

Relaxation Time Spectra of Linear and Crosslinked Polymers

E. KONTOU

Department of Theoretical and Applied Mechanics, The National Technical University of Athens GR-15773, Greece

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ABSTRACT: In this work, an attempt has been made to define a unique relaxation time spectrum for different types of polymeric materials. Empirical models for the relaxation spectrum, proposed for linear flexible polymers in the literature, have been used. A systematic determination of the parameters defining the relaxation time spectrum has been made from dynamic mechanical data. It has been shown that the resulted expression for the relaxation modulus could then be used to calculate the stress response of the materials to various deformations. The strain rate dependence of yield behavior could also be predicted. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 679–684, 1998

Key words: relaxation time spectrum; relaxation modulus; yielding; linear viscoelasticity

INTRODUCTION

The stress response of a polymeric material to various deformations may be predicted by either a linear or nonlinear model of viscoelasticity if an equation of the relaxation modulus $G(t)$ is available.¹

Polymers are characterized by a spectrum of multiple relaxation times due to the various modes of relaxation a polymer chain can undergo. The longest relaxation time corresponds to the relaxation of a whole chain, while the shorter one corresponds to the relaxation of short parts of the molecules.²

Relaxation phenomena in polymeric materials have been widely defined with the aspect of cooperativity between segments relaxing simultaneously.

The master curve of the relaxation modulus² of an amorphous polymer involves three stages: stage 1 for the segmental relaxation, stage 2 for the transition zone, and stage 3 attributed to the entangled molecules.²

Stage 1 may be satisfactorily described with the Kohlraush–Williams–Watts (KWW) equation, as follows³:

$$G(t) = G_0 \exp \left[- \left\{ \frac{t}{\lambda_c} \right\}^b \right] \quad (1)$$

where G_0 is the unrelaxed modulus, b is equal to 0.5 for most of the polymers, and λ_c is the relaxation time. Its reciprocal value is almost equal to the radial frequency for the dielectric loss maxima at the glass transition.

Although the KWW equation begins to fail at very short times, it successfully describes stage 1, exhibiting a sharp cut off at longer times. Beyond this range is the extended relaxation stage 2, corresponding to the transition state and obeying a power law, as follows:

$$G(t) = \frac{G_0}{e} \left(\frac{t}{\lambda_c} \right)^{-n} \quad (2)$$

where e is the base of the natural logarithm, and n is equal to 0.5. This stage is molecular-weight-dependent and extends further as molecular weight increases.

Around time λ_c , eqs. (1) and (2) can overlap. The slope of -0.5 is the same as predicted by Rouse's theory,⁴ and the unrelaxed modulus in Rouse's theory is the rubber-like elastic modulus.

Stage 3 is also molecular-weight-dependent,

exhibiting a plateau zone (the entanglement effect) and a terminal zone due to the flow of the material.

Usually a continuous function $H(\ln t)$ is more preferable than a discrete spectrum of relaxation times.

Then the relationship between relaxation spectrum H and the relaxation modulus $G(t)$ is as follows:

$$G(t) = \int_{-\infty}^{+\infty} H(\ln(\lambda)) \exp\left(-\frac{t}{\lambda}\right) d \ln \lambda + G_e \quad (3)$$

where G_e is the relaxed or equilibrium modulus.

Various theories,⁴⁻⁸ based on molecular dynamics, predicted a unique relaxation time spectrum. Two of them are the spectrum of Rouse,⁴ as mentioned above, scaling with $\lambda^{-0.5}$; and the spectrum developed by Doi,⁵ based on the reptation theory of de Gennes, which scales as $\lambda^{0.5}$. These theories predict the physical meaning of macroscopically measured material functions and the associated parameters. However, as it is mentioned in Baumgaertel et al.,⁹ there is no quantitative agreement with experimental data for the dynamic moduli $G'(\omega)$ and $G''(\omega)$.

Ferry¹⁰ presented several empirical methods of approximating relaxation time spectrum H from rheological data.

In Baumgaertel et al.,⁹ a relaxation time spectrum obtained with the superposition of two power laws has been shown to describe the linear viscoelastic behavior of linear flexible polymers in the flow and entanglement region.

This spectrum may be written as

$$H(\lambda) = n_e g_0 \left\{ \left(\frac{\lambda}{\lambda_c} \right)^{-n_g} + \left(\frac{\lambda}{\lambda_{\max}} \right)^{n_e} \right\} \quad \text{for } \lambda \leq \lambda_{\max}$$

$$H(\lambda) = 0 \quad \text{for } \lambda > \lambda_{\max} \quad (4)$$

where g_0 is the plateau modulus; λ_{\max} is the longest relaxation time of the material; n_e and n_g are the slopes of the spectrum in the entanglement and high-frequency glass transition zones, respectively; and λ_c is the crossover time to the glass transition.

The first term corresponds to the high-frequency glass transition region, while the second term describes the relaxation in the entanglement region.

From the other hand, another empirical for-

mula for the relaxation spectrum H may be proposed, based on the interesting observation of Catsiff and Tobolsky¹¹ that the logarithmic relaxation modulus in the transition zone fits the normal distribution curve. The proposed form of the spectrum is of the type

$$H(t) = \frac{h}{\sqrt{\pi}} \exp\left(-\left(h \log \frac{t}{\lambda_m}\right)^2\right) \quad (5)$$

where λ_m is the relaxation time of the mean size strand, and h is a parameter defining the width of the distribution. Parameter h is equal to $1/(d2\wedge.5)$, where d is the standard deviation of the probability density function. This function expresses the probability of the number of strands characterized with a relaxation time between λ_m and t . Therefore, the incremental modulus between two successive times is a measure of the population of modes with relaxation time between them.

Once the distribution of relaxation times is defined, various linear viscoelastic functions such as storage and loss moduli can be obtained in terms of the relaxation spectrum H , as follows:

$$G'(\omega) = \int_{-\infty}^{+\infty} H \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} d \ln \lambda + G_e \quad (6)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H \frac{\omega \lambda}{1 + \omega^2 \lambda^2} d \ln \lambda \quad (7)$$

where ω is the frequency in rad/s.

Moreover, the relationship between the relaxation modulus $G(t)$ and the relaxation spectrum $H(\ln \lambda)$ is as follows:

$$G(t) = G_e + \int_{-\infty}^{+\infty} H \exp\left(-\frac{t}{\lambda}\right) d \ln \lambda \quad (8)$$

In this study, dynamic mechanical data for two different types of materials, namely, low density polyethylene characterized by linear flexible molecules and an epoxy resin based on an amine-cured DGEBA, which is an almost highly dense network, have been used to fit the parameters of the relaxation spectrum functions mentioned above. In this way, a unique expression for the relaxation time spectrum H has been defined empirically, in terms of dynamic mechanical analysis. This expression has been shown to be a material property, as being able to describe experimental results obtained at a totally different time

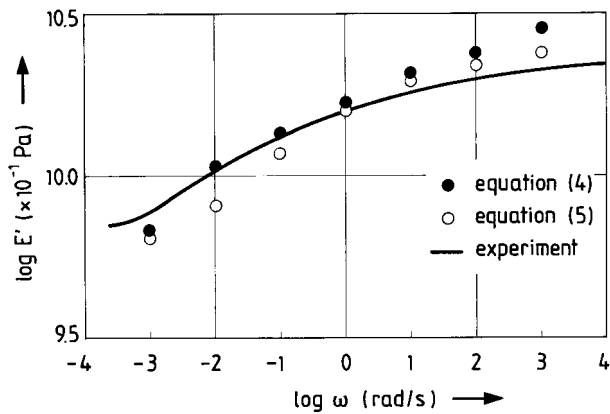


Figure 1 Master curve of storage modulus for linear polyethylene: Solid line represents the experimental data of Matsuoka²; (●) represents eq. (4); (○) represents eq. (5).

scale, namely, tensile and compression stress-strain results of the materials tested.

MATERIALS AND EXPERIMENTAL

The experimental results for a linear polyethylene of high molecular weight are shown in Figure 1, where a master curve at 30°C for the tensile storage modulus versus frequency in a logarithmic scale has been plotted. These data have been taken from Matsuoka.²

A different type of material has also been studied in the same analysis. It is an epoxy resin based on DGEBA and cured with triethylene tetramine (8% per weight of epoxy), and post-cured at 120°C for 24 h.

A Dynastat and Dynalizer apparatus was used for the measurement of the moduli E' and E'' . This apparatus could apply a sinusoidal load of maximum amplitude 100N on a cylindrical specimen mounted between a long upper rod connected to a load cell and a short lower rod coupled to a displacement transducer and connected to a motor, which was a coil, suspended in the gap of a permanent pole magnet. By passing a servo-controlled current through the coil, the specimen could be subjected to various sinusoidal loads of prescribed amplitude and frequency. By taking into account the rigidity of the load cell and the type and dimensions of the specimen, the storage and loss moduli may be calculated. Measurements were carried out at frequencies from 0.1 to 100 Hz and at temperatures of 40–130°C.

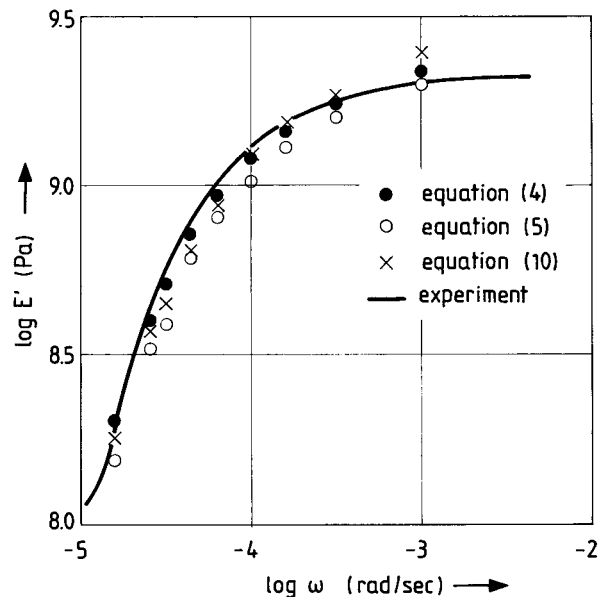


Figure 2 Master curve of storage modulus for the epoxy resin: Solid line represents the experimental data; (●) represents eq. (4); (○) represents eq. (5); (×) represents eq. (10).

The obtained master curve from the various isotherms is plotted in Figure 2.

Apart of the dynamic mechanical properties, the stress-strain behavior in respect to the deformation rate has also been examined. Tensile stress-strain tests for linear polyethylene at three different strain rates, data taken from Matsuoka,² are presented in Figure 3.

On the other hand, compression stress-strain curves for two different rates of deformation for

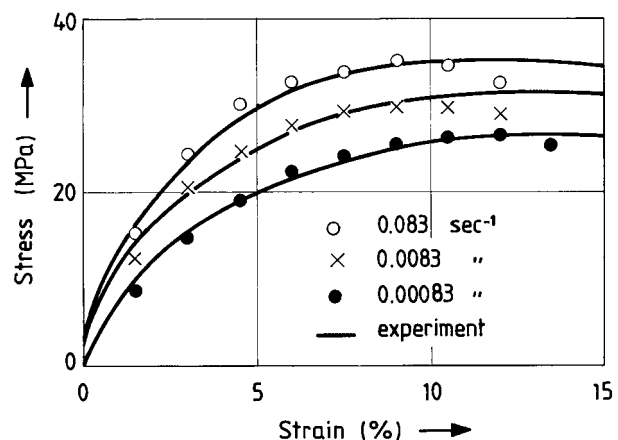


Figure 3 Tensile stress-strain data for linear polyethylene at three strain rates: Solid lines represent the experimental data of Matsuoka²; points represent the viscoelastic model combined with eq. (4).

the epoxy resin used, have also been obtained in Figure 5.

These tests have been carried out at room temperature, with an Instron 1121 type tester, at two strain rates 6.83×10^{-3} and $4.62 \times 10^{-4} \text{ s}^{-1}$. The corresponding curves are presented in terms of true stress versus true strain, where an isovolume type of deformation has been assumed.

RESULTS AND DISCUSSION

The relation between stress and strain, at small deformations, for a viscoelastic material can be described by the Boltzmann superposition principle, as follows:

$$\tau = \int_{-\infty}^t G(t-s) \dot{\gamma}(s) ds \quad (9)$$

where τ is the stress, $G(t)$ is the relaxation modulus, and $\dot{\gamma}$ is the rate of deformation.

On the other hand, the nonlinear viscoelastic behavior may be described with the use of nonlinear continuum models.

In all cases, however, it is necessary to define the modulus with an explicit mathematical function, such as eqs. (6) or (8).

Therefore, it is necessary to have a discrete relaxation spectrum H that can be determined by fitting a set of parameters to the experimental data. Then, a form of $G(t)$ can be obtained, resulting in a constitutive equation, able to describe the corresponding stress-strain data.

However, the problem is more interesting and more complex if the relaxation spectrum obtained with this procedure can be treated as a material characteristic.

For the case of linear polyethylene, the parameters associated with the two power laws of eq. (4) have been evaluated using eq. (6) for $G'(\omega)$ in respect to the experimental data for $E'(\omega)$ of Figure 1. The relationship $G = E/2(1 + \nu)$ has also been taken into account, where the Poisson ratio ν was taken equal to 0.3.

The fitting of parameters in all cases, as well as all the calculations, have been made with the use of the software "Mathematica".¹²

The estimated values of these parameters are summarized as follows: n_e equals 0.1; n_g equals 0.01; λ_c equals 100 s; λ_{\max} equals 10^4 s; and g_0 equals 600 MPa.

For the same material, linear polyethylene, the formula of relaxation spectrum given by the prob-

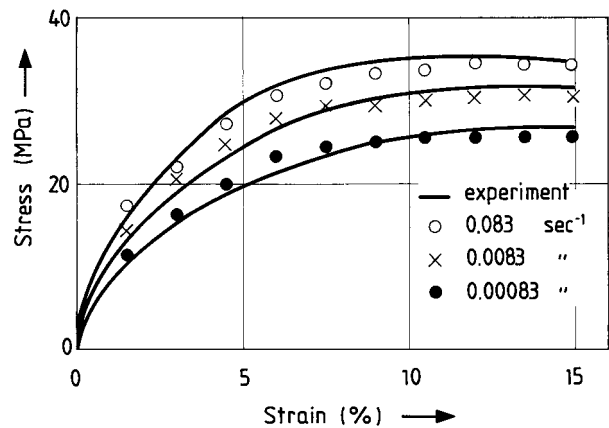


Figure 4 Tensile stress-strain data for linear polyethylene at three strain rates: Solid lines represent the experimental data of Matsuoka²; points represent the viscoelastic model combined with eq. (5).

ability density function of eq. (5) has also been used in an analogous procedure.

The results of both treatments are shown in Figure 1, where a similar approximation to the experimental data has been obtained.

After the function for H has been evaluated, eq. (8) has been combined with eq. (9) for the description of tensile data of Figure 2. Parameter h was fitted to be equal to 2.

The numerical evaluation of eqs. (8) and (9) has been made with the above-mentioned software. The results for three different strain rates are shown in Figures 3 and 4.

It must be mentioned here that the relaxation spectrum of eq. (4) deals with the glass transition and chain disentangling, while the experimental data of Figure 1 are referring to the α -process of semicrystalline polymer, including also part of the above T_g (α -relaxation) region of the material. Therefore, the molecular parameters that are evaluated for the relaxation spectrum consist a combination of different relaxation regions, as it is also defined by the superposition of two terms in eq. (4).

From the other hand, the stress-strain experimental data of Figure 3 are carried out at room temperature, close to the reference temperature of experimental data of Figure 1. Moreover, in Figure 3, what can be termed small strain properties, i.e., tensile modulus and yield stress, is presented. Large-scale plastic deformation, cold drawing, and failure are not included. The non-crystalline portion of polyethylene is liquid-like or rubbery at room temperature. One of the earliest treatments,¹³ has considered the elastic modulus of PE to result from deformation of amorphous

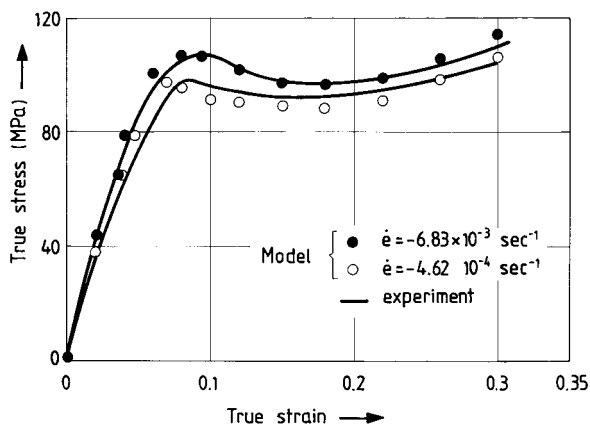


Figure 5 Compression stress–strain data for the epoxy resin at two different strain rates: Solid lines represent experimental data; points represent the viscoelastic model combined with eq. (4).

“tie molecules” obeying inverse Langevin statistics. The correspondence between tensile behavior and melt elasticity is consistent with rubber-like elasticity manifested through entanglements. After the initial elastic part of the stress–strain curve, macroscopic yielding is assumed to be controlled by the onset of slip within the lamellar crystals, provided that the amorphous regions are compliant and weak compared to the crystals. At room temperature, where the α -process is already activated, intracrystalline shear is facilitated by thermally generated twist or kink defects.¹⁴ This irreversible shear of the crystallites has been demonstrated by Young et al.¹⁵ by X-ray studies.

Due to the above-mentioned mechanisms, parameters associated with the spectrum of eq. (4), representing the viscoelastic behavior of linear polymers in the flow and entanglement regime, can be used for the description of yield behavior of PE at small deformations.

Besides, concerning the relaxation spectrum of eq. (5), it has been defined for the transition zone, or stage 2 of relaxation,² associated with the external viscosity, which resists the tendency of chains to slip past their neighbors. As it is observed from Figure 4, the same parameters, evaluated from fitting the experimental data of Figure 1 with eq. (5), were able to predict the stress–strain curve of PE.

Following the same procedure for the epoxy resin, it has been found that the two power laws relaxation spectrum of eq. (4) can be fitted well to the experimental data of Figure 2 with the associated parameters taking the values: n_e equals n_g equals 0.4, λ_e equals 100 s, λ_{\max} equals 10^4 s, and g_0 equals 1200 MPa.

Using these parameter values to the constitutive eq. (9), the compression stress–strain data could be predicted, as shown in Figure 5, for two different strain rates. A more detailed analysis for yield behavior, including temperature and rate effects on yield stress, has been made elsewhere,¹⁶ where the dependence of relaxation time on yield stress has been taken into account. The complete description of the yield behavior of the epoxy tested, including the strain hardening, could be made with the addition of an extra term in eq. (9), corresponding to the G_e term of eq. (8), related to the resistance to the plastic flow of the material. The value of G_e was fitted to be 350 MPa. This parameter denotes the deformation resistance that the material has to overcome once molecular alignment occurs, altering the configurational entropy. Instead of this term, a back stress tensor may be alternatively introduced, related to the gradient of the entropy change.¹⁷

Under constant rate straining, glassy polymers show nonlinear viscoelastic behaviors, such as yielding and cold flow. Various models have been proposed to explain this behavior, taking into account some structural change in the polymeric structure.¹⁸ Recently, experimental results have been reported, verifying the shear induced structural transition in various polymer glasses. Agreement in relations between activation enthalpy and activation entropy for the steady plastic flow in the post-yield range and the corresponding ones in the molten state of the same polymer constitute direct evidence for the transition of the glass structure into liquid one in the post-yield range. Therefore, a change in the relaxation mechanism in the largely deformed glass has been verified, leading to a satisfactory description of the stress–strain data of Figure 5, with molecular parameters referring to eq. (4) and associated with glass transition and entanglement regime.

On the other hand, the normal distribution function of relaxation times, defined by eq. (5), was not possible to describe the stress–strain behavior of the epoxy with the same parameter values used for the fitting of the storage modulus of Figure 2.

Considering that epoxy is mainly characterized by a chemical network with rather short molecular chains with decreased flexibility, it has been assumed that the term of eq. (4) related to the entanglements should be omitted. By taking into account only the first term of eq. (4), the master curve of Figure 2 was fitted satisfactorily in the transition region. The parameter values were n_g

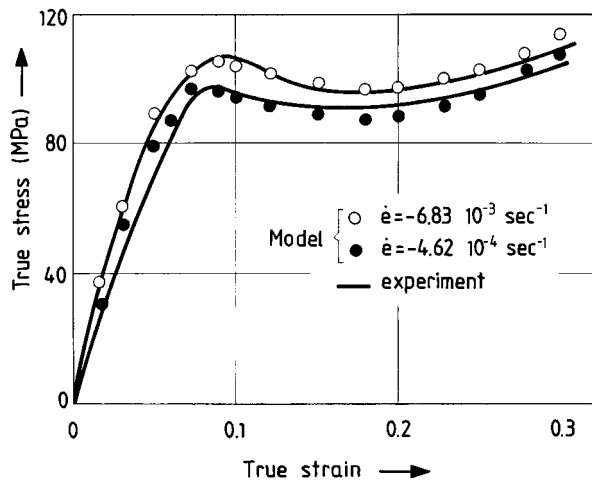


Figure 6 Compression stress–strain data for the epoxy resin at two different strain rates: Solid lines represent experimental data; points represent the viscoelastic model combined with eq. (10).

equals 0.1 and λ_c equals 100 s. The relaxation spectrum H then takes the form

$$H(t) = g_0 \left(\frac{t}{\lambda_c} \right)^{-n_g} \quad (10)$$

and is consistent with the well-known Rouse model, describing stage 2 of relaxation. The same parameter values used in the numerical evaluation of eqs. (8), (9), and (10) resulted to a satisfactory fitting of the stress–strain curves in Figure 6. Parameter G_e takes the value of 350 MPa.

From the above analysis, it is implied that the relaxation time spectrum based on the superposition of two power laws may represent a unique relaxation spectrum for different types of molecular structures. It has also been shown that this spectrum can be treated as a material characteristic and, consequently, may be used for the prediction of yield behavior of the material studied.

CONCLUSIONS

In this study, a method is presented of obtaining a relaxation time spectrum H equation, based on dynamic mechanical analysis experimental data. The relaxation time spectrum H has been defined following two semiempirical equations, developed mainly for linear flexible polymers. The determination of associated parameters has been made by fitting the data from dynamic mechanical ex-

periments in terms of a generalized Maxwell model. The parameters associated with spectrum H were defined as those that best approximate the entire range of experimental results.

The same procedure has been followed for the following two types of materials: a high molecular weight linear polyethylene, and a crosslinked epoxy resin.

The relaxation spectrum could then be treated as a material characteristic, leading to the description of the stress–strain behavior of these materials with the same set of parameters, in terms of a viscoelastic constitutive equation.

It has been found that for both types of materials, the relaxation spectrum H based on the superposition of two power laws expresses an explicit function for the relaxation modulus $G(t)$.

Concerning the epoxy resin, a power law analogous to that of Rouse's theory for H , but with a different exponent value, leads to a satisfactory prediction of the relaxation modulus and, consequently, the yield behavior of the material.

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