JOURNAL OF MATERIALS SCIENCE 27 (1992) 1475–1478

Study of shrinkage in biaxially oriented isotactic polypropylene

B. LEROUX*, T. ELMES‡, P. MILLS
ICI Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough,
Cleveland TS6 8JE, UK

A description is given of a "dual network" model which can be used as a basis for understanding correlations between the temperature dependence of shrinkage in biaxially oriented polypropylene films, along with film-forming parameters such as draw temperature and draw ratio. Although the model is presented in its most simplified form, and the structures of the networks are considered to be determined solely by their crystallinities, agreement between theory and experiment is promising.

1. Introduction

To produce thermoplastic polymer specimens of high degrees of chain orientation by mechanical deformation requires deformation to take place at a temperature and rate where the mechanical response of the polymer can be described as rubbery [1]. This implies that the polymer chains are present in a "network" structure. In the case of an amorphous polymer, the sub-chains of the network would be created by chain entanglements [2, 3]. However, in semi-crystalline polymers crystallites can also generate sub-chains [4].

Descriptions of networks of amorphous polymers are well developed [5, 6] and remarkable correlations between network structures and mechanical properties have been made [7]. This, however, is not the case for semi-crystalline polymers. In order to describe the network structure fully it would be necessary to have information on the size distribution of crystallites, the nature of crystallite surfaces, and the spatial distribution of crystals. The matter is greatly complicated by the fact that the network structure will change during deformation. Indeed, sub-chains of "taut-tie molecules", first described by Peterlin [8] and now widely accepted to exist, are a consequence of the breakup and redistribution of crystallites present in the undeformed specimen.

Stabilization of oriented thermoplastics can be achieved by quenching the deformed polymers beneath their glass transition temperature. However, for semi-crystalline polymers, stabilization can also be achieved if during the quench further crystallization occurs. It is this latter circumstance which is of interest here.

The metastability of such an oriented semi-crystalline polymer is reflected in the irreversible reduction in orientation (i.e. shrinkage) that occurs in the polymer during subsequent heating. Depending on the temperature, the molecular process involved can include amorphous relaxation [9], crystal melting and annealing [10], or crystal perfection [11]. What have yet to be developed, however, are models which combine this molecular information on deformation, stabilization and shrinkage, and enable semi-quantitative predictions of the effect of the deformation history of an oriented semi-crystalline polymer on its subsequent shrinkage behaviour. Nowhere is this need greater than in the production and use of biaxially oriented films. The main processing variables to be considered are draw ratio, draw temperature and draw rate. Application of these films in packaging relies on the film having good dimensional stability at printing and storage temperatures.

This paper describes such a model for polymers drawn at temperatures within the melting range of the polymer. In the stabilized polymer there will therefore be two groups of crystals, those present during draw and those formed during stabilization. As suggested above, to make any sort of progress has required making some gross simplifications and assumptions. As in a rubber, shrinkage is considered to be driven by the increase in entropy of oriented sub-chains. However, it would be opposed by the reduction in entropy of a network produced in a deformed state. The mechanics of "dual networks" of this type have been described by Kramer *et al.* [12, 13].

The model is evaluated by undertaking experimental measurements of shrinkage in a series of biaxially oriented polypropylene (BOPP) films drawn under different conditions.

2. The model

Fig. 1 shows the stages of formation and relaxation of dual networks. Imagine an elastic network, n', deformed to a draw ratio λ_0. A second network, n'', is then formed in this state of strain. If the load is then

---

**Present address*: 17 Rue des Coteaux, 14760 Brettevile, Sur Odon, France.
‡Present address: PROPAFILM R + T, ICI Films, Tewin Road, Welwyn Garden City, Hertfordshire, AL7 1HD, UK.

0022-2461

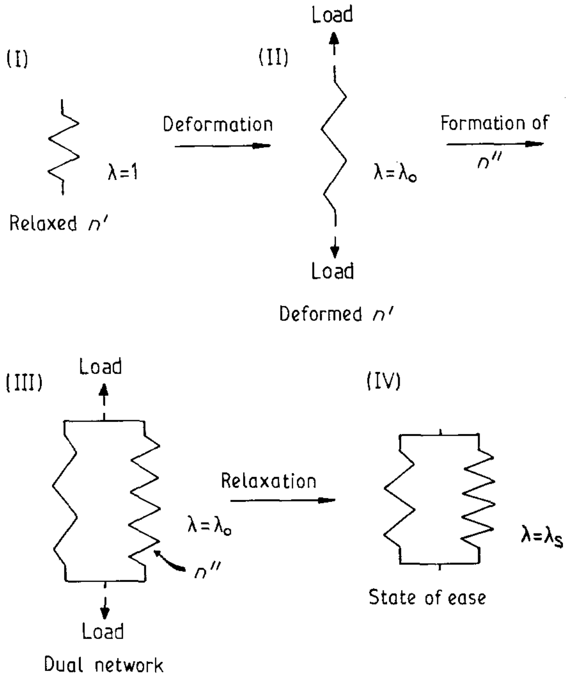

Figure 1 Stages of formation and relaxation of dual networks.

removed from this dual network, then n' wants to contract to $\lambda = 1$. However, since n'' was introduced in the deformed state, it wants to maintain the draw ratio λ_0. Thus the sample shrinks to a state of ease, λ_s, where the tension of n' balances the compression on n''. For this dual network, the empirical stored energy function can be written as [14]

$$W = W' + W'' \tag{1}$$

where

$$W' = C_1(\lambda_x'^2 + \lambda_y'^2 + \lambda_z'^2) + C_2'(\lambda_x'^2\lambda_y'^2 + \lambda_y'^2\lambda_z'^2 + \lambda_z'^2\lambda_x'^2) \tag{2}$$

$$W'' = C_1''(\lambda_x''^2 + \lambda_y''^2 + \lambda_z''^2) + C_2''(\lambda_x''^2\lambda_y''^2 + \lambda_y''^2\lambda_z''^2 + \lambda_z''^2\lambda_x''^2) \tag{3}$$

The prime quantities refer to n' and the double prime quantities to n''. For a rubber which is biaxially deformed

$$\lambda_x' = \lambda_s, \qquad \lambda_y' = \lambda_s, \qquad \lambda_z' = \lambda_s^{-2}$$
$$\lambda_x'' = \lambda_s/\lambda_0, \qquad \lambda_y'' = \lambda_s/\lambda_0, \qquad \lambda_z'' = (\lambda_0/\lambda_s)^2$$

A state of ease will occur when

$$(\mathrm{d}W/\mathrm{d}\lambda_s)\lambda_0 = 0 \tag{4}$$

If the sub-chains within the network are assumed to obey Gaussian statistics, $C_2'' = C_2' = 0$, while

$$C_1'/C_1'' = \nu'/\nu'' \tag{5}$$

where ν is the sub-chain density in the network.

From Equations 1–5

$$\nu'/\nu'' = (\lambda_0^6 - \lambda_s^6)/(\lambda_0^2\lambda_s^6 - \lambda_0^2) \tag{6}$$

In the case of a rubber, the two networks can be formed chemically and/or by using ionizing radiation. For the BOPP films considered here, draw took place at temperatures within the melting range of the polymer. It will be assumed that ν' is determined by the crystallinity present at the draw temperature. The value of ν'' is assumed to be determined by the crystallinity produced when quenching the sample.

3. Experimental procedure

Plaques of polypropylene (ICI Propathene) were prepared by compression moulding. The moulding temperature was 230 °C, the pressure approximately 6 MPa, and the moulding time 2 min. The moulding was then quenched in iced water. The dimensions of the plaque were 60 × 60 × 1.5 mm thick. The density of the plaques was in the range of 0.900 to 0.903 g cm^{-3}, which corresponds to a weight fraction crystallinity of approximately 40 %.

The films were prepared using a T.M. Long stretcher. The variables were draw temperature, T_D, and machine draw ratio, λ_M. Draw was undertaken simultaneously in two perpendicular directions, the machine strain rate being 0.33 s^{-1}. While still under constraint, the films were immediately rapidly cooled to room temperature using cold air.

Measurements of shrinkage were undertaken using a Perkin Elmer thermo-mechanical analyser (TMA). Specimens in the form of rectangular strips were cut along both principle draw directions. After the specimen had equilibrated at 25 °C, its temperature was raised to a programmed temperature, T_S, as rapidly as possible (60 °C min^{-1}). The time taken to stabilize at T_S was approximately 5 min. The dimensional changes of the specimen were continuously monitored.

After mechanical equilibrium within the specimen had been attained, the specimen was cooled as rapidly as possible (30 °C min^{-1}) back to 25 °C and the dimensions of the specimen monitored. The advantage of using TMA is that information on the kinetics of shrinkage can be readily obtained, and the accuracy of measurement is ± 0.5 %. However a 'contact' method of this type means an upper limit on T_S of 160 °C before specimens would be significantly deformed by measurement.

4. Results

Fig. 2 shows the type of output obtained from the TMA. The kinetics of shrinkage in BOPP will be

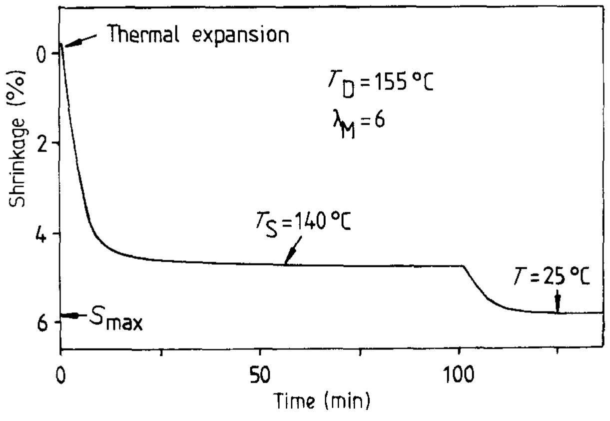

Figure 2 Output from TMA.

discussed in a future publication. This study is concerned only with S_{max}, the maximum amount of shrinkage which can be obtained by annealing a specimen at T_S.

Fig. 3 shows the dependency of S_{max} on T_S (Fig. 3a) and λ_M (Fig. 3b). Values of S_{max} increase with increasing T_S. It is clear that shrinkage is most marked at temperatures above those where crystal melting has occurred, the rate of increase in S_{max} with T_S increasing right through to $T_S = T_D$. For a given value of T_S, S_{max} increases with decreasing T_D and increasing λ_M.

5. Evaluation of the model

In the modelling, it is assumed that the sub-chain densities ν' and ν'' are determined by the crystallinities associated with each network. Fig. 4 shows a typical melting endotherm obtained from a film specimen using differential scanning calorimetry (DSC). The crystallinity beneath T_D would have to be associated with n''. That above T_D could however be associated with n' and n''.

As the temperature of specimens is raised, the initial melting will therefore be of crystals associated with n''. In order to use Equation 6 to determine the new value of λ_s as a consequence of the change in ν'/ν'' it is of course necessary to resolve the question of the crystallinity associated with n' and to determine a value of λ_0.

If deformation during film formation was entirely elastic, then it would of course equal λ_M. This would mean maximum values of shrinkage of 83 and 88 %, for $\lambda_M = 6$ and 8, respectively. However the values of shrinkage of specimens heated above their melting point (Fig. 3) are much lower, showing that considerable plastic flow has occurred during deformation.

The procedure that has been adopted is therefore to assume that at T_D, $\nu'' = 0$. From S_{max} at $T_S = T_D$, λ_S can then be determined as

$$\lambda_S = 1/(1 - S_{max}) \qquad (7)$$

For ν'/ν'' given by the ratio of areas highlighted in Fig. 4, λ_0 can then be determined from Equation 6.

Table I summarizes the parameters and values used in the determination of λ_0. Encouragingly, there is an increase in λ_0 with decreasing T_D and λ_M.

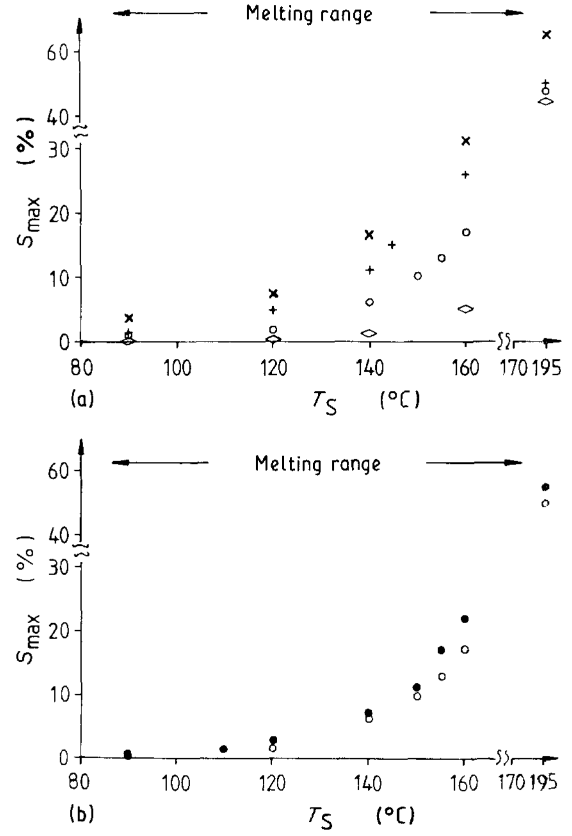

Figure 3 Experimental measurements of the dependency of S_{max} on T_S. (a) λ_M = constant = 6; T_D = (×) 145; (+) 150; (○) 155; (◇) 160 °C. (b) T_D = constant = 155 °C, λ_M = (●) 8; (○) 6.

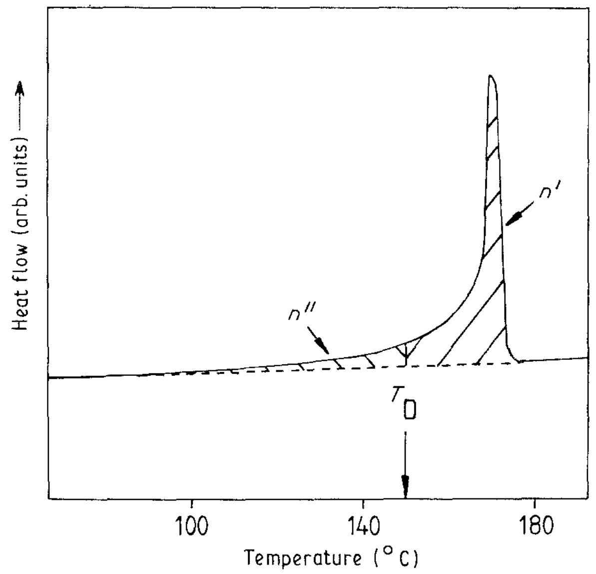

Figure 4 DSC scan of film specimen; assignment of crystallinity associated with n and n. T_D = 150 °C; λ_M = 6.

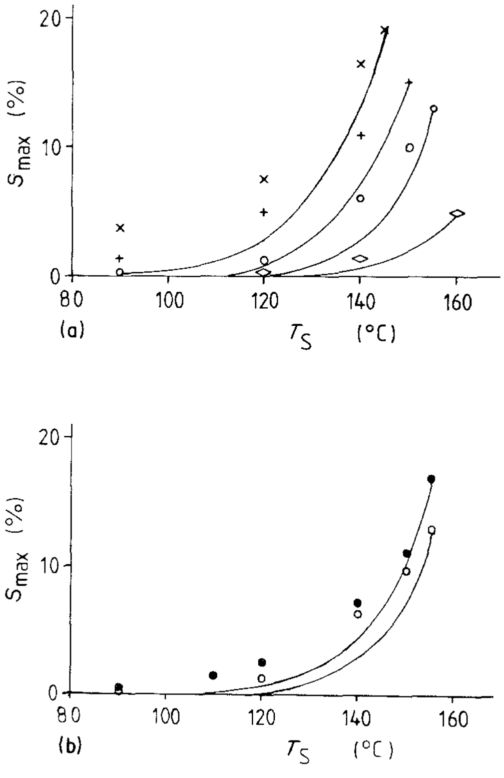

Figure 5 Evaluation of model: (—) model; symbols, experiment. (a) λ_M = 6; T_D = (×) 150, (○) 155; (●) 160 °C. (b) T_D = 155 °C; λ_M = (○) 6, (●) 8.

TABLE I Model parameters and values

T_D (°C)	λ_M	S_{max} (%) $T_S = T_D$	v/v $T = 25°C$	λ_S $T = 25°C$	λ_0
145	6	19	10.1	1.23	2.25
150	6	15	3.9	1.18	1.66
155	6	13	3.2	1.15	1.51
160	6	5	2.2	1.05	1.15
155	8	17	3.0	1.20	1.63

Figure 5 shows a comparison of experiment and model. Qualitatively the agreement is excellent, the model predicting the observed increase in shrinkage with decreasing T_D and λ_M. Given the assumptions and simplifications that have been made, quantitative agreement between experiment and model is also remarkably good. It is interesting to note, however, that the model consistently underestimates the extent of shrinkage, the variance being more marked at lower T_D. One possible explanation which has emerged during a study of the kinetics of shrinkage in BOPP films is that due to the high viscosity of film specimens at room temperature, specimens such as these which have been drawn and then quenched might not have been in a state of ease at room temperature (data to be published).

6. Conclusion

A model based on the mechanics of 'dual networks' in rubbers is a promising route for description of the shrinkage behaviour of biaxially oriented polypropylene films.

References

1. I. M. WARD in "Mechanical Properties of Solid Polymers" (Wiley, New York, 1983) p. 79.
2. R. S. PORTER and J. F. JOHNSON, *Chem. Rev.* **66** (1966) 1.
3. W. W. GRAESSLEY, *Adv. Polym. Sci.* **16** (1974) 1.
4. P. J. MILLS, J. N. HAY and R. N. HAWARD, *J. Mater. Sci.* **20** (1985) 501.
5. P. G. deGENNES, *J. Chem. Phys.* **55** (1971) 572.
6. M. DOI and S. F. EDWARDS, *J. Chem. Soc. Faraday Trans.* 2 **74** (1978) 1789.
7. C. S. HENKEE and E. J. KRAMER, *J. Polym. Sci.* **22** (1984) 721.
8. A. PETERLIN, *J. Mater. Sci.* **6** (1971) 91.
9. M. P. W. WILSON, *Polymer* **15** (1974) 277.
10. R. G. C. ARRIDGE and P. J. BARHAM, *ibid.* **19** (1978) 654.
11. J. M. PETERSON, *J. Polym. Sci. Polym. Lett.* **7** (1969) 231.
12. O. KRAMER, R. L. CARPENTER, V. TY and J. D. FERRY, *Macromolecules* **7** (1974) 79.
13. O. KRAMER and J. D. FERRY, *ibid.* **8** (1975) 87.
14. A. GREENE, K. J. SMITH and A. CIFERRI, *Trans. Faraday. Soc.* **61** (1965) 2772.

Received 25 October 1990
and accepted 25 March 1991