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Stress - Optical Behaviour of Polymers

Ian M. Ward

Summary: The collaborative research between Stepto and colleagues at Manchester University and Ward and colleagues at Leeds University is discussed in terms of its general significance for understanding the development of molecular orientation which occurs during the stretching of polymers. Cross-linked polyethylene and polyethylene terephthalate are chosen as the key examples, with particular reference to their stress optical behaviour. Infra-red spectroscopy is shown to be a valuable tool to validate the methodology developed by Stepto and his colleagues for modelling the behaviour of rubber-like networks.

Keywords: birefringence; polyethylene; polyethylene terephthalate; stress/strain

Introduction

It is very appropriate to honour Professor Robert Stepto by a special session of Polymer Networks 2006 and to attempt to explain the wider significance of his research. The joint research between Manchester and Leeds University on the stress optical behaviour of polymers is important for two principal reasons. First, the development of optical anisotropy with deformation gives complementary information to that obtained from stress-strain measurements and provides insight into the molecular basis of the deformation mechanisms involved. Secondly, the optical birefringence of fibres and films can be used as a processing tool for industrial processes and give information regarding the influence of molecular orientation on mechanical properties, especially modulus and tensile strength.

The Stress Optical Behaviour of Polymers

The collaborative researches between the University of Manchester and Leeds have brought together and provided a deeper understanding of two strands of research.

First, there is the stress-optical behaviour of rubber and cross-linked polyethylenes which was extensively studied by Treloar[1] and Saunders[2] and their collaborators in the period 1945–1970. Secondly, there is the stress-optical behaviour of polyethylene terephthalate (PET) studied by Ward and his colleagues, initially at ICI Fibres, during the period 1954–1990. The ICI research stemmed from the observation in the early 1950's that the tensile drawing behaviour of PET was extraordinarily sensitive to the presence of a small degree of birefringence in the fibres after the initial melt spinning stage of the two stage spinning and drawing process[3] (Figure 1).

This observation could be satisfactorily understood by proposing that in the spinline the fibre was being stretched in the rubber-like state above T_g so that the spun fibre was like a frozen stretched rubber. On subsequent heating above T_g this spun yarn developed an entropic force. Detailed measurements of the stress-optical behaviour were undertaken by Pinnock and Ward[4] and used to characterise the processing route as well as the spun yarns. Because it is much easier to measure the birefringence than the stress in the spinline, the determination of the stress-optical constant was important in enabling a detailed

IRC in Polymer Science and Technology, School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK
Fax: (+44) 0113 3433846
E-mail: I.M.Ward@leeds.ac.uk

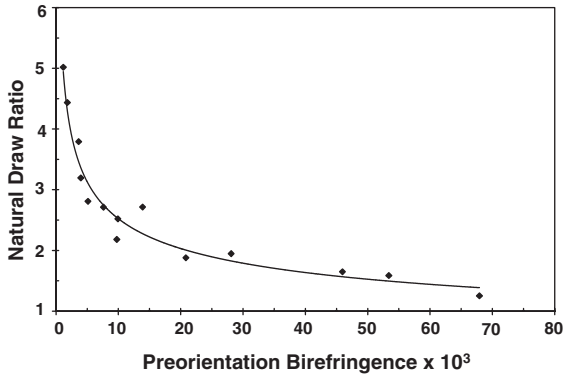

Figure 1.
Influence of preorientation birefringence on the natural draw ratio of PET fibres.

understanding of the mechanics of the fibre spinning process.

This research was also important in establishing the importance of the formation of a molecular network at the spinning stage which is subsequently deformed to define a network draw ratio. The recognition that the properties of the final fibre relate to the network draw ratio and not to that imposed in the tensile drawing stage was of great importance and is of general validity.[5] (Figure 2)

For example, it was the key to the development of high modulus and high strength polyolefine fibres[6] and the related recognition that the processing of polymers in the solid state can be understood in terms of true stress/true strain strain rate relationship which is a cornerstone in the quantitative modelling of polymer processes.[7]

Theoretical Modelling of Stress-Optical Behaviour

The stress-optical behaviour of rubbers and melt spun PET was initially interpreted using the 1942 theory of Kuhn and Grün.[8] This theory asserts that the true molecular network can be replaced by an idealised network of N_o chains/unit volume, each chain containing a number n of freely jointed links (called random links) of length ℓ'.

The values of n and ℓ' for the equivalent freely jointed chain are determined by assuming that these are identical to the values of $\langle r^2 \rangle$ and r_{max} for the real chain. The Kuhn and Grün model was very attractive with regard to the prediction of a constant relationship between birefringence and stress, because both related to the simple finite strain measure $(\lambda^2 - \lambda^{-1})$ where λ is the deformation ratio imposed on the polymer. The absolute value of this relationship- the stress optical coefficient - was, however, not very clearly defined and in the case of PET the number of random links was very small (<5) which cast doubt on the basic validity of the model. Eventually, it came to be recognised that the model of a network of Gaussian freely jointed chains was inadequate and also that the assumption of a constant stress-optical coefficient did not apply.

A major advance in our understanding of these issues stems from the Monte Carlo model developed by Stepto and his co-workers[9,10] which is based on detailed molecular representations of network chain structures and directly addresses the problem of some chains in a rubber network reaching maximum chain extension. The basis of the Manchester/Leeds collaboration was that the Stepto model could address the developments of molecular orientation and hence the optical birefringence as well as the stress in deformed rubber-like networks.[11] Here the key issue is to relate the orientation of chain segments to the overall deformation of the molecular

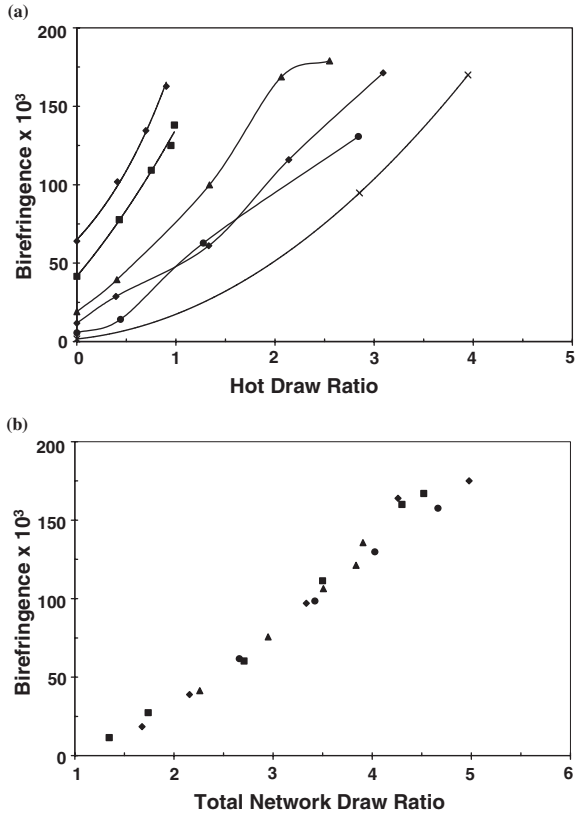

Figure 2.
Birefringence Vs. (a) Actual hot draw ratio, (b) Total network draw ratio for drawn PET fibres and their spun yarn precursors.

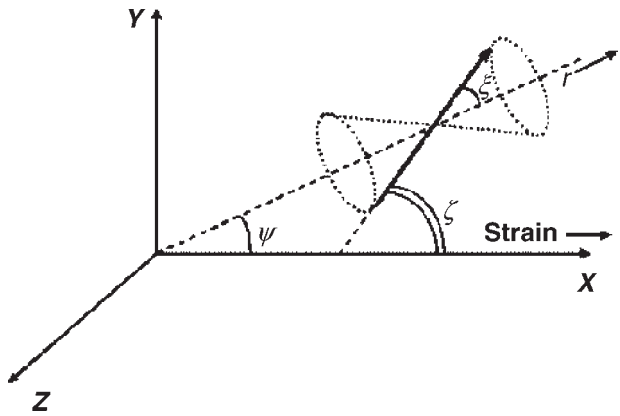

Figure 3.
Orientation angles: ξ, between segment vector and chain vector r ψ, between r and the uniaxial strain direction ζ, the angle between the segment vector and the chain direction.

network. Figure 3 shows how the orientation angle ξ between a segment vector and a chain vector r relates to the angle ψ between r and the uniaxial strain direction and ζ the angle between the segment vector and the strain direction.

For birefringence and infra-red measurements of molecular orientation in samples with fibre symmetry we require the average value of

$$P_2(\cos\zeta) = 1/2(3\cos^2\zeta - 1)$$

The Legendre addition theorem gives the average value of

$$\langle P_2(\cos\zeta)\rangle = \left\langle \langle P_2(\cos\xi)\rangle_i P_2(\cos\psi_i)\right\rangle$$

where $\langle P_2(\cos\xi)\rangle_i$ is found for each chain and the product is formed for the deforming network.

For polyethylene, RIS calculations showed that $\langle P_2(\cos\xi)\rangle_i$ was proportional to 1/n to a very good approximation where n is the number of links in a chain between junction points of the network (Figure 4).

With $\langle P_2(\cos\xi)\rangle_i = \kappa/n$

the stress optical coefficient can be shown to be

$$C = \frac{\kappa}{3}\frac{M_o}{\rho RT}\Delta\,\tilde{n}_{\max}$$

where M_o is the average molecular mass, ρ is density, R the gas constant, T absolute temperature and $\Delta\,\tilde{n}_{\max}$ is the maximum birefringence for a fully oriented polymer.

In addition to providing a satisfactory prediction of Saunders' stress optical data on cross-linked polyethylene, the Leeds/Manchester collaboration also showed that this rescaling approach could be used in conjunction with NMR spin- echo data to determine the rheological entanglement length in PE melts.[12] These latter results drew extensively on previous research at Leeds by Ries, Brereton and others.

Stress-Optical Behaviour of PET Fibres and Films

In PET the modelling of the deformation is more complicated than for PE because there are two molecular parts, a glycol residue and a terephthaloyl residue. It is

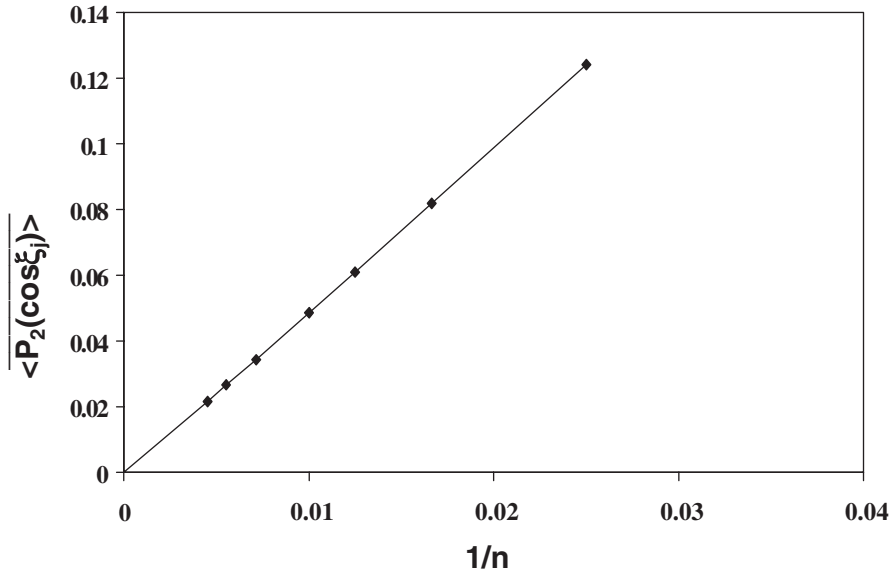

Figure 4.
$\langle P_2(\cos\xi)\rangle_i$ vs. 1/n for RIS model.

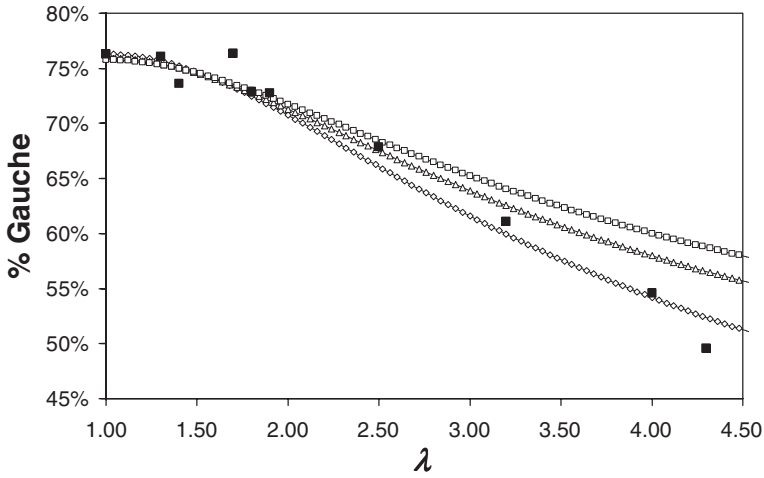

Figure 5.
Experimentally measured values of gauche content as a function of the draw ratio λ (■), compared with theoretically predicted values for networks of 9 (◇), 10 (△) and 11 (□) repeat units per chain at 523 K.

possible to take into account changes in conformation (gauche/trans for the glycol residue, cis/trans for the terephthaloyl residue) and to provide quantitative predictions for changes in conformational states as well as molecular orientation. Infra-red spectroscopy was therefore used to determine changes in gauche/trans ratio and molecular orientation of the terephthaloyl residue for comparisons with the theoretical modelling. The initial gauche/trans content was chosen to be consistent with the infra-red data and the neutron diffraction determination of $\langle r^2 \rangle$ by Fischer and his colleagues.

The key infra-red results shown in Figure 5 and 6 confirm that the conformational changes in gauche/trans content and the terephthaloyl orientation are both consistent with stretching an entangled molecular network with about ten PET units per network chain[13] The molecular modelling

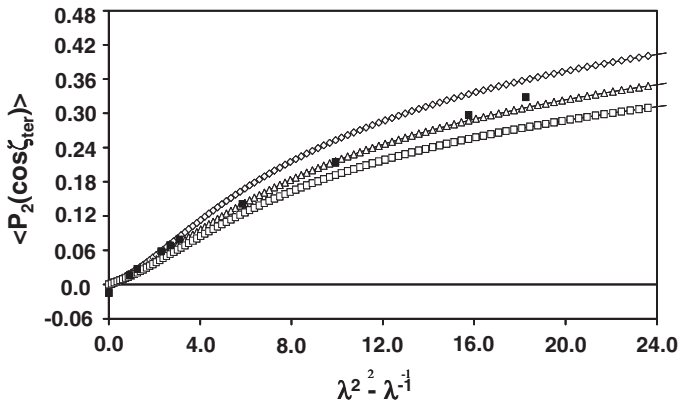

Figure 6.
Average experimental values of the terephthaloyl segment orientation as a function of $\lambda^2 - \lambda^{-1}$ (■), compared with theoretically predicted values for networks of 9 (◇), 10 (△) and 11 (□) repeat units per chain at 523 K.

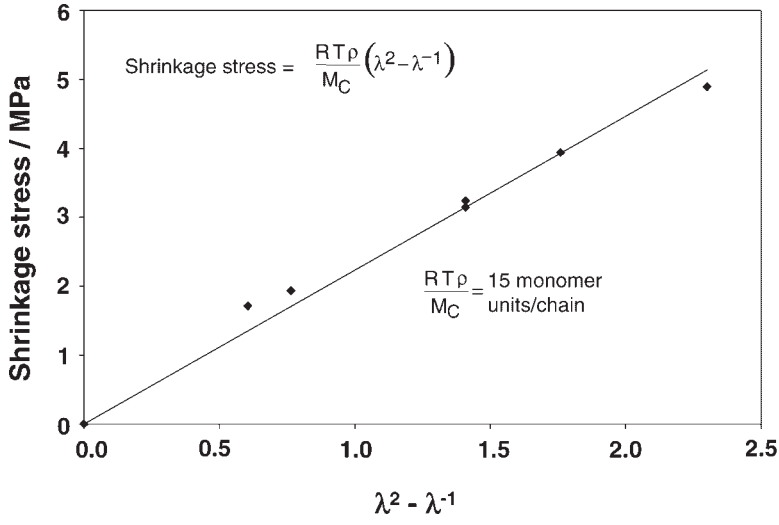

Figure 7.
Shrinkage stress at 80 °C of drawn PET samples Vs. (λ^2-λ^{-1}).

was also used to calculate the development of birefringence with deformation and combined with measurements of the shrinkage force produced when the oriented samples are heated above the glass transition temperature i.e. to 80 °C (Figure 7). The shrinkage force data are consistent with about 15 monomer units per network chain compared with 10 for the FTIR data. Two explanations can be offered for this difference. Either not all chains are effective in developing stress or there is a distribution of network chain lengths where shorter chains make a greater contribution to the changes in conformation and molecular orientation.

A major issue regarding the deformation of PET has been the extent to which the onset of crystallisation would affect these predictions based on a rubber-like network. To examine this, Ward and co-workers[14] monitored the behaviour in real time during the uniaxial drawing of PET fibres using dynamic FTIR spectroscopy and in situ WAXS measurements at the Daresbury Synchrotron Radiation Source. The

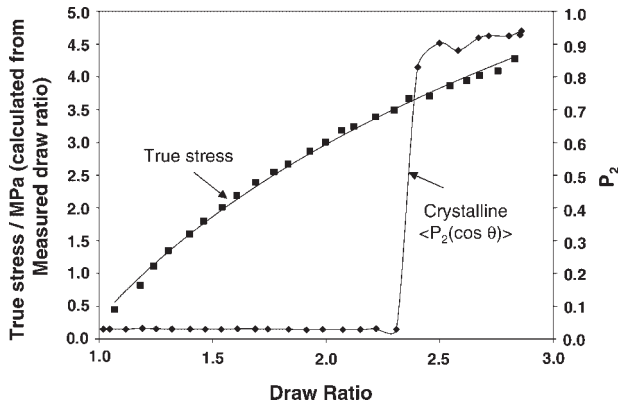

Figure 8.
Crystalline orientation $\langle P_2(\cos\theta)\rangle$ vs Draw Ratio.

onset of crystallisation, defined as the point at which the $\bar{1}05$ reflection could be first observed in the X-ray diffraction pattern, did not correlate with any abrupt change in the FTIR spectra nor with any feature on the stress strain curve. As shown in Figure 8 the crystallites formed at a draw ratio of about 2.3 with very high orientation ($P_2 > 0.8$). It appears that crystallisation occurs after molecular orientation so that the molecular modelling is directly relevant to the development of structure in the drawing process. This result also explains why the properties of the drawn yarns relate to a very good approximation to the network draw ratio irrespective of the nature of the division of the network stretching between the melt extrusion/ spinning stage and the hot drawing stage of the process.

Conclusion

It has been a pleasure to review the very productive collaborative research on the deformation of polymer networks between the Universities of Manchester and Leeds and to emphasise the major contribution to this research by Professor Robert Stepto and his colleagues.

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