JOURNAL OF MATERIALS SCIENCE 17 (1982) 747–752

A model for the stress–strain behaviour of toughened polystyrene

Part 2

S. D. SJOERDSMA, D. HEIKENS
Eindhoven University of Technology, Laboratory for Polymer Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The general stress–strain relationship derived in an earlier paper is applied to analyse experimental stress–strain curves of polystyrene–polyethylene blends. It is concluded from the stress and temperature dependence of the rates of craze initiation and craze growth that these rates can be described by means of the Eyring relationship. By inserting this result in the general stress–strain relationship, experimental stress–strain curves could be compared with stress–strain curves as predicted by the model. For constant strain rate experiments and constant stress rate experiments a good agreement was obtained, proving the applicability of the model.

1. Introduction

In a previous paper [1] an equation was derived that describes the stress–strain behaviour of polymers that deform by crazing. This equation is based on the observations that the stress–strain behaviour of crazed toughened polymers is well approximated by a linearly elastic series model of uncrazed polymer and crazes [1, 2]. The amount of polymer drawn into the crazes as fibrillar craze material can be calculated from the rate of craze initiation and the rate of the surface drawing process of the craze fibrils. This is combined with an expression that relates the amount of craze material with craze strain, to obtain a general stress–strain relationship, i.e.,

$$\frac{1}{f}k_i k_g = \frac{1}{p\sigma + r}\left[\frac{d\sigma}{dt}\left(\frac{1}{k_g}\frac{dk_g}{d\sigma} + \frac{2p}{p\sigma + r}\right)\right.$$
$$\times\left(\frac{d\sigma}{dt}\frac{p\epsilon + r/E_{TPS}}{p\sigma + r} - \frac{d\epsilon}{dt}\right)$$
$$\left. + \frac{d^2\epsilon}{dt^2} - \frac{p\epsilon + r/E_{TPS}}{p\sigma + r}\frac{d^2\sigma}{dt^2}\right]. \quad (1)$$

Here k_i is the rate of craze initiation, defined as the rate of craze surface formation normal to the stress direction per volume toughened polystyrene (TPS) and k_g is the rate of the surface drawing process of the craze fibrils. The strain of the tensile specimen is given by ϵ while σ is the applied stress. p and r are constants depending on the modulus of uncrazed toughened polystyrene, E_{TPS}, the craze modulus, E_{cr}, and the expansion factor, f, where f denotes the volume of the crazes that originates if 1 cm^3 PS is converted into craze material. p and r are defined as follows

$$p = \frac{f}{E_{cr}} - \frac{1}{E_{TPS}}, \quad (2)$$

and

$$r = f - 1. \quad (3)$$

If the rates of craze initiation, k_i, and of the surface drawing process, k_g, are expressed as functions of stress and time, Equation 1 can be solved to calculate stress–strain behaviour if the strain–time behaviour is known, and vice versa. However, due to the opacity of toughened polymers it is not possible to determine k_i and k_g in a direct way, e.g. optically. Thus a direct verification of Equation 1 is not possible. However, this relation can be used to evaluate k_i and k_g from stress–strain experiments.

2. Experimental procedure

The 85 wt% polystyrene (PS) to 15 wt% polyethylene (PE) tensile specimens were prepared as described previously [1].

0022–2461/82/030747–06$03.22/0

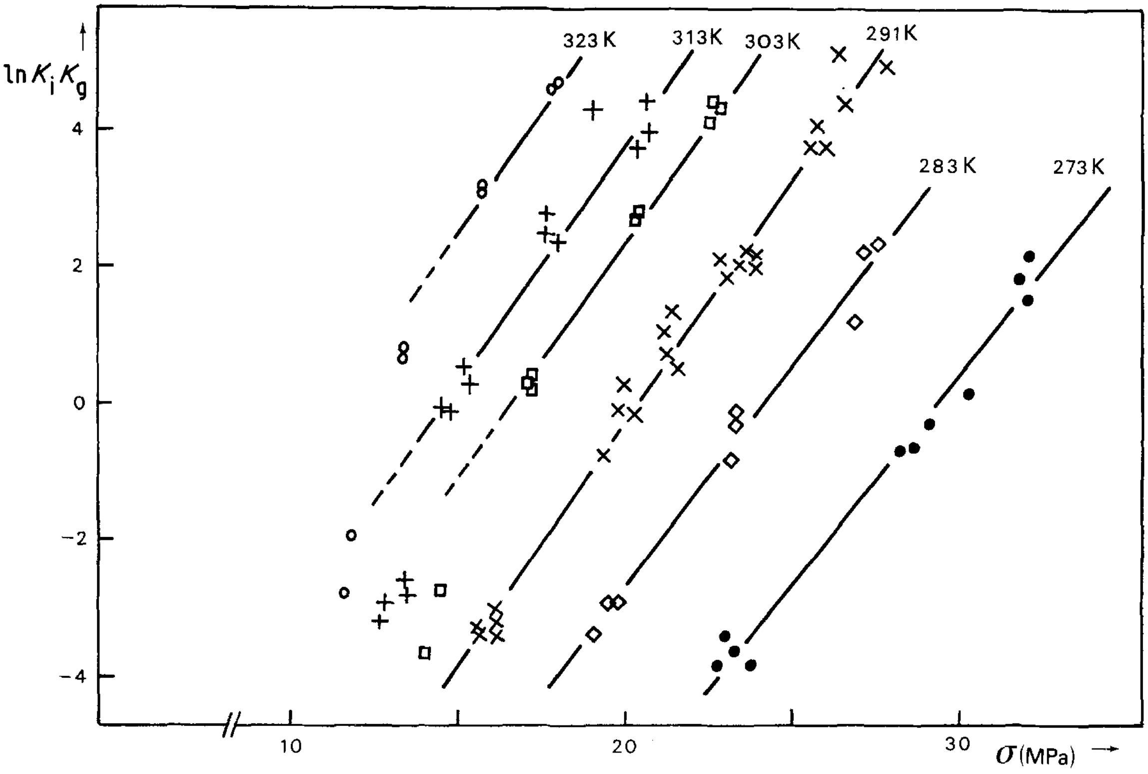

Figure 1 Dependence of $\ln k_i k_g$ on stress at various temperatures.

Constant strain-rate tests were performed on a thermostatted Instron tester, equipped with a HBM linear voltage displacement transducer (LVDT) to determine strain independently. Signals from the Instron load cell and the LVDT were obtained through a HBM amplifier.

Constant stress-rate tests were performed on a Zwick model 1474 tensile tester.

3. Results and discussion

3.1. Stress dependence of crazing in constant strain rate experiments

In order to obtain values for k_i and k_g stress–strain curves at constant strain rates have been analysed. At yield point ($d\sigma/dt = 0$) during constant strain-rate experiments ($d^2\epsilon/dt^2 = 0$) Equation 1 reduces to

$$\frac{1}{f}k_i k_g = -\frac{p\epsilon + r/E_{\mathrm{TPS}}}{(p\sigma + r)^2}\frac{d^2\sigma}{dt^2}. \qquad (4)$$

So by evaluating $d^2\sigma/dt^2$, σ and ϵ at yield point, the product $k_i k_g$ can be calculated as p and r are known constants [1]. By doing this at different strain rates and temperatures the stress and temperature dependence of $k_i k_g$ can be determined.

In Fig. 1 $k_i k_g$ is plotted logarithmically against stress. At all temperatures a linear relationship between $\ln k_i k_g$ and σ was found, except at some instances at high temperatures and low strain rates. These deviations may well result from the existence of a critical crazing stress [3] and are not taken into consideration in the following discussion.

The linear relationship between $\ln k_i k_g$ and stress suggests the following expressions for k_i and k_g,

$$k_i = a \exp(b\sigma) \qquad (5)$$

and

$$k_g = c \exp(d\sigma), \qquad (6)$$

where a, b, c and d are constants, which is also in accordance with previous findings that at constant stress k_i and k_g are not time-dependent [1]. The slope of the plot of $\ln k_i k_g$ against stress then equals $b + d$, while extrapolation to $\sigma = 0$ yields ac. Results for the PS–PE blend are given in Table I.

3.2. Constant stress rate experiments

If Equations 5 and 6 are inserted in the general stress–strain relationship (Equation 1) then it can be shown that in order to solve this relation numerically only b or d needs to be determined.

TABLE I Values of various constants at different temperatures

T (K)	$b+d$* ($\mathrm{MPa^{-1}}$)	b ($\mathrm{MPa^{-1}}$)	d ($\mathrm{MPa^{-1}}$)	$\ln ac$*
273	0.62 (3)			− 18.1 (9)
283	0.65 (3)			− 15.6 (8)
291	0.70 (2)	0.15	0.55	− 14.3 (4)
303	0.68 (5)			− 11.3 (1.1)
313	0.70 (5)			− 10.1 (8)
323	0.69 (2)			− 7.7 (4)

*Figures in brackets are the standard deviations of the proceeding figure.

Values for b and d can be obtained separately from constant stress-rate experiments, i.e., $\mathrm{d}\sigma/\mathrm{d}t > 0$, $\mathrm{d}^2\sigma/\mathrm{d}t^2 = 0$. For constant stress-rate experiments Equation 1 can be solved to obtain

$$\epsilon = \frac{ac}{f}(p\sigma + r)\left\{\frac{\exp\left[(b+d)\sigma\right]}{b(b+d)} - \frac{\exp(d\sigma)}{bd} + \frac{1}{d(d+b)}\right\}\frac{1}{(\mathrm{d}\sigma/\mathrm{d}t)^2} + \frac{\sigma}{E_{\mathrm{TPS}}}. \qquad (7)$$

Equation 7 predicts a linear relation between the strain, ϵ, of a sample at a given stress and the reciprocal square of the stress-rate, $(\mathrm{d}\sigma/\mathrm{d}t)^{-2}$. Such a relationship is indeed found for experiments at 20° C, as shown for three stresses in Fig. 2. The slope contains the unknown constants b and d. As the sum $b + d$ is known from constant strain-rate experiments, b and d can be calculated separately, completing the set of constants needed to solve the generalized stress–strain relationship (Table I). However, as the constant stress-rate experiments have been performed on a different tensile testing machine than that used for the constant strain-rate experiments, values for b and d thus obtained may contain some inaccuracy.

In Figs 3 and 4 experimental stress–strain curves for constant strain-rate and constant stress-rate experiments are compared with the predictions of the model. In all cases a good agreement between experiment and the model is obtained. Not only the general features of the experimental curves such as yielding, the point of inflection after yielding, and the increase of yield stress and yield-strain with strain-rate are predicted, but the quantitative predictions of the model are good as well.

3.3. Temperature dependence of crazing

The exponential dependence on stress of the product $k_\mathrm{i}k_\mathrm{g}$ suggests stress-activated processes with rates that can be described with the Eyring flow equation [4]

$$k_\mathrm{i} = 2A_\mathrm{i}\exp\left(\frac{-\Delta H_\mathrm{i}^*}{kT}\right)\sinh\left(\frac{\gamma_\mathrm{i}V_\mathrm{i}^*\sigma}{kT}\right) \qquad (8)$$

and

$$k_\mathrm{g} = 2A_\mathrm{g}\exp\left(\frac{-\Delta H_\mathrm{g}^*}{kT}\right)\sinh\left(\frac{\gamma_\mathrm{g}V_\mathrm{g}^*\sigma}{kT}\right), \qquad (9)$$

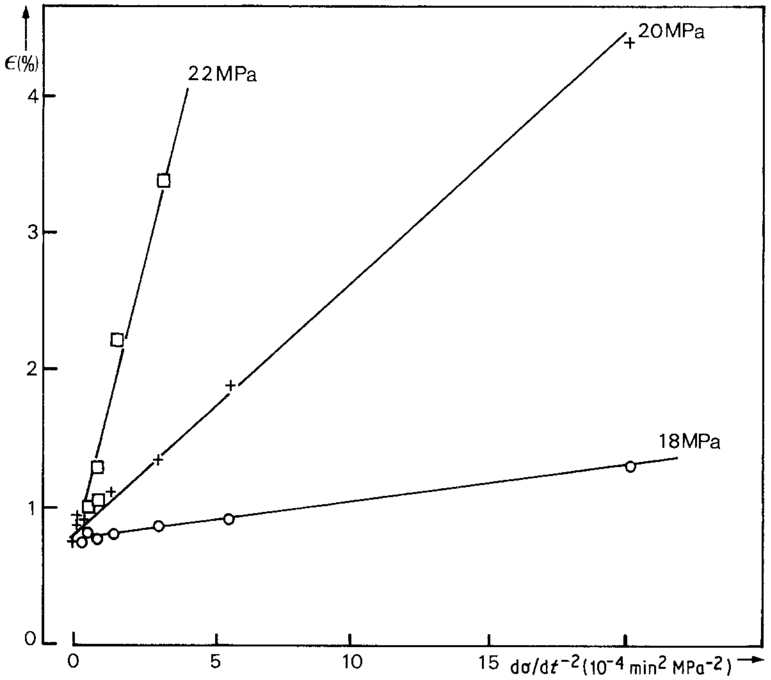

Figure 2 Stress-rate dependence of strain in constant stress-rate experiments at various stresses.

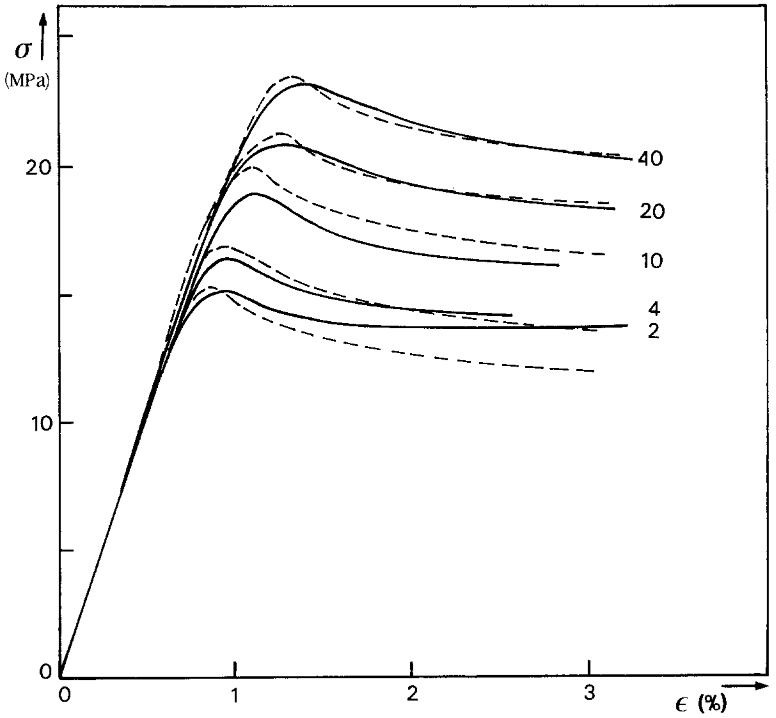

Figure 3 Experimental stress–strain curves (solid lines) and model predicted stress–strain curves (broken lines) obtained during constant strain-rate experiments. The strain-rates (% min^{-1}) are as indicated.

where γ is a stress concentration factor, A is a constant that contains the frequency factor belonging to the rate coefficient, ΔH^* and V^* are the activation enthalpy and volume and the subscripts i and g refer to initiation and growth, respectively, as $2 \sinh (\gamma V^* \sigma / 4kT)$ is well approximated by $\exp (\gamma V^* \sigma / 4kT)$ if the argument is large.

The use of Equations 8 and 9 is supported by the following: surface craze initiation in terms of numbers of crazes is well described for many glassy polymers in air and in liquids by the Eyring equation [5–7]. Furthermore, it has been proposed that neck propagation of glassy polymers is more or less comparable with the surface drawing

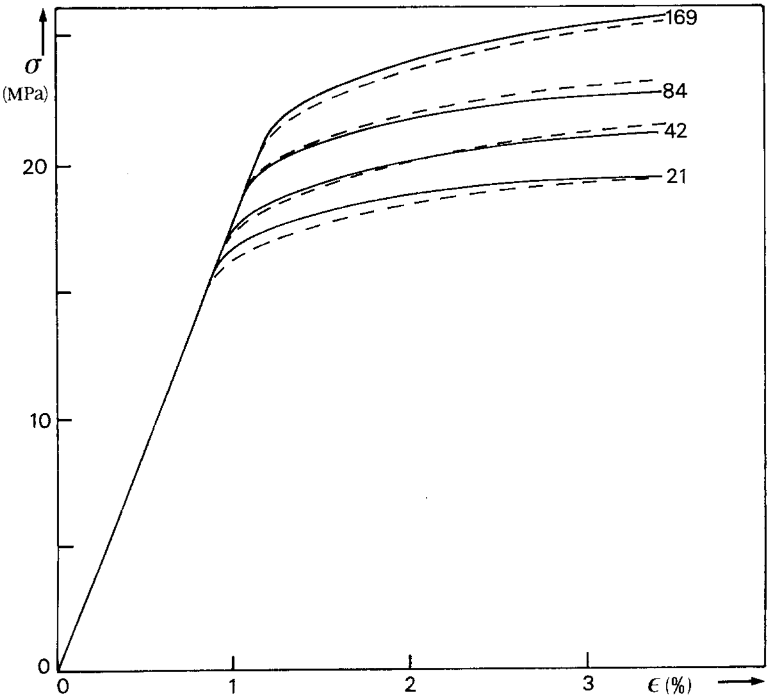

Figure 4 Experimental stress–strain curves (solid lines) and model predicted stress–strain curves (broken lines) obtained during constant stress-rate experiments. The stress-rates (MPa min^{-1}) are as indicated.

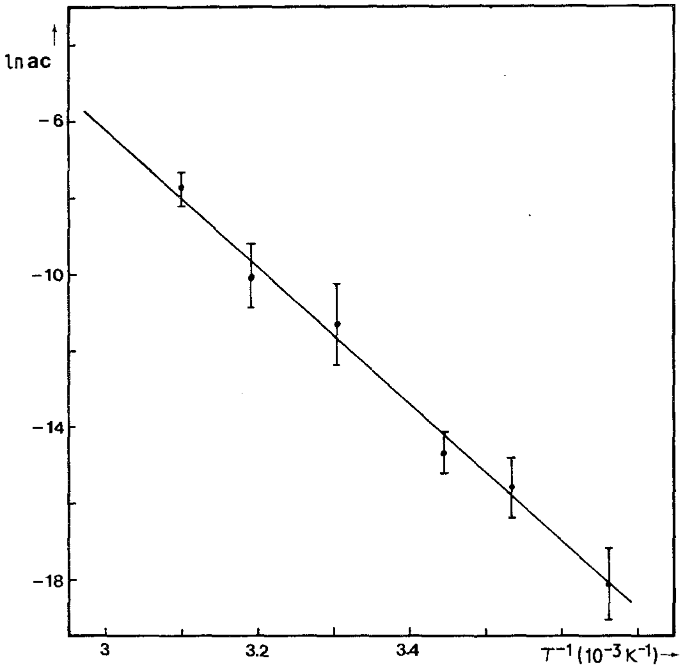

Figure 5 Plot of ln *ac*, as determined from the results represented in Fig. 1, against the reciprocal temperature.

process during craze thickening (the rate of which is given by k_g) [8]. From the kinetics of neck propagation it was concluded that this process is stress activated [8, 9], and its rate can be described by the Eyring flow equation, which is again in accordance with our findings concerning the surface drawing process.

Further evidence of the validity of the Eyring flow relationship was obtained from the temperature dependence of the $k_i k_g$ term. As predicted by the Eyring flow equation, a linear relationship was found between ln *ac* and the reciprocal temperature (see Fig. 5). From the slope, a value of $\Delta H_i^* + \Delta H_g^* = 149\,\text{kJ mol}^{-1}$ is calculated, which is comparable with the activation enthalpy found for the overall rate of crazing in high impact polystyrene (HIPS) i.e., 155 kJ mol^{-1} [10, 11], and with the activation enthalpy of craze yielding, 178 J mol^{-1} [12]. From the low dependence of $b + d$ on temperature (see Table I) it can be concluded that the term $\gamma_i V_i^* + \gamma_g V_g^*$ is approximately proportional to the temperature. This is not in disagreement with the Ree–Eyring theory [13] and has been observed for craze yielding as well [12]. At 20° C a value of 2.4 nm^3 was found for $\gamma_i V_i^*$ whilst $\gamma_g V_g^*$ was 8.8 nm^3. These are reasonable values that may be compared with the activation volumes of shearing of PS homopolymers which are in the range of 3.3 to 6.8 nm^3 [9].

4. Conclusion

The model can be extended in a number of ways to enlarge its predictive range. One possibility is, for instance, the incorporation of some form of craze termination by assuming either a stop in craze initiation or a stop in craze growth. Another possibility is to make use of the three-spring model developed before [1] which allows a more accurate description of a decrease in strain. However, these improvements all involve one or more extra parameters that must be known or must be adjusted to obtain a good fit. The underlying model, which does not contain any adjustable parameters, has proved to be a useful tool in determining the stress and temperature dependence of the rates of craze initiation and craze growth.

The validity of the model is shown by the good qualitative and quantitative predictive characteristics for constant strain-rate and constant stress-rate experiments. Therefore the model offers possibilities for further studies on the effect of PS–PE co-polymer addition and the effect of changes of the PE volume-fraction on crazing characteristics.

Acknowledgements

We are grateful to the N.V. Philips' Gloeilampenfabrieken for allowing us to use their tensile testing facilities. Experimental work by P. F. Butzelaar and F. Zee is also gratefully acknowledged.

References

1. S. D. SJOERDSMA and D. HEIKENS, *J. Mater. Sci.* **17** (1982) 741.
2. J. HOARE and D. HULL, *Phil. Mag.* **26** (1972) 443.
3. R. N. HAWARD, in "The Physics of Glassy Polymers" edited by R. N. Haward (Applied Science Publishers Ltd., London, 1973) p. 340.
4. H. EYRING, *J. Chem. Phys.* **4** (1936) 283.
5. I. NARISAWA and T. KONDO, *Int. J. of Fract. Mech.* **8** (1972) 435.
6. K. IISAKA, Y. NISHIMOTO and K. SHIBAYAMA, *J. Polymer Sci., Polymer Phys. Ed.* **17** (1979) 791.
7. M. KITAGAWA, *ibid.* **17** (1979) 663.
8. N. VERHEULPEN-HEYMANS, *Polymer* **21** (1980) 97.
9. T. E. BRADY and G. S. Y. YEH, *J. Macromol. Sci.-Phys.* **B9** (1974) 659.
10. B. MAXWELL and L. F. RAHM, *Ind. Eng. Chem.* **41** (1949) 1988.
11. R. F. BOYER, *Polymer Eng. Sci.* **8** (1968) 161.
12. J. N. SULTAN and F. J. McGARRY, *ibid.* **14** (1974) 282.
13. T. REE and H. EYRING, *J. Appl. Phys.* **26** (1955) 793.

Received 3 June
and accepted 24 July 1981