Towards a Method of Exploring the Limits of Low Frequency Time-Temperature Superposition Models in Predicting the High Frequency Response of Epoxy-Amine Resins

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CENTRE OF EXCELLENCE

Introduction

- Material responses over 0.1-2000 Hz are a cause for concern for a variety of industries
- Time-temperature superposition is one method of probing a materials response over a wide range of frequencies and temperatures from low frequency data
- There are three main challenges with using TTS as a method, the problems are outlined below and potential solutions identified

Experimental

Two epoxies were manufactured and Dynamic Mechanical Analysis (DMA) was performed to obtain both the shear damping properties and the glass transition temperatures of the two materials.

Time-temperature superposition performed done using a 0.05 % strain, a logarithmic frequency sweep over the range 1-100 Hz and a step temperature increase of 5 °C between 0-180 °C.

The master curves were generated using the procedure below.

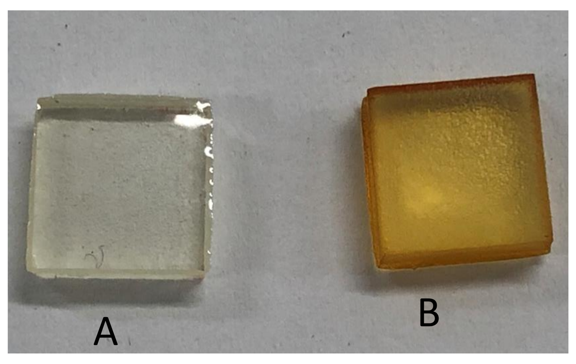

Figure 1: Epoxy resin samples made from bisphenol A diglycidyl ether and A: 3-diethylaminopropylamine. B: 5-Amino-1,3,3-trimethylcyclohexanemethylamine

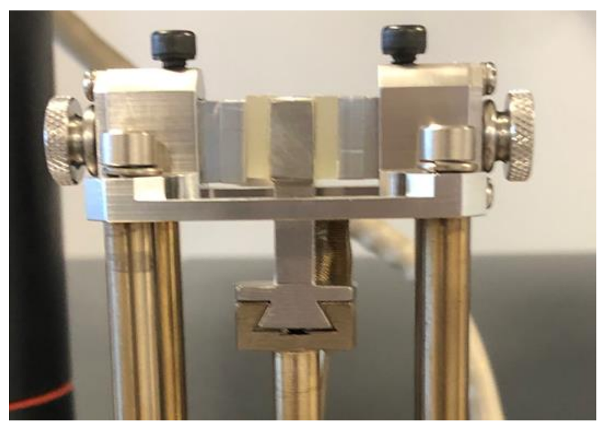

Figure 2: DMA shear clamp with epoxy sample in place.

Step 1: select refence temperature → Step 2: determine initial shifts → Step 3: refine shifts → Step 4: calculate WLF and Arrhenius parameters

Step 1 and Challenge 1

The reference temperature is an arbitrarily selected temperature within the experimental data. It is very much a personal choice and will differ for all materials.

Potential solution: Often the reference temperature may be the glass transition for the material.

Our solution: was to use a reference temperature approximately within the middle of the isotherm plot (Figures 3 and 4). For the shear data this was found to be different to the glass transition temperatures of the materials.

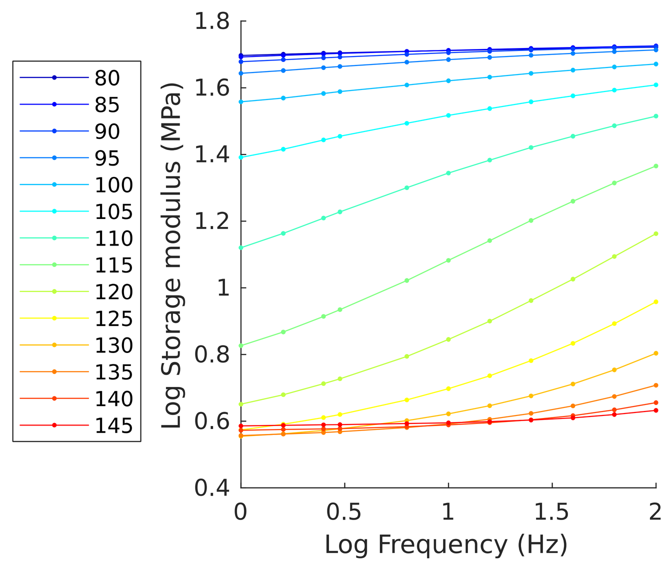

Figure 3: Epoxy and 3-Diethylaminopropylamine Log storage modulus vs Log frequency

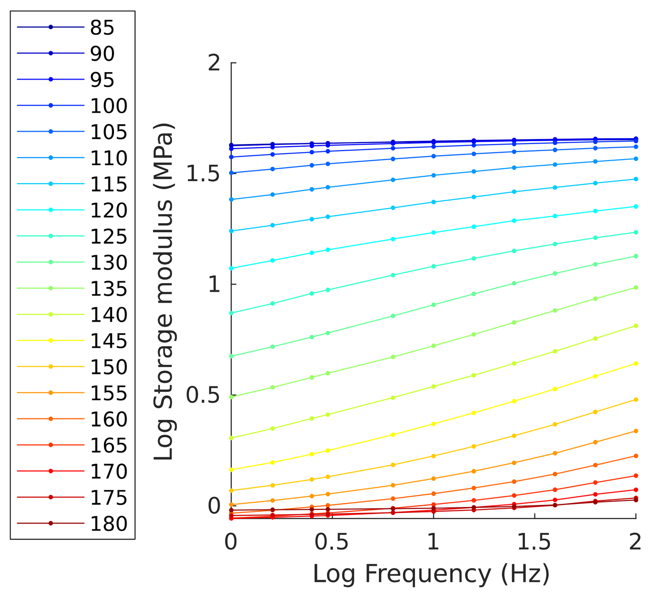

Figure 4: Epoxy and 5-Amino-1,3,3-trimethylhexanemethylamine Log storage modulus vs Log frequency

Steps 2 and 3 and Challenge 2

After shifting the data around the reference temperature a master curve is created. For the Storage modulus this looks like a typical "s" shape (Figures 5 and 6). The "s" shape is dependant on the analyst. Here a lot of operator bias can be introduced.

Potential solution: Using software will remove some operator bias.

Our solution: To validate the master curves by performing experiments at higher frequencies in line with the ASTM standard E756-05.

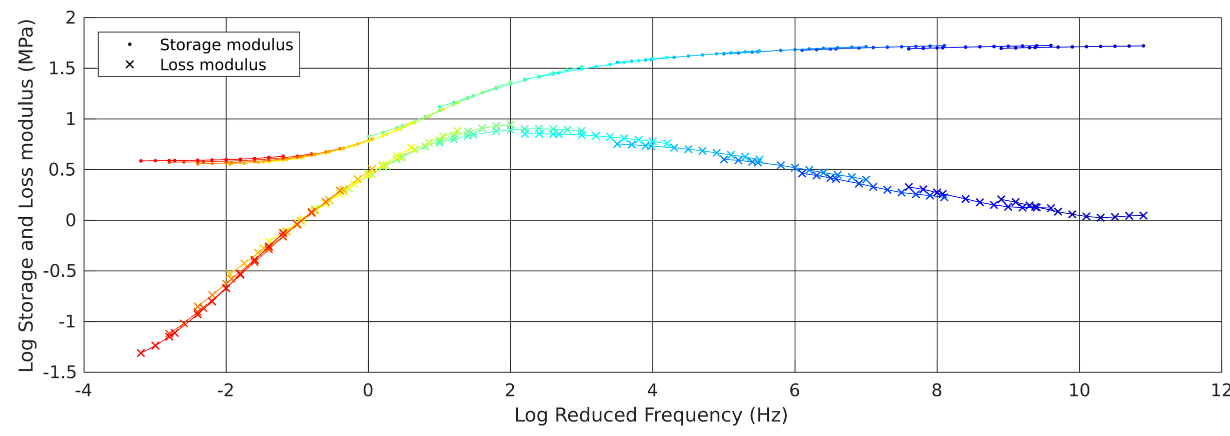

Figure 5: Epoxy and 3-Diethylaminopropylamine master curve for storage modulus

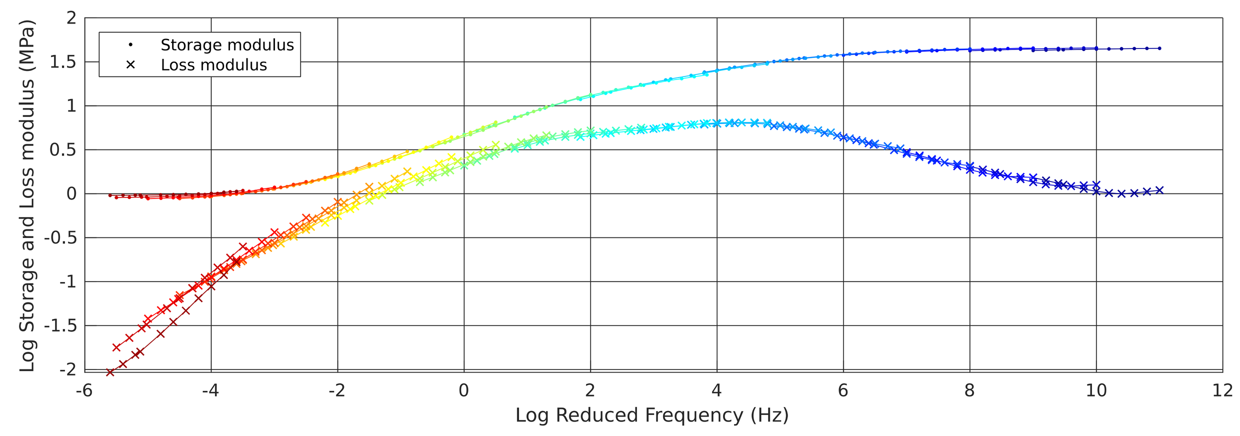

Figure 6: Epoxy and 5-Amino-1,3,3-trimethylhexanemethylamine master curve for storage modulus

Step 4 and Challenge 3

To date there are multiple different shift equations that could be used ranging from the traditional Williams-Landen-Ferry and Arrhenius to newer ones of polynomial and double shift equations.

Our solution: Is to use the Williams-Landen-Ferry (WLF) and Arrhenius due to this being the most frequently used throughout literature.

$\log[\alpha(T)] = T_A\left(\frac{1}{T}-\frac{1}{T_0}\right)$ Arrhenius shift equation

$\log[\alpha(T)] = -C_1\frac{(T-T_0)}{B_1\,(T-T_0)}$ Williams-Landen-Ferry shift equation

Figures 7 and 8 show the trends of the data and how they best fit to the WLF and Arrhenius equations.

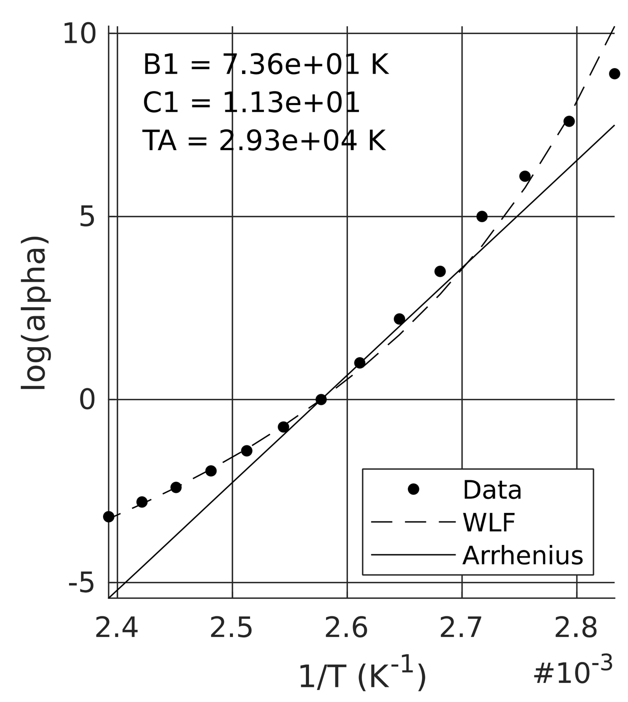

Figure 7: Epoxy and 3-Diethylaminopropylamine shift factors

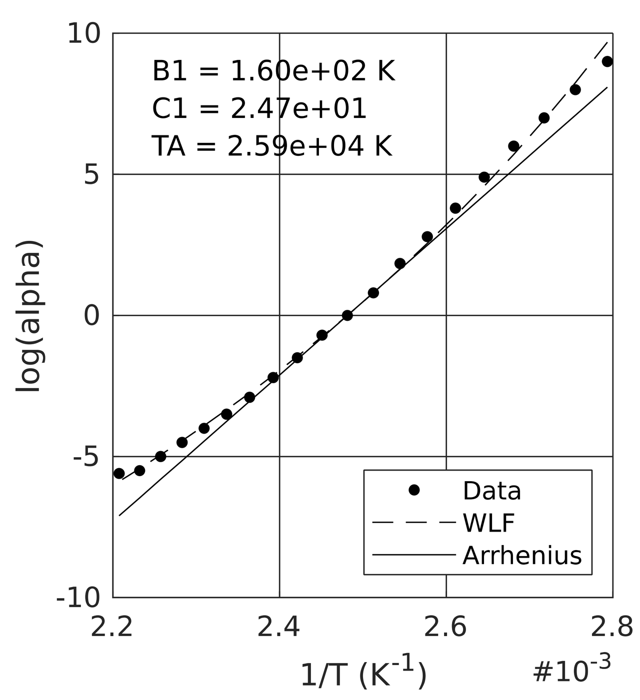

Figure 8: Epoxy and 5-Amino-1,3,3-trimethylhexanemethylamine shift factors

Conclusions

- Three solutions have been presented to overcome the challenges of TTS
- A good initial starting point for Challenge 1 is to select a reference in the middle of the isotherm plot
- Validating the master curves through high frequency experiments and working close to literature are adopted as approaches to overcoming Challenges 2 and 3

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