EFFECT OF LOW TEMPERATURE SHIFT FACTOR MODELING ON PREDICTED PART QUALITY

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Abstract

The effect of low temperature modeling of the time-temperature shift factor on the prediction of residual stress and warpage of injection-compression molded compact discs is studied for an optical grade polycarbonate. Predicted residual stress and warpage with WLF and Arrhenius shift factors truncated at different temperatures indicate that the truncation temperature has a significant effect on the predicted part qualities. A double domain approach is employed to fit the shift factor with WLF function above T_g and an asymptotic function below T_g, and the simulation results are compared with the experimental observations. The comparison shows that the double domain shift factor yields good model fit and part quality prediction of injection-compression molded compact discs.

Introduction

Polymers exhibit time-dependent properties called viscoelasticity. The time-dependent properties are also highly temperature-dependent. For thermo-rheologically simple polymers, the time and temperature are correlated by a time-temperature superposition, which implies that time and temperature are generally equivalent in affecting the relaxation modulus of polymers. The time-temperature transformation is implemented by a shift factor. The WLF equation [1], which is based on free volume theory, was proposed as an empirical expression for the shift factor, and has been frequently utilized to model the temperature dependence of many different polymeric materials. The typical temperature range in which WLF works well is between T_g and T_g+100°C, where T_g is the glass transition temperature of polymers. At temperatures well below T_g, the WLF equation deviates significantly from the test data. While such low temperature rheology modeling will not significantly alter the flow conductance, flow behavior, or pressure distribution in simulation, it is vital to predicting many long-term physical properties such as stress relaxation, creep, warpage, birefringence, and others.

Given that the WLF equation is not applicable for temperatures below T_g, researchers have resorted to alternative ways of describing the shift factor at low temperatures. Some have truncated the shift factor directly at T_g [2, 3], and others have used an Arrhenius type shift factor [4-6]. For the optical grade polycarbonate (PC) considered in the current study and many other polymers, the shift factor below T_g is not linear in a log(a_T)-T plot as will be elaborated in the following section. As such, the Arrhenius type equation has to be similarly truncated at a certain temperature. Although this truncation is motivated to match observations from material tests, it is to a large extent arbitrary. This study investigates the effect of truncation error of the shift factor on the predicted part quality attributes including thermal stress and warpage of compact discs molded using an optical grade PC, and proposes a function to describe the shift factor for polymers below T_g.

WLF Equation and Dynamic Mechanical Test Data

The WLF function has the form:

$$\log a_T = -\frac{C_1\left(T - T_{ref}\right)}{C_2 + T - T_{ref}} \qquad (1)$$

where a_T is the time-temperature shift factor, T_{ref} is a reference temperature to which the master curves are generated by shifting the dynamic mechanical test data at other temperatures, and C_1 and C_2 are material coefficients to be determined by fitting the test data of the shift factor with the WLF function.

Fig. 1 (a) shows the storage and loss moduli of the PC from dynamic mechanical tests in the temperature range of 100°C to 280°C. The master curves of the storage and loss moduli generated by shifting the test data to a reference temperature of 150°C are shown in Fig. 1 (b) with the corresponding shift factor shown in Fig. 1 (c). The glass transition temperature of the PC in this study under atmospheric pressure is 143°C, with a pressure dependence of $3.81 \cdot 10^{-7}$ °C·Pa^{-1}, both determined from p-v-T tests. As is observed from Fig. 1 (c), the shift factor just below T_g increases rapidly as the temperature decreases until about 125°C, where there is an inflection and the slope becomes concave downward. From 150°C to 125°C, the shift factor in the log(a_T)-T plot exhibits a linear behavior, which can be well described by an Arrhenius type of equation. For temperatures below 125°C, the shift factor asymptotically approaches a value of about $1.0 \cdot 10^8$. Similar experimental observations of the shift factor behavior below T_g for a polycarbonate, Lexan LS, is reported in [7].

The storage and loss moduli in frequency domain directly sourced from the dynamic mechanical tests are not readily utilized in numerical simulation. It is preferable to convert the dynamic moduli in the frequency domain to a linear relaxation modulus $G(t,T)$ in the time domain, which has the form:

$$G(t,T) = G_e + \sum_{i=1}^{m} g_i e^{-\frac{t}{a_T \theta_i}} \tag{2}$$

where G_e is the equilibrium modulus, m is the number of the relaxation modes, and g_i and θ_i is a discrete set of relaxation moduli and relaxation times. The relaxation spectrum is obtained by fitting a model to the master curves of the storage and loss moduli from the dynamic mechanical tests.

Effect of Low Temperature Errors

In order to study the effect of low temperature modeling of the shift factor on predicted thermal stress and warpage, the shift factor obtained by shifting the dynamic mechanical test data is fitted by the WLF equation and an Arrhenius type of equation. The fitted shift factor is truncated at certain temperatures below T_g. The prediction of thermal stress and warpage is performed by a simulation of injection-compression molding of compact discs reported in [9].

Apart from the reasons discussed in the first section, it is obvious from Fig. 1 (c) that if all the test data of the shift factor in the temperature range of 100^{o}C to 280^{o}C were to be utilized to fit a WLF equation, the error would be too large. As a first try, only the test data from 120^{o}C to 280^{o}C is utilized to fit the WLF equation, and the WLF fit is to be truncated at 140^{o}C, 135^{o}C, 130^{o}C, and 120^{o}C in the simulation. Below the truncation temperature, the shift factor is set constant and equal to the value at the truncation temperature. This selection of test data is arbitrary with the consideration of utilizing as many test data points as possible without introducing much larger errors. The test data and the fitted curve are shown in Fig. 2 with the WLF coefficients listed in Table 1.

Fig. 3 shows the simulation results of warpage and residual stress of a disc after 20 seconds of ejection with different truncation temperatures. It can be seen that the truncation temperature has a great effect on the predicted warpage and thermal stress. The warpage with the truncation temperatures of 140^{o}C and 135^{o}C is much greater than the warpage with truncation temperatures of 130^{o}C and 120^{o}C. The tensile stress in the core and the surfaces of the disc and the compressive stress in the layers immediately within the surfaces with the truncation temperatures of 140^{o}C and 135^{o}C are much lower than with the truncation temperatures of 130^{o}C and 120^{o}C. The reason is that the truncation of the shift factor at higher temperatures reduces the shift factor significantly, resulting in greatly reduced characteristic relaxation times. This effect is equivalent to significantly reducing the relaxation modulus below the truncation temperature. As the truncation temperature decreases from 140^{o}C to 120^{o}C, the residual stress and warpage become robust since the truncation error is much smaller with the truncated shift factor getting closer and closer to the test data thanks to the decreased change rate of the shift factor.

A second try is performed by fitting the WLF equation with the test data from 130^{o}C to 280^{o}C. This temperature range allows for lower fitting errors of the shift factor for the temperatures from 150^{o}C to 130^{o}C, but the fit deviates significantly from the test data for temperatures blow 130^{o}C. The fitted shift factor is then truncated at 140^{o}C, 135^{o}C, 130^{o}C, and 120^{o}C in the simulation. The test data and the fitted curve are shown in Fig. 4 with the WLF coefficients listed in Table 1. Fig. 5 shows the warpage simulation with different truncation temperatures. The truncation error has similar effect as in the first try, except that the truncation temperatures of 140^{o}C and 135^{o}C yield much smaller warpage.

Finally, only the test data from 150^{o}C to 280^{o}C are utilized to fit the WLF equation, and the shift factor is truncated at 140^{o}C, 135^{o}C, 130^{o}C, and 125^{o}C in the simulation. The test data and the fitted curve are shown in Fig. 6 with the WLF coefficients listed in Table 1. In this case, the WLF fits the test data in that temperature range very well, but deviates significantly for temperature below 150^{o}C. Fig. 7 shows the warpage simulation with different truncation temperatures. The result for a truncation temperature of 120^{o}C is not shown here because the shift factor goes to nearly infinity causing numerical errors in the simulation. At low temperatures, the WLF shift factor causes the material to be over-rigid because of the significant deviation from test data. Surprisingly, the truncation temperatures of 135^{o}C and 130^{o}C yield result close to the experimental data (ref. Fig. 12). But the disc warps toward the other direction at truncation temperature of 125^{o}C because of the over-rigidity.

As can be seen in the above trial cases, at some well-selected lower truncation temperatures, the predicted short term warpage is close to the experimental data. However, the fitting and truncation error of the shift factor still affects the relaxation behavior of the polymers, and will cause prediction errors for the long-time properties. Since the prediction of long-time properties of polymers based on test data obtained over relatively short timescales has to consider the physical aging effect [10], it would not be accurate with the time-temperature shift only. But for illustration purpose, the physical aging effect is neglected, and simulation results of warpage for a relaxation time of 200,000 seconds at room temperature are shown in Fig. 8.

Modeling of shift factor at low temperatures by an Arrhenius type shift factor is also studied. The shift factor is fitted by a single parameter function:

$$a_T = e^{-b(T-T_{ref})} \tag{3}$$

with the test data between 130°C and 280°C, resulting in the coefficient b=0.65°C^{-1}. Then the shift factor is similarly truncated at 140°C, 135°C, 130°C, and 120°C. The shift factor and the simulation results are shown in Fig. 9 and Fig. 10 respectively. As expected, the results are very close to the WLF trial case two except much smaller warpage for the 140°C truncation temperature. Similarly, truncation of an Arrhenius type of shift factor at arbitrary temperatures below T_g where on the $\log(a_T)$-T plot the shift factor changes from linear to non-linear shape is expected to cause prediction errors for long-time properties.

Proposed Function for Shift Factor below T_g

A search was unsuccessfully conducted to determine a physically motivated model of the shift factor behavior that was C2 continuous, wherein a few coefficients of the model could be estimated from test data. Currently, the following function is proposed for modeling the shift factor of polymers below T_g:

$$\log(a_T) = \frac{a\left(1-\exp\left(-\left(b\left(T_{ref}-T\right)\right)^c\right)\right)}{d+\exp\left(-\left(b\left(T_{ref}-T\right)\right)^c\right)} \tag{4}$$

with a, b, c, and d are the coefficients determined by fitting the shift factor test. Such S-shaped functions [11] are well known and provide a constant value of the shift factor at low temperatures, and Arrhenius type behavior at the interface between the two domains. The set of coefficients offers modeling flexibility to closely fit data for polymers displaying similar shift factor behavior as the PC used in this study.

A double domain shift factor with WLF function above T_g, and the proposed function below T_g is shown in Fig. 11. The coefficients for the WLF and the proposed functions are listed in Table 1 and Table 2 respectively. The proposed function shows good fit in the temperature range of 100°C to 145°C, and has an asymptotic behavior for temperatures below 100°C, which is coherent with the much greater relaxation time at lower temperatures. It is observed that the separation of high and low temperature domains enables significant improvement in the model fit at both low and higher temperatures. Fig. 12 shows the comparison of the predicted warpage of the disc with the double domain shift factor and the measured data. It can be seen that the simulation with the double domain shift factor yields good warpage prediction.

Conclusions

The time-temperature shift factor of PC shows a non-linear behavior on $\log(a_T)$-T plot at temperature below T_g, which cannot be described by WLF or Arrhenius type of equations. Approximated shift factor by fitting partial test data with the WLF equation and truncating at certain temperatures at or below T_g can cause significant prediction errors with the truncation temperature of T_g causing greater errors than lower truncation temperatures. Although the Arrhenius type shift factor below T_g can relatively accurately predict the short-term properties of polymers, it may cause prediction errors for the long-term properties. While selection of truncation temperature can be tricky, the double domain shift factor solution offers a "trouble-free" approach. Future work is needed for extending and validating the models in the current study to other thermoplastic polymers.

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Table 1. WLF coefficients of PC

Temp. Range	T_{ref} (°C)	C_1	C_2 (°C)
120~280°C	150	11.60	71.74
130~280°C	150	10.13	53.32
150~280°C	150	8.83	35.70

Table 2. Coefficients for proposed shift function of PC

Coefficient	a	b (°C^{-1})	c	d
Value	1.96	0.13	0.98	0.25

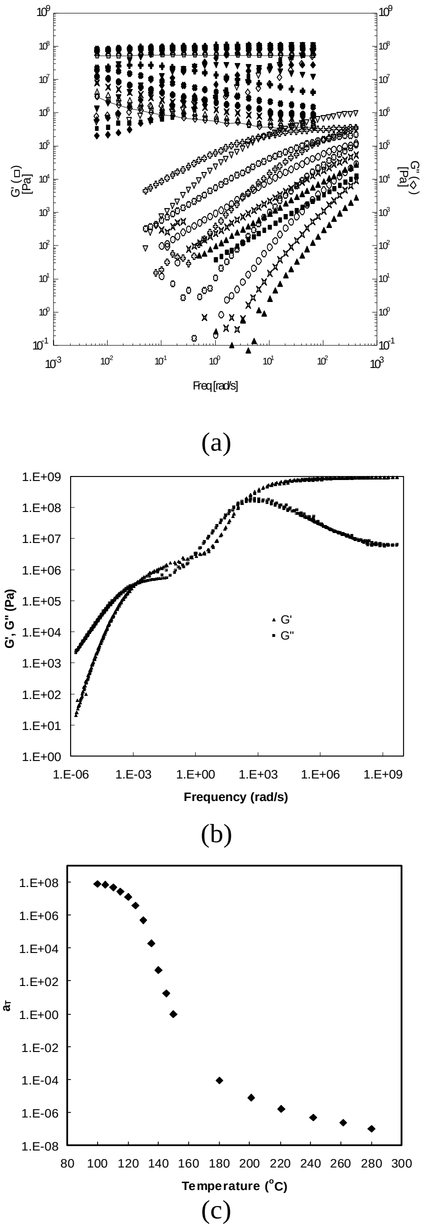

Fig. 1 (a) Dynamic storage and loss moduli of PC in the temperature range of 100°C~280°C, (b) the corresponding master curves at a reference temperature of 150°C, and (c) the shift factor.

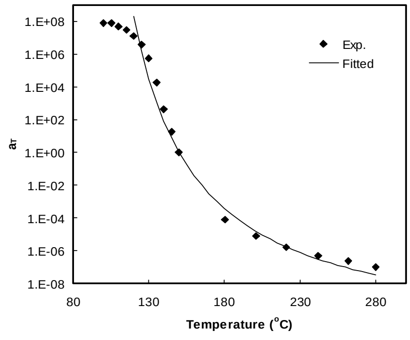

Fig. 2 Shift facotor test data and WLF fit (120~280°C).

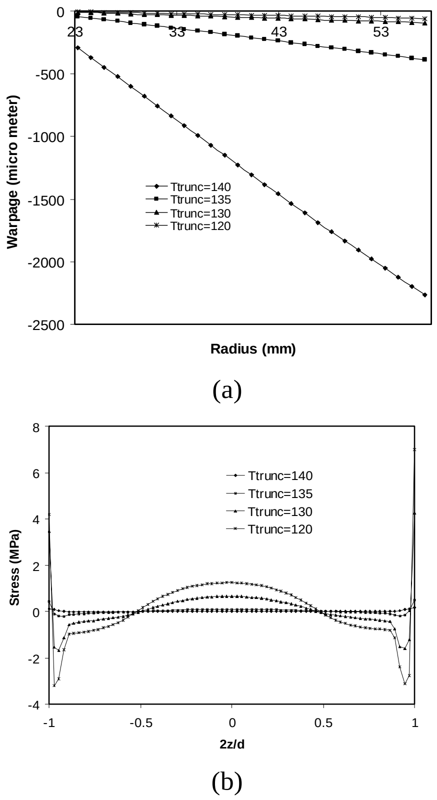

Fig. 3 Comparison of predicted warpage (a) and thermal stress (b) of a disc with different truncation temperatures of the WLF shift factor.

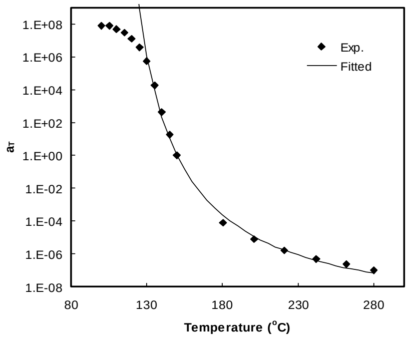

Fig. 4 Shift facotor test data and WLF fit (130~280°C).

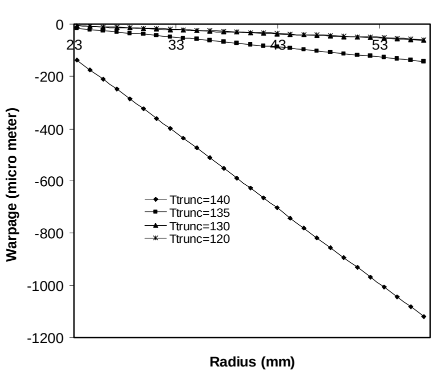

Fig. 5 Comparison of predicted warpage of a disc with the WLF shift factor shown in Fig. 4.

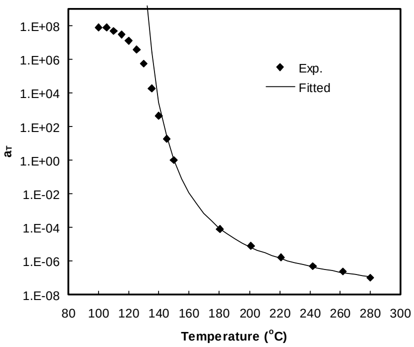

Fig. 6 Shift facotor test data and WLF fit (150~280^{o}C).

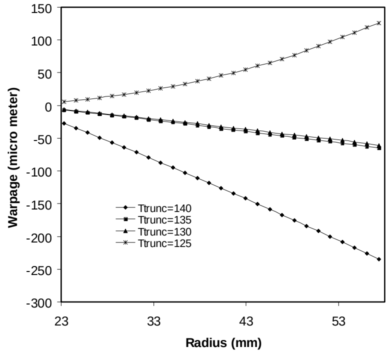

Fig. 7 Comparison of predicted warpage of a disc with the WLF shift factor shown in Fig. 6.

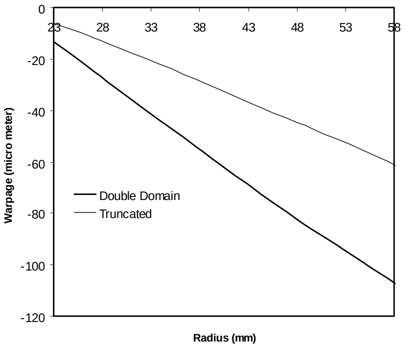

Fig. 8 Comparison of predicted warpage of a disc after 200,000s of relaxation at room temperature. The double domain shift factor is shown in Fig. 11, and the WLF shift factor is as shown in Fig. 6 truncated at 130^{o}C.

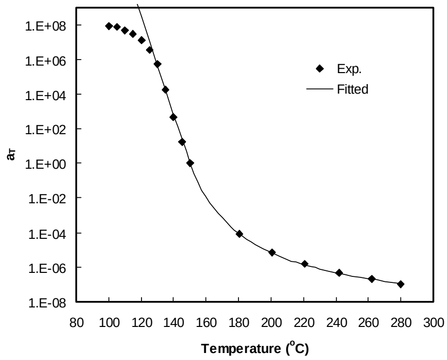

Fig. 9 Shift facotor test data and double domain fit. Fitted curve: WLF above T_g, and Arrhenius (130~145^{o}C) below T_g.

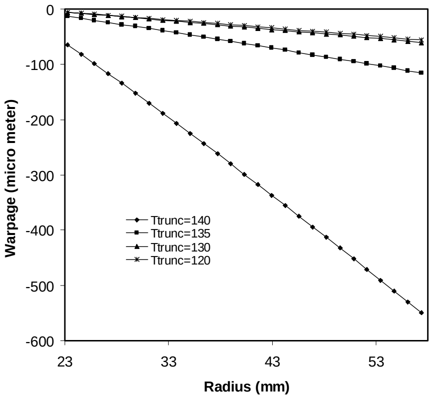

Fig. 10 Comparison of predicted warpage of a disc with the WLF shift factor shown in Fig. 9.

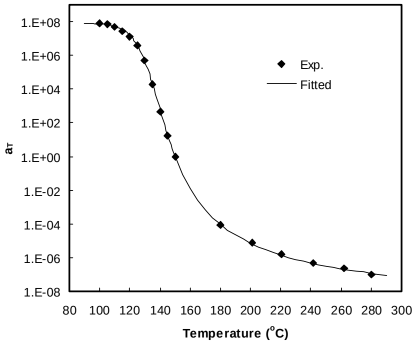

Fig. 11 Shift facotor test data and double domain fit. Fitted curve: WLF above T_g, and the proposed function below T_g.

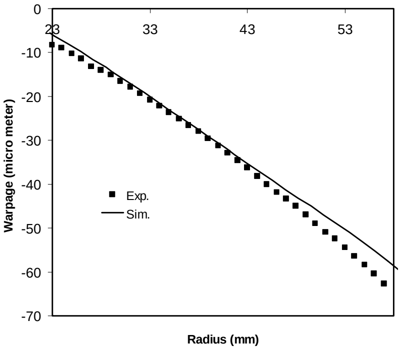

Fig. 12 Comparison of predicted and measured warpage of a disc with the shift factor shown in Fig. 11.