

## RHEOLOGY APPLICATIONS NOTE

### Application of Time-Temperature Superposition Principles to Rheology

#### Theory

Polymeric materials, because of their viscoelastic nature, exhibit behavior during deformation and flow which is both temperature and time (frequency) dependent. For example, if a polymer is subjected to a constant load, the deformation or strain (compliance) exhibited by the material will increase over a period of time. This occurs because the material under a load undergoes molecular rearrangement in an attempt to minimize localized stresses. Hence, compliance or modulus measurements performed over a short time span result in lower/higher values respectively than longer-term measurements. This time-dependent behavior would seem to imply that the only way to accurately evaluate material performance for a specific application is to test the material under the actual temperature and time conditions the material will see in the application. This implication, if true, would present real difficulties for the rheologist because the range of temperatures and/or frequencies covered by a specific instrument might not be adequate, or at best might result in extremely long and tedious experiments..

Fortunately, however, there is a treatment of the data, designated as the method of reduced variables or time-temperature superposition (TTS), which overcomes the difficulty of extrapolating limited laboratory tests at shorter times to longer-term, more real-world, conditions. This TTS treatment is well grounded in theory (1,2,3) and can be applied to the rheology data obtained from oscillation experiments.

The underlying bases for time/temperature superpositioning are (1) that the processes involved in molecular relaxation or rearrangements in viscoelastic materials occur at accelerated rates at higher temperatures and (2) that there is a direct equivalency between time (the frequency of measurement) and temperature. Hence, the time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and transposing (shifting) the resultant data to lower temperatures. The result of this shifting is a “master curve” where the material property of interest at a specific end-use temperature can be predicted over a broad time scale.

The amount of shifting along the horizontal (x-axis) in a typical TTS plot required to align the individual experimental data points into the master curve is generally described using one of two common theoretical models. The first of these models is the Williams-Landel-Ferry (WLF) equation :

$$\log A_t = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}$$

where  $C_1$  and  $C_2$  are constants,  $T_0$  is the reference temperature (in K),  $T$  is the measurement temperature (in K), and  $A_t$  is the shift factor. The WLF equation is typically used to describe the time/temperature behavior of polymers in the glass transition region. The equation is based on the assumption that, above the glass transition temperature, the fractional free volume increases linearly with respect to temperature. The model also assumes that as the free volume of the material increases, its viscosity rapidly decreases.

The other model commonly used is the Arrhenius equation :

$$\log A_t = \frac{E}{R(T - T_0)}$$

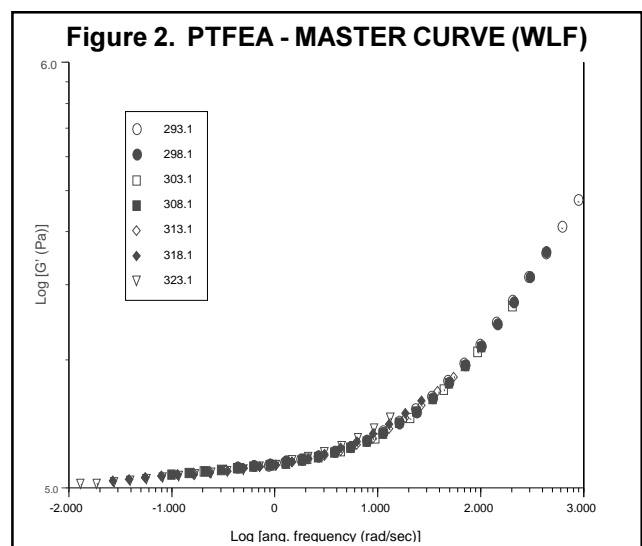
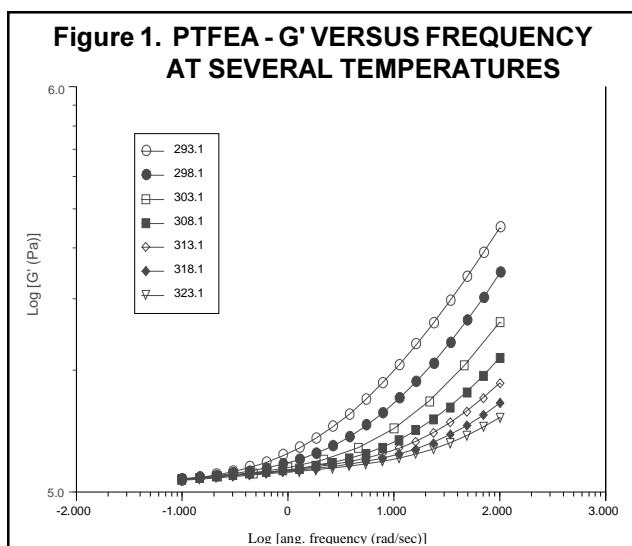
where  $E$  is the activation energy associated with the relaxation,  $R$  is the gas constant,  $T$  is the measurement temperature,  $T_0$  is the reference temperature, and  $A_t$  is the time-based shift factor. The Arrhenius equation is typically used to describe behavior outside the glass transition region, but has also been used to obtain the activation energy associated with the glass transition.

## TA Instruments TTS Software

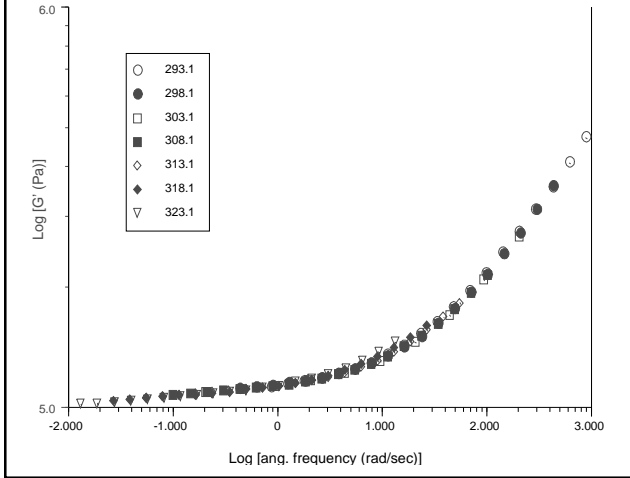
The TA Instruments TTS Software [PN 15366 (U.S.); PN 5366 (Europe & Export)]\* is an option which expands the capabilities available under the oscillation mode in *Rheology Solutions*. The software allows the operator to take the  $G'$ ,  $G''$ ,  $J'$ ,  $J''$ , or  $\tan \delta$  curves plotted from multiple oscillation experiments and shift those curves to superimpose on a selected reference temperature curve (i.e. form a master curve). This shifting can be performed manually by the operator or automatically by the software. The amount of shifting required to superimpose the data onto the reference curve can be subsequently fitted to several available theoretical models to determine which best describes the data and to determine the associated shift factors. Furthermore, once the master curve is obtained, it can be stored as a "data file" for subsequent recall and overlay with the master curves from similar materials (to compare differences in behavior) or other master curves for the same material (to compare behavior at different end-use temperatures).

The TTS Software conforms to the Windows™ (GUI) format with many ease-of-use features such as tool bars, icons, and point & click mouse interactions. In addition, the automatic shifting capability makes it possible for even an inexperienced operator to rapidly generate master curves and evaluate alternative theoretical models. Furthermore, TTS is fully supported in *Rheology Navigator* to allow completely unattended experimental evaluation and master curve generation once the sample has been loaded.

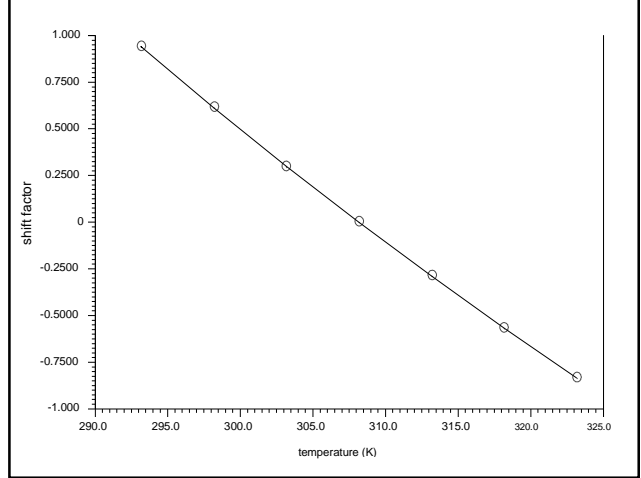
Figures 1-5 show the steps involved in a typical application of the TTS Software. Figure 1 shows the  $G'$  curves obtained for polytetrafluoroethylene acetate (PTFEA) as a function of frequency at several temperatures. Figures 2 and 3 are the resultant master curves after shifting the initial curves to a reference temperature of 308 K (35°C) using the WLF and Arrhenius models respectively. Figures 4 and 5 are plots of the shift factors expected for the respective models (solid lines) versus the actual shift factors obtained from the automatic curve-fitting routine in the software (open circles). The shift factors obtained for both models exhibit good agreement with theory, indicating that either model can be used to predict behavior for PTFEA in this temperature region. Figures 6 and 7 summarize the key constants derived from these plots. If the agreement between the theoretical shift factors and those obtained from automatic shifting is not satisfactory, the operator has the option to manually adjust the shift factors in Figures 4 and 5 to agree completely with theory and generate a new master curve. In this example, that process is not necessary. Comparing the original  $G'$  results in Figure 1 to the master curves in Figures 2 or 3, it is easy to see that the TTS treatment in this material has increased the range for predicting modulus change versus time (frequency) by at least two decades over the range covered just by the raw experimental data.



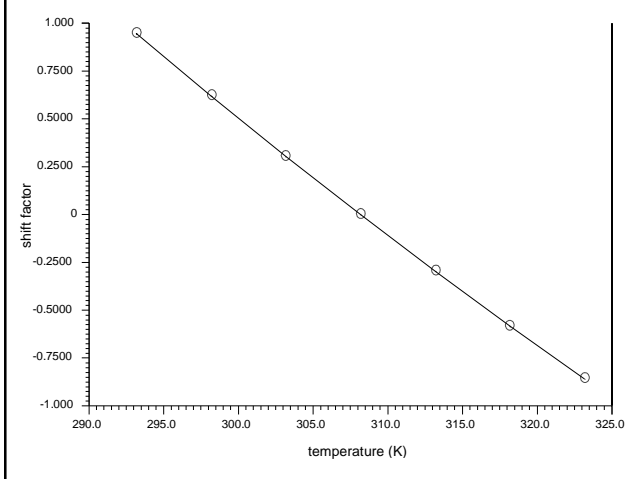
**Figure 3. PTFEA - MASTER CURVE (ARRHENIUS)**



**Figure 4. WLF SHIFT FACTORS**



**Figure 5. ARRHENIUS SHIFT FACTORS**



**Figure 6. WLF ANALYSIS RESULTS**

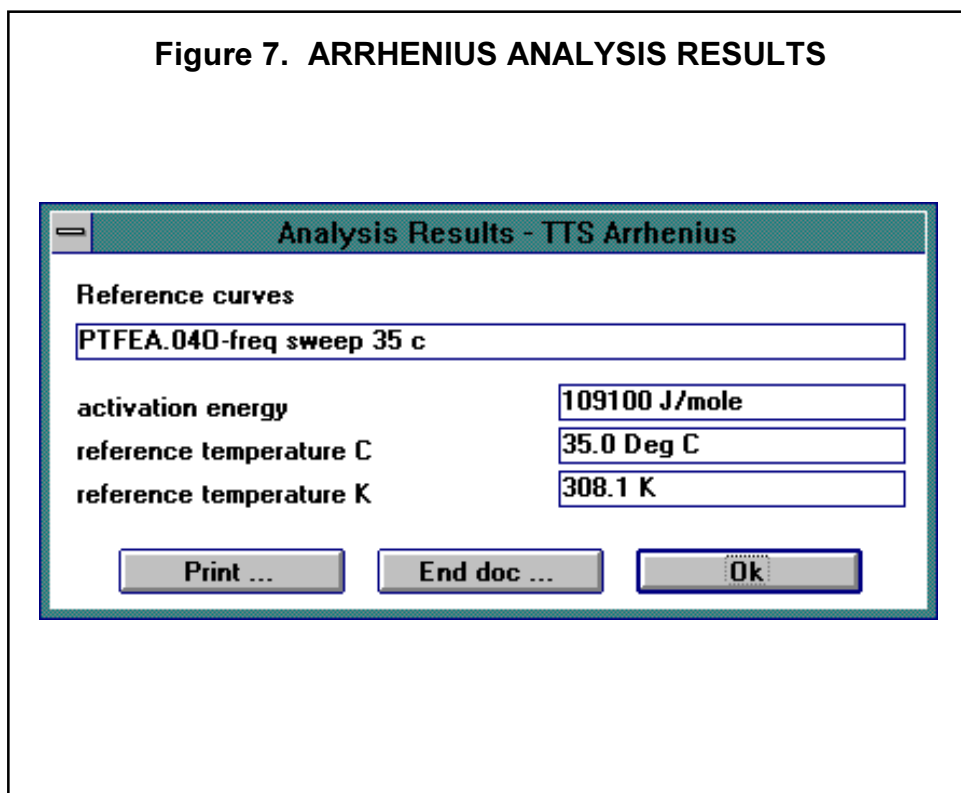
**Analysis Results - TTS WLF**

Reference curves  
 PTFEA.040-freq sweep 35 c

c1	14.67
c2	248.9
reference temperature C	35.0 Deg C
reference temperature K	308.1 K

Print ...    End doc ...    Ok

**Figure 7. ARRHENIUS ANALYSIS RESULTS**



## REFERENCES

1. A.V. Tobolsky, *Properties and Structures of Polymers*, Wiley, New York, 1960.
2. J.D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.
3. M.L. Williams, R.F. Landel, and J.D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

\*TA Instruments TTS Software was developed in collaboration with Dr. Richard Chartoff & his coworkers, University of Dayton, Center for Basic & Applied Polymer Research.

---

For more information or to place an order, contact:

**TA Instruments, Inc.**

109 Lukens Drive  
New Castle, DE 19720  
Telephone: (302) 427-4000  
Fax: (302) 427-4001

**TA Instruments N.V./S.A.**

Gent, Belgium  
Telephone: 32-9-220-79-89  
Fax: 32-9-220-83-21

**TA Instruments, Ltd.**

Leatherhead, England  
Telephone: 44-1-372-360363  
Fax: 44-1-372-360135

**TA Instruments S.A.R.L.**

Paris, France  
Telephone: 33-01-30489460  
Fax: 33-01-30489451

**TA Instruments GmbH**

Alzenau, Germany  
Telephone: 49-6023-30044  
Fax: 49-6023-30823

**TA Instruments Japan K.K.**

Tokyo, Japan  
Telephone: 813-5434-2771  
Fax: 813-5434-2770

---

Internet: <http://www.tainst.com>