is found with experiments. The parameters describing the evolution of yield stress with time proved to follow the rule of mixtures.

The proposed methodology is a promising addition to the range of tools available for optimizing design and properties of polymer products. If both components of a miscible blend are adequately characterized, the properties of any blend composition can be predicted, and thus the combination of composition, product geometry and processing conditions can be optimized in a fully numerical environment without performing a single product related test.

5 Conclusions

The yield stress of a polymer glass, i.e. polycarbonate, can be accurately predicted based on the processing conditions used, by following a modeling approach using an effective time. Here this approach is validated for a miscible blend of polycarbonate with a polyester and good agreement is found with experiments. The parameters describing the evolution of yield stress with time proved to follow the rule of mixtures.

The proposed methodology is a promising addition to the range of tools available for optimizing design and properties of polymer products. If both components of a miscible blend are adequately characterized, the properties of any blend composition can be predicted, and thus the combination of composition, product geometry and processing conditions can be optimized in a fully numerical environment without performing a single product related test.
References


Date received: August 21, 2008
Date accepted: February 8, 2009

Bibliography

DOI 10.3139/217.2224
Intern. Polymer Processing
XXIV (2009) 2; page 167–173
© Carl Hanser Verlag GmbH & Co. KG
ISSN 0930-777X

You will find the article and additional material by entering the document number IPP2224 on our website at www.polymer-process.com