Polymer Testing 32 (2013) 961–971

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Test method

A simple and effective scheme for data reduction of stress relaxation incorporating physical-aging effects: An analytical and numerical analysis

Rui Miranda Guedes [a,*], José Lopes Morais [b]

[a] INEGI – EXPMAT – Experimental Mechanics and New Materials & Department of Mechanical Engineering, Faculty of Engineering of the University of Porto, 4200-465 Porto, Portugal
[b] CITAB/UTAD, Apartado 1013, 5001-801 Vila Real, Portugal

ARTICLE INFO

Article history:
Received 26 February 2013
Accepted 22 April 2013

Keywords:
Polymers
Viscoelasticity
Physical aging
Stress relaxation
Time-Aging Time Superposition Principle

ABSTRACT

A simple methodology for obtaining viscoelastic parameters from the stress relaxation tests incorporating physical-aging effects is presented. The method assumes that the experimental data are in the linear viscoelastic domain. Three different mathematical representations of the viscoelastic stress relaxation modulus are analysed and used. Experimental data obtained from literature and simulated data with a random error are used to evaluate the proposed methodology. It is proved that it can capture very well the relaxation modulus of polymers irrespective of the mathematical representation used for the relaxation modulus. Moreover, the methodology proved to be reasonably insensitive to random noise. Extrapolation predictions were also evaluated for the proposed models with very good results.

1. Introduction

Physical aging is a manifestation of a slow evolution of a polymer towards thermodynamic equilibrium by time-dependent change in volume, entropy and mechanical properties including viscoelastic properties. In the work of Struik [1], periodic creep strain measurements were performed to register the effects of physical aging on creep compliance. The test starts after quenching the specimen from the glass temperature (T_g) to a lower temperature designated as the aging temperature. The aging time (t_a) measures the elapsed time after that occurrence. The periodical creep tests cannot last more than 0.1 t_a to minimize the aging effect during the creep tests. These short-term creep curves are a “snap-shot” of the viscoelastic properties at each aging time.

The time-aging time superposition is the paramount principle for data reduction of short-term creep or stress relaxation curves into a reference or master curve using horizontal and vertical shift factors. Accordingly to Bradshaw and Brinson [2], until then, shifting was done by visual inspection to decide the use (or not) of vertical shift. Many used subjective notions, depending on their previous experience, to produce inconsistent results. In this context, Bradshaw and Brinson [2] proposed an automated method based on error minimization. The procedure was based on the concept of “total reference curve”, i.e. the reference curve was obtained using the information of all short-term curves. For each step, an iterative procedure determines the new reference curve and the new shift factors until convergence is attained.

Since the functions used in viscoelastic models belong to the power law type (with three material parameters one being the time exponent), other authors used a different

* Corresponding author. DEMEC, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal. Tel.: +351 22 508 14 00.
E-mail address: rmguedes@fe.up.pt (R.M. Guedes).

0142-9418/$ – see front matter
http://dx.doi.org/10.1016/j.polymertesting.2013.04.009

approach to incorporate the information of all short-term curves in the reference or master curve [3,4]. The general idea is to calculate all the exponents for each curve to obtain the averaged value of one of them. This averaged exponent is used to recalculate the two remaining parameters for each curve.

In this work, a different approach is proposed. The present methodology assumes that the time exponent parameter of the viscoelastic model is unaffected by the physical aging. Therefore, the common exponent, global and constant, is the one that minimizes the sum of square errors of all curves. The present approach applies the previous concepts, i.e. uses the information of all curves to determine the optimal global exponent. Hence, this is equivalent to performing a rotation of each curve, this rotation being given by the difference between the global exponent and the optimal exponent of each curve. The present methodology was implemented for three different mathematical representations of the stress relaxation modulus. The final exercise used simulated experimental stress relaxation modulus data to assess the precision of the method. An artificial perturbation, which assigned a random error of ±1.5% maximum to each observation, was used to evaluate the sensibility of the method to noisy data. The average method [3,4] was used for comparisons purposes.

Finally, extrapolation exercises were performed using long-term relaxation modulus data to evaluate the extrapolation capability of the models.

2. Linear viscoelasticity

The integral form is the most usual way to represent viscoelastic constitutive models. The main reason is related to its handy form to represent experimental data. Moreover, the integral form is very convenient if temperature, moisture and aging effects are to be included. The integral form is naturally deduced from the Boltzmann superposition principle application [5]. Assuming that the stress history is imposed we have

$$\varepsilon(t) = \int_0^t S(t-\tau)\frac{\partial\sigma(\tau)}{\partial\tau}d\tau \qquad (1)$$

where $S(t)$ is the creep compliance.

During a creep test under a constant stress $\sigma = \sigma_0 H(t)$, the creep strain $\varepsilon(t)$ is measured. If the material is in the linear range, the creep compliance is stress independent and is given as

$$S(t) = \frac{\varepsilon(t)}{\sigma_0} \qquad (2)$$

If the strain history is imposed then we have

$$\sigma(t) = \int_0^t E(t-\tau)\frac{\partial\varepsilon(\tau)}{\partial\tau}d\tau \qquad (3)$$

where $E(t)$ is the relaxation modulus.

In a relaxation test, $\varepsilon = \varepsilon_0 H(t)$, the time dependent stress $\sigma(t)$ is measured. If the material is in the linear range the relaxation modulus is strain independent and is given as

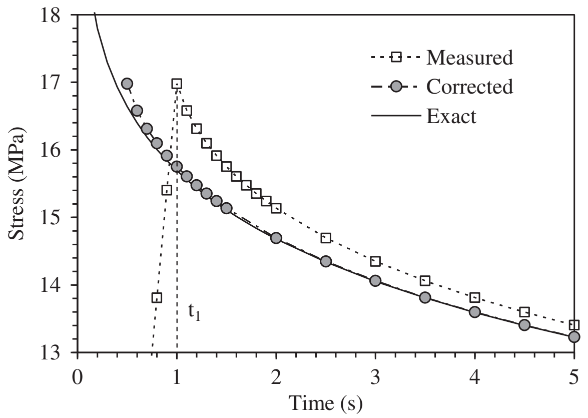

Fig. 1. Comparisons between exact, measured and corrected time-dependent stresses for a simulated stress relaxation test by applying a constant strain rate ramp, followed, at time t_1, by a constant strain.

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \qquad (4)$$

The limits of linear viscoelastic behavior can be given in terms of energy limit [6]. For some polymers it was verified that the energy limit of linear viscoelasticity is independent of the strain rate, temperature and moisture. The energy limit of linear viscoelastic (LVE) behavior, $W_{LVE} = (\sigma_{LVE}\varepsilon_{LVE})/2$ being σ_{LVE} and ε_{LVE} limit stress and strain of linear viscoelasticity respectively, is 1.2 N.mm/mm^3 for epoxy resins and 1.07 N.mm/mm^3 for PEEK [6]. This approach allows establishing the linear viscoelastic limits in a simple way.

3. Mathematical representation of relaxation modulus

The kernel function of the integral representation (3), i.e. the relaxation modulus, can be given by different functions. The simplest one is the so called power law (PL), in the present study given as

$$E_{PL}(t) = E_{0PL} - \left(\frac{t}{\tau_{PL}}\right)^{n_{PL}} \qquad (5)$$

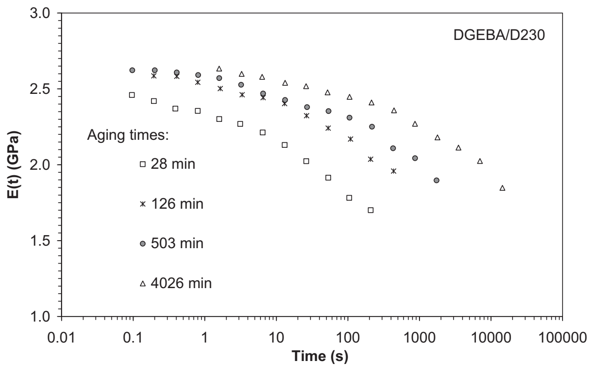

Fig. 2. Stress relaxation modulus curves for DGEBA/D230 measured by Lee and McKenna [11] at different aging times.