

# Some New Operational Modes and Parameters of Stress Relaxation for the Viscoelastic Characterization of Solid Polymers. II. The “Vertical-Shift” Mode and Intrinsic “Time–Strain Clock”

V. N. Kytopoulos, G. D. Bourkas, E. Sideridis

National Technical University of Athens, Department of Engineering Science, Section of Mechanics, 5 Heroes of Polytechnion Avenue, GR-157 73 Athens, Greece

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**ABSTRACT:** As in part I of this study, in the same manner in the present part II as well, by the same *modus operandi* way, an attempt was made to introduce, by means of a given operational mode, some further practical parameters for a “by-eye” but well-proven experimental viscoelastic characterization of a polymeric solid. Thus, through consideration of the peculiar vertical shift behavior of the apparent modulus ( $\bar{E}$ ) of isotactic polypropylene (iPP) and based on the KWW model, it is shown that, in an empirical and a formalistic sense, a relevant effective or equivalent (single) characteristic relaxation time can be introduced which can give some new interpretations for the linear and nonlinear viscoelastic behavior of a polymeric material, as that of a “time–strain clock,” which, as an intrinsic function, is responsible for a functional time–strain shift of the relaxation

time and, at the same time, for a shift toward to a more linear or to a more nonlinear behavior. In the above context of attempts, another functional relationship was shown, the so-called spectral shift function and its corresponding parameter of nonlinearity strength, through which some further interpretations and characterizations connected with the existence of the permanent internal stress could be made. Finally, the introduction of the so-called spectral isostrains and their corresponding “spectral inversion point” complete the “set” of the operative parameters proposed for the above-mentioned purpose. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 138–148, 2003

**Key words:** poly(propylene) (PP); relaxation; modeling; viscoelastic properties; modulus

## INTRODUCTION

Just as spectral analysis of thermal radiation, and, after that, spectroscopy, in general, contributed to the most detailed characterization and in-depth study of a material in physics, in the same way, the “spectral” distribution of the relaxation modulus, that is, the so-called mechanical spectroscopy, contributed to the study of the polymers’ mechanics. Thereby, there have been, and are still, huge research efforts to find the relaxation “spectrum” through experimental and theoretical facts. The most popular experimental methods were, and still are, the ones of Alfrey and Ferry–Williams,<sup>1,2</sup> which describe the zeroth (Alfrey) and first and second degrees (Ferry–Williams) of approximations. The Tobolsky<sup>3</sup> method has a quite limited application, as it *a priori* accepts a general, very simple distribution (box distribution) which mainly describes only the high spectrum times. Here, we should refer to the recent experimental study<sup>4</sup> where the relaxation time spectrum is approached by a Gaussian spectral

distribution in order to describe the stress-relaxation behavior of isotactic polypropylene (iPP) over a wide range of strain, time, and temperature by means of extended numerical computational steps. On the other hand, it is generally accepted, by almost all experts, that Alfrey’s method is the most practical one and, therefore, we intend to apply it to some following calculations for the evaluation of the corresponding parameters.

Apart from the spectrum itself, the meaning of the relaxation time has great importance. The determination of a “characteristic” relaxation time, which will describe the viscoelastic behavior of a material, is, today, a subject for the study of polymers. For this purpose, so far, we distinguish two basic ways: the theoretical and the experimental. In the first way, it is introduced indirectly by means of several notions, such as the so-called stress–clock function,<sup>5</sup> volume clock,<sup>6</sup> and total strain<sup>7</sup>—a new interpretation of the relaxation time. Here, we have to remind one of the older notion of the temperature-dependent intrinsic time, which was already introduced by Leaderman in 1943.<sup>8</sup>

In the second more empirical and more direct way, we distinguish mainly the experimental studies,

Correspondence to: V. N. Kytopoulos.

where, by means of some general models such as the KWW,<sup>9</sup> the power Law,<sup>9</sup> and the logarithmic-law of Matsuoka,<sup>9</sup> an attempt is made to find out a single characteristic time.

In part II of this investigation, we introduce and try to prove using the so-called *modus operandi* way new notions of some operative parameters such as of the single effective characteristic relaxation time, spectral shift function, and spectral inversion point which can describe in a relatively more practical supplementary and/or complementary manner the viscoelastic behavior of solid polymers.

### GENERAL THEORETICAL CONSIDERATIONS

A basic and practical method for the determination of a characteristic relaxation time is the adjustment of the experimental relaxation data on several semiempirical functions, which, used as models, will eventually be able to describe the molecular mobility of a material. Also, from the correlation coefficient  $r^2$  of the best fit, it will be possible to extract some essential conclusions for each model. One of the most "flexible" and versatile models is the Kohlrausch one (or KWW), which is amply used for describing the polymers' mechanics on a macrostructural and microstructural basis.<sup>9,10</sup> This model is expressed by a function of the relaxation modulus as follows:

$$E(t) = E_0 \exp[-(t/\tau_c)^n] \quad (1)$$

Kohlrausch had already discovered, in 1847, that the above equation could well approach the following one:

$$E(t) = \int_0^\infty g(\tau) \exp[-t/\tau] d\tau \quad (2)$$

which, in turn, can mathematically be expressed as

$$\lim_{N \rightarrow \infty} \sum_{i=1}^N E_0 \exp[-t/\tau_i] = \int_0^\infty g(\tau) \exp[-t/\tau] d\tau \quad (3)$$

This last relation describes, in other words, a viscoelastic body with an infinite number  $N$  of Maxwell elements, in a parallel connection, and is also known as the Maxwell-Wiechert body. In the Kohlrausch equation, the parameter  $n$  characterizes the line width of the spectral distribution of the relaxation time itself. Therefore, if  $n = 1$ , the spectrum consists of one line, which means that there is only one active mode of relaxation time for the whole body. As  $n$  is reduced, the distribution becomes wider and this means that there are more active modes of relaxation times.

TABLE I  
Parameters of Polymer Material

Property	
MFI (230°C/2,16 kg)	15.4
MFI (190°C/2,16 kg)	6.1
$M_w$	257,500
$M_n$	59,000
$D$	4.3

In the same equation,  $\tau_c$  is a characteristic relaxation time which is required for the reduction of the initial modulus  $E_0$  to  $1/e$  of the initial value. Consequently, this model is very simple and practical as it describes the viscoelastic behavior through only three parameters:  $n$ ,  $\tau_c$ , and  $E_0$ . Therefore, apart from the fact that, in most cases and with the help of best fit, this model approaches well and satisfactorily the experimental facts, it has also a basic natural notion in connection to the kinetic mechanisms of the molecular mobility.<sup>9</sup> Of course, it is necessary to point out that these three parameters are consecutively changing under deformation (stress) and temperature.

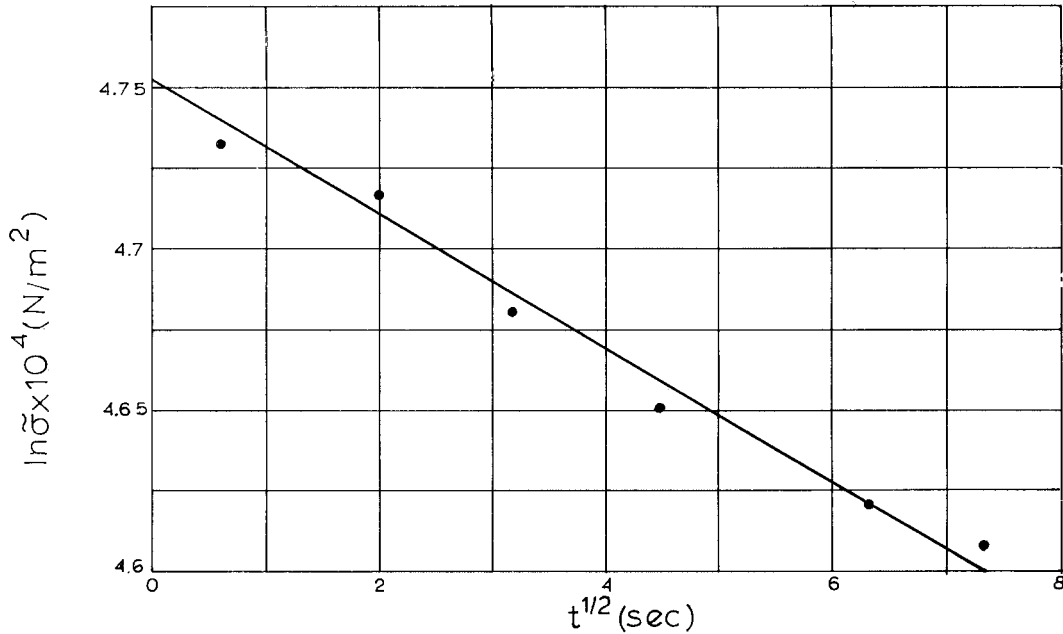
Another empirical model which often correctly describes the relaxation phenomena is the one shown below with the following simple equation (power law):

$$E(t) = E_0 (t/\tau_c)^{-\beta} \quad (4)$$

It is well known that, in general, the KWW model should describe very well the viscoelastic behavior of a solid polymer in the first stage of the relaxation spectrum (solidlike state) while the power law should respond in the second stage (transition) of the spectrum. In this sense, estimations give  $n \cong 0.5$  and  $\beta \cong 0.6$  for polymers in a thermodynamically equilibrium state.<sup>9</sup>

### EXPERIMENTAL

Particular knowledge of certain constructive parameters on every polymer material, other than general properties and definitions, is required before the material enters the experimental stages. Some of these parameters, like the melt-flow index, (MFI), the molecular mass and weight distribution, and the heterogeneity index ( $M_n$ ,  $M_w$ ,  $D$ ), are given in Table I. Further characteristics of the PP used can be found in the references given in part I of this study. Isotropic materials were obtained at 150°C from compression-molded sheets with a thickness of 0.30 cm. The sheets were afterward cooled at room temperature. From these sheets, dog-bone specimens were cut which were tested in stress relaxation. All tests were carried out at room temperature ( $\approx 24^\circ\text{C}$ ) and using an Instron-type tensile machine.



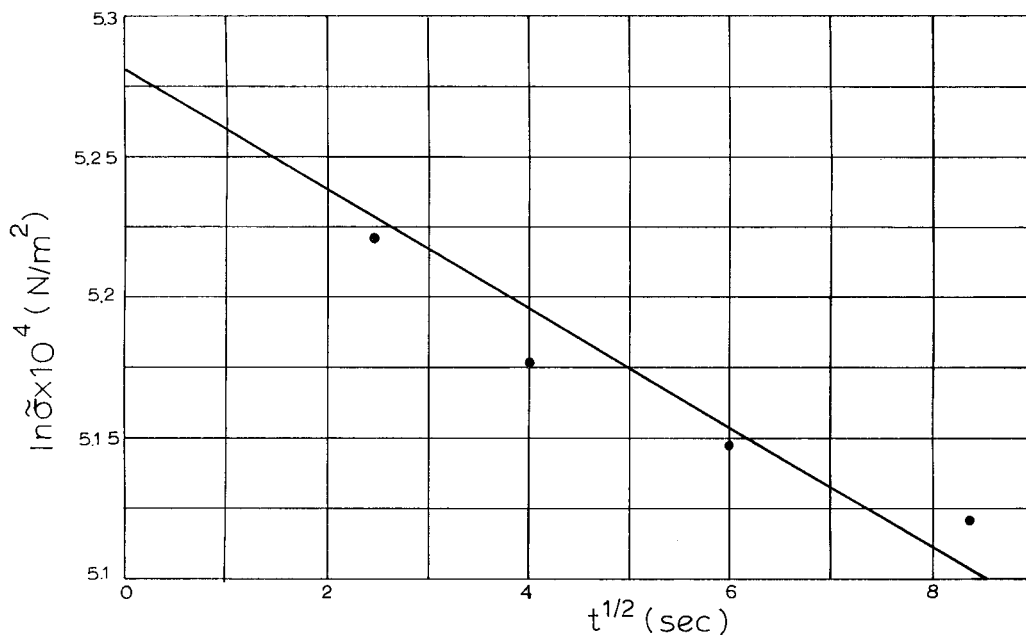
**Figure 1** Linear regression best-fit plot of apparent stress the evidence of response to the KWW model,  $\epsilon_0 \cong 1\%$ . Linear regression:  $y = \alpha + \beta x$ , with  $y = \ln \bar{\sigma}$  and  $x = t^{1/2}$ ,  $r^2 \approx 0.98$ ,  $n \approx 0.5$ .

**RESULTS AND DISCUSSION**

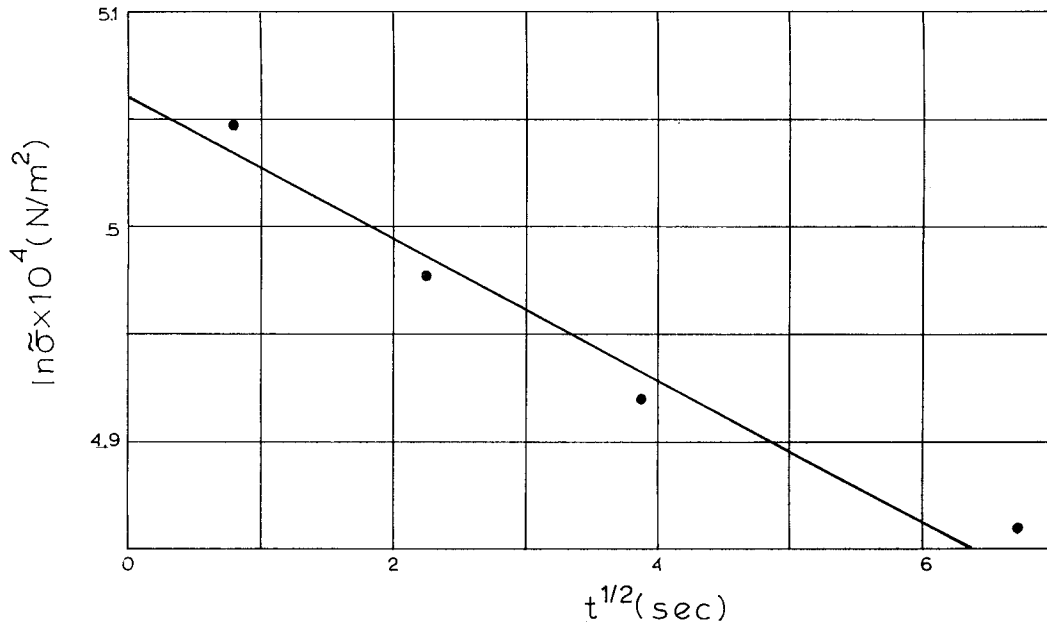
**Formalistic estimations of an effective characteristic relaxation time**

Already in part I of this investigation from the first experiments, it appeared that, for the apparent modulus  $\tilde{E}$ , there is a general trend for a better response of the KWW model than the power law model. The

above-mentioned apparent modulus is defined as that modulus which derives from experimentation with a finite loading time. The supplementary measurements carried out in this article better confirmed and proved this trend. Thus, for example, in the plots of Figures (1) and (2), the curves for the response of the apparent stresses,  $\bar{\sigma}$ , to the KWW model using linear regression in the form  $\ln \bar{\sigma} - t^{1/2}$  are given for different initial



**Figure 2** Linear regression best-fit plot of the apparent stress relaxation for evidence of response to the KWW model,  $\epsilon_0 \approx 2\%$ . Linear regression procession as in Figure 1,  $r^2 \approx 0.97$  and  $n \approx 0.5$ .



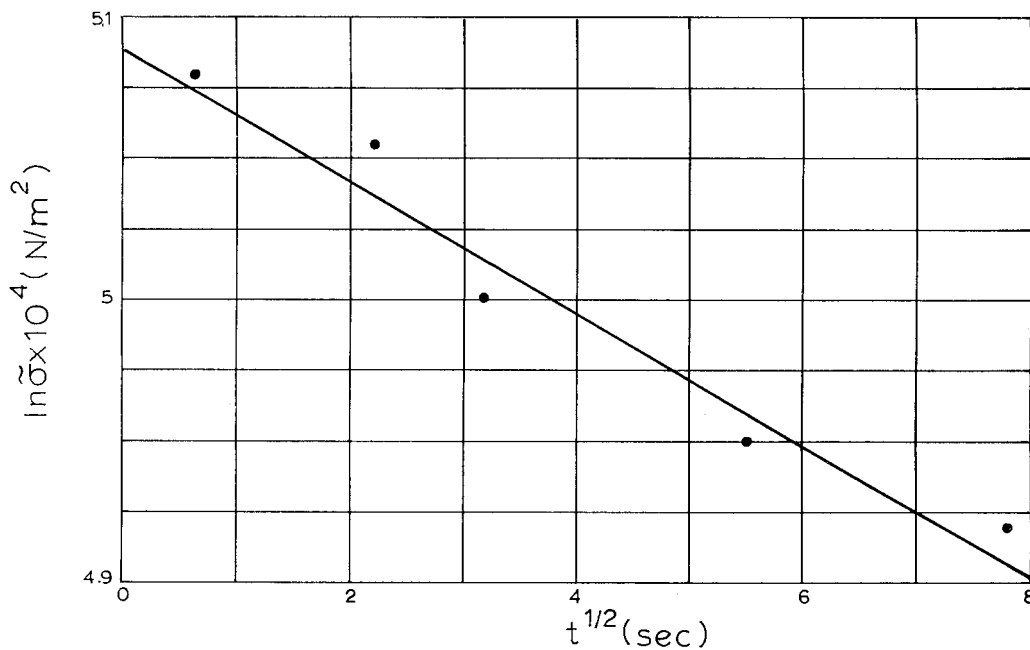
**Figure 3** Linear regression best-fit plot for KWW response at  $\dot{\epsilon}_0 \approx 10^{-3}$  ( $n \approx 0.5$ ,  $r^2 \approx 0.98$ ).

strains. In this way, in each curve of these figures, the parameters of the respective best-fitted function was found by the aid of Table Curve-2D fitting software of Jandel Scientific. Herefrom appears the relatively good stability of the model from the relatively small variation of the correlation coefficient  $r^2$ . The stability of the model becomes more evident even from the little influence of the strain rate appearing in Figures (3)–(5).

The power-law model is shown in the linear  $\ln - \ln$  plot of Figure 6, from where we assess a constant

power index  $\beta \approx -0.3$  for various strains. This value is in contradiction with that given by Matsuoka,<sup>9</sup> where  $\beta \approx -0.6$ . Therefore, by taking as the “correct” model the KWW one, because it fits very well the experiments for  $n \approx 0.5$ , the value given by Matsuoka,<sup>9</sup> we shall use it as a reference model in this work.

Now, taking into consideration the aforementioned remarks and based on the KWW model, we can go through a formal “transformation” to an equivalent nonlinear modulus:



**Figure 4** Linear regression best-fit plot for KWW response at  $\dot{\epsilon}_0 \approx 10^{-2}$  ( $n \approx 0.5$ ,  $r^2 \approx 0.97$ ).

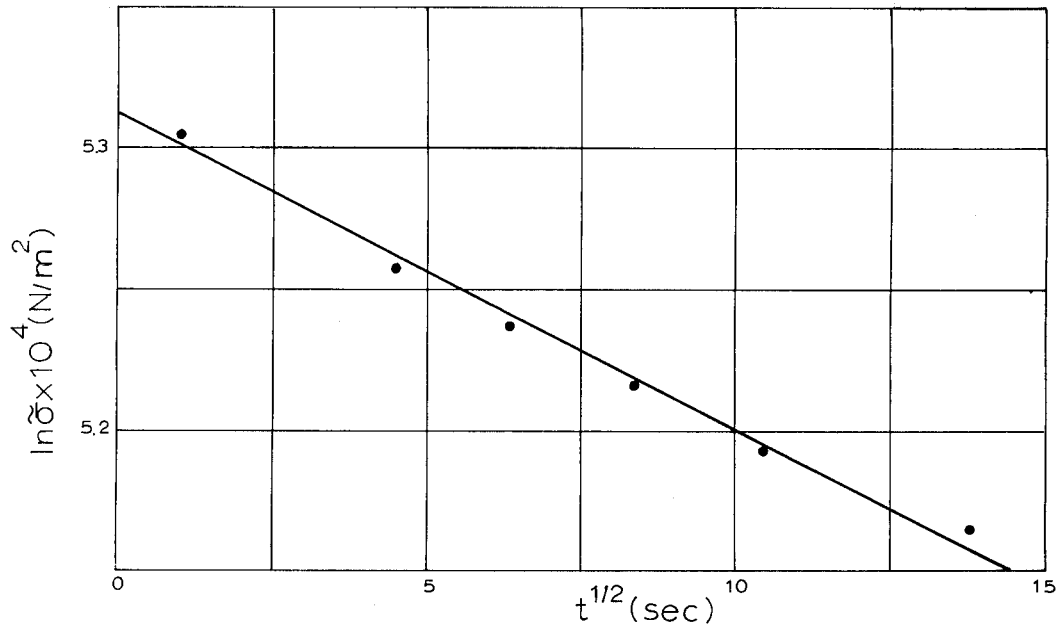


Figure 5 Linear regression best-fit plot for KWW response at  $\dot{\epsilon}_0 \approx 3 \times 10^{-2}$  ( $n \approx 0.5$ ,  $r^2 \approx 0.96$ ).

$$\begin{aligned} \tilde{E}_\epsilon(t) &= \tilde{E}_0 e^{-(t/\tau_c)^n} = \tilde{E}_0 e^{-t^n [1/\tau_c^n + B/t^n]} = \tilde{E}_0 e^{-(t/\tau_c)^n - B} \\ &= \tilde{E}(t)g(\epsilon), \quad \text{with } g(\epsilon) = e^{-B} \quad (5) \end{aligned} \quad \tilde{\tau}_c^n(\epsilon, t) = \frac{1}{1/\tau_c^n + B/t^n} = \frac{(\tau_c \cdot t)^n}{t^n + \tau_c^n \cdot B}$$

from where it is deduced that

or

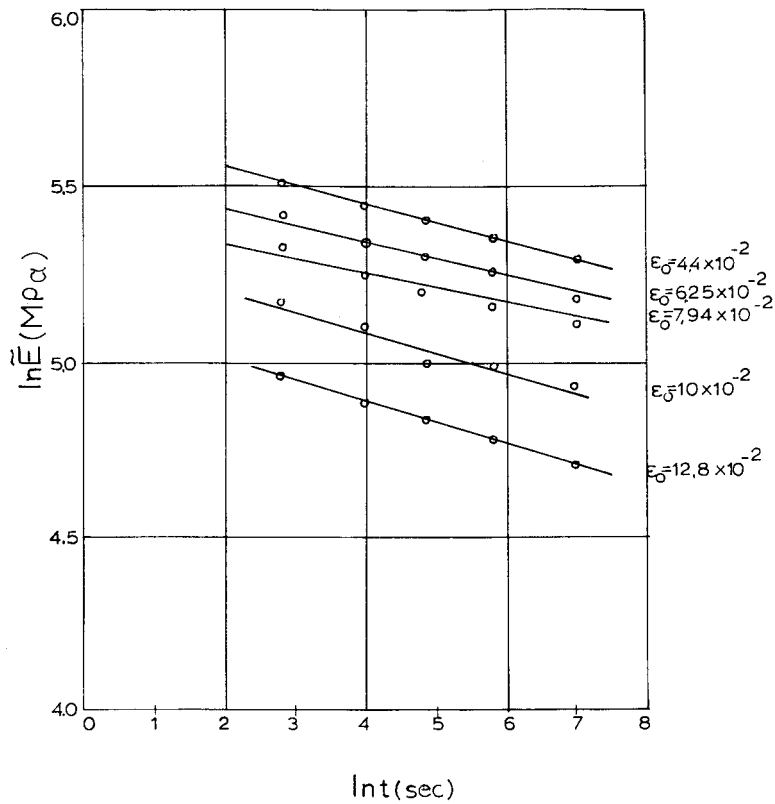


Figure 6 Plot for power-law response for different initial loading strains,  $\epsilon_0$  (for strain rate  $\approx 10^{-3}$ /s).

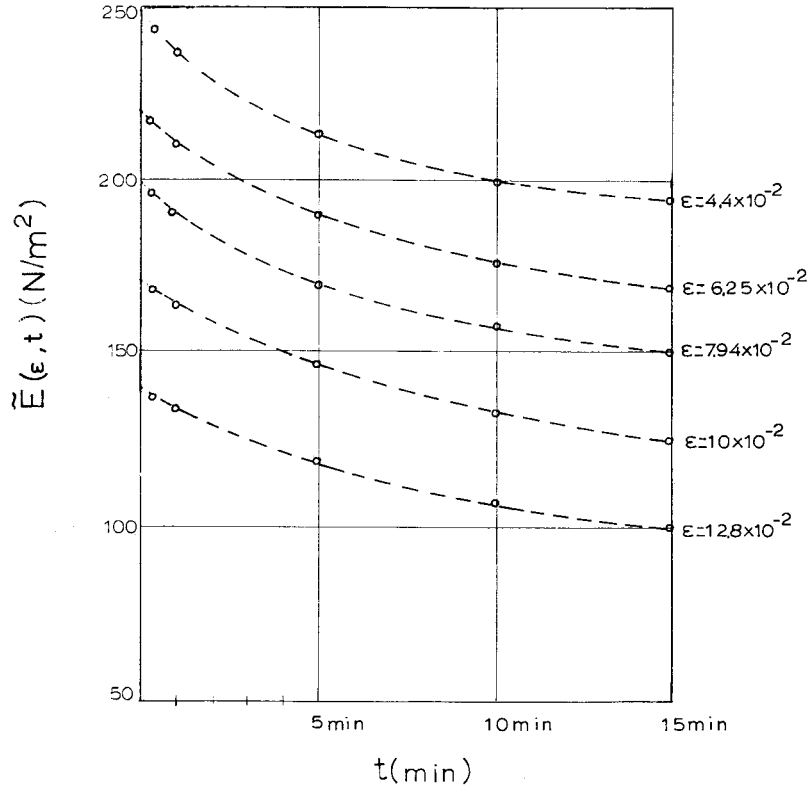


Figure 7 Vertical-shift evidence of the apparent moduli with deformational variation (for strain rate  $\approx 10^{-3}$ /s).

$$\tilde{\tau}_c(\epsilon, t) = \frac{\tau_c \cdot t}{t \left[ 1 + \left( \frac{\tau_c}{t} \right)^n B \right]^{1/n}} = \frac{\tau_c}{\left[ 1 + \left( \frac{\tau_c}{t} \right)^n B \right]^{1/n}} \quad (6)$$

[As will be shown later,  $B$  is a function of the strain (deformation)]. Based on this context, we can formally introduce a new effective or “equivalent” characteristic relaxation time  $\tilde{\tau}_c$ , which must be a function of both strain ( $\epsilon$ ) and observation time ( $t$ ). Of course, this occurs for a specific condition, that is,  $\tilde{E}_e(t) = \tilde{E}(t)g(\epsilon)$ , where the nonlinear modulus can be expressed as a product of two functions with different variables, that is, of the linear modulus and of a strain function.

At this place, it seems quite “attractive” to devise the notion of this equivalent characteristic relaxation time ( $\tilde{\tau}_c$ ) which could describe, in a different way, some physical aspects of the viscoelastic behavior. In this sense, eq. (6) could represent a evolution function with time for an increase of the internal viscosity, which leads to a “time-hardening” behavior as it occurs, for example, in a creeping material.

Now, from Figure 7, we can deduce a strong vertical shift of the modulus curves with the deformational variation. A similar shift was found also in ref. 4. Based on the curves of Figure 7, we calculated the vertical shift factor as follows: We considered as a reference the modulus  $\tilde{E}_e$ , which corresponds to strain  $\approx 1\%$ , where  $\tilde{E}_\epsilon \geq \tilde{E}_1 \approx \tilde{E}$  (linear). So, for a given time

$t = \text{const}$ , we measured the vertical distance of each curve from the time axis and we calculated the ratios:

$$\frac{\tilde{E}_1}{\tilde{E}_\epsilon} = g(\epsilon) \quad (7)$$

The curve calculated in this way is shown in Figure 8, while the following linear relation can be obtained:

$$\ln g(\epsilon) = A\epsilon_0 - c \Rightarrow g(\epsilon) = e^{A\epsilon - c} = e^{-B} \quad (A > 0, \quad c > 0) \quad (8)$$

and

$$B = -A\epsilon_0 + c \cong -1/3\epsilon_0 + 1.1 \quad (9)$$

After simple algebra, it can be shown that eq. (6) has sense only when  $t > (-B)^{1/n}\tau_c$  and for  $-B > 0$  or when  $\epsilon_0 > 3\%$ . These findings may be interpreted by the fact that, in the “early” steps of observation times,  $t < \tau_c$ , the “time-strain clock” of the viscoelastic nonlinearity is working well, and as time goes on, for  $t \gg \tau_c$ , this “clock” tends to remain in rest, which means that  $\tilde{\tau}_c(\epsilon, t) \rightarrow \tau_c = \text{const}$ .

Now, we can make, be it so, a formalistic correlation of eq. (6) with the notion of the stress-clock function.<sup>5</sup>

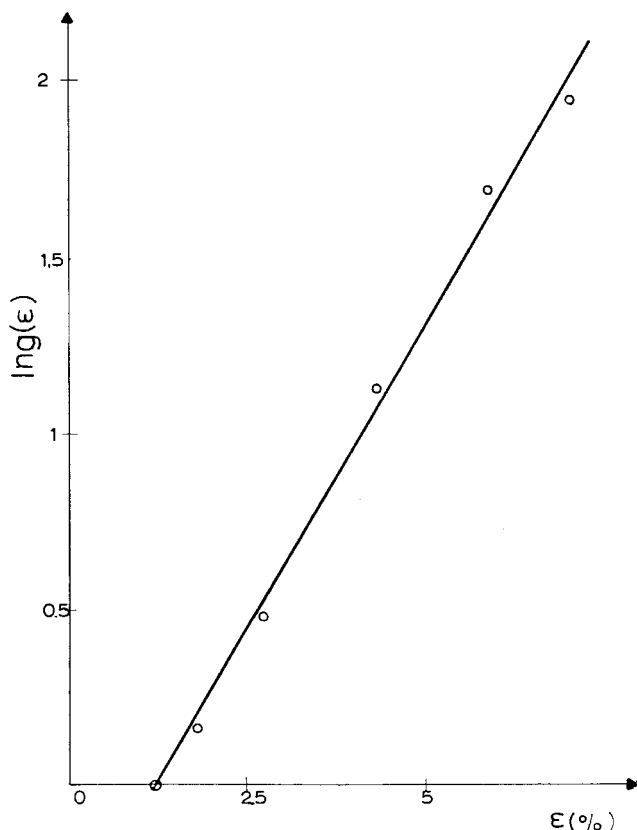


Figure 8 Logarithmic plot of vertical shift versus strains.

Thus, in that study for a simplified example of a Maxwell model, the relationship

$$E(t) = \frac{3kE(0)}{\varepsilon_0} \bar{\tau}_c \frac{1}{1 - K\bar{\tau}_c}$$

with  $\bar{\tau}_c = \tau_c/[b(\sigma)]$ , where  $b(\sigma)$  is the so-called stress-clock function, is given. Now, by comparing with eq. (6), we see that

$$b(\sigma) = \left(1 + \frac{\tau_c}{t} B\right)^{1/n} = f(t, \varepsilon)$$

thus having a "formal mapping" from the "stress space" to the "time-strain space," which is expressed by a time-strain clock function.

Consequently, because iPP presents a so-called general peculiar viscoelastic behavior, through the relation  $\tilde{E}_\varepsilon(t) = \tilde{E}(t)g(\varepsilon)$ , the nonlinear behavior can be expressed by the linear one, provided that  $g(\varepsilon)$  is known. Furthermore, if the  $\tilde{E}_\varepsilon(t)$  behavior of a polymer, for a given deformation  $\varepsilon$ , is known, it is possible to apply it on any other deformation. In this way, it is possible, when necessary, to apply many of the theoretical explanations stated in Appendices A/B and in part I of this investigation, related to the virtual modulus.

In this sense, eventually, for all polymers having the aforementioned general viscoelastic behavior, we can define an "intrinsic," characteristic relaxation time  $\bar{\tau}_c(\varepsilon, t)$ , which could modify the well-known notion of the "internal stress-clock function," connected to the nonlinear viscoelastic behavior and "rename" it, for example, an "internal time-strain clock function." From all the aforementioned, it can be argued that the nonlinear behavior of iPP, expressed by its general viscoelastic peculiarity [eqs. (5) and (7)] in conjunction with some other relatively more complicated methods and techniques of analyzing the nonlinearity, as, for example, in refs. 11 and 12, can be now studied more effectively.

### Formalistic approach of a more general characteristic relaxation time

Now, if we want to have a body model with a dashpot of an Eyring type (process activated-stress-biased dashpot), then this model is primarily turned into a nonlinear one. The Eyring's dashpot behavior can be expressed by the known relation

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left[-\frac{\Delta H}{RT}\right] \sinh\left[\frac{v\sigma}{RT}\right] \quad (10)$$

This relation is more accurate in expressing the material's behavior as it takes into consideration certain parameters, such as the temperature and the molecular mobility by the activation volume. Furthermore, we will try to better understand this problem.

If in the basic Maxwell-Wiechert model the "Newtonian dashpot" is substituted with an Eyring one, then for a stress relaxation with a given  $\varepsilon_0 = \text{const}$ , the following known differential equation is provided:

$$\dot{\sigma}/E_i = -[\dot{\varepsilon}'_0] \sinh(\sigma v_i/kT) \quad (11)$$

which we can integrate as

$$\int_{\sigma_0}^{\sigma_1} \frac{d\sigma}{\sinh(\sigma v_i/kT)} = -\int_0^t \dot{\varepsilon}'_0 E_i dt \quad (12)$$

Using the transformations  $z = \sigma$  and  $a = v_i/kT$ , we have

$$\int_{z_0}^{z_1} \frac{dz}{\sinh az} = \frac{1}{a} \text{Lnth} \frac{az}{2} = \frac{KT}{v_i} \text{Lnth}(v_i \sigma_i / KT2) \Big|_{\sigma_0}^{\sigma_1(t)} \quad (13)$$

Thus, the solution of eq. (11) is

$$\frac{kT}{v_i} \{\text{Lnth}[v_i \sigma_1 / KT2] - \text{Lnth}(v_i \sigma_0 / 2KT)\} = -At \quad (14)$$

where  $A = \varepsilon'_{0i} E_i$  ( $\varepsilon'_{0i}$  is a preexponential factor of the initial deformation rate).

If it is considered that, in general, the following relation is valid:

$$\frac{\nu\sigma}{2KT} \ll 1 \quad (15)$$

and also using the Taylor expansion, we have the approximation

$$\ln \left[ \text{th} \left( \frac{\nu_i \sigma}{2KT} \right) \right] \cong \ln \left[ \frac{\nu_i \sigma}{2KT} \right] \quad (16)$$

Then, eq. (14) is modified as

$$\ln[\sigma_1/\sigma_0] = -At\nu_i/KT \quad (17)$$

$$\sigma_1/\sigma_0 = \exp[-At\nu_i/KT]$$

and taking  $\sigma_0 = \sigma(t = 0)$ , we have

$$\sigma_1(t) = \sigma(0)e^{-t/\tilde{\tau}_i} \quad \text{and} \quad E_i(t) = E_i(0)e^{-t/\tilde{\tau}_i} \quad (18)$$

where

$$\tilde{\tau}_i = \frac{kT}{E_i \nu_i} \frac{1}{\varepsilon'_{0i}} = \text{const [s]}$$

and which is an equivalent or an effective elementary relaxation time. In other words, eq. (18) represents the general form of an "effective nonlinear Maxwell element" with its corresponding "effective" relaxation time  $\tilde{\tau}_i$ .

Now going from a discrete distribution to a continuous one, we have

$$\lim_{N \rightarrow \infty} \sum_{i=1}^N E_i(t) = \int_0^{\infty} g(\tilde{\tau}) e^{-t/\tilde{\tau}} d\tilde{\tau} = E(t) \quad (19)$$

with  $\tilde{\tau}_i \rightarrow \tilde{\tau}$ . Using the Kohlrausch principle, we have

$$E(t) \cong E(0)e^{(-t/\tilde{\tau}_c)^n}, \quad (20)$$

with  $\tilde{\tau}_c = f(\varepsilon_0, T, \bar{\nu})$ , where  $\bar{\nu}$  is an equivalent activation volume, which represents the molecular and the morphological states of the polymeric solid.

Of course, all the above-mentioned are based on the assumption given by relation (15), which is valid if we take some experimental data known for PP, such as "activation volume" =  $\nu \leq \ln m^3 = 10^{-27} m^3$ ,  $\sigma_{\max} \leq 1 \text{ kp/mm}^2 = 0.1 \text{ MPa}$ ,  $T \cong 300 \text{ K}$ , from which we can estimate

$$\frac{\sigma_{\max} \nu}{2KT} \cong 10^{-2} \ll 1$$

that is, condition (15). From the above-mentioned, it can be argued that the effective characteristic relaxation time  $\tilde{\tau}_c$ , which we have introduced, may be of a more general form than those given in eq. (6). In this sense, we would be able to express it as  $\tilde{\tau}_c = f(\varepsilon, \bar{\nu}, T, \sigma, t)$ . For this function, we can give the following simple formalistic interpretation and/or correlations: The strain dependence can be related to the "total strain" model of Valanis<sup>7</sup> and/or to eq. (6); the volumetric dependence, to the "volume-clock" model of Shay and Caruthers<sup>6</sup>; the stress dependence, to the "stress-clock" model of Bernstein and Shokooch<sup>5</sup>; the temperature dependence, to the temperature-dependent intrinsic time model of Leaderman<sup>8</sup>; and, finally, the time dependence, to eq. (6).

### Spectral shift function

The apparent relaxation spectrum  $\tilde{H}(\tau)$  of iPP was estimated through Alfrey's approach as follows:

$$\tilde{H}(\tau) = - \left. \frac{d\tilde{E}(t)}{d \ln t} \right|_{t=\tau} \quad (21)$$

Consequently, for a precise calculation of the "Alfrey's slopes," it is necessary to use an apparent modulus curve with a logarithmic time scale. Such curves are shown in Figure 9, where  $\tilde{H}(\tau)$  is given by the slope of each curve which changes with strain  $\varepsilon_0$ . Figure 10 was constructed in a similar way, taking for the ordinate the slope values from the  $\sigma(t) - \ln t$  plots. The plot in Figure 10 is the so-called Lee's technique for the evidence of the permanent internal (strain-induced) stresses. Now, we can see that, by extrapolating to a "zero slope" (spectrum), it still remains a negative stress (strain), that is, we should have, after unloading, permanent (residual) internal stresses in the material.

The final plot of the spectral curve  $\tilde{H}(\tau)$  is given in Figure 11, from which the following linear equation arises:

$$\tilde{H}(\tau) \cong -a\varepsilon + \beta \quad (22)$$

with  $a \cong 1$  and  $\beta \cong 1.1 \text{ MPa}$ , meaning that we have the behavior of a linear spectral shift with the deformational change.

From the above equation, we can deduce three characteristic parameters which can, in more detail, characterize a material. These are  $a$ , the viscoelastic nonlinearity strength,  $\beta$ , the "zero" strain spectrum which approaches the one of linear behavior (for very small deformation), while  $\varepsilon_c = \beta/a$  is a fictive-critical strain



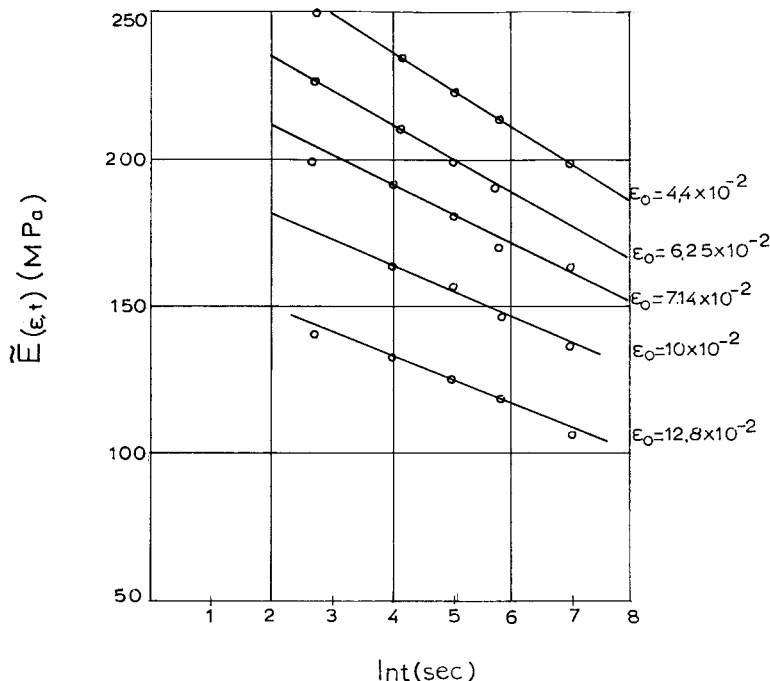


Figure 9 Logarithmic time plot of relaxation moduli (Alfrey's slopes) for different loading strains.

point at which the spectrum "vanishes," in the sense of passing into the viscoplastic state. Here, the flow of the material accelerates the slippage phenomena between the macromolecules and the "physical meaning" of the elastic modulus disappears.

From the above, it is deduced that the Alfrey's approach given by eq. (21) was applied on a nonlinear material, and, therefore, in conjunction with the peculiar eq. (5), we can similarly assume that  $\tilde{H}_\epsilon(\tau) = \tilde{H}(\tau)g(\epsilon)$ , from where it is concluded that

$$\tilde{H}_\epsilon(\tau) = - \left[ \frac{d\tilde{E}(t)}{d \ln t} \right] [g(\epsilon)] = -a\epsilon + \beta \cong -\epsilon + 1.1 \quad (23)$$

In the first parentheses, we have the (Alfrey's) linear spectrum, which, as shown before, can be well approached for  $\epsilon \rightarrow 0$  (or for a very small deformation) by giving a value of about 1. Now, from the above, we can extract the following relation:

$$g(\epsilon) \cong \epsilon - 1 \quad (24)$$

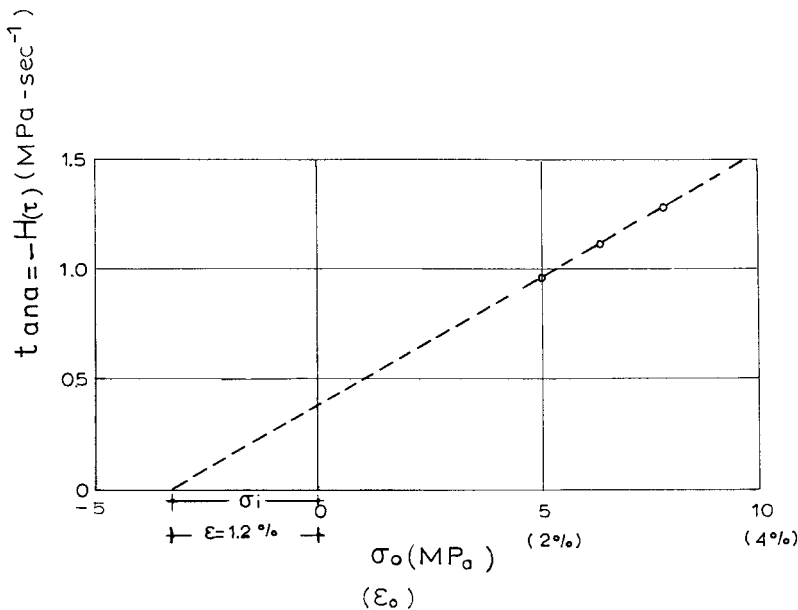


Figure 10 Changes of Alfrey's slopes with stress (strain) (for strain rate  $\approx 10^{-3}/s$ ).

This function is similar to Figure 10, which, as mentioned, gives us the slope changes, as shown in Figure 9, for different loading strains. By taking  $\varepsilon = 0$  from eq. (24), we have  $g(\varepsilon) \cong -1$ , that is, it is a "negative" or fictive spectral distribution, which must lead to the existence of "negative" or remanent internal stresses. From all the above, we can corroborate the existence of the peculiar, nonlinear, viscoelastic behavior of iPP, given by eqs. (5) and (6), and, at the same time, the existence of the internal residual stresses.

**Spectral inversion point and "isostrains"**

From the relationship  $\tilde{H}(\tau) = \tau g(\tau)$ , we arrive at the relation

$$g(\tau) = \frac{\tilde{H}(\tau)}{\tau} = \frac{h}{\tau}, \quad \text{where } h = \text{const} \quad (25)$$

This constant is derived from Figure 9, where, for a given deformation (strain) and according to Alfrey's approach, we obtain a constant spectrum (boxlike distribution) during the experimental observation time. The aforementioned equation is a hyperbola, with some characteristic points such as  $\tau_s = \sqrt{h}$  and  $a_s = \sqrt{2h}$ , as shown in the sketch of Figure 12.

For a given known  $h = \tilde{H}(\varepsilon)$  taken from Figure 11, we can now construct the curves of Figure 13, which

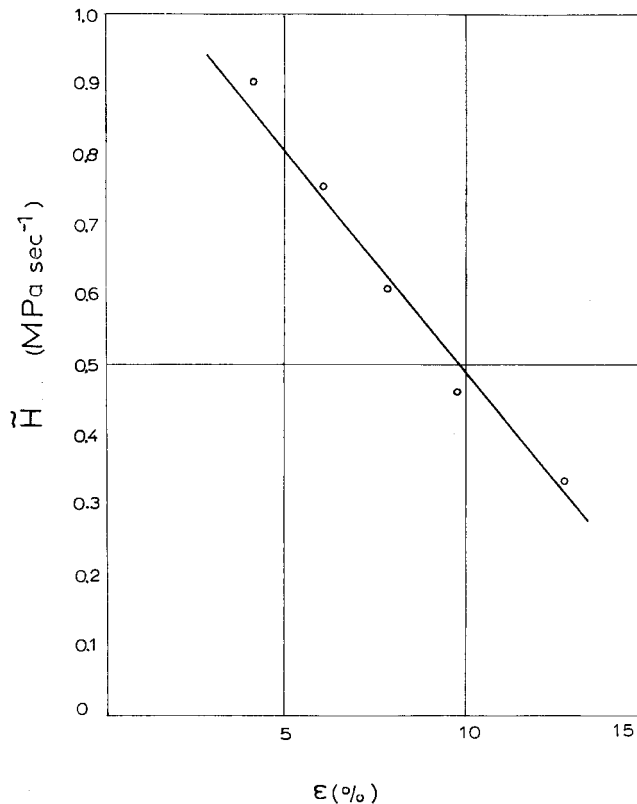


Figure 11 Strain dependence of the spectral density.

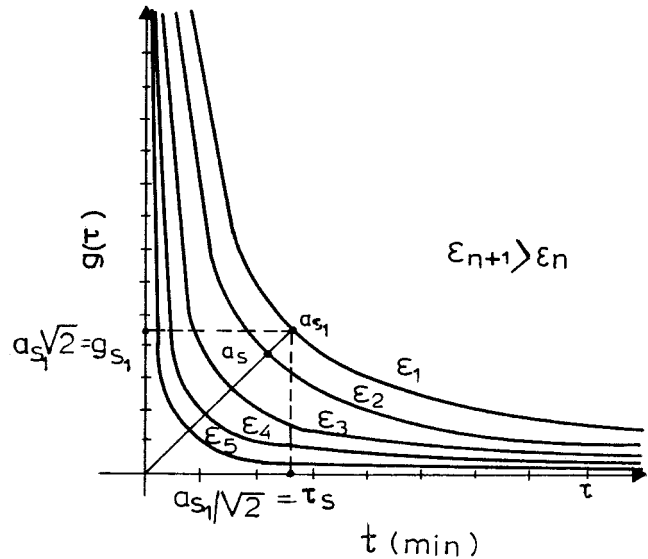


Figure 12 Schematic characteristic points of the spectral isostrains (hyperbolas).

are the hyperbolas for constant deformations, and call them spectral "isostrains." Therefore,  $a_s$  may represent a kind of shift factor and, at the same time,  $\tau_s = a_s/\sqrt{2}$ , an "inversion point" of the spectral density  $g(\tau)$ . In other words, this point can exist in the sense that the maximal change in the rate of the spectral density coincides with the point of maximum curvature. Therefore, for  $\tau > \tau_s$ , the density  $g(\tau)$  changes very slowly, while for  $\tau < \tau_s$ , it changes very fast. In this context, this point can be further regarded as a critical "metastable" point of the spectral density. Thus, the greater is  $\tau_s$ , the slower is the transition from linear to nonlinear behavior. This means, in conclusion, that, with an increasing strain, the material's "instability" of the linear viscoelastic state increases and that, at the same time, the material behaves as a more nonlinear viscoelastic.

**CONCLUSIONS**

In this article, there has been an effort to introduce, in a modus operandi way, certain effective-notional parameters for a more practical characterization of the linear and nonlinear viscoelastic behavior of polymers using the example of iPP.

Depending on the algorithmus used and its parametric response, this effort has shown the following:

- (a) Through approximations made by the aid of the Best-Fit software, it has been shown that iPP is satisfactorily characterized by the KWW model and less satisfactorily by the power law. Based on this evidence, the KWW model was taken as a reference for all purposes.

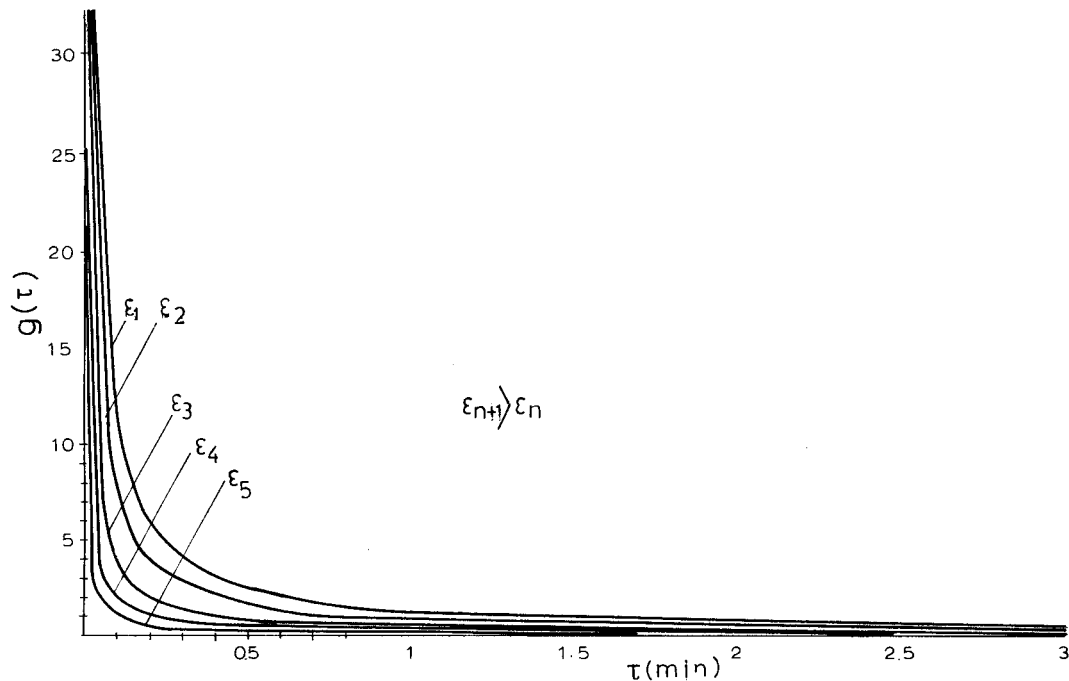


Figure 13 Calculated spectral isostrains for strains  $\varepsilon_1 = 1\%$ ,  $\varepsilon_2 = 2\%$ ,  $\varepsilon_3 = 4\%$ ,  $\varepsilon_4 = 6\%$ , and  $\varepsilon_5 = 8\%$ .

- (b) The nonlinear viscoelastic behavior of iPP has been proved through the peculiar vertical shift. The correlation of this behavior with the KWW model leads to a formalistic introduction of an equivalent characteristic relaxation time as a function of the observation time  $t$  and strain  $\varepsilon$ . In this context, the vertical shift's apparent behavior is related to an intrinsic time-strain function. Consequently, the known notion of the internal stress-clock function could be modified as an internal time-strain clock function, something which demands further studies.
- (c) The introduction of a so-called spectral shift function and its corresponding spectral inversion point can provide us with further, relevant internal parameters for a more practical characterization of material's viscoelastic behavior. In this sense, it was shown that this function can be related to a coefficient of nonlinear viscoelastic strength, whereas the inversion point, to a transitional behavior from linear viscoelastic to nonlinear viscoelastic state.
- (d) By implementing of a (single) characteristic effective relaxation time through an Eyring-type modeling, it is proposed to give a very general formalistic interpretation of this time. This is done by expressing it in the form of a function  $\tau_c$

$= f(t, \varepsilon, \tilde{v}, T, \sigma)$ , where the parameters are  $t$ , observation time;  $\varepsilon$ , strain;  $\tilde{v}$ , equivalent activation volume;  $T$ , temperature; and  $\sigma$ , the stress.

- (e) The experimental evidence of the above-proposed internal time-strain relaxation function for the investigated material, iPP, can take place for an initial strain above about 3%, which means a nonlinear viscoelastic control behavior of this function.

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