Development of a Time Temperature Superposition Program

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Motivation

- PVC has up to 40% by weight of plasticizers, the most common one is di (2-ethylhexyl)phthalate (DEHP)
- DEHP plasticizers leach out into the environment and degrade into more toxic metabolites [1].
- The “green” plasticizer project lead to possible alternatives for DEHP.
- Long term performance of “green” plasticizers has been compared to DEHP. [2]
- There is need to compare the performance of “green” plasticizers at processing time by using storage modulus.

Rheology

Oscillatory deformation experiments of polymer melts measure the storage modulus G’(t) and the loss modulus G’’(t). G’(t) measures the energy stored and recovered per oscillation cycle [3].

The range of these measurements is limited by the rheometer, high and low frequencies cannot be measured due to low accuracy and inconvenience respectively [3].

For rheologically simple polymers changing the temperature is equivalent to shifting the G’(t) curve vertically (b_T) and horizontally (a_T) [4]. This is used to extend the measured range of G’(t) w.r.t. a reference temperature T_r.

$$b_T G'\left(T, \frac{t}{a_t}\right) = G'(T_r, t)$$

b_T is given by the ratio $\frac{T_r}{T}$ [3]. Values for a_T are obtained by shifting curves to obtain superposition. For polymers well above glass transitions temperature, a_T should follow an Arrhenius relationship [4].

$$a_T(T) = \exp\left[\left(\frac{E_a}{R}\right) * \left(\frac{1}{T} - \frac{1}{T_r}\right)\right]$$

The shifting of rheological data is called time temperature superposition, and the result is called a “master curve”. The success of the superposition can be confirmed by simply looking at the shifted data [4].

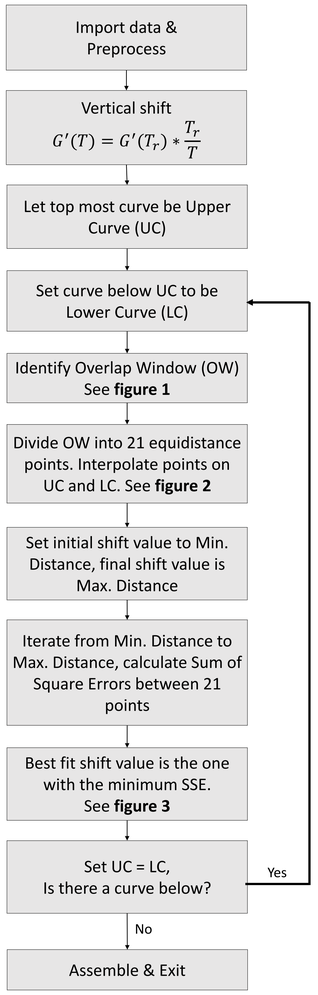
Objective

- Build a user friendly program that will perform robust time temperature superposition.
- Fit the shift factors to the empirical Arrhenius relationship

Methods

MATLAB was used to build the entire program. The algorithm was written in many sub functions to enable maintenance, if necessary. The Graphical User Interface Design Environment (GUIDE) was used to build the application.

The Algorithm



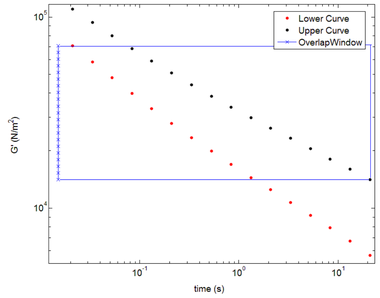


Figure 1. Identification of Overlap Window

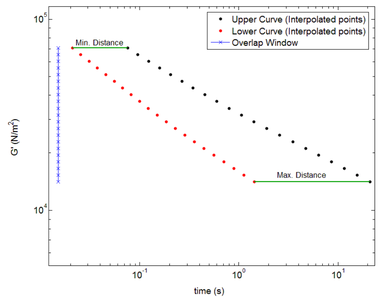


Figure 2. Interpolated points on UC and LC in overlap window

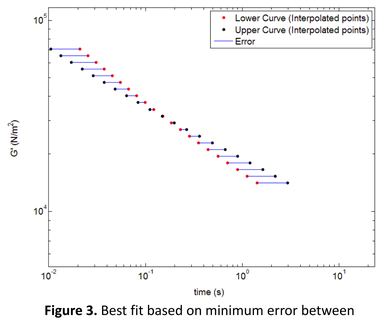


Figure 3. Best fit based on minimum error between interpolated points of UC and LC

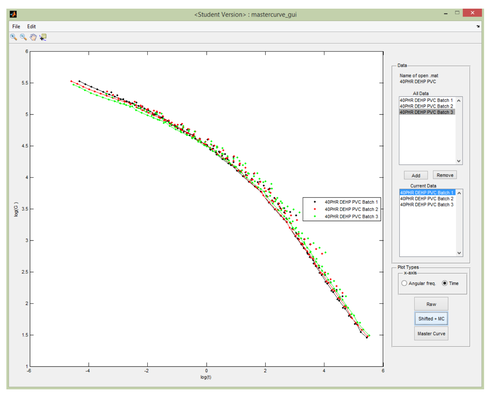


Figure 4. MATLAB application for the algorithm

A graphical user interface was built to use the algorithm and provides the following functionalities:

- Import data series
- View raw data
- View shifted curves
- View master curve
- Open/Save workspace
- Export processed data to excel sheet

Results

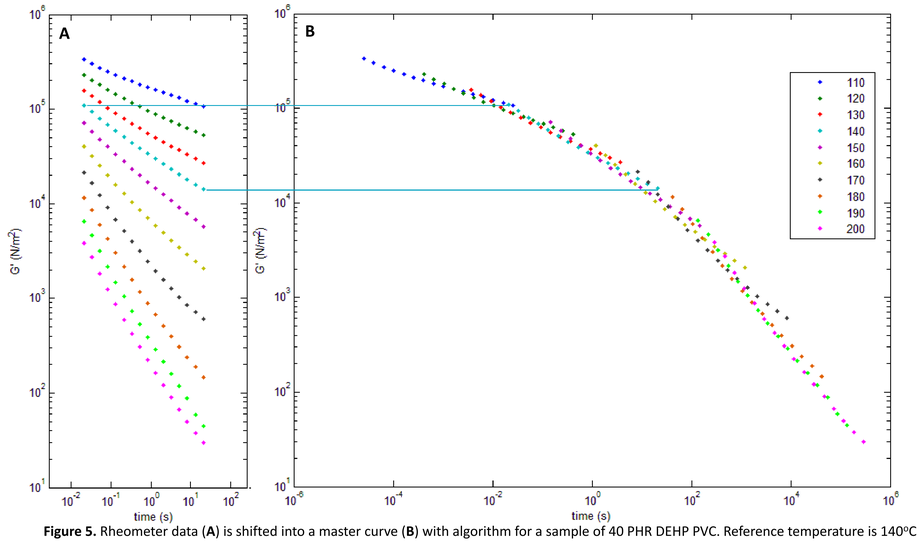


Figure 5. Rheometer data (**A**) is shifted into a master curve (**B**) with algorithm for a sample of 40 PHR DEHP PVC. Reference temperature is 140°C

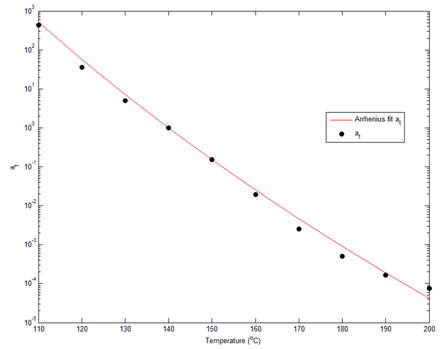


Figure 6. Shifted values obtained are fit to an Arrhenius relationship.

Conclusion

A program that performs time temperature superposition was successfully designed and built. The program will be used to reliably and conveniently generate Master Curves for the green plasticizer project.

Acknowledgment

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References

[1] Horn et al. *Water Research*, 2004, **38**(17): p. 3693-3698
[2] Hanno et al. *Chemosphere* **86**(2012): p. 759-766
[3] Ferry, *Viscoelastic properties of polymers (1980)*
[4] Dealy and Plazek, *Rheology Bulletin*, **78**(2): p. 16-21