

Development of orientation in glassy polycarbonate at high strains

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(Received 13 November 1986; revised 23 February 1987; accepted 3 March 1987)

Birefringence has been measured on yielded specimens of polycarbonate in simple tension in creep and stress relaxation. The pseudo-affine and random-chain affine models both fail to describe the experimental relationship between birefringence (or orientation) and strain. A new model assuming affine deformation of chain ends and non-random chains is presented, adequately describing the trends of experimental data.

(Keywords: molecular orientation; birefringence; glassy state; post yield; polycarbonate)

INTRODUCTION

It is general practice to describe development of orientation in partially crystalline polymers in the glassy state using Kratky's¹ pseudo-affine model (e.g. Spegt *et al.*², McBrierty and Ward³ and Biangardi⁴). In this model, anisotropic units rotate as rigid rods in an affinely deforming isotropic matrix. The model has also been applied by Biangardi⁴ and Mitchell *et al.*⁵, among others, to orientation of amorphous polymers in the glassy state, although there is no justification for a two-phase model in this case. Kashiwagi *et al.*⁶ have even applied the model to analysis of room temperature birefringence of poly(methyl methacrylate) (PMMA) deformed in the rubbery state. Orientation in the rubbery state is more usually described by Kuhn and Gr \ddot{u} n's⁷ random-chain affine model (e.g. Purvis and Bower⁸ and Cunningham *et al.*⁹); in this model, end-to-end vectors joining crosslinks (or 'entanglement points') deform affinely, and the chain is free to assume a random configuration between these points. Brown and Mitchell¹⁰, Raha and Bowden¹¹ and Zanker and Bonart¹² attributed discrepancies to a strain-dependent entanglement density whereas Kahar *et al.*¹³ attributed them to deviations from the statistical theory following an expression of the Mooney-Rivlin type.

Brown and Windle¹⁴ have discussed the shortcomings both of the pseudo-affine model and of the random-chain affine model with variable entanglement density. They introduce a two-parameter model, separating strain into an 'extensional' and an 'orientational' component, successfully describing stress-strain and orientation-strain relationships in the rubbery state¹⁵ (and Mitchell *et al.*¹⁶) and giving the general trends of glassy state behaviour¹⁷.

In Erman and Flory's^{18,19} description of crosslinked rubbers, diffuse entanglements are taken into account as restrictions on fluctuations of junctions, leading to non-affine deformation of end-to-end vectors. The theory describes birefringence in the rubbery state reasonably well; however, it has been shown by Gottlieb and Gaylord²⁰ that the theory breaks down completely (as do all existing theories of the rubbery state) when applied to stress-strain behaviour in swollen networks. Also, since the effect of entanglements is approximated by

constraints on junctions (i.e. on chemical crosslinks) it does not appear possible to extrapolate the theory to thermoplastics.

It is interesting to note that all reasonably successful descriptions of the trends of deformation behaviour in polymers require at least two components of strain: orientational and extensional^{14,16}, phantom network with fluctuations¹⁸, 'glide' mode and 'diffusional' mode (Lefebvre *et al.*²¹), uniformly affine and random chain affine (Picot *et al.*²² and Maconnachie *et al.*²³). This expresses the experimental fact that birefringence is not a unique function of strain, but also depends on time (at constant strain) or equivalently on strain history¹³ as observed by Qayyum and White^{24,25} and Hammack and Andrews²⁶. Single component models, giving a one to one correspondence between orientation and strain^{1,7} are clearly inadequate. Strictly speaking, two-component models only apply to the rubbery state; in the glassy state, description of the stress-strain behaviour has been shown by Bauwens²⁷ to require three components (Hookean spring, Eyring dashpot and rubbery-elastic spring).

The most convincing model to date of orientation behaviour in the glassy state has been given by Brown and Windle^{14,17}. One drawback of their model, however, is that it ignores the fact that orienting units are joined into chains. The purpose of this paper is to propose an alternative model of orientation in the glassy state and to compare it with classical theories and with experimental data on birefringence in polycarbonate.

EXPERIMENTAL

Polycarbonate (PC) was chosen for this investigation, both because it is amorphous and because birefringence depends only on orientation of main chain segments, polarizability anisotropy being far greater for the phenyl ring than for the methyl side-groups.

Tensile specimens with flared ends and a gauge section $4 \times 0.8 \text{ cm}^2$ were cut from a commercially available sheet of polycarbonate (Makrolon, Bayer) 2 mm thick. The specimens were drawn in an Instron tensile tester at 0.5 cm min^{-1} at room temperature until the neck had reached the flared ends. After unloading, the strain was

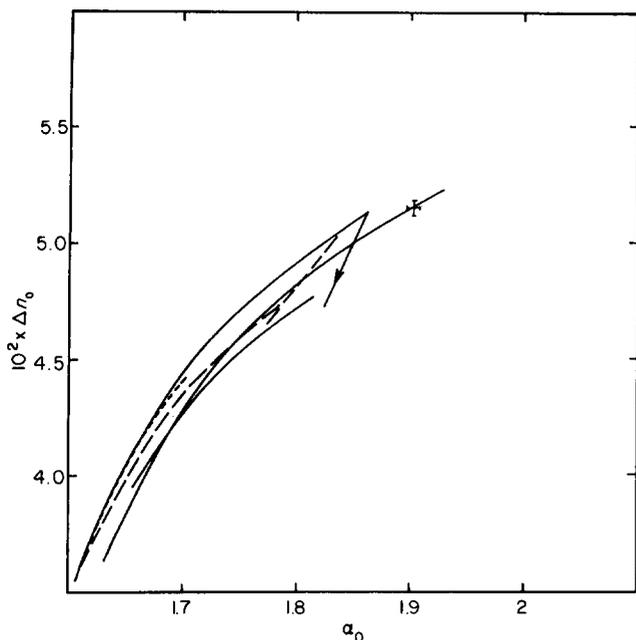


Figure 1 Residual birefringence against residual draw ratio at room temperature. Points omitted for clarity. —, Creep; ----, stress relaxation. Downward arrow indicates recovery. Error bars indicate uncertainty on variation of residual birefringence and draw ratio

determined from the change in cross-sectional area, and birefringence was measured in white light between crossed polars by comparison with a reference sample of known birefringence. The specimens were loaded in creep at nominal stresses (referred to the initial cross-section) ranging from 44 to 50 MPa at room temperature and from 32 to 44 MPa at 62°C. Strain was measured with a dial gauge and birefringence was measured between crossed polars in sodium light ($\lambda = 589.3 \text{ nm}$) by counting fringes. A few samples were tested in stress relaxation, the total strain being stepped up regularly once relaxation had become negligible. Two short samples with flared ends and no gauge section were tested under the same conditions to obtain an estimate of the effect of creep of the tail pieces on strain measurements. It was found that the correction required to account for this effect was equivalent, within 2%, to assuming a gauge length of 50 mm instead of the nominal value, i.e. 40 mm. A few samples were tested below yield at room temperature, in creep and in tension at constant elongation rate.

For most samples a period of recovery of at least 24 h was allowed between sample preparation and testing. In order to determine whether variations in recovery time had any effect on subsequent behaviour, one sample was tested at room temperature within 30 min of preparation, and one was tested at 62°C without unloading.

RESULTS

Birefringence Δn was determined from fringe order f as:

$$\Delta n = \frac{\lambda f}{e_0(\alpha_0/\alpha)^{1/2}} \tag{1}$$

where λ is the wavelength of sodium light (589.3 nm), e_0 and α_0 are the thickness and draw ratio of the drawn sample prior to reloading and α is the current draw ratio. Birefringence at a given strain was found to increase with

stress. This effect was assumed to be due to the purely elastic contribution of stress to birefringence and strain, which was found on unloading to be proportional to stress within experimental error. This contribution was evaluated from:

$$\Delta n_e = A\sigma \tag{2}$$

$$\Delta \alpha_e = \frac{\alpha\sigma}{E} \tag{3}$$

where σ is true stress, $A = 7.4 \times 10^{-5} \text{ MPa}^{-1}$ and $E = 3400 \text{ MPa}$ at 20°C ($6.5 \times 10^{-5} \text{ MPa}^{-1}$ and 3700 MPa respectively at 62°C). These are average values obtained from the immediate response on unloading. The slightly higher modulus at 62°C might simply reflect the lower stresses required at this temperature. These contributions were subtracted from all results obtained on samples under load, in order to convert them to an equivalent unstressed state. Corrected or residual values will be denoted by subscript 'o'. They are relatively insensitive to variations of A and E in creep; in stress relaxation experiments, the major cause of variation of birefringence is the change in stress, making results sensitive to any uncertainty in A and E , and consequently making them more difficult to interpret.

When Δn_o is plotted against α_o (Figure 1), curves obtained at different loads are extremely similar in shape, and differences between these plots do not depend on load. Remaining scatter appears to be traceable to differences in the initial state of the samples (i.e. after preparation but prior to testing). In Figures 2 and 3, results obtained on different samples have been arbitrarily shifted to superpose the shape of the final parts of the plots (i.e. long times and high strains). The shifts are not given, as they are extremely difficult to interpret: widely varying combinations of initial strain and birefringence can be obtained, depending on the strain at

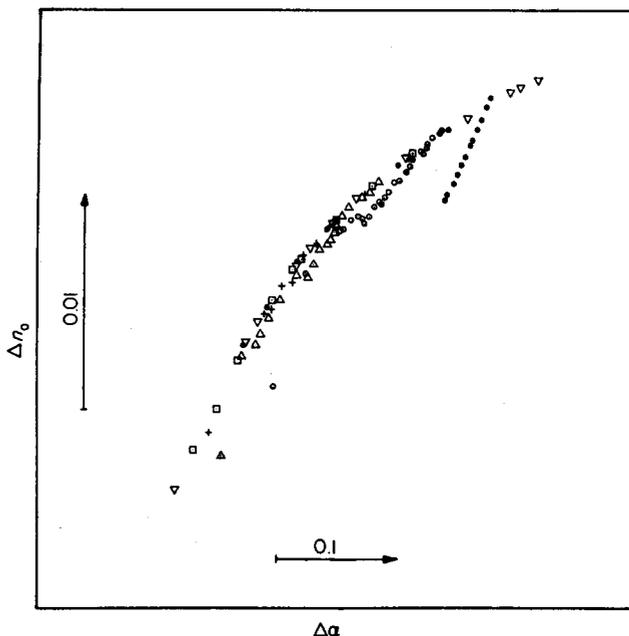


Figure 2 As Figure 1 but curves shifted to superpose long-term portion. +, 52.5 MPa; ∇, 48.8 MPa; ●, 46.4 MPa and recovery after same; □, 44.2 MPa; ○, △, stress relaxation

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