Three-Dimensional Thermorheological Behavior of Isotactic Polypropylene Across Glass Transition Temperature

N. Woicke, M. Keuerleber, B. Hegemann, P. Eyerer

Institute for Polymer Testing and Polymer Science (IKP), University of Stuttgart, Pfaffenwaldring 32, 70569 Stuttgart, Germany

ABSTRACT: The aim of this work was to determine the three-dimensional thermorheological behavior of isotactic polypropylene (i-PP) in the region of its glass transition temperature (T_g) by a master curve. The i-PP is a widespread polymer with a $T_g \sim 0°C$. Dynamic mechanical analysis (DMA) at varying frequencies and temperatures and bulk tests at varying temperatures and times are carried out to obtain the relaxation spectra. Traditionally, the combination of time and temperature is done for thermorheological simple material by the creation of a master curve based on the Arrhenius or William–Landel–Ferry (WLF) equation. This investigation shows that these equations do not fit the behavior across the glass transition of i-PP. Instead, a new arc tangent function is derived. Additionally, it can be shown that the shifting factors differ from shear to bulk load. Therefore, the mode of mechanical stress seems to have an influence on the thermorheological behavior. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 877–880, 2004

Key words: polypropylene; rheology; glass transition temperature

INTRODUCTION

For polymers, it is important to consider the time- and temperature-dependent mechanical material behavior. The description of this behavior can be done by using master curves, which combine temperature and time by a time-temperature shift. This is a well-known method[1] to simplify the thermorheological behavior. The well-established way to describe the time–temperature shift is the Arrhenius or William–Landel–Ferry (WLF) equation.[1] The shifting factors are normally determined by one-dimensional tests but are also applied to three-dimensional problems.

The aim of this study was to model the three-dimensional thermorheological behavior of isotactic polypropylene (i-PP) by generating master curves. Since a lot of material properties change drastically at glass transition temperature (T_g), this is a critical area of modeling and is the focus of the following dispatch.

THEORETICAL BACKGROUND

Strain and stress are three dimensional. At small strains, the Boltzmann superposition principle[1] is valid. The strain ε_{ij} and stress σ_{ij} can be split into two parts[1]:

$$\varepsilon_{ij} = e_0 + e_{ij} \tag{1}$$

$$\sigma_{ij} = s_0 + s_{ij} \tag{2}$$

The tensors s_0 and e_0 describe the hydrostatic pressure and the resulting volume change. s_{ij} is a pure shear matrix and e_{ij} is the change in form connected to s_{ij}. Equations (1) and (2) are relevant for elastic and nonelastic material behavior. For information about all three dimensions, it is necessary to test the bulk properties as well as the shear behavior.

It is shown for amorphous polymers[2,3] that the thermomechanical and rheological behavior can be correlated by a shifting factor. If this is possible, the polymer is called thermorheological simple.

Usually, for shifting between time and temperature, the Arrhenius equation is used. This equation evolves from reaction kinetics and can be derived from the Van't Hoff equation:[4]

$$\frac{d(\ln \dot{\varepsilon})}{dT} = \frac{E}{RT^2} \tag{3}$$

$$\ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} = \ln a_T = \int_{T_0}^{T} \frac{E}{RT^2} \, dT = \frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{4}$$

Correspondence to: N. Woicke (woicke@ikp.uni-stuttgart.de).
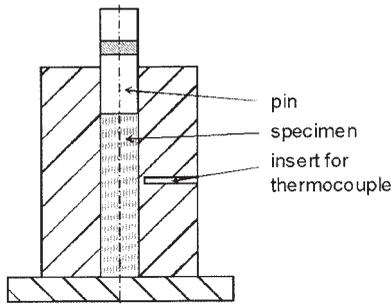
Figure 1　Testing device for the bulk tests.

where a_T is the shifting factor between the strain rate $\dot{\varepsilon}$ at temperature T and $\dot{\varepsilon}_0$ at the reference temperature T_0. R is the general gas constant and E is the change in the specific enthalpy.

Equation (4) was adapted for the description of the rheological behavior at varying temperatures of polymers.

Williams et al.[3] observed for amorphous polymers that the T_g has an important influence on the shifting factor. Based on the free volume theory, they developed a dependency according to eq. (4)[3]:

$$\ln a_T = B\left(\frac{1}{f(T_0)} - \frac{1}{f(T)}\right) \qquad (5)$$

$$f(T) = f_0 + \alpha_f(T - T_g) \qquad (6)$$

where f is the fractional free volume at temperature T, f_0 is the fractional free volume at T_g, α_f is the thermal expansion above glass transition, and B is a model parameter. Equation (5) is called the WLF equation and needs three material-dependent parameters: f_0/B, α_f/f_0, and T_g. If the reference temperature T_0 is the T_g, eq. (5) simplifies to the more commonly known and established equation:

$$\ln a_T = \frac{B\alpha_f}{f_0}\left(\frac{(T - T_g)}{f_0 + \alpha_f(T - T_g)}\right) \qquad (7)$$

The study from WLF[3] was done on amorphous polymers (polystyrene and polyisobutylene) and other glasses at high temperatures. Equation (7) was derived for data at 50 to 100 K above T_g.

EXPERIMENTAL

Material

The material investigated is I-PP MOPLEN HP500L from Basell Polyolefins GmbH, Frankfurt, Germany. The molecular weight is M_w = 288560 g/mol (M_n = 81993 g/mol). The specimens (according to DIN EN

ISO 527 Type 1A) were injection molded (melt temperature of 230°C and tool temperature of 50°C).

Shear

The shear properties are measured with a torsional Rheometer RMS-800/RDSII from Rheometrics in a dynamic mechanical analysis (DMA) mode. The samples have a geometry of $4 \times 10 \times 40$ mm^3 between the clamping devices and are cut out of tensile bars. The frequency range is between 0.055 and 55 Hz, and the temperature range is between −70 and +90°C. The testing mode is torsional with a maximum strain of 0.1% in the peripheral area. Therefore, the theory of Saint-Vénant[5] is used for the correct calculation of the shear stress.

Bulk

The bulk tests are executed with a special testing device (Fig. 1) on a Zwick 1476 universal test machine. The massive steel body of the testing device prevents any displacement in the circumferential direction, while the pin is compressing the rectangular specimen. The samples have the geometry of $4 \times 10 \times 70$ mm^3 and are manufactured from the parallel section of tensile bars. Therefore, the DMA and bulk specimens have the same morphology and processing background.

With this testing device, the bulk longitudinal modulus can be measured. All tests were relaxation tests at 1% strain. The temperature varied between −30 and +40°C.

RESULTS AND DISCUSSION

Shear

The wicket plot[6] is an easy method to identify thermorheological simple materials. It shows loss modulus G'' versus storage modulus G' for all temperatures and frequencies as it can be seen in Figure 2. A devi-
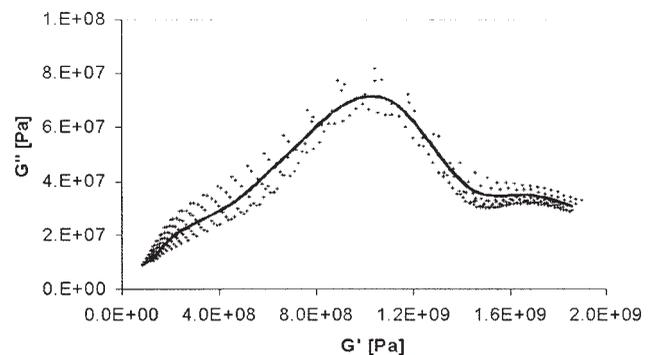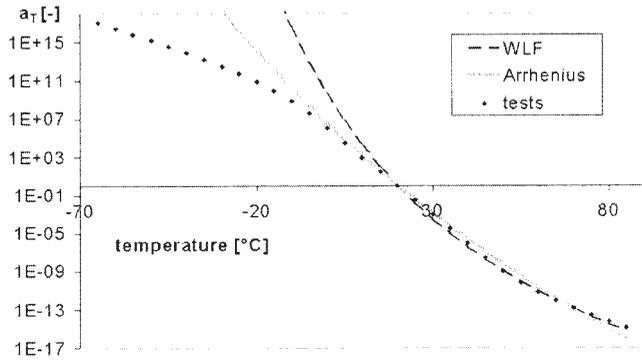

Figure 2　Wicket plot of shear tests.

Figure 3 Shifting factors a_{TS} for shear ($T_0 = 20°C$) with WLF and Arrhenius fit.

ation exists but all measurements follow the course of the mean behavior (solid line). The storage modulus G' is used for the time–temperature shift.

The Arrhenius or WLF equation does not fit the shear factors a_{TS} well (Fig. 3). This problem was already investigated in an other research.[7]

In a new approach, eq. (3) (Van't Hoff) is expanded empirically and integrated

$$\frac{d(\ln \dot{\varepsilon})}{dT} = \frac{A}{1 + C(T - T_g)^2} \tag{8}$$

$$\ln a_T = \int_{T_0}^{T} \frac{A}{(1 + C(T - T_g)^2)} dT = \frac{A}{\sqrt{C}} [\arctan(\sqrt{C}(T - T_g))$$

$$- \arctan(\sqrt{C}(T_0 - T_g))] \tag{9}$$

A, C, and T_g are used as material-dependent parameters. Equation (9) fits the test data very well (Fig. 4).

To explain the good fit of eq. (9), a closer look at the free volume theory around the T_g has to be done.
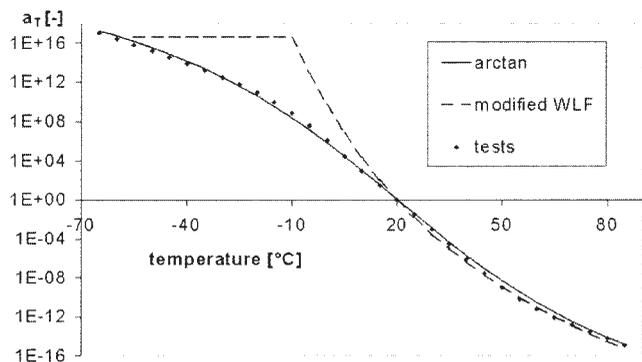

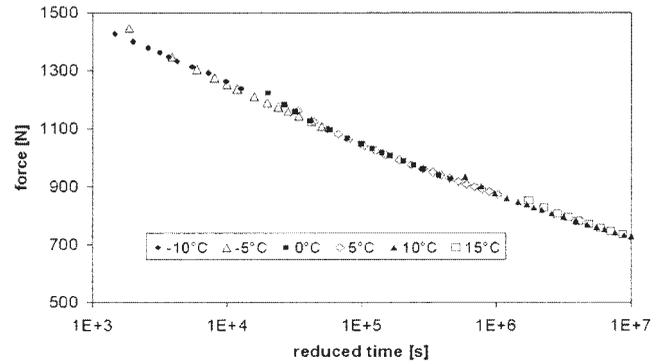**Figure 4** Shifting factors a_{TS} for shear ($T_0 = 20°C$) with modified WLF and arc tangent fit.

Figure 5 Master curve for relaxation tests between −10 and 15°C.

Equation (6) must be specified for this temperature range

$$f(T) = f_0 + \alpha_f(T - T_g) \text{ for } T > T_g$$

$$f(T) = f_0 \text{ for } T < T_g \tag{10}$$

The resulting modified WLF is

$$\ln a_T = B\left(\frac{1}{f(T_0)} - \frac{1}{f(T)}\right) \text{ for } T > T_g$$

$$\ln a_T = B\left(\frac{1}{f(T_0)} - \frac{1}{f_0}\right) = \text{const} \quad \text{for } T < T_g \tag{11}$$

The plot of eq. (11) (modified WLF) and eq. (9) (arc tangent) can be seen in Figure 4. There is a good coincidence between the modified WLF, the arc tangent, and the test results for temperatures > 20°C. At temperatures < 20°C, the modified WLF curve diverges dramatically from the test results around the T_g and changes abruptly to a horizontal line. This line again fits test results at lower temperatures. The arc tangent curve is in the region of the T_g, smoother than the modified WLF, and follows the test results. At low temperatures, the arc tangent also approaches this limit.

Bulk

According to the DMA tests, the thermorheological simple behavior of the material in bulk tests must be investigated. Here, a wicket plot is not possible. Therefore, the measured forces are displayed as a function of the reduced time τ (Fig. 5):

$$\tau = \frac{t}{a_T} \tag{12}$$

In eq. (12), a_T are the time–temperature shift factors for the relaxation tests and t is the measured time. In
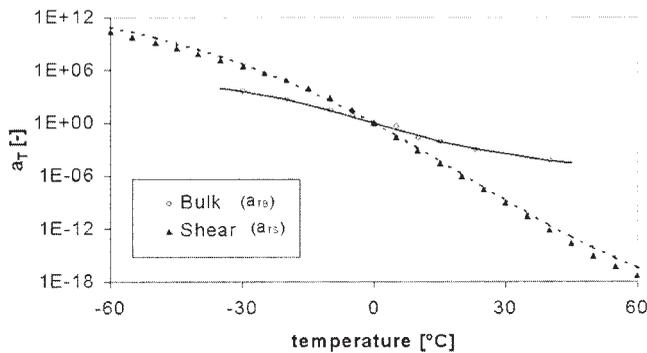
Figure 6 a_{TS} and a_{TB} and their description by the arc tangent function ($T_0 = 0°C$).

Figure 5, there are reduced data in the area between −10 and 15°C, which is representative for all measured data. There is a large conformance, which supports the validity of the shifting procedure.

The resulting shift factors can also be described by an arc tangent function (Fig. 6). However, the bulk factors a_{TB} differ from the factors a_{TS} derived for the shear behavior

$$A_S \neq A_B, \quad C_S \neq C_B, \quad T_{gS} \neq T_{gB} \qquad (13)$$

CONCLUSION

DMA at varying frequencies and temperatures and bulk tests at varying temperatures and times were carried out on i-PP to obtain the relaxation spectra. Traditionally, the combination of time and temperature was done by the creation of a master curve based on Arrhenius or WLF equations. Both equations diverge from the experimental data in the region below the T_g.

Instead, the Van't Hoff equation was expanded empirically and integrated to derive a new arc tangent function. This new function fits the experimental data very well. Therewith, it is possible to describe the bulk and shear behavior.

The thermorheological behavior of i-PP around glass transition is dependent on the mode of mechanical load. Shear tests resulted in totally different shifting factors than bulk tests. Therefore, testing must be carried out at two different and independent modes of loads to determine the whole three-dimensional thermorheological behavior.

Further investigations will show if this new approach can be generalized for semicrystalline polymers around glass transition.

References

1. Menges, O. Materials Science of Polymers for Engineers; Hanser Verlag: Munich, 1995; Chapter 2.
2. Ferry, J. D. Vicoelastic properties of polymers, 3rd ed.; Wiley: New York, 1980; Chapter 11.
3. Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701–3707.
4. Taschenbuch der Chemie, 2nd ed.; Schwister, K., Ed.; Hanser Verlag: Leibzig, 1996; Chapter 7.
5. Beitz, W.; Küttner, K.-H. Dubbel, Taschenbuch für den Maschinenbau, 17; Auflage: Springer Verlag, Berlin, Heidelberg, 1990; Chapter C2.
6. Jones, D. I. G. Handbook of Viscoelastic Vibration Damping; Wiley: Chichester, 2001; Chapter 5.
7. Lewen, B. Das nichtlineare viskoelastische Verhalten von Kunststoffen am Beispiel der Zeit-Temperatur-Verschiebung und derq Uerkontraktion; Dissertation RWTH, Aachen 1991; Chapter 3.