

Modeling of the mechanical response of solid semicrystalline polymers

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Mechanical properties of most of the solid materials are commonly determined experimentally. Predictions on what would be the material response under a certain load are hard because such a response also depends on the processing of the material. However, a model on the mechanical response would be helpful for the industry because it gives relevant information beforehand, needed to improve the design of new materials to be produced.

Within this framework, we will try to develop a mathematical model to predict the mechanical response of solid polymers. The mechanical behavior under dynamic loading depends on elastic as well as viscous properties, so we pretend to determine the linear viscoelastic features based on the theory developed by Ferry¹. From viscoelasticity, we aim at elucidating a plausible morphology and molecular structure of the system through the macroscopic data, being that this property contain information on it¹²³.

To validate the model and find the model parameters we have available data corresponding to dynamic mechanical analysis experiments of polyethylene bars in the linear regime.

Nevertheless, the problem will not have a trivial solution because the polymer studied is not amorphous. A straight fitting to the literature available models for the amorphous polymers is not possible⁴ and no time-temperature superposition with a single shift can be found³. It has to be taken into account that the polymer has a semicrystalline structure and their mechanical relaxation is complex⁵.

Hence, we pretend that the microscopic mechanism leading to complex response can be depicted using a Generalized Maxwell model, as it has already been done by Klompen⁶, with a small modification, which is represented by a combination of springs and dashpots and can be mathematically expressed by a real and an imaginary part:

$$G^* = G' + iG'' \quad (1)$$

$$G'(\omega) = k + \int_0^\infty d\tau \frac{(\omega\tau)^2 \tilde{E}(\tau)}{1 + (\omega\tau)^2} \quad (2)$$

$$G''(\omega) = \eta\omega + \int_0^\infty d\tau \frac{(\omega\tau) \tilde{E}(\tau)}{1 + (\omega\tau)^2} \quad (3)$$

where G^* is the shear complex modulus, G' and G'' are the storage and loss modulus, ω is the frequency, τ is

the relaxation time, \tilde{E} is the contribution of the modulus at each relaxation time, k is the elasticity constant and η is the pure viscous term.

The determination of the model parameters has been achieved by performing a parameter estimation as a global optimization problem using a simulated annealing algorithm to solve it. The probabilistic metaheuristic for global optimization brings the system from an arbitrary initial state to a state with the minimum possible “free energy”.

Once the minimization is done it can be said that the Generalized Maxwell model is capable to satisfactorily fit the experimental data, available for the dynamic response, with the model proposed for both, the storage and the loss modulus.

A discrete relaxation spectrum is obtained for each experiment at a given temperature. The region where we have the data is where a lower deviation is obtained and as we move away from this window, some points with higher error appear. At different temperatures the spectrum keeps the same pattern but with some changes in position and height.

The elasticity constant k added in parallel to the generalized Maxwell model decreases substantially as the temperature approaches the melting point, as expected. The pure viscous term η also added in parallel, presents a maximum on the glass-transition temperature.

We consider that the results obtained are meaningful and the description of the microscopic structure could be done from them as next step. Further interpretation on the internal structure of the polymers might be done with that information obtained.

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² Rodriguez. F (1996): *Principles of Polymer Systems*, 4th. ed., Taylor and Francis, Washington.

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⁴ Tobolsky, AV. 1956 *J. Appl. Phys.* 27, 673-685

⁵ Boyd, RH. 1985 *Polymer* 26, 1123-1133

⁶ Klompen, Edwin T.J (2005): *Mechanical properties of solid polymers: constitutive modeling of long and short term behavior*, Technische Universiteit Eindhoven, Eindhoven.