Group Interaction Modelling as a tool for predicting polymer properties

Malvina Constantinou, Supervisor: Dr David M. Williamson

Cavendish Laboratory, University of Cambridge

Introduction

Group Interaction Modelling (GIM) is a useful modelling tool for predicting polymer properties, laid out by David Porter[1]. It was developed as a compromise between physically fundamental principles and industrially useful empirical tools. GIM uses information from the chemical identity and morphological structure of a polymer to predict bulk material properties.
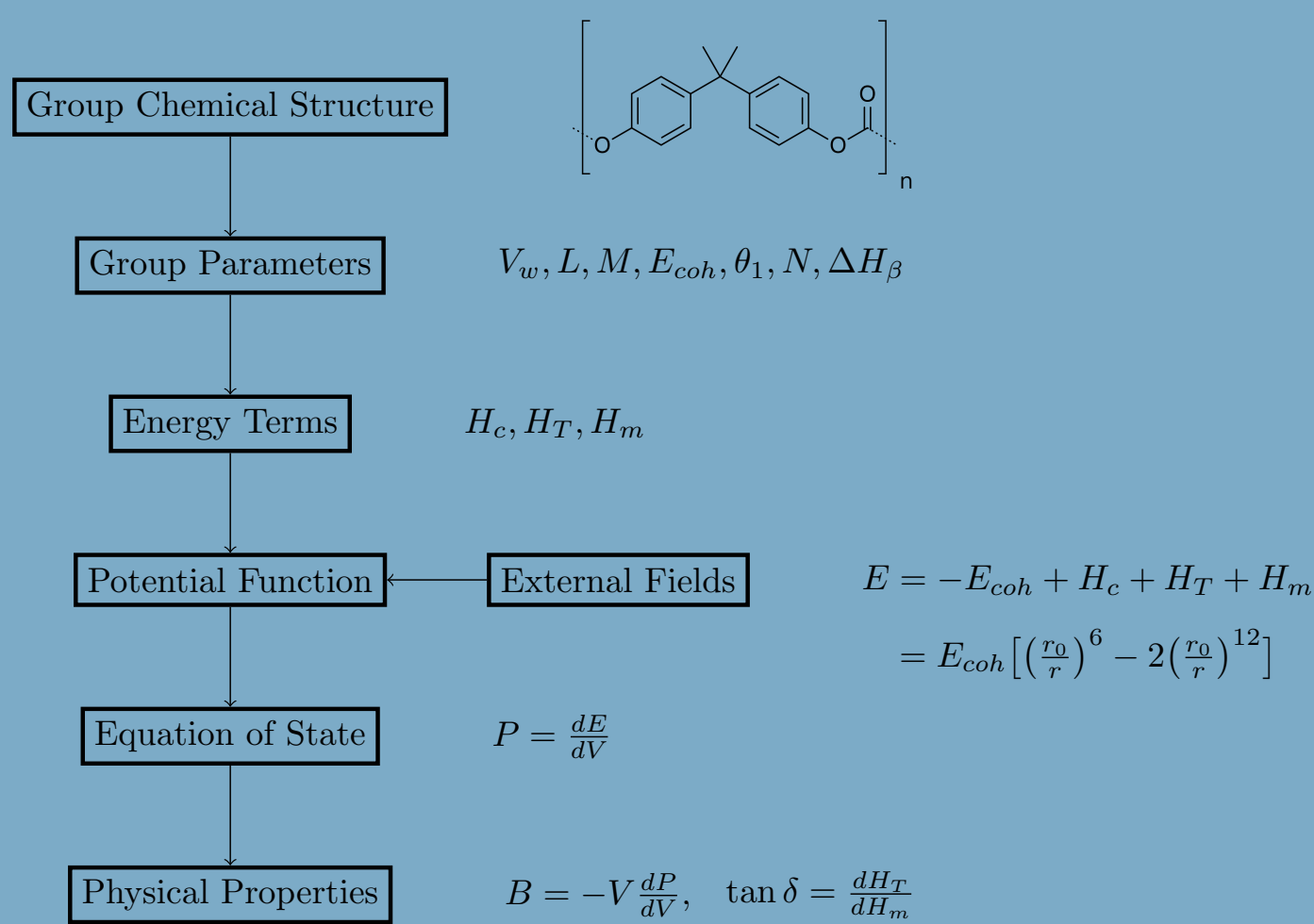

Group Chemical Structure

Group Parameters $\quad V_w, L, M, E_{coh}, \theta_1, N, \Delta H_\beta$

Energy Terms $\quad H_c, H_T, H_m$

Potential Function / External Fields
$$E = -E_{coh} + H_c + H_T + H_m$$
$$= E_{coh}\left[\left(\frac{r_0}{r}\right)^6 - 2\left(\frac{r_0}{r}\right)^{12}\right]$$

Equation of State $\quad P = \frac{dE}{dV}$

Physical Properties $\quad B = -V\frac{dP}{dV}, \quad \tan\delta = \frac{dH_T}{dH_m}$

Fig. 1: Flow chart showing how GIM gets from the chemical structure of the polymer to its bulk properties.

How GIM Works

1. Obtain the main input parameters from the characteristic group of atoms (often the repeating mer group):

- Dimensions: Van-der-Waals volume V_w, length L and molar mass M per mer.
- Energy parameters: cohesive energy E_{coh}, related to the mer interaction potential well depth, the reference temperature of skeletal vibrations θ_1 and any activation energies ΔH_β of secondary relaxations.
- Vibrational degrees of freedom in the molecule: divided into skeletal modes (N), which oscillate the chain segment centre of gravity about the chain axis, and atomic group modes(N_E), which only contribute in storing heat.
- The parameters can be obtained via a variety of methods, from atomistic molecular simulations to group-contribution methods. Tabulated values exist for common polymers[1], whereas new polymers can pose a challenge.

2. Derive energy terms: H_c is the configurational energy, which takes different values for amorphous and crystalline structures, H_T is the internal thermal energy, and H_m is mechanical energy of deformation. We may include other external energy terms.

3. Combine energy contributions into a potential function, which relates the interaction energy to the distance r between adjacent chains.

4. Derive the equation of state and solve it to obtain material properties using thermodynamic definitions.

Experimental Methods

- **Materials:** The measurements included here were made on **BPA polycarbonate**, whose repeating unit is shown in Fig. 1, and **Cross-linked polystyrene**. GIM input parameters are well known for these polymers and suggested values are given in the literature [1, 2].
- **Volumetric heat capacity** measurements were carried out using a transient plane source method [3], achieving measurements in the temperature range 20-450 K.
- **Coefficient of thermal expansion (CTE)** was measured via laser dilatometry, in a house-designed kit allowing a temperature range 120-420 K with controlled heating and cooling rates.
- **Dynamic Mechanical Analysis (DMA)** is used to measure the complex mechanical modulus, as well as the loss tangent of the polymer.

Polycarbonate: CTE

The coefficient of thermal expansion, α, is the most direct probe into N:

$$\alpha = \frac{1.38N(T)}{E_{coh}(T)}\frac{\left(\frac{6.7T}{\theta_1}\right)^2}{1+\left(\frac{6.7T}{\theta_1}\right)^2} \qquad (1)$$

noting that N increases in steps, upon transition temperatures. The observed glass transition temperature(T_g) shifts with heating rate $\dot\epsilon$. The model predicts T_g at a given strain rate:

$$T_g = 0.224\theta_1 + 0.0513\frac{E_{coh}}{N} - 50 + \frac{1280 + 50\ln(\theta_1)}{\ln\left(\frac{2\pi f_0}{\dot\epsilon}\right)} \qquad (2)$$

Here, we have translated the heating rate in the experiment to an equivalent thermal strain rate, by considering the strain caused by the thermal expansion of the material. The thermal strain rate $\dot\epsilon$ can be obtained from the heating rate Q and the linear thermal expansion coefficient β, using the relation: $\beta = \frac{1}{l}\cdot\frac{dl}{dt}\cdot\frac{dt}{dT} = \frac{\dot\epsilon}{Q}$.
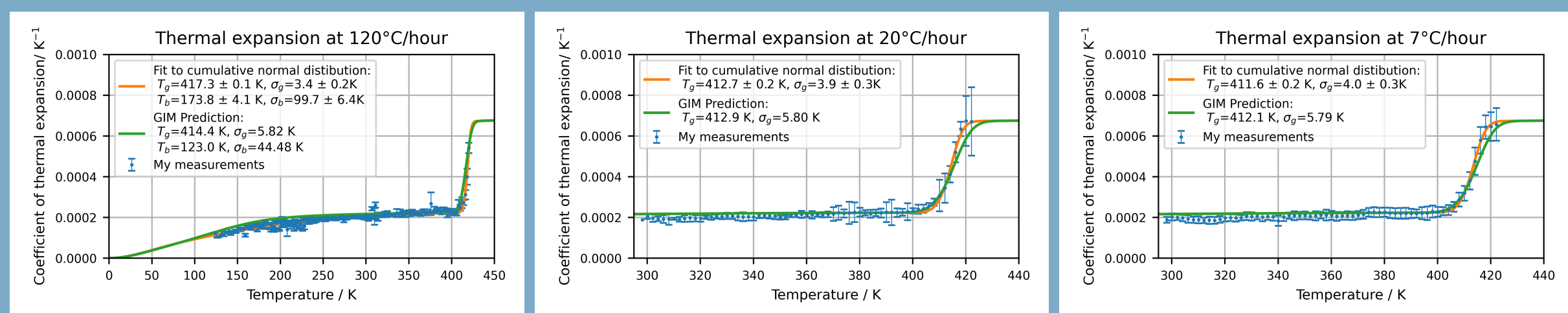

Fig. 2: Thermal expansion results at different heating rates. GIM calculations were performed using the equivalent thermal strain rates.

Polycarbonate: Heat Capacity

The GIM expression for the specific heat capacity is:

$$C_T = C_{skeletal} + C_{atomic}$$
$$= \frac{N(T)R\left(\frac{6.7T}{\theta_1}\right)^2}{1+\left(\frac{6.7T}{\theta_1}\right)^2} + \sum_{N_E}\frac{R\left(\frac{\theta_E}{T}\right)^2\exp\left[\frac{\theta_E}{T}\right]}{\left(\exp\left[\frac{\theta_E}{T}\right]-1\right)^2} \qquad (3)$$

The presented results highlight that the change in mobility of main-chain phenyl rings upon the secondary transition cause θ_1 to change with temperature. If this is not taken into account, the prediction is inaccurate in the low temperature region. Also, we consider the thermal strain rate of this experiment, as above, to capture the observed glass transition temperature.
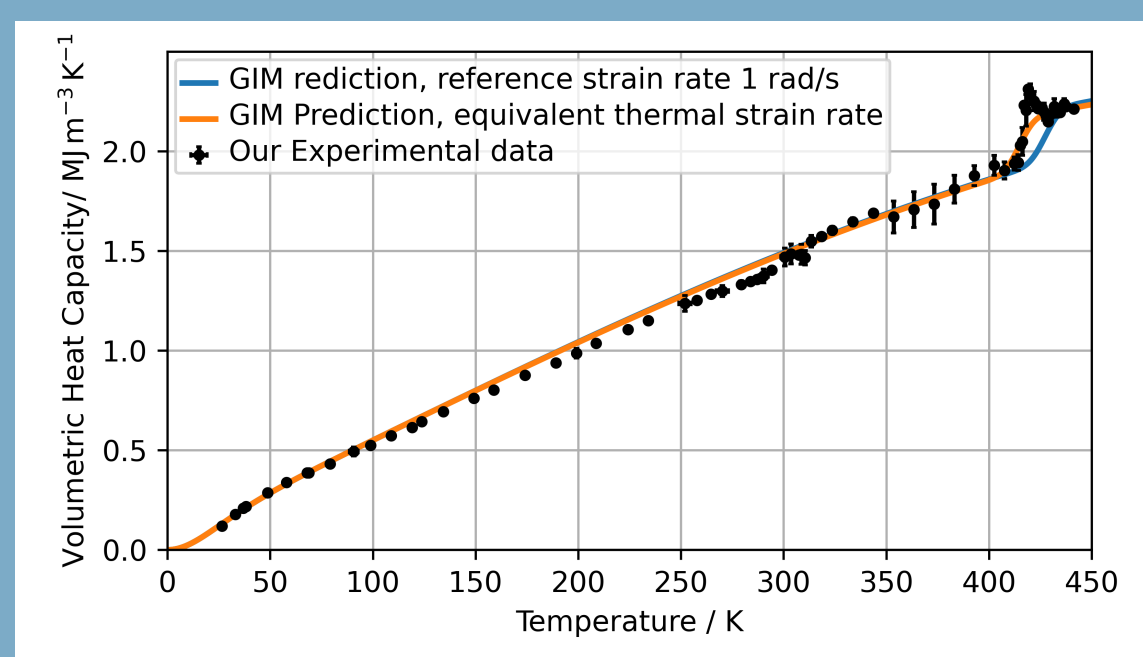

Fig. 3: Measurements of volumetric heat capacity of polycarbonate, compared with GIM predictions.

Polycarbonate: Time-Temperature Superposition

Time-temperature superposition is a characteristic behaviour of polymers, where increasing the temperature is equivalent to increasing the timescale. As a result, the glass transition temperature increases with increasing strain rate, as predicted in Equation 2 and observed in our experiments.

Fig. 4: Measured glass transition temperatures against strain rate, including thermal experiments and a reference DMA result at 1Hz.

Cross-linked Polystyrene: Information from CTE

GIM can help us deduce structural information for a sample, from limited experimental input. Below is an example using cross-linked polystyrene. The effect of cross-linking is a decrease in average number of skeletal degrees of freedom per mer (N). Here, we use T_g obtained from thermal expansion measurements at three different rates, to get an average of 5.6 skeletal degrees of freedom per mer, instead of 6 with no cross-linking, which suggests there is one cross-link for every 15 mers.
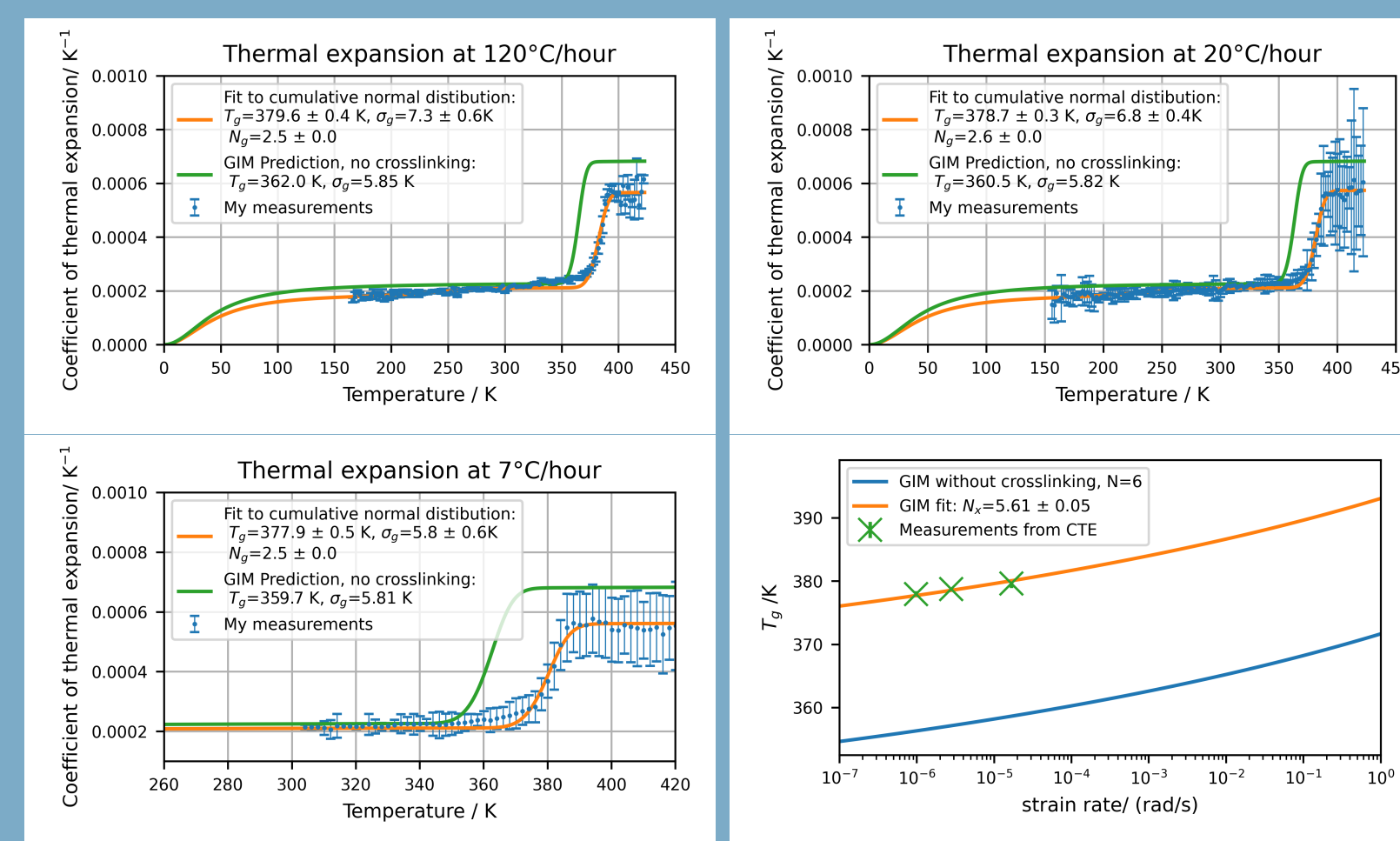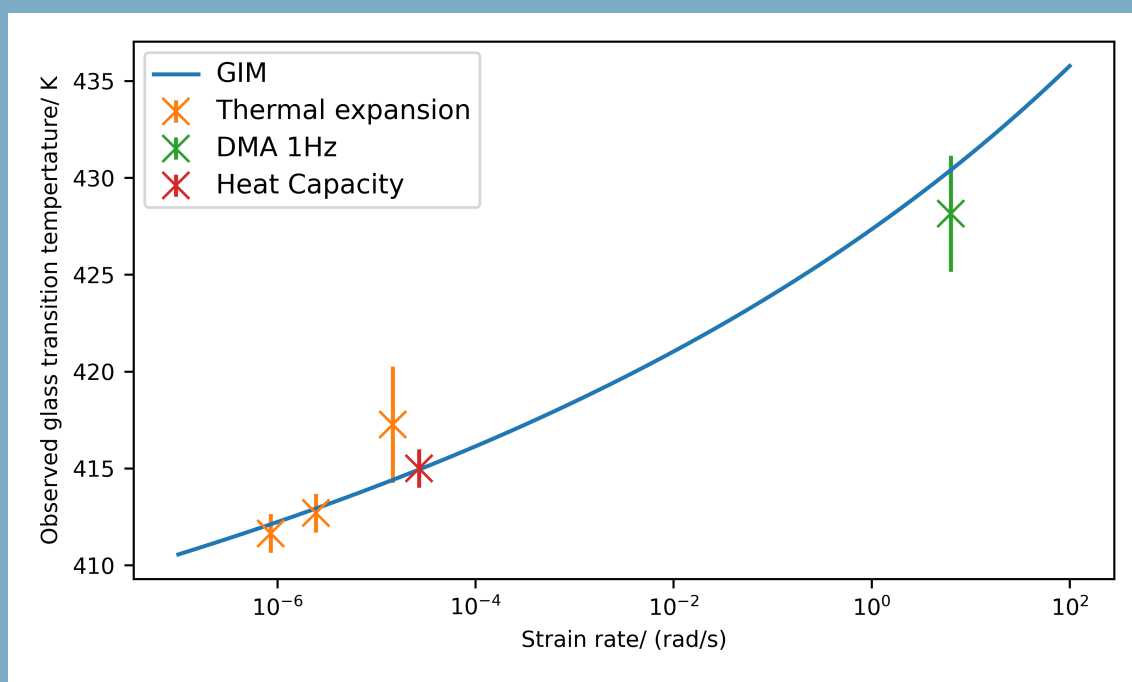

Fig. 5: CTE data for cross-linked polystyrene and how these are used to work out the parameter N and hence the degree of cross-linking. The number of degrees of freedom associated with the glass transition are fitted for, showing that these are also likely to be affected by cross-linking.

Conclusions

- GIM proves to be a powerful tool for predicting polymer properties.
- Converting heating rates to thermal strain rates, allows the comparison of thermal and mechanical timescales, via time-temperature superposition.
- Care must be taken with changes in θ_1, when a main-chain group is involved in a secondary transition.
- GIM allows for acquisition of structural information (e.g. the degree of cross-linking) from limited experimental data.

Further Work

- Further mechanical measurements for polycarbonate, to illustrate the predictive power of the model.
- Investigating a new bio-derived polymer, in order to expand the model to make predictions for newly-discovered polymers.
- Identifying the best method to obtain GIM input parameters, which can be appropriate to as wide a range of polymers as possible.

References and Acknowledgements

[1] D. Porter, Group Interaction Modelling of Polymer Properties. Marcel Dekker inc., 1995.

[2] D. Porter and P. J. Gould, "Predictive nonlinear constitutive relations in polymers through loss history," International Journal of Solids and Structures, vol. 46, pp. 1981–1993, 2009.

[3] ISO-22007-2, "Plastics - determination of thermal conductivity and thermal diffusivity -part 2: Transient plane heat source (hot disk) method.," International Organisation for Standardization, Tech. Rep., 2008.