Temperature–Strain Rate Transformations with Isotactic Polypropylene at Finite Strains

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Synopsis

The possibility of applying Ferry's superposition principle to the entire stress–strain curve of oriented isotactic polypropylene is studied. Sufficient data to prove the applicability of the principle is not available, but from published information it is shown that if superposition is valid for this material, then the shift factors are independent of strain and apply to the breaking extension as well as points along the stress–strain curve.

Introduction

It has been shown by Ferry[1] and co-workers that for many amorphous polymers at temperatures above their glass transition, the effect of a temperature change is to shift the curve of dynamic modulus (or other viscoelastic functions) against the logarithm of the frequency (or time) in a direction parallel to the frequency (or time) axis without change of shape. This is known as the principle of time–temperature superposition since it follows that a series of curves at different temperatures can be superimposed to form a master curve, and provide values of a shift factor which is a function of temperature. The application of this principle at finite strains, and in particular to stress–strain curves, has however received little attention.

To study its application to stress–strain curves, it is necessary to construct a curve of stress at a given strain against strain rate from a family of stress–strain curves measured at different rates. From similar curves at different temperatures, the possibility of superposition and the dependence of shift factor on strain can be studied. Data sufficient for this are not available at present, but the author[2] has published results showing the effect of temperature at a fixed strain rate and strain rate at a fixed temperature on the stress–strain curve of oriented isotactic polypropylene. By using these results and assuming that the superposition principle is valid it is possible to study how the shift factor depends on strain. This is done in the work reported here.

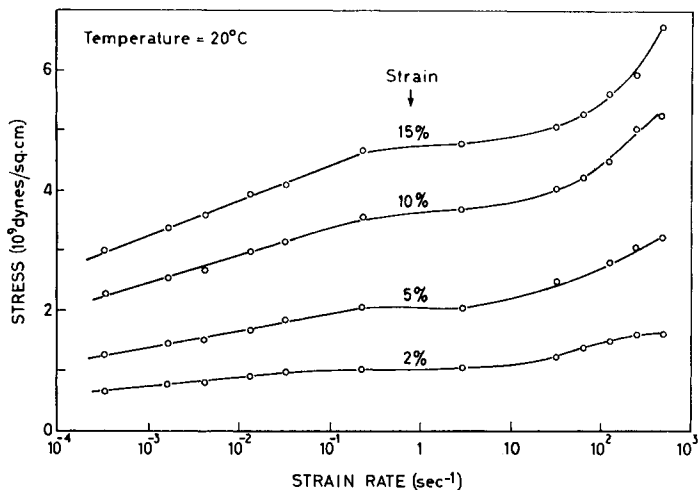* Present address: Department of Physics, Manchester College of Science and Technology, Manchester, England.

Fig. 1. Variation of stress with rate for isotactic polypropylene.

The assumption that time–temperature superposition is valid for iso-tactic polypropylene over the temperature range used is questionable for two reasons: firstly, this is a semicrystalline polymer, and secondly, the temperature range passes through the transition temperature. However, Nagamatsu[3] has shown that, provided crystallinity remains constant, superposition is possible with semicrystalline polymers, and Ferry[1] quotes cases where superposition has been successfully applied at temperatures below the glass transition, though this calculation must be treated as an entirely separate case from that at temperatures above the transition.

Method of Calculation

The results of the experiment in which strain rate was varied are plotted in Figure 1 and of that in which temperature was varied in Figure 2. From these figures were determined the temperatures and strain rates at which the values of stress at a given strain were equal. The values of strain rate were divided by the value of strain rate used in the experiment in which temperature was varied and the resultant ratio, which is equivalent to the shift factor a_T used by Ferry,[1] is plotted in Figure 3 against the reciprocal of the absolute temperature. This is done for three different strains.

Discussion

The small variation in shift factor with strain which is shown in Figure 3 might be significant, or it could be caused by differences between the Instron tensile tester used in the experiment in which rate was varied and the Cambridge extensometer used in that in which temperature was varied. That this latter possibility is the more likely explanation is indicated by the fact that an effect of strain is shown at $\log a_T = 0$. At this point, conditions
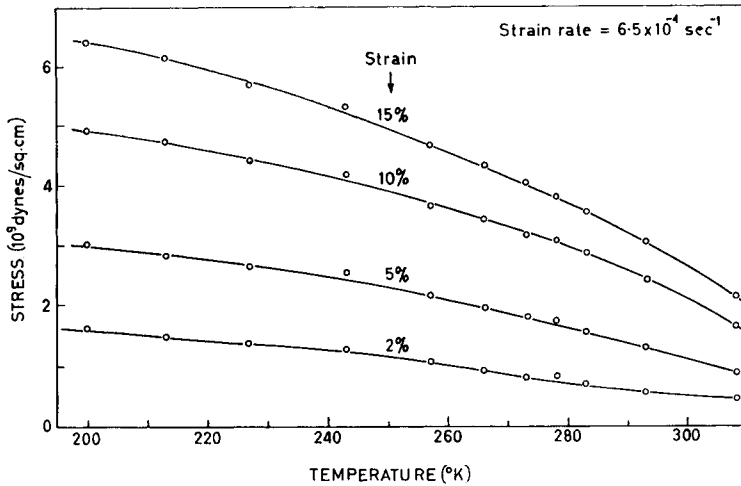
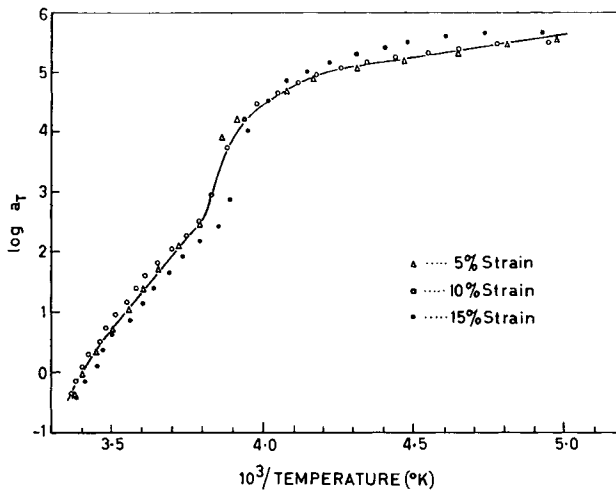Fig. 2. Variation of stress with temperature for isotactic polypropylene.

Fig. 3. Dependence of transformation factor on temperature for isotactic polypropylene.

of temperature and strain rate are identical in each experiment, and so this cannot be a real effect but reflects differences between the testing machines. It is therefore concluded that within experimental error the shift factor is independent of strain.   From this two conclusions follow: the changes in shape in the stress–strain curve are the same, whether they be produced by increasing the strain rate or decreasing the temperature, and that if superposition is valid at any strain with this material, it must be valid at all strains.

According to Ferry,[1] log a_T should vary linearly with $1/T$ for a semicrystalline material.   In Figure 3 it will be seen that there are two sections over which this is substantially true, but that there is a very pronounced
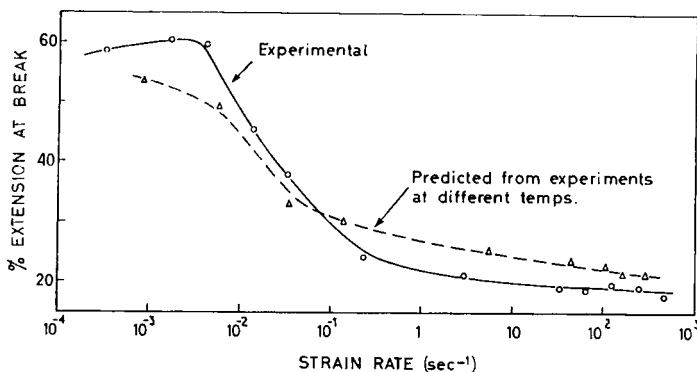
Fig. 4. Rate dependence of breaking extension of isotactic polypropylene predicted from temperature dependence.

discontinuity between them. This arises because, whereas there is a range of strain rate in which the stress–strain curve is substantially rate-independent, there is no range of temperature in which a similar effect occurs.

As the discontinuity is approached from the high temperature side the apparent activation energy (the slope of the curve) increases rapidly, which is characteristic of the approach to a glass transition. According to Reding[4] (from dilatometric data) this transition occurs at 255°K. with isotropic polypropylene, the same temperature as that at which the discontinuity occurs. It would seem likely therefore that the discontinuity is associated with the glass transition. If this is so, it follows that the region of strain rate in which the stress–strain curve is substantially rate-independent is also associated with the glass transition. Also, the significance of the values of a_T at the lower temperatures becomes dubious, because these are obtained by transposition through a glass-transition temperature.

The values of log a_T given by the line drawn in Figure 3 have been used to predict the dependence of breaking strain on rate from the experimentally determined dependence of breaking strain on temperature. The values are plotted in Figure 4 and compared with directly determined values. It is seen that the range of strain rate in which breaking extension drops rapidly with increasing rate is correctly predicted, indicating that the drop in breaking extension has the same cause whether it is produced by increasing strain rate or decreasing temperature.

It had been concluded previously that this was not so.[2] This conclusion was based on the fact that whereas the decrease in breaking extension with decreasing temperature appeared to be accompanied by an increase in modulus, the decrease with increasing strain rate was not. The moduli were determined from the initial slopes of the stress–strain curves, and it would now seem that this is an unreliable measurement.

It has been suggested by Vincent[5] that with a polymer which extends through a "neck," the fall in breaking extension with increasing rate could be caused by the transition from isothermal to adiabatic extension.

He argues that when the temperature rises during extension it will not be possible for a stable neck to form and the testpiece will break. The fall in breaking extension with decreasing temperature cannot be explained in this manner since all experiments were done at a low, constant rate. Hence it follows that the suggestion does not provide a true explanation of the fall in breaking extension with increasing rate.

Conclusions

From the foregoing it may be concluded that if the time–temperature superposition is valid for isotactic polypropylene, then the shift factor a_T is independent of strain and also applies to the breaking extension. From this it follows that the changes in the shape of the stress–strain curve and of the breaking extension which are produced by increasing the strain rate are identical with those which are produced by decreasing the temperature and must therefore have the same basic cause.

References

1. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, Chap. 11.
2. Hall, I. H., *J. Polymer Sci.*, **54**, 505 (1961).
3. Nagamatsu, K., *Kolloid-Z.*, **172**, 141 (1960).
4. Reding, F. P., *J. Polymer Sci.*, **21**, 547 (1956).
5. Vincent, P. I., *Polymer*, **1**, 425 (1960).

Résumé

On a étudié la possibilité d'appliquer le principe de superposition de Ferry à l'entièreté de la courbe tension-élongation du polypropylène isotactique orienté. On n' a pas suffisamment de résultats pour prouver que ce principe est d'application mais à partir de données de la littérature on peut montrer que, si le principe de la superposition était valable pour ce matériel, les facteurs de glissement seraient indépendants de l'élongation et s'appliqueraient aussi bien à la tension de rupture qu'aux différents points de la courbe tension-élongation.

Zusammenfassung

Die Anwendbarkeit des Ferryschen Superpositionsprinzips auf die gesamte Spannungs-Dehnungs-Kurve von orientiertem isotaktischen Polypropylen wurde untersucht. Zum Beweis der Anwendbarkeit dieses Prinzips liegen nicht genügend experimentelle Daten vor. Aus den veröffentlichten Arbeiten geht jedoch hervor, dass im Falle der Gültigkeit der Superposition für diese Substanz die Verschiebungsfaktoren von der Dehnung unabhängig und sowohl auf die Bruchdehnung als auch auf Punkte längs der Spannungs-Dehnungs-Kurve anwendbar sind.