

# Nonlinear Viscoelastic Model for the Prediction of Double Yielding in a Linear Low-Density Polyethylene Film

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**ABSTRACT:** Tensile testing and tensile creep experiments for linear low-density polyethylene in a thin-film form were examined and analyzed in terms of a nonlinear viscoelastic model. The proposed model, based on two distinct thermally activated rate processes (Eyring models), was proved to describe the double-yield-point tensile behavior of the material tested. The required model parameters were eval-

uated from the corresponding creep-strain curves, and this revealed the relationship between the main aspects of the inelastic behavior of polymers, that is, the monotonic loading and creep response. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3519–3527, 2004

**Key words:** polyethylene (PE); yielding; creep

## INTRODUCTION

The study of the deformation behavior of polymers during creep procedures is important and useful for the identification of viscoelastic and physical aging effects. Moreover, the origin of creep deformation controls the long-term behavior of polymeric materials, whereas the imposition of specific loads for a period of time is very common for engineering applications. Therefore, the theoretical and experimental examination of creep is a matter of great interest.

Many works have dealt with the creep of polymers; some of them are based on empirical equations developed for describing the high-temperature creep of metals.<sup>1–3</sup>

A widely used approach for creep procedures is the Eyring model.<sup>4</sup> According to this model, creep is a thermally activated process, occurring because of the motion of molecular units from one position to another under the imposition of a stress field. The Eyring approach has been used to study, among other things, the creep behavior of ultrahigh-molecular-weight polyethylene fibers.<sup>5,6</sup> However, extensive studies of the yield behavior of poly(methyl methacrylate) and polycarbonate over a wide range of strain rates and temperatures by Roetling<sup>7</sup> and Bauens<sup>8</sup> have shown that the yield stress increases more rapidly with increasing strain rate and decreasing temperature at low temperatures and high strain rates than at high temperatures and low strain rates. Therefore, it has been

proposed that the Eyring equation can be extended, under the assumption that there is more than one activated rate process, the stresses being additive.

Although several works have dealt with ultrahigh-molecular-weight polyethylene fibers,<sup>5,6,9</sup> creep behavior and verification of the creep mechanism, especially for semicrystalline materials, remain problematic.

In an analogous way, the prediction of the inelastic behavior of solid polymers, in terms of monotonic and cyclic loading, complementary to creep and relaxation, is of great importance. The nonlinear viscoelasticity and viscoplastic response of polymers have been the subjects of many works.<sup>10–14</sup>

In most cases, all these aspects of deformation are treated separately. The need for the development of a unified model, representing the nonlinear viscoelastic yield and postyield viscoplastic response of solid polymers has been emphasized by many authors.<sup>15,16</sup> Related to this and reported in an interesting work,<sup>16</sup> a model has been presented that can describe the experimental results of strain rate compression tests at different temperatures and creep data. In this approach, a constitutive model based on the distributed nature of the microstructural state and the thermally activated evolution of the glassy state is considered. More recently, another constitutive model<sup>17</sup> has been presented, leading to the evaluation of the rate of plastic deformation in glassy polymers. Through this analysis, yielding and postyielding can be described, and the identification of a nonlinear viscoelastic response during creep experiments is also possible.

Apart from this, the study of the ultimate properties of polyethylenes has been the subject of many works<sup>18–22</sup> because of the variety of their applications.

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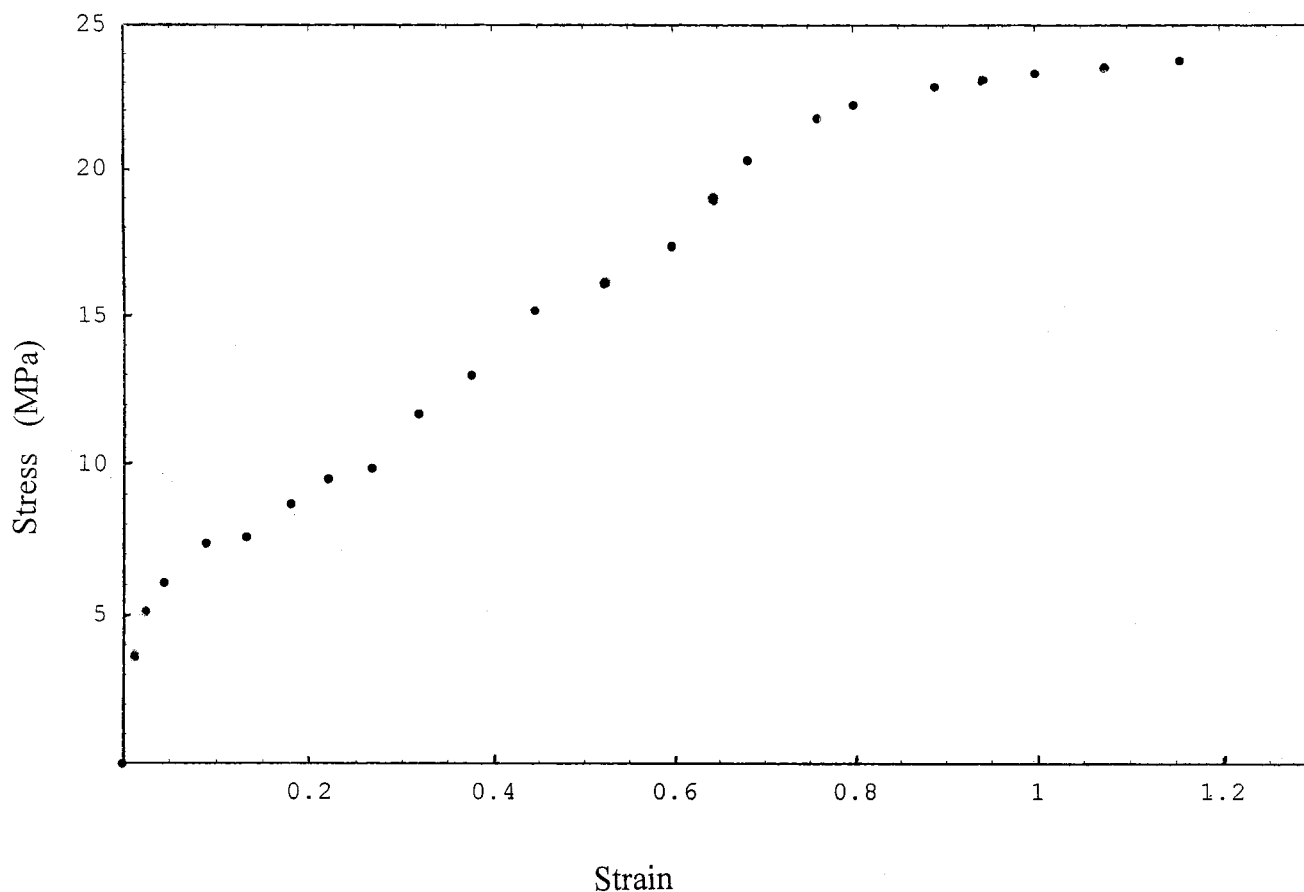


Figure 1 Tensile nominal stress-strain curve of an LLDPE film.

These material types present a broad range of solid structures, from highly crystalline lamellar morphologies to the granular morphology of low-crystallinity copolymers. An interesting classification of homogeneous ethylene-octene copolymers is presented in ref. 20. The varying material morphology results in tensile behavior, changing from typical necking, cold drawing, and strain hardening to a uniform elastomeric deformation as the comonomer content increases.

In this work, a linear low-density polyethylene (LLDPE), provided as a thin film, was studied in terms of the tensile strain rate and tensile creep experiments. Double yielding, exhibited by tensile testing, was analyzed with a nonlinear viscoelastic model, and the results were combined with a creep procedure that was performed very systematically at various stress levels between the two yield stresses that were found.

## EXPERIMENTAL

### Materials

Lupolen, provided by Mornos Co., Theva, Greece, a commercial type of LLDPE prepared with traditional Ziegler-Natta catalysts, was examined. The material

was provided in the form of a thin film obtained by injection blowing. The raw material properties were as follows: density =  $0.923 \text{ g/cm}^3$  and melt-flow index =  $0.80 \text{ g/10 min}$ . The content of butene, used as a comonomer, was 7 wt %.

### Procedures

#### Differential scanning calorimetry

The material was heated at a constant heating rate of  $40^\circ\text{C/min}$  from the ambient temperature up to  $160^\circ\text{C}$  to erase the previous history. It was then held for 10 min and subsequently cooled to  $0^\circ\text{C}$  at a cooling rate of  $20^\circ\text{C/min}$ . The sample was then heated at a rate of  $10^\circ\text{C/min}$ , and a thermogram was recorded. With respect to the heat of fusion of  $290 \text{ J/g}$  for a perfect crystal,<sup>23</sup> the crystallinity of the material in the thin-film form was 41.7%.

#### Tensile testing

Tensile experiments were performed at room temperature with an Instron 1121 tester (Buckinghamshire, England). Film specimens, 0.06 mm thick, 15 mm

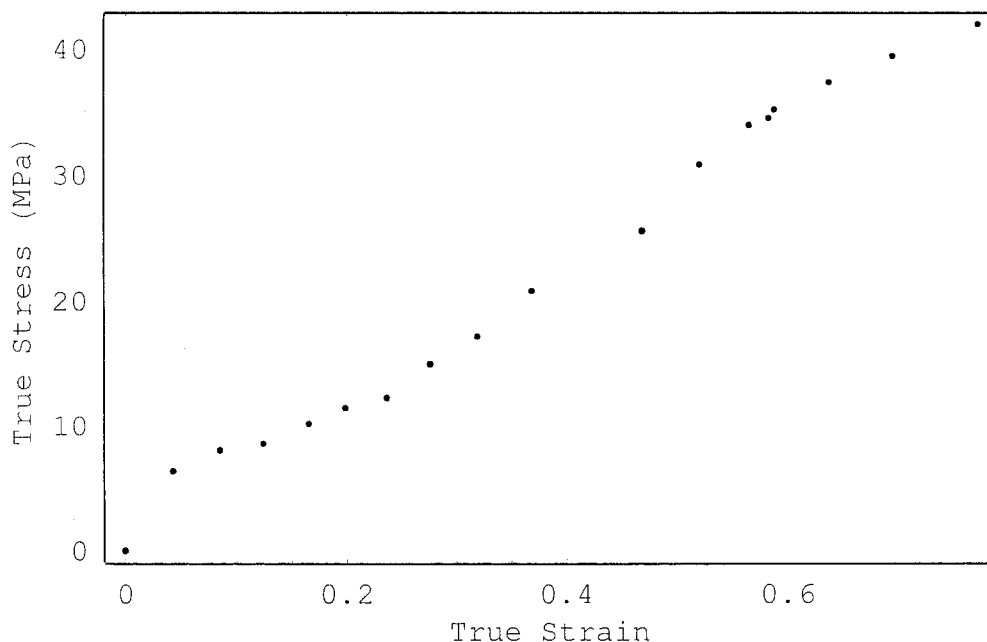


Figure 2 Tensile true stress-strain curve of an LLDPE film.

wide, and 150 mm long on average, were stretched at a crosshead speed of 15 mm/min. A representative stress-strain curve is shown in Figure 1. In this curve, two distinct yield points can be observed at 7.5 and 20 MPa. The engineering stress-strain curve was then replotted in terms of a true stress-strain curve; this is presented in Figure 2. As expected, the true stress-strain curve attains higher values because the nominal stress is multiplied by the term  $1 + \log(1 + \epsilon)$ , where  $\epsilon$  is the strain, but the two yield points are preserved at 7.5 and 35 MPa.

#### Creep testing

The specimens for tensile creep experiments were stripes 15 mm wide and 100 mm long. A different sample was used for each creep experiment to prevent the influence of permanent flow due to the previous loading of the sample.

In every case, the creep load was applied for a period of 2 h at room temperature. Seven different stress levels below the first yield point, and six stress levels above it, up to the second yield stress were applied.

The deformation was measured very accurately at every localized region along the total gauge length. The experimental method was based on a noncontact method using a laser extensometer, which has been described in detail elsewhere.<sup>24</sup> Typical creep curves were then obtained, as presented in Figures 3 and 4.

The instantaneous response was followed by a decreasing rate of primary and secondary creep. When

the imposed stress was much lower than the first yield stress, a rather linear viscoelastic response was detected through the observation of the relative position of the creep-strain curves (Fig. 3). The same effect was not observed in the second group of creep curves (Fig. 4) because some of the material underwent plastic deformation. The experimental data of Figures 3 and 4 were replotted on a double-logarithmic scale and are shown in Figure 5, from which the early time response has been omitted. The material response at this stage was considered to be unreliable because of the effects of increasing time.

#### CONSTITUTIVE MODEL

Figure 1 shows a nominal stress-strain curve for the LLDPE film examined. There are two distinct yield points at 7.5 and 20 MPa. Analogous behavior can be observed in the true stress-strain plots of Figure 2, in which the second yielding is exhibited at 35 MPa. The yielding of glassy and semicrystalline polymers is usually manifested by a single yield point. In several works, however, double-yield points for low-crystallinity ethylene copolymers and branched polyethylenes under tension have been reported.<sup>25-29</sup>

This behavior can be attributed either to the broad distribution of the crystal thickness<sup>30</sup> or to the association and subsequent dissociation of co-units during the second step of yielding.<sup>31</sup>

In the following, a viscoelastic model is presented that is proposed to predict the tensile behavior of the material tested. In our analysis, the double-yield point

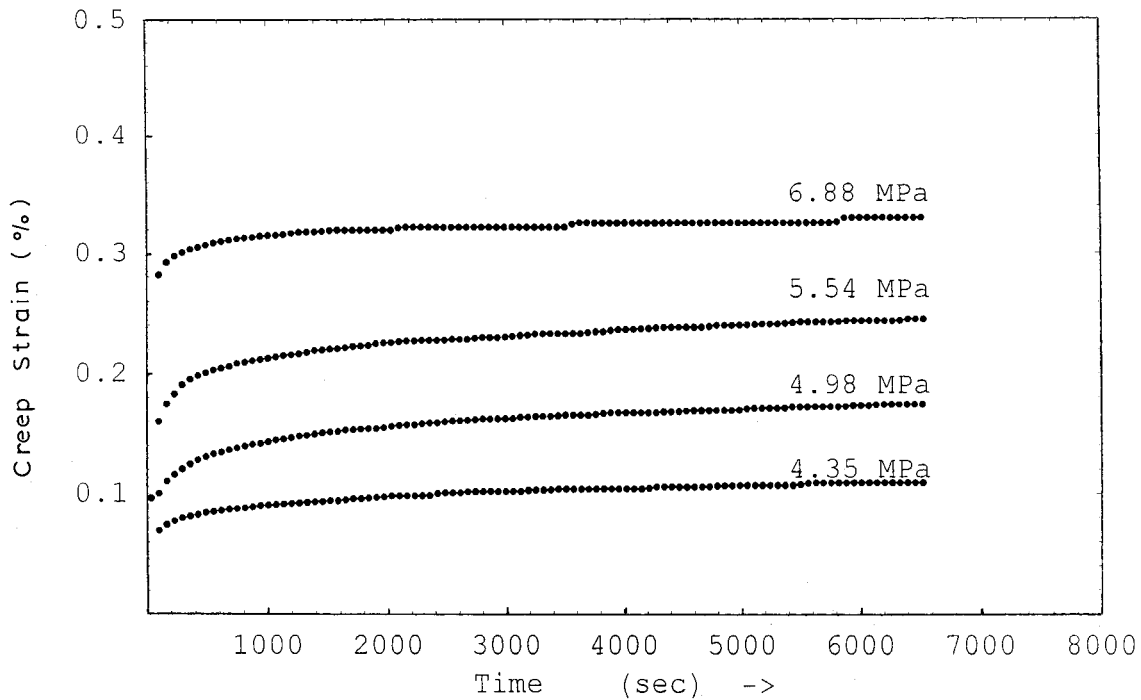


Figure 3 Creep-strain curves of an LLDPE film at three stress levels below the first yield point of 7.5 MPa.

is treated as an effect arising from the combination of two thermally activated rate processes using different activation parameters. Therefore, the yield mechanism is modeled as a parallel association of two Eyring dashpots. One is in parallel connection with a Langevin spring, and these two elements are

subsequently connected to a second Langevin spring, as shown in Figure 6. The latter acts as a source of material resistance to large deformations. In series with this model, an elastic spring is connected to obtain the total macroscopic material response.

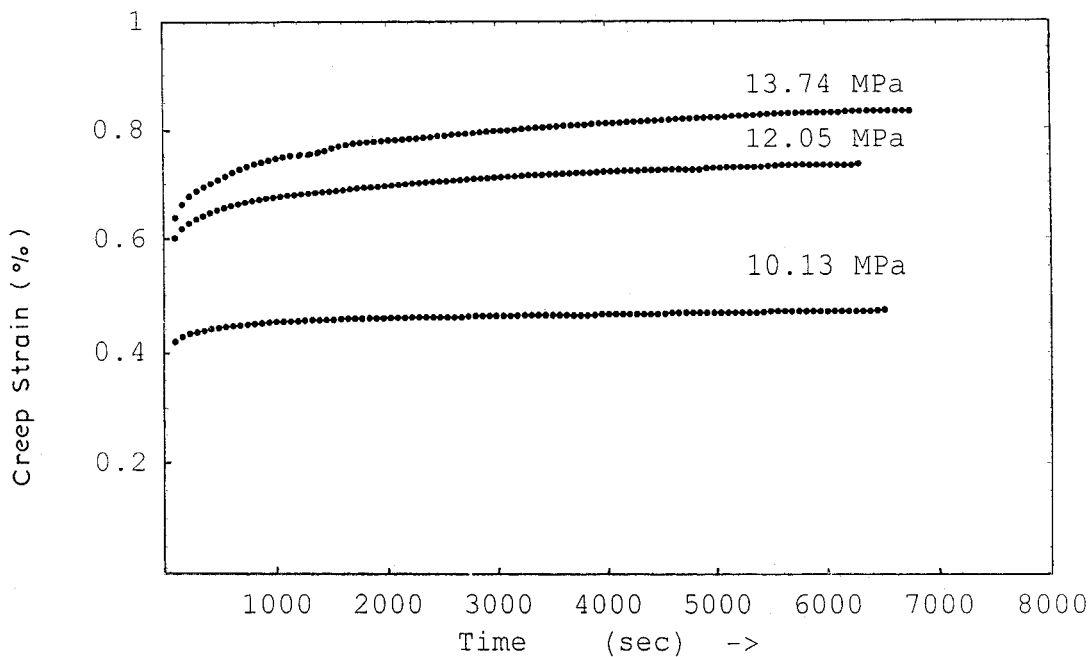


Figure 4 Creep-strain curves of an LLDPE film at four stress levels above the first yield point of 7.5 MPa.

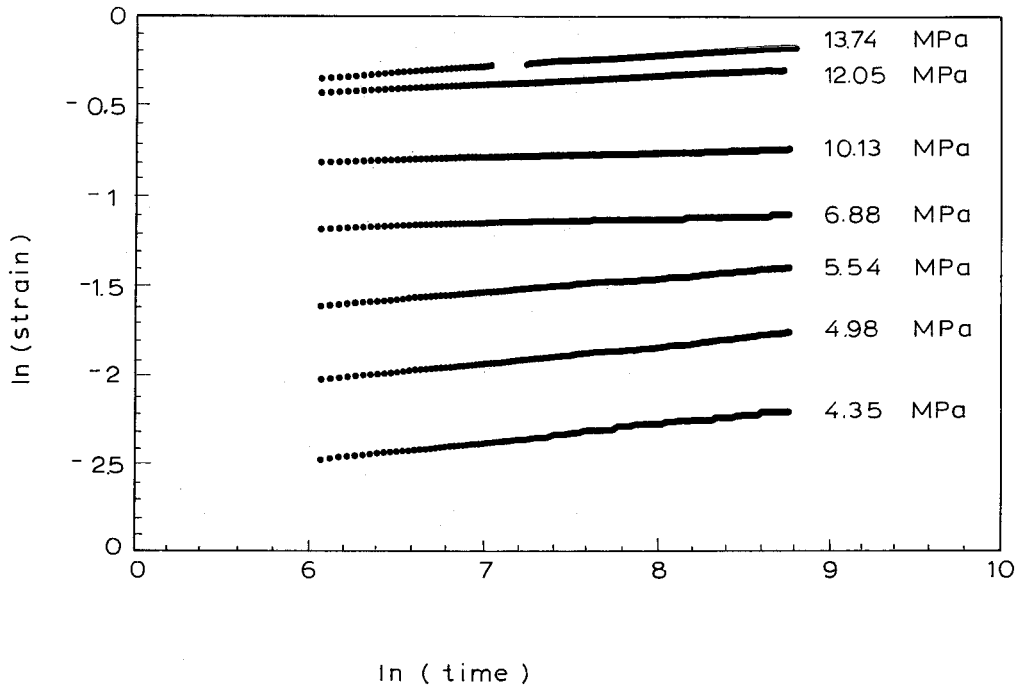


Figure 5 Creep strain versus the time on a double-logarithmic scale at various stress levels.

According to the proposed model, there is a first deformation process, which can be described by the following equation:

$$\dot{\epsilon}_{p1} = \dot{\epsilon}_0 \exp \left[ \frac{v_1(\sigma - \sigma_{int1})}{kT} \right] \quad (1)$$

where  $\sigma$  is the total applied stress,  $\dot{\epsilon}_0$  is the pre-exponential factor,  $k$  is the Boltzmann constant,  $T$  is the

temperature, and  $v_1$  is the activation volume of the first thermal activated process.  $\sigma_{int1}$  is an internal stress:

$$\sigma_{int1} = C_{R1} \frac{\sqrt{N_1}}{3} \left[ \alpha_p L^{-1} \left( \frac{\alpha_p}{\sqrt{N_1}} \right) - \alpha_p^{-1/2} L^{-1} \left( \frac{1}{\sqrt{\alpha_p} \sqrt{N_1}} \right) \right] \quad (2)$$

$\alpha_p$  is a stretch ratio obtained from the total strain after the subtraction of the plastic part:

$$\alpha_p = 1 + \epsilon_{p1} - \epsilon_{p2} \quad (3)$$

where  $C_{R1}$  is the rubbery modulus and  $N_1$  is the number of equivalent links.<sup>32</sup> The stress-strain properties of ultralow-density polyethylene and other thermo-plastic elastomers have been accordingly modeled by Haward<sup>33</sup> through the application of non-Gaussian chain statistics.

The rate deformation of the second thermally activated process can similarly be described as follows:

$$\dot{\epsilon}_{p2} = \dot{\epsilon}_0 \exp \left[ \frac{v_2(\sigma_{int1} - \sigma_{int2})}{kT} \right] \quad (4)$$

where  $\dot{\epsilon}_0$  is the pre-exponential factor and  $v_2$  is the activation volume.  $\sigma_{int2}$  is the corresponding internal stress of the second Langevin spring, being parallel to the second Eyring dashpot:

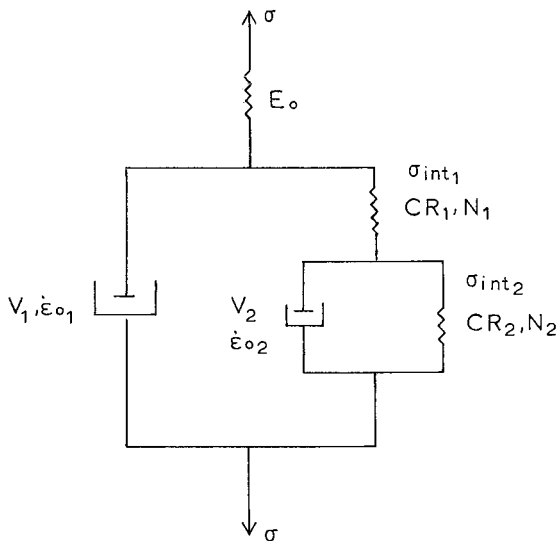


Figure 6 Schematic presentation of the applied viscoelastic model.

**TABLE 1**  
 **$k_2$ ,  $v$  and  $\dot{\epsilon}_0$ .**

Group	$\dot{\epsilon}_0$ (s <sup>-1</sup> )	$v/kT$ [(MPa) <sup>-1</sup> ]	$k_2$ (MPa)
First	$\dot{\epsilon}_{0_1} = 10^{-9.0}$	$v_1/kT = 5$	25
Second	$\dot{\epsilon}_{0_2} = 10^{-10}$	$v_2/kT = 1.2$	20

$$\sigma_{int_2} = C_{R_2} \frac{\sqrt{N_2}}{3} \left[ \alpha_{p'} L^{-1} \left( \frac{\alpha_{p'}}{\sqrt{N_2}} \right) - \alpha_{p'}^{-1/2} L^{-1} \left( \frac{1}{\sqrt{\alpha_{p'} \sqrt{N_2}}} \right) \right] \tag{5}$$

where

$$\alpha_{p'} = 1 + \epsilon_{p_2} \tag{6}$$

$N_2$  and  $C_{R_2}$  are the equivalent number of links and the rubbery modulus for the second source of material resistance at large deformations, respectively.

The total strain ( $\epsilon_{tot}$ ) is given as follows:

$$\epsilon_{tot} = \epsilon_{p_1} + \epsilon_0 \tag{7}$$

where  $\epsilon_0$  is the strain of the Hookean spring.

Thus, the total material response is simply given by a Hookean equation, in which the effective tensile modulus ( $E_0$ ) is multiplied by the total strain:

$$\sigma = \epsilon_0 E_0 \tag{8}$$

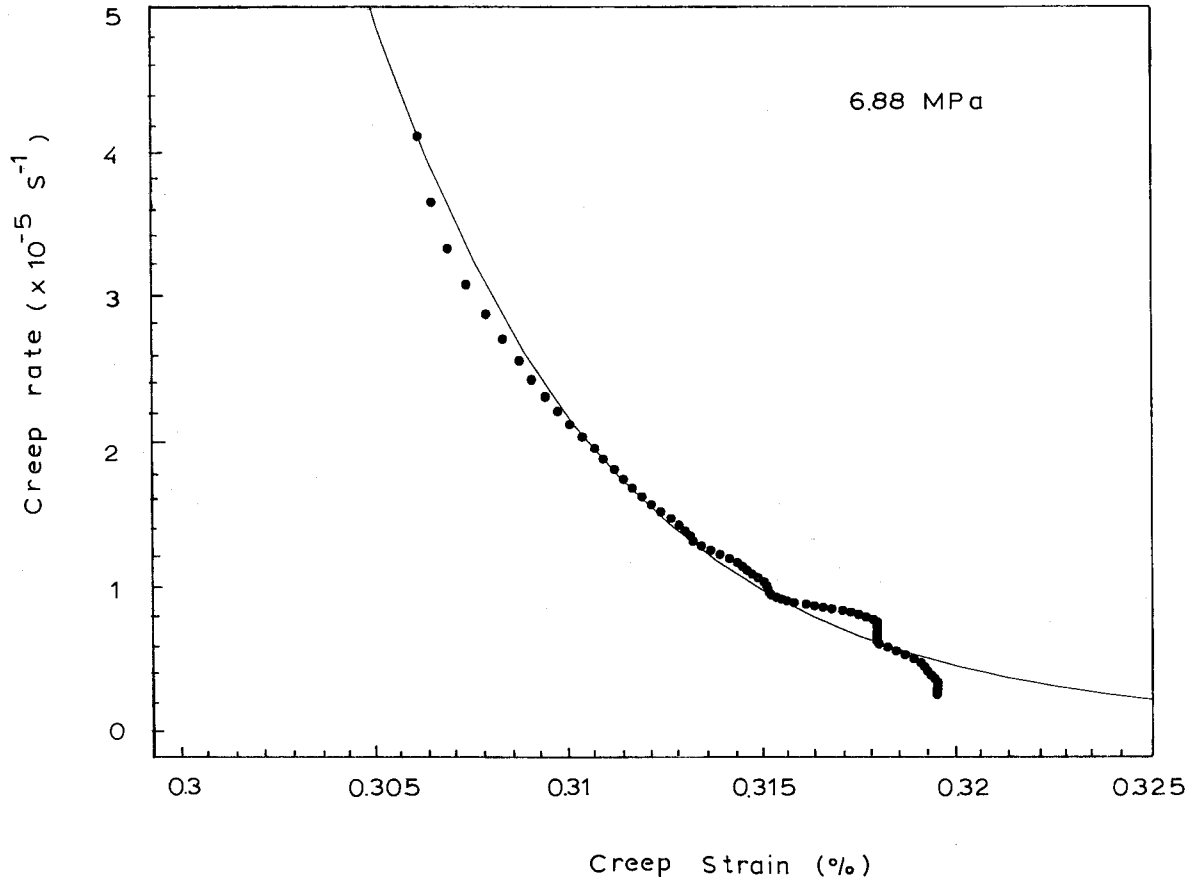
By solving numerically eqs. (1)–(8), we can obtain the corresponding constitutive stress–strain relation if the model parameters  $\dot{\epsilon}_{0_1}$ ,  $\dot{\epsilon}_{0_2}$ ,  $v_1$ ,  $v_2$ ,  $C_{R_1}$ ,  $C_{R_2}$ ,  $N_1$ , and  $N_2$  can be evaluated.

**CALCULATION OF THE MODEL PARAMETERS**

The corresponding creep-strain curves are presented in Figures 3 and 4, and the whole set of curves is presented on a double-logarithmic scale in Figure 5. According to the theory of thermal activation, as proposed by Eyring<sup>4</sup> and used by Bauens-Crowet et al.,<sup>34</sup> the creep rate takes the following form:

$$\dot{\epsilon} = A e^{-\frac{Q}{kT}} e^{(\sigma - \sigma_{int})v/kT} = \dot{\epsilon}_0 e^{(\sigma - \sigma_{int})v/kT} \tag{9}$$

where  $A$  is a constant,  $Q$  is the activation energy, the term  $A e^{-(Q/kT)}$  can be replaced by the pre-exponential



**Figure 7** Creep rate versus the creep strain for a stress level of 6.88 MPa: (●) experimental data and (—) fitting.

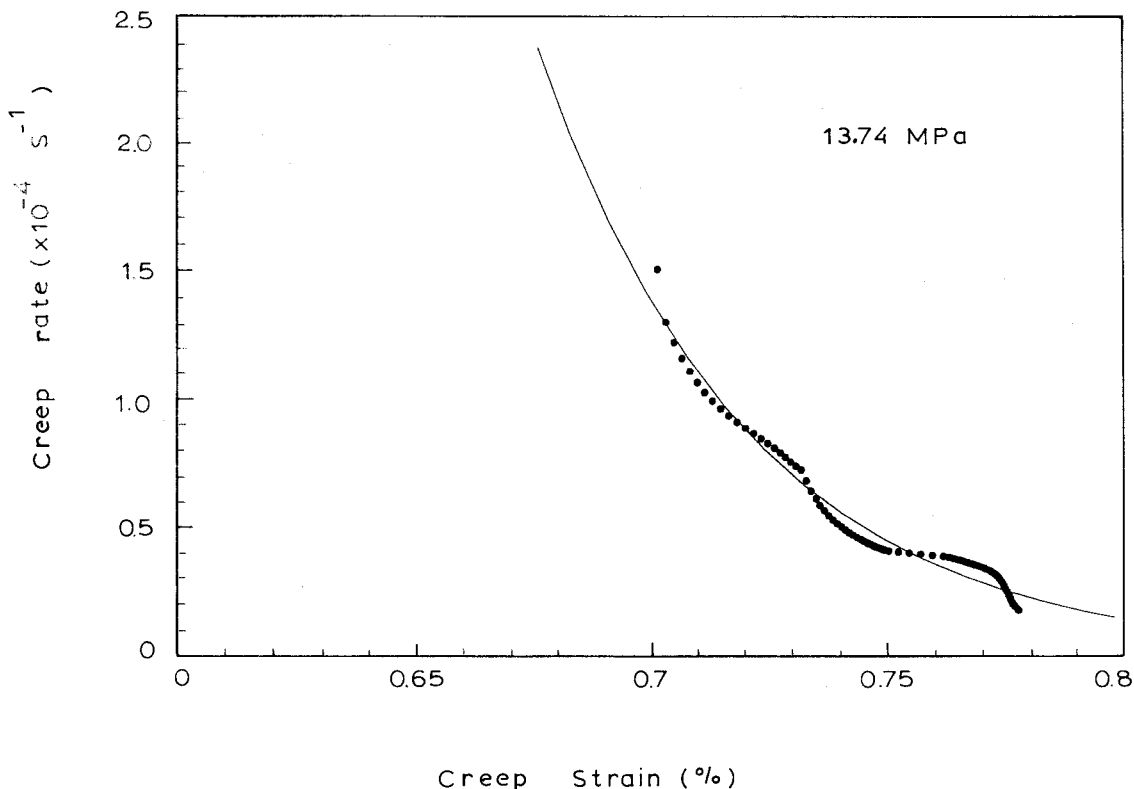


Figure 8 Creep rate versus the creep strain for a stress level of 13.74 MPa: (●) experimental data and (—) fitting.

factor  $\dot{\epsilon}_0$ , and  $v$  is the activation volume.  $\sigma_{int}$  is an internal stress that opposes the applied stress, and it is proportional to the amount of strain that will be recovered:

$$\sigma_{int} = k_2 \epsilon_R \tag{10}$$

where  $k_2$  is a constant proportional to the temperature and  $\epsilon_R$  is the recoverable strain. Equation (10) is a Hookean representation, treated equivalently to a Langevin equation, that is used to simulate the internal stress with rubber elasticity behavior.

Equations (9) and (10) have been combined with the experimental data of Figures 4 and 5 as follows: the nonlinear-fit procedure has been applied with the software Mathematica,<sup>35</sup> and it has also been taken into account that the experimental data should be separated into two groups, that is, one group of data before the first yielding takes place and a second group after the first yielding up to the second yield stress. The parameters  $k_2$ ,  $v$ , and  $\dot{\epsilon}_0$  have been evaluated and are listed in Table I. The quality of fitting in the curves of the creep-strain rate versus the creep strain is shown in Figures 7 and 8 for representative load levels (6.88 and 13.74 MPa) for the two sets of experimental data.

Under the assumptions that the accumulation of strain in a creep procedure may be treated similarly to

the increment of strain in a tensile experiment<sup>17</sup> and that both effects are based on the same mechanism, the parameter values obtained from creep experiments have been used to predict the constant crosshead speed of polyethylene film.

Combining eqs. (1)–(8) and associating the parameter values of the first and second groups with the first [eq. (1)] and second thermal activation processes [eq. (4)], we have proved that the tensile stress–strain curve of Figure 2 can be predicted in a very satisfactory way. The theoretical and experimental data are shown in Figure 9. The integration has been made numerically with small time steps up to a high convergence.

$N$  and  $C_R$  for both processes have been estimated to produce an average Langevin plot that is close to the line obtained with the fitted values of constant  $k_2$  of eq. (10). According to this assumption, the parameter values are  $N_1 = 1.2$ ,  $C_{R1} = 2$  MPa,  $N_2 = 1.2$ , and  $C_{R2} = 1$  MPa.

$E_0$  has been taken to be 180 MPa, as given by the initial slope of the stress–strain curve.

From this analysis, it may be summarized that the first yielding (at a low strain) is associated with that population of crystal blocks that are characterized as larger and more perfect, and that the yield is related to

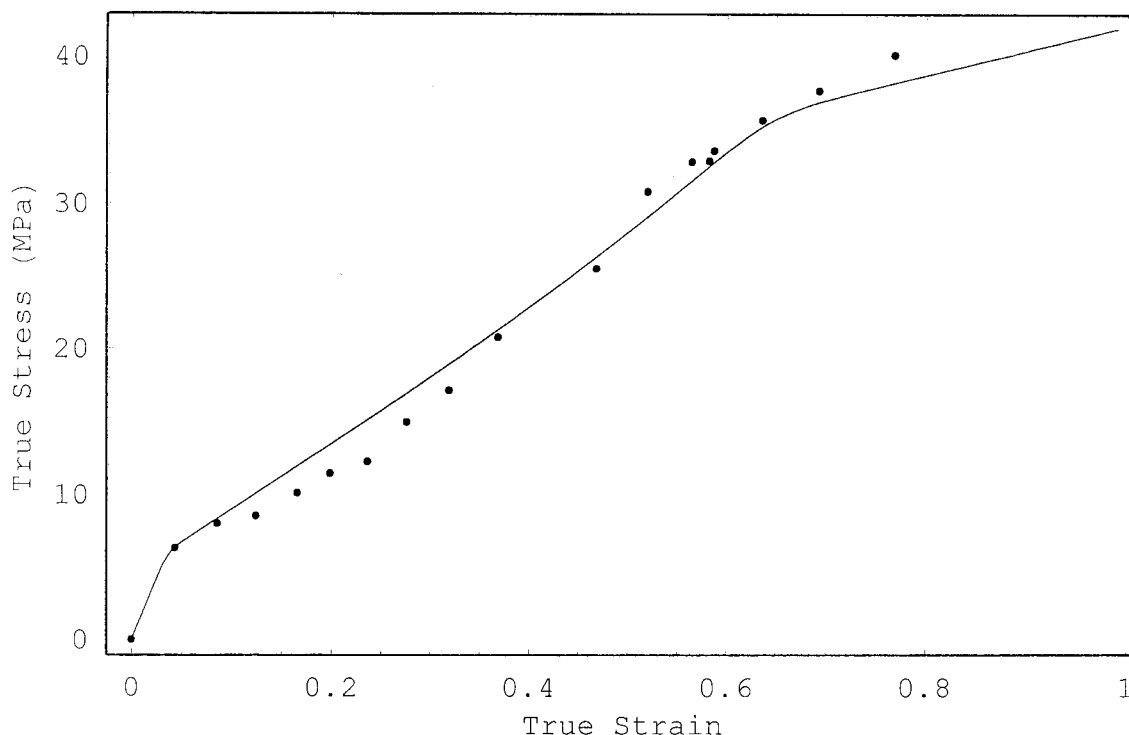


Figure 9 True stress-strain curve of an LLDPE film: (●) experimental data and (—) theoretical predictions.

slip along planes parallel to the chain axis, which is the main process of plastic deformation in polymeric crystals. During the same stage, the amorphous (tie) chains, connecting adjacent crystalline blocks, act as load-transfer agents. The function of these chains is related to the internal stress, which emerges in the plastic flow, in addition to the effective flow stress. Afterward, the second mechanism takes place, involving the homogeneous shear of the smaller crystalline regions as well as the relative slippage of amorphous regions. Initially, the first stage is predominant, and after  $\sigma_{int_1}$  becomes high enough, the second process starts to be important. The  $v_1$  value of this process, which generally represents the volume of the polymer segment needed to move as a whole for yielding to occur, is equal to  $20 \text{ nm}^3$ , that is, larger than  $v_2$ , which is equal to  $5 \text{ nm}^3$ . During the second stage,  $\sigma_{int_2}$  leads to a slight hardening behavior after the second yielding, as presented in the experimental stress-strain curve. The proposed model, which involves two distinct thermally activated processes connected in parallel, has been proved to be reliable for the prediction of the double-yield point exhibited. The fact that the model parameters have been obtained from creep-strain experiments, under the assumption that strain accumulation follows the same mechanism in both creep and constant-crosshead-speed experiments, provides further evidence for the validity of our assumptions.

## CONCLUSIONS

A type of LLDPE material in the form of a thin film was examined in tension and creep experiments. Contrary to the single yield stress usually exhibited by these polyethylenes, the polyethylene film appeared to have two distinct yield points. A nonlinear viscoelastic model, based on two distinct thermally activated rate processes, was found to describe this double-yield-point response. The model parameters were calculated from the material creep-strain curves with the Eyring approach. The different values obtained for the activation volumes of the two processes ( $20$  and  $5 \text{ nm}^3$ ) led to the conclusion that different parts of the material structure participated in the yield process in the two procedures. The observed strain hardening was attributed to the tie chains among the crystalline regions, and it was also modeled with two internal stresses, each of them being significant at different stages of deformation.

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