Polym. Bull. (2009) 63:773–778
DOI 10.1007/s00289-009-0152-x

A contribution to the interpretation of polymer viscoelasticity in DMTA testing

Cleuza Maria Wasilkoski · Gabriel Pinto De Souza · Leni Akcelrud

Received: 24 September 2008 / Revised: 29 April 2009 / Accepted: 25 August 2009 /
Published online: 10 September 2009

Abstract Some ideas relevant to the prevailing viscoelasticity interpretations of dynamic mechanical thermal analysis (DMTA) experiments are presented. The main aspect is the inclusion of kinetic energy and inertia as variables, seeing the relaxing mass constantly increasing during strain, assigning inertial variation and not viscosity to energy dissipation. The equations developed make it possible to obtain the values of important viscoelastic properties, under in any experimental condition, with the data taken from previous experiments.

Keywords Elastic properties · Polymers · Viscoelasticity

Introduction

One of the most important characteristics of polymeric materials is viscoelasticity, and DMTA is an important tool to characterize the viscoelastic behavior of solid polymers [1–8]. In this work, we present a contribution to the treatment of DMTA data based on the inclusion of the variation of kinetic energy and inertia of the sample during the test. The physical system taken as a reference for the proposed mathematical modeling of the tensile deformation process is based on the affine

C. M. Wasilkoski
Instituto de Tecnologia para o Desenvolvimento (LACTEC), Centro Politécnico, P. O. Box 19067, Curitiba, PR CEP 81531-990, Brazil

C. M. Wasilkoski · G. P. De Souza · L. Akcelrud
Programa de Pós-Graduação em Engenharia (PIPE), Universidade Federal do Paraná, Curitiba, PR 81531-990, Brazil

L. Akcelrud (✉)
Departamento de Química, Centro Politécnico, Universidade Federal do Paraná, P. O. Box 19081, Curitiba, PR 81531-990, Brazil
e-mail: leni@leniak.net

model, which assumes that the chain segments can be treated as independent entities and are strained in the same proportion as the bulk. The applied stress will move the entanglement points to new positions, altering the distance among each other in the transverse and longitudinal directions in relation to the applied force. The shifting to the new position of each segment depends on its interaction with the immediate neighborhood, that is, on the cooperative macromolecular movement and on the mass of the chain itself. The straining will progressively become more difficult due to the incorporation of neighboring chains to the movement and, therefore, the mass to be dragged away tends to increase progressively as well. After this point, new applied stresses will result in larger differences in mechanical responses in each direction. This interpretation sees the mass of the moving chain segments constantly increasing during the process of straining. For purposes of mathematical modeling, the average volumetric stress will be considered as acting in each segment. This situation can be seen as a linear oscillator, in which the damping term is the sum of the dissipative, viscous effects and the mass of the added fluid. Consequently the problem is treated as a variable mass question, in agreement with the model described by Landau and Lifshitz [8]. The response of the sample to the straining has been characterized by the conformational geometry of the polymer molecules, which will be modified during the experiment according to their inertial variation [9]. The braking force which depends on the added mass from the surroundings during the movement is taken into account in our equation as an out-of-phase component in relation to the linear oscillator movement. This way the linearity between stimulus and response inherent to DMTA measurements is sustained. The developed equations based on these ideas should match the experimentally obtained curves, establishing the dependency of the complex modulus E^* and tanδ with the experiment variables.

Results and discussion

As the polymer chains in the amorphous state are randomly placed, a large part of the mechanical energy put into the system is used to align the chains (torque), which varies continuously along the straining process. Therefore, there is a variation in the momentum of inertia of the system $\mathrm{I}(t)$. Newton's second law can describe all the events occurring during the deformation process:

$$\mathrm{I}(t)\frac{d^2\varepsilon(t)}{\mathrm{d}t^2} + \frac{\mathrm{d}I(t)}{\mathrm{d}t}\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t} + \eta\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t} + k\,\varepsilon(t) = \sigma_{\mathrm{S}} + \sigma_{\mathrm{D}}e^{i\omega t}. \qquad (1)$$

Since DMTA experiments are performed in a linear regime, the relationship between applied force and response has to obey this condition as well. The responses relative to the dynamic and static stimuli ε_{D}, ε_{S} are measured separately. The response to the dynamic force is contained in the amplitude of the dynamic deformation and in the dephasing (δ) between the applied stress and the resulting strain, whereas the response to the static stress is measured as the total deformation of the sample (δ S). Accordingly, one has:

$$\varepsilon(t) = \varepsilon_S(t) + \varepsilon_D e^{i(\omega t - \delta)} \tag{2}$$

$$\frac{d\varepsilon(t)}{dt} = \frac{d\varepsilon_S(t)}{dt} + i\omega\varepsilon_D e^{i(\omega t - \delta)} \tag{3}$$

$$\frac{d^2\varepsilon(t)}{dt^2} = \frac{d^2\varepsilon_S(t)}{dt^2} - \omega^2\varepsilon_D e^{i(\omega t - \delta)} \tag{4}$$

$$\begin{aligned} &\left[-\omega^2 I(t) + i\omega\left(\frac{dI(t)}{dt} + \eta\right) + k\right]\varepsilon_D e^{i(\omega t - \delta)} + \text{(dynamic response)} \\ &\left[\frac{d^2\varepsilon_S}{dt^2} + \left(\frac{dI(t)}{dt} + \eta\right)\frac{d\varepsilon_S}{dt} + k\varepsilon_S\right] = \sigma_S + \sigma_D e^{i\omega t} \text{ (creep response).} \end{aligned} \tag{5}$$

The creep component is due to the static force continuously operating in order to maintain the sample in the appropriately aligned position. In a DMTA experiment, one has

$$\left[-\omega^2 I(t) + i\omega\left(\frac{dI(t)}{dt} + \eta\right) + k\right]\varepsilon_D e^{i(\omega t - \delta)} = \sigma_D e^{i\omega t} \tag{6}$$

$$\varepsilon_D = \frac{\sigma_D}{\left[(k - \omega^2 I(t))^2 + \omega^2\left(\frac{dI(t)}{dt} + \eta\right)^2\right]^{\frac{1}{2}}} \tag{7}$$

$$e^{-i\delta} = \frac{\left[(k - \omega^2 I(t)) - i\omega\left(\frac{dI(t)}{dt} + \eta\right)\right]}{\left[(k - \omega^2 I(t))^2 + \omega^2\left(\frac{dI(t)}{dt} + \eta\right)^2\right]^{\frac{1}{2}}} \tag{8}$$

$$E\prime = k - \omega^2 I(t) \tag{9}$$

dT/dt stands for the heating rate (β) which remains constant during the experiment.

$$E'' = \omega\left(\frac{dI(T)dT}{dT\ dt} + \eta\right) \tag{10}$$

$$tg\delta = \frac{\omega\left(\frac{dI(t)}{dt} + \eta\right)}{(k - \omega^2 I(t))} = \frac{\omega\left(\frac{dI(T)}{dT}\frac{dT}{dt} + \eta\right)}{(k - \omega^2 I(t))} \tag{11}$$

$$\int_{M_1}^{M_2} dI = \frac{1}{\beta\omega}\int_{T_1}^{T_2} E''dT \tag{12}$$

Taking volume, length, and elastic modulus as V, L, and E, we have

$$\sigma = E\varepsilon \equiv \frac{\text{Force}}{\text{Area}} = E\frac{\Delta L}{L} \text{and} \frac{dM}{V} = \frac{L^2}{V}\left(\frac{1}{\beta\omega}\int_{T_1}^{T_2} E''dT\right). \tag{13}$$

According to Eq. 9, the stored energy E' can be seen as a spring with a elastic constant k and an inertial component $I(t)$, k is a function of temperature, and

undergoes an accentuated decay during a phase transition. $I(t)$ also varies with temperature since it decreases with increase in temperature. Both parameters are intrinsic properties of the material at a given temperature, and do not depend on the test conditions. The shift to higher temperatures of E′ and tanδ is illustrated in Figs. 1 and 2 and can be calculated from Eq. 11 that establishes tanδ as a function

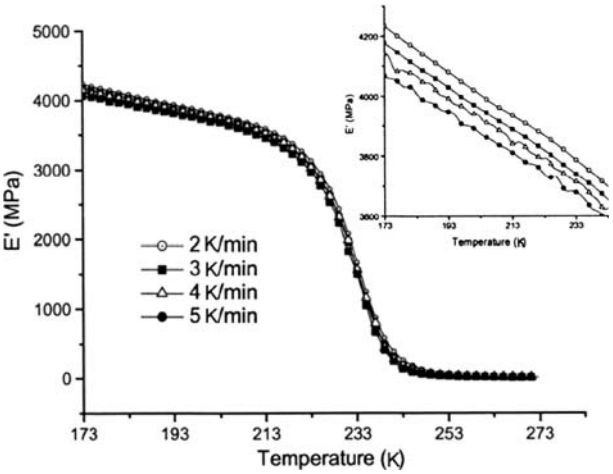

Fig. 1 Elasticity modulus as a function of temperature measured at several heating rates at 0.5 Hz

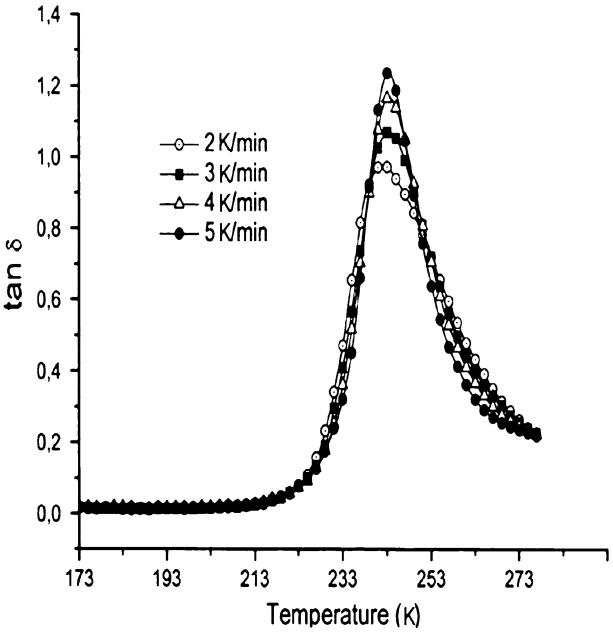

Fig. 2 tanδ as a function of temperature measured at several heating rates at 0.5 Hz

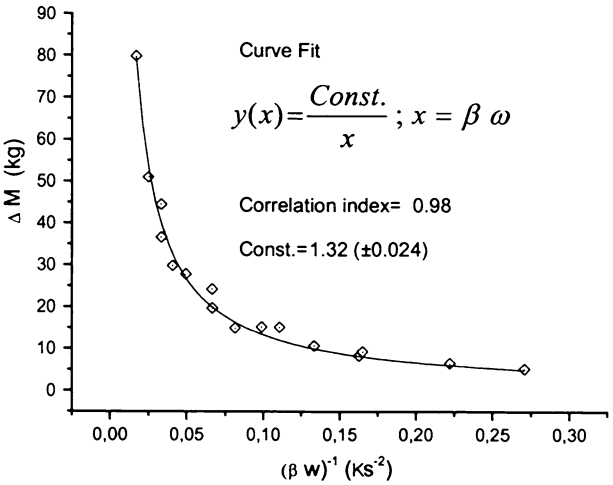

Fig. 3 Relaxed mass in function of the temperature measured at several frequencies and heating rates

of the heating rate. The DMTA essays were performed with frequencies of 0.5, 1, 2, and 3.33 Hz and at heating rates of 2, 3, 4, and 5 °C/min for each one. The material chosen for this trial was NBR [poly(acrylonitrile-*co*-butadiene)] and the same sample was used for all the experiments, without removing it from the equipment.

Figure 3 was obtained by plotting the variation of the mass involved in the deformation process during the test (using Eq. 11) against the testing parameters (frequency and heating rate). The corresponding curve is a hyperbola that describes the material's mobility (and hence damping) and is specific of the system under testing. The immediate consequence of this result is the possibility of obtaining E″ for a different set of experimental conditions without actually performing the test, by simply extracting E″ from the previously drawn curve for the material under analysis. Taking into account that E′ is an intrinsic parameter, which depends only on the temperature and thus is independent of the test conditions, its value is the same as the one used for the construction of the characteristic hyperbole. Therefore, tanδ can be directly obtained.

Conclusions

An alternative way of interpreting DMTA tests is presented, introducing the variation of kinetic energy in the calculations, seeing the relaxing mass constantly increasing during straining, assigning inertial variation to energy dissipation. Plotting the variation of the mass involved in the deformation process during the test in function the testing parameters (frequency and heating rate) the obtained curve is a hyperbole, that describes the material's mobility (and hence damping) and is specific of the system under testing. The universal validity of the concepts presented is currently under investigation, using semicrystalline and amorphous polymer systems.

Acknowledgments The authors wish to acknowledge LACTEC (Instituto Tecnologico para o Desenvolvimento-Brazil) and CNPq (Conselho Nacional de Pesquisas—Brazil) for the financial support.

References

1. Menard KP (1999) Dynamical mechanical analysis: a practical introduction to techniques and applications. CRC Press, Boca Raton
2. Furukawa J (2003) Physical chemistry of polymer rheology. Springer, Berlin
3. Mark JE (1984) Physical properties of polymers. ACS, Washington
4. Mark JE (2007) Physical properties of polymers handbook. Springer, New York
5. Ferry JD (1960) Viscoelastic properties of polymers. Wiley, New York
6. Sepe MP (1998) Dynamical mechanical analysis for plastics engineering. Plastics Design Library, New York
7. Grosberg AY (1998) Theoretical and mathematical models in polymer research. Modern methods in polymer research and technology, Academic Press, Boston
8. Landau LD, Lifshitz EM (1987) Fluid mechanics, 2nd edn. Pergamon, New York
9. Facchinetti ML, Langre E, Biolley FJ (2004) Coupling of structure and wake oscillatorsin vortex-induced vibrations. J Fluid Struct 19:123–140