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D.S.A. De Focatiis and C.P. Buckley (2011), *Craze initiation in glassy polymers: quantifying the influence of molecular orientation*, Polymer, 52 (18), pp 4045-4053. doi: 10.1016/j.polymer.2011.06.044

D.S.A. De Focatiis and C.P. Buckley (2011), *Prediction of frozen-in birefringence in oriented glassy polymers using a molecularly-aware constitutive model allowing for finite molecular extensibility*, Macromolecules, 44 (8), pp 3085–3095. doi: 10.1021/ma102906z

D.S.A. De Focatiis, J. Embery and C.P. Buckley (2010), *Large deformations in oriented polymer glasses: experimental study and a new glass-melt constitutive model.* Journal of Polymer Science Part B: Polymer Physics, 48 (13), pp 1449-1463. doi: 10.1002/polb.22028

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PREDICTION OF CRAZING AND BIREFRINGENCE IN ORIENTED GLASSY POLYMERS

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Abstract

A study has been made of how crazing stress and birefringence of oriented glassy polymers can be predicted, for a polymer of given molecular weight, following a given melt processing history. The ROLIEPOLY (RP) polymer rheological model proposed by Likhtman and Graham (2003) was employed, together with the Kramer theory of crazing (1983). The predictions were tested by comparison with results of a new experimental study of crazing and birefringence in monodisperse grades of polystyrene, following model melt-stretching histories. The RP model produced accurate predictions of orientation and hence birefringence, provided that the prior melt-stretching process occurred on a time-scale slower than the entanglement Rouse relaxation time τ^{e} . Similarly, the crazing stress was predicted successfully with the model under the same conditions; the only adjustable parameter being the single parameter of the Kramer theory.

Introduction

There is currently great interest in further development of computational tools for simulation of polymer processes and products, to include prediction of solid state properties and hence product performance in service. A well-known feature of glassy polymers is the phenomenon of crazing under load: the formation of visible, apparently crack-like, defects prior to fracture. Each craze is a planar region of localized deformation and cavitation, with its lower density and hence refractive index causing total internal reflection from craze boundaries, causing a superficial resemblance to cracks. The stress required to initiate crazing is known to be sensitive to any molecular orientation in the product, frozen-in during previous melt-processing. Therefore, it is highly desirable to be able to predict crazing in silico, during computer-based optimization of a product and its manufacturing process. Furthermore, so that optimization could extend to specification of the grade of polymer, predictions would ideally include sensitivity to important molecular parameters such as polymer molecular weight and its distribution.

The present study was aimed at achieving this goal. The approach adopted was to combine experimental study of a group of monodisperse and polydisperse polystyrenes as a model system, with development of a numerical simulation tool, for modeling the development and freezing-in of molecular orientation during processing. Results are shown here for two monodisperse polystyrenes.

In the experimental study, the polystyrene materials were subjected to a set of well-defined melt-stretching histories, and their resulting craze initiation stress at room temperature was measured (parallel to the direction of uniaxial orientation). In addition, to provide an independent validation of the predictions of molecular orientation, the optical birefringence was measured for each oriented polystyrene sample.

Numerical simulations of identical melt-stretching processes, incorporating awareness of molecular chain length, were achieved by exploiting the molecularly-based ROLIEPOLY polymer melt rheological model proposed by Likhtman and Graham [1]. It has found wide success in simulating correctly the flow of monodisperse polymer melts along closed channels (see for example, Bent et al. [2]). Its reliability for polydisperse polymers is currently unclear. In this paper we limit application of the model to monodisperse polystyrene. In the present work, it was employed within a "glass-melt" constitutive model for an amorphous polymer, that extends its use to the freezing-in of molecular orientation in the glassy state [3]. Predictions of molecular orientation were used to predict birefringence and crazing stress (via the model proposed earlier by Kramer [4]). Finally, the predictions were critically assessed, by comparison with results of the experimental study.

Materials and experimental methods

The materials for which data are reported here were two samples of monodisperse linear atactic polystyrene (PS) (PDI = $M_w/M_n < 1.15$), synthesized by living anionic polymerization (kindly provided by Dr Lian Hutchings of the University of Durham). Molar mass measurements were performed by size exclusion chromatography on a Viscotek TDA 302 machine with refractive index,

viscosity and light scattering detectors. The polymers are referred to here as AF ($M_w = 2.62 \times 10^5$ g/mol) and AG ($M_w = 5.18 \times 10^5$ g/mol) for consistency with previous publications on these materials [3].

To characterize the linear viscoelastic melt rheology, as needed for fitting the rheological model, dynamic mechanical analysis of the polymers in shear was carried out using an Ares L2 rheometer with 10 mm parallel plates (results kindly provided by Dr John Embery of the University of Leeds). The temperature range between 130°C and 230°C was used. Curves of *G*' and *G*'' versus log(frequency) were time-temperature shifted to provide master curves for each polymer at a reference temperature of 170°C. From these, the linear viscoelastic relaxation spectrum for each polymer was obtained.

Isotropic bars of the two materials were formed by compression moulding, using a hydraulic press with the mould heated to 170°C. Repeatable surface roughness was ensured by using a disposable aluminium foil liner for the mould. Molecular orientation was introduced in a controlled manner by axial melt-stretching of the bars in an Instron 4204 testing machine with an environmental chamber, at a range of temperatures T above $T_{\rm g}$, at a constant crosshead velocity corresponding to a nominal strain rate of 0.02 s⁻¹. The bars were held in pneumatic grips and stretched uniaxially to a range of draw ratios λ between 2 and 8, and then quenched to below T_{g} , using a cold aerosol spray. A cooling rate through $T_{\rm g}$ of 15°Cs⁻¹ approximately was achieved. In some experiments, stress relaxation for a time t_{dwell} , at constant grip displacement, was allowed after stretching, before quenching. Strain during melt-stretching was measured using an Instron non-contact video extensometer.

Three versions of the orientation procedure were employed, to explore systematically the roles of three process variables.

Procedure I: Stretching temperature *T* was varied from 105°C to 135°C, with constant stretch $\lambda = 3$, and constant stretch rate 0.02 s⁻¹, and immediate quenching.

Procedure II: Dwell time t_{dwell} was varied between 1 s and 10^6 s, for constant $T = 120^{\circ}$ C, $\lambda = 3$, stretch-rate = 0.02 s⁻¹. *Procedure III*: Stretch λ was varied from 2 to 7, for constant $T = 120^{\circ}$ C, stretch-rate = 0.02 s⁻¹, and immediate quenching.

In-plane birefringence of the oriented bars $\Delta n = n_3 - n_1$ was measured using an Olympus BX51 transmission optical microscope, with polarising optics and a Berek rotary compensator, in white light at room temperature. Axis 3 was defined as the direction of stretching, and axis 1 the in-plane transverse direction.

The measurement of tensile stress required to initiate visible crazes was made using a customized procedure, designed to work with miniature specimens, to enable the study of unusually small quantities of material. Experimental details are described by the authors elsewhere [5]. All measurements were made with specimens soaked in analytical reagent grade diethylene glycol (DEG), for a minimum of 1 day prior to testing. Specimens with approximate dimensions 7 mm x 2 mm x 0.3 mm were cut from the oriented bars parallel to their axes, and after prior soaking were subjected to three-point bend creep tests, while still immersed in DEG.

A low power optical microscope was used to determine the position where crazing was just initiated after application of a given bending load for a given creep time (300 s for all the results shown here). Application of the theory of beam bending then gave the value of the crazing stress.

Theoretical predictions

Crazing stress and birefringence in an oriented polymer depend on orientation of the molecules. Each molecule at any instant has an end-to-end vector \mathbf{R} . Meltstretching induces two forms of deviation of the \mathbf{R} vectors from their counterparts \mathbf{R}_0 in the fully relaxed, isotropic case. First: the distribution of directions of \mathbf{R} vectors becomes non-random, i.e. there is preferred alignment of end-to-end vectors. Second: the distribution of directions of molecular sub-units within a molecule becomes nonrandom, giving molecular stretching, and hence a change to the magnitude of \mathbf{R} . A statistical measure of the average orientation, encompassing both effects, is given by the orientation tensor T, defined (using <...> to indicate averaging over all molecules)

$$T \equiv \frac{3 < RR^{\mathrm{T}} >}{< R_0^2 >} \tag{1}$$

thus T = I in the isotropic limit. The ROLIEPOLY model comprises a set of differential equations governing the evolution of T, that may be solved numerically for any given melt-deformation history, for a monodisperse polymer. The only input data required are the linear viscoelastic spectrum of the melt, polymer chain length, and the histories of velocity gradient and temperature. Details and physical justification for the model were given previously by Likhtman and Graham [1]. In the present work a modified version of the equations was employed, allowing for finite extensibility (FE) of the molecules.

Theories for prediction of crazing stress have been proposed by several authors. Indeed, the present authors, in an earlier phase of the work reported here, proposed a model for the rate-dependent crazing of isotropic glassy polymers in tension, based on competition between disentanglement and chain scission mechanisms for the formation of the new surfaces of craze fibrils [6]. This yields a value for the crazing stress $\,\sigma_{
m c}^{
m iso}\,$ of the isotropic polymer, and its variations with temperature, strain-rate and molecular weight. When the polymer contains preferred molecular orientation, however, it is well-known that the crazing stress deviates from its isotropic value. The process of crazing was studied in detail by Kramer and co-workers - see the review by Kramer [4]. On the basis of detailed microscopic studies of crazes in isotropic and oriented polymers, they proposed the following. The effect of molecular orientation in a glassy polymer is to give rise to an entropic back-stress, or conformational stress $\sigma_{\rm conf}$, that must be overcome in addition to the intrinsic (isotropic) crazing stress σ_{c}^{iso} , which is itself unaffected by orientation. Thus the increase in tensile crazing stress in the direction of the orientation process is predicted to be given by:

$$\sigma_{\rm c} - \sigma_{\rm c}^{\rm iso} = \sigma_{\rm conf} / \beta \tag{2}$$

where β is a scalar constant for a given polymer and σ_{conf} is the component in this direction of the stress tensor σ_{conf} . This stress is obtained from *T*, again allowing for finite extensibility (neglecting any volume change):

$$\boldsymbol{\sigma}_{\text{conf}} = G_{\text{e}}\left(\frac{F(\lambda)}{\lambda}\right) \left[\boldsymbol{T} - \lambda^{2}\mathbf{I}\right]$$
(3)

where G_e is the plateau modulus, $\lambda = \sqrt{\frac{1}{3} \text{tr} T}$ is the rms molecular stretch, and the factor $F(\lambda)$ can be written as follows for a chain of maximum possible stretch λ_{max}

$$F(\lambda) = \mathscr{G}^{-1}\left(\frac{\lambda}{\lambda_{\max}}\right) / \mathscr{G}^{-1}\left(\frac{1}{\lambda_{\max}}\right)$$
(4)

where $\mathscr{I}^{-1}(x)$ is the inverse Langevin function. The maximum stretch λ_{\max} is computed for any given polymer as that of the equivalent Kuhn chain between entanglements: in terms of the number of bonds between entanglements $n_{\rm b}$, the characteristic ratio C_{∞} , and the carbon-carbon backbone bond angle $\theta_{\rm b}$. It is given by

$$\lambda_{\max} = \sqrt{\frac{n_{\rm b}}{C_{\infty}}} \sin\left(\theta_{\rm b}/2\right) \quad . \tag{5}$$

In applying the ROLIEPOLY model in the present work, the multi-mode form was used, reflecting the linear

viscoelastic relaxation spectrum. Then each mode has its own corresponding stretch λ , and hence stress from equation (3). The total conformational stress was obtained by summing over the spectrum.

From the orientation tensor T, the birefringence Δn may also be obtained, as follows

$$\Delta n = C_{\rm e} G_{\rm e} \left(T_{33} - T_{11} \right) H \left(\frac{\lambda_k}{\lambda_{\rm max}} \right) / H \left(\frac{1}{\lambda_{\rm max}} \right)$$
(6)

where C_c is the (dominant) conformational contribution to the stress optical coefficient, and H(x) is a function that expresses the finite extensibility of the molecules, as follows

$$H(x) \equiv \frac{5}{3x^2} \left[1 - \frac{3x}{\mathscr{G}^{-1}(x)} \right]. \tag{7}$$

Parameters of the model

The parameters of the model were found using the procedure described earlier in this context by De Focatiis et al. [3]. The first step was to establish the generic molecular parameters for polystyrene. The microscopic theory of linear rheology of polymer melts proposed by Likhtman and McLeish [7] was fitted to the linear rheological data for shear of both materials simultaneously, using the 'Reptate' toolbox [8]. This yielded the entanglement shear modulus $G_e = 318$ kPa, the entanglement molar mass $M_e = 13140 \text{ g mol}^{-1}$ and the Rouse relaxation time of one entanglement length $\tau^{e} = 6.97$ $\times 10^{-4}$ s at the reference temperature $T^* = 170^{\circ}$ C. With $M_{\rm e}$ obtained in this way, and the known parameters for PS $C_{\infty} = 10$, and $\theta_{\rm b} = 109.28^{\circ}$, the maximum stretch of interentanglement strands can be obtained from equation (5): $\lambda_{\rm max} = 4.09$.

For each material, the longest (whole molecule) Rouse time and reptation time were then computed for the reference temperature following Collis et al. [9] as

$$\tau_1^{R^*} = Z^2 \tau^e$$

$$\tau_1^{d^*} = 3 \left(1 - \frac{2.38}{Z^{0.5}} + \frac{4.17}{Z} - \frac{1.55}{Z^{1.5}} \right) Z^3 \tau^e$$
(8)

where $Z = M / M_e$ represents the number of entanglements per molecule.

Finally, starting with the longest reptation time as that given by the second of equations (8), a discrete

normalized shear relaxation spectrum $v_k(\tau_k^d)$ was fitted to the linear shear rheology data for each material, with one mode of reptation per decade of time. For modes other than the slowest, an effective *Z* was computed by applying the second of equations (8) to τ_k^d , and the corresponding Rouse time τ_k^R found from the first of equations (8). The relaxation spectrum for each material was also extended down into the glassy region, as described by De Focatiis et al. [3], but this is not important for the present application of the model.

To complete the prediction of birefringence, a value for the conformational part of the stress-optical coefficient is required: C^c . When orientation in glassy PS is quenched-in by rapid cooling from the melt, this governs the dominant contribution to the birefringence. The value used in this work was $C^c = -4.5 \times 10^{-9}$ Pa⁻¹, applicable to monodisperse and polydisperse PS [10]. It is negative because of the dominance of the pendant phenyl group in the PS monomer unit, such that alignment of the molecular backbone causes a perpendicular alignment of the phenyl groups.

Experimental tests of the model

The first prediction to be tested was the stress-optical rule, and its nonlinearity arising from finite extensibility of the molecules, in the most highly oriented specimens.



Figure 1 Measurements of optical birefringence plotted against the stress just prior to quenching after melt-stretching, for both materials and all three procedures (symbols); the full line shows the prediction of the model, while the dashed line shows the prediction if finite extensibility is neglected.

Fig. 1 shows birefringence plotted versus the stress measured at the time of quenching after the meltstretching process, for both materials and all three procedures employed. Two features are prominent. Firstly, at the lowest stresses, the relationship is linear with a gradient predicted correctly by the model using the value for stress-optical coefficient given above. Secondly, there are some data near a birefringence of -0.01 lying significantly above the predicted line: these data correspond to melt-stretching on the sub-entanglement length-scale, as seen also at low temperatures in Fig. 2. Thirdly, although only limited experimental data are available, the points appear to start to break away from the linear relation at higher stresses. This is predicted by the physical model: as the molecules become stretched and aligned the birefringence tends to saturate, while the stress increases more rapidly reflecting finite extensibility (from equations (3) and (6)). The dashed and full lines in Fig. 1 show the theoretical predictions, with finite extensibility switched off, and on respectively.

The predictions of birefringence were further tested by comparison with experimental values, for the two materials melt-stretched according to Procedures I, II and III. In each case, the predictions were produced by numerical simulation of the melt-stretching procedure, using the constitutive model outline above. No further adjustable parameters were employed in calculating the birefringence.



Figure 2 Measurements of birefringence as a function of melt-stretching temperature T, for orientation according to Procedure I (symbols). Predictions were obtained using numerical simulations with the constitutive model (lines).

Thus Fig. 2 shows birefringence versus temperature of melt-stretching, for bars oriented according to Procedure I, for the two monodisperse PS materials.

At the highest temperatures, the predictions of the model including finite extensibility are in clear agreement with experiment. The model captures well the fall-off in birefringence resulting from increasing molecular relaxation during melt-stretching. At the lowest temperatures in the range, however, the measured birefringences for both materials, which are in close agreement, deviate upwards relative to the predictions. Also indicated on this graph is the temperature where the $\tau^{\rm e}$ based Weissenberg number $Wi_{\rm e}$ for the melt-stretching process reaches unity. It is interesting to note that the deviations occur where $Wi_{\rm e}>1$.

Fig. 3 shows birefringence versus t_{dwell} for PS bars of polymer AF, oriented according to Procedure II. It can be seen that there is close agreement between experimental data (symbols) and predictions of the model with finite extensibility (solid line). Again the model captures accurately the decrease in birefringence arising from molecular relaxation, in this case occurring during the dwell following melt-stretching. Superimposed on the graph are the times were the Deborah numbers based on τ^{e} and τ^{R} are unity. The agreement in this case extends right across the range of time-scales, from Rouse relaxation of an entanglement strand to relaxation of the whole molecule.



Figure 3 Measurements of birefringence as a function of post-drawing dwell time t_{dwell} for melt-stretching of material AF according to Procedure II (symbols). Predictions were obtained using numerical simulations with the constitutive model (lines). Also shown are the times at which the Deborah numbers based on t^{R} and t^{R} are equal to unity.

Finally Fig. 4 shows the variation of birefringence with the applied draw ratio, for melt-stretching of material AG according to Procedure III. Again, the experimental measurements (symbols) are compared with predicted values, obtained by simulations of the melt-stretching process (lines). The model with finite extensibility provides excellent agreement with the experimental data for the full range of draw ratios.



Figure 4 Measurements of birefringence as a function of draw ratio, for melt-stretching of material AG according to Procedure III (symbols). Predictions were obtained using numerical simulations with the constitutive model (lines).

In summary, these tests of the model showed good agreement between measured and computed birefringence, using the model with finite extensibility, for melt-stretching at temperatures sufficiently above T_g . However, under some conditions the birefringence is underpredicted using the present model (Fig 2). This is associated with molecular stretching at the subentanglement level (Wi_e >1).

To test the ability of the model to predict tensile crazing stress, specimens were cut from the oriented bars and tested in miniature 3-point bending as described above. Results were compared with the results of numerical simulation, via equation (2), as shown in Figure 5. The model predicts proportionality between the increase in crazing stress and the conformational stress, with a constant of proportionality that is independent of molecular weight. Both predictions are seen to be verified in Figure 5, although this breaks down where the entanglement scale Weissenberg number exceeds unity.

Again, as seen before in Figs 1 and 2, the model provides good predictions *until* there is significant stretch at the sub-entanglement length-scale. From fitting the linear portion of the graph in Fig. 5 (where $Wi_e < 1$) to equation (2), the constant of the Kramer model is found to be $\beta = 0.064$ for monodisperse PS.



Figure 5 Measurements of the increase in tensile crazing stress relative to the isotropic case, as a function of the conformational stress (computed from the birefringence using the master curve in Figure 3 for experimental measurements). Drawing was performed according to Procedure I. Also identified is the portion of the data set for which $W_{i_e} > 1$. Also shown is the linear relationship predicted by Kramer's theory using $\beta = 0.064$ (solid line).

Conclusions

The work described in this paper has proposed, and experimentally tested, a procedure for predicting two important solid-state properties of oriented glassy polymers: the birefringence (widely used as a measure of molecular orientation); and the crazing stress.

The method of prediction employs the molecularlybased ROLIEPOLY rheological model for polymers proposed by Graham and Likhtman, extended to accommodate finite molecular extensibility, and to allow cooling through the glass transition.

The model allows evolution of the molecular orientation tensor T to be tracked during numerical simulation of any given melt-stretching history, and hence its final value in the glassy state to be predicted. The resulting birefringence can then be predicted, and the crazing stress can also be predicted by invoking Kramer's theory of crazing.

Experimental results show close agreement with predictions when molecular orientation is primarily on a length-scale equal to, or greater than, the entanglement length. However, the effects of molecular stretch at shorter length-scales are not captured consistently by the model in its present form. This is the subject of ongoing research.

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