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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

Other relevant articles:

D.S.A. De Focatiis and C.P. Buckley (2008), *Determination of Craze Initiation Stress in Very Small Polymer Samples,* Polymer Testing, 27 (2) pp. 136-145. doi: 10.1016/j.polymertesting.2007.08.006

D.S.A. De Focatiis, C.P. Buckley and L.R.Hutchings (2008), *Roles of Chain Length, Architecture and Time in the Initiation of Visible Crazes in Polystyrene*, Macromolecules 41(12) pp. 4484-4491. doi: 10.1021/ma702157m

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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The Initiation of Environmental Stress Crazes in Polystyrenes with Process-Induced Anisotropy

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Abstract

In order to investigate the effect of molecular orientation at different length scales on the initiation of crazes in polystyrene, oriented tapes are produced by hot drawing at different temperatures and relaxing while hot for different times. The 300s isochronal craze initiation stress in diethylene glycol is then measured in 3-point bending creep experiments on beams cut from the oriented tapes. There is a correlation between craze initiation stress and optical birefringence and increases in craze initiation stress of as much as a factor of 5 compared with the isotropic have been recorded. The most dramatic change in craze initiation is observed where samples are drawn in less than the Rouse entanglement time τ_e.

1 Introduction

The susceptibility to crazing is an important criterion in evaluating the performance of optically clear amorphous polymers such as atactic polystyrene. It has been previously reported that molecular orientation affects both the morphology [1] and the micromechanics [2] of crazes. In this study we investigate the effects of molecular orientation at different length-scales, induced by controlled process histories, on the stress at which crazes initiate.

2 Materials and Methods

Oriented tapes 0.3-0.7mm thick were produced from isotropic compression-moulded bars of linear atactic polystyrene with a weight-average molar mass M_W = 230,000g/mol and polydispersity index M_W/M_N = 2.35 obtained from Dow as GP PS680E. The tapes were hot-drawn in an Instron 4204 testing machine fitted with environmental chamber at a nominal strain rate of $0.02s^{-1}$. The drawing temperature and subsequent relaxation prior to freezing using a cold spray were chosen in order to allow relaxation of the molecules at different length scales, as calculated from molecular theory applied to polystyrene [3]. Table 1 gives values of the Rouse relaxation time of an entanglement segment τ_e, the Rouse time τ_R and the reptation time τ_d, as well as the relaxation time t_r for which tapes are held at the drawing temperature prior to freezing, and the total experiment time t_x (the sum of the drawing time and any relaxation) for the temperatures used in the drawing experiments. Strain was measured during the hot-drawing procedure using a non-contact video extensometer and the stress-strain curves are shown in Figure 1.

Temperature (ºC)	Rouse and reptation times			Post-drawing relaxation t_r (s)	Experiment t_x (s)
	τ_e (s)	τ_R (s)	τ_d (s)		
105	721	130000	18700000	0	$200 < \tau_e$
115	65	11900	170000	300	$\tau_e < 500 < \tau_R$
125	2.2	401	5760	1800	$\tau_R < 2000 < \tau_d$
135	0.2	31	448	1800	$\tau_d < 2000$

Table 1: Relaxation times τ_e, τ_R and τ_d at the 4 drawing temperatures compared with the post-drawing relaxation time t_r and the total experiment time t_x.

Small rectangular beam specimens were cut from the oriented tapes with the beam axis aligned parallel to the drawing direction, and the optical birefringence was measured on each beam using an Olympus microscope fitted with polarisers and a thick Berek compensator. The 300s isochronal craze initiation stress in tension σ_c was then measured by subjecting the beams to 3-point bending at constant load after 24 hours of saturation in diethylene glycol. The width of the crazed region under the applied load was measured within 1 hour of unloading the samples

using a low power optical microscope employing the reflective property of the crazed region and σ_c was then determined from simple beam theory.

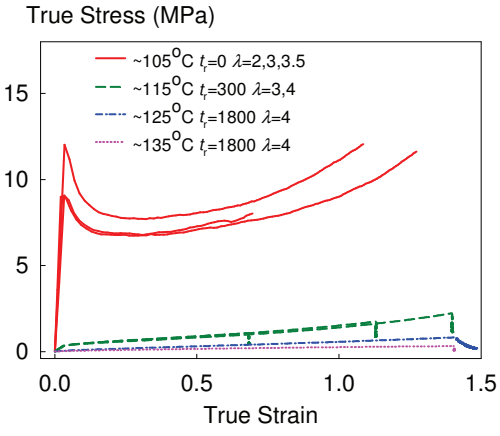

Figure 1: Stress-strain response of the tapes measured during the drawing experiments to stretches λ=2,3,3.5 and 4 and during the subsequent relaxation t_r.

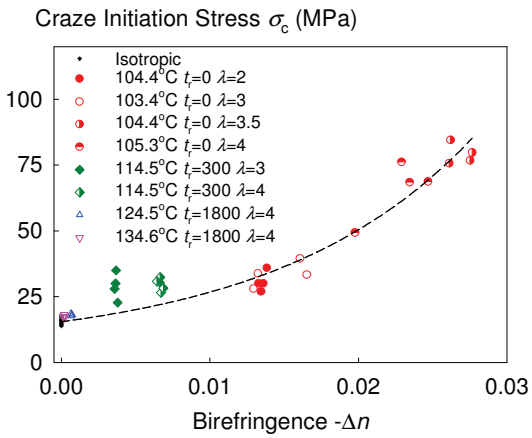

Figure 2: Craze initiation stress as a function of optical birefringence -Δn measured on beam specimens cut from the drawn tapes. Curve guides the eye through samples drawn at 105ºC.

3 Results and Discussion

Figure 2 shows the measured σ_c as a function of -Δn for the full range of beam samples tested. Samples cut from tapes where $t_x < \tau_e$ show a substantial rise in σ_c with -Δn. The behaviour is highly sensitive to the drawing temperature in this regime, and small changes in temperature have a large effect on the final birefringence. Samples from tapes where $\tau_e < t_x < \tau_R$ exhibit a smaller increase in σ_c at the same stretch. Samples from tapes where $\tau_R < t_x < \tau_d$ and $\tau_d < t_x$ show little to no change in σ_c compared with isotropic material.

4 Conclusions

The increase in σ_c in oriented polystyrene is most affected by short range molecular relaxation at times of the order of τ_e and by stretches greater than 3. The most dramatic increase in σ_c is observed where samples are drawn and frozen in less than τ_e. Samples which have been drawn and allowed to relax for a time greater than τ_e can show some increase in σ_c compared with the isotropic case provided the relaxation time is less than τ_R (see diamonds in Figure 2). We can speculate that the length scale associated with an increase in σ_C is longer than the length scale associated with optical birefringence. Further experiments are planned on samples drawn at 105ºC to smaller stretches in order to shed light on this observation.

5 Acknowledgements

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6 References

[1] P. Beardmore and S. Rabinwitz, *Craze formation and growth in anisotropic polymers*, Journal of Materials Science, **10**, 1763-1770 (1975)

[2] N.R. Farrar and E.J. Kramer, *Microstructure and mechanics of crazes in oriented polystyrene*, Polymer, **22**, 691-698 (1981)

[3] M.W. Collis, A.K. Lele, M.R. Mackley, R.S. Graham, D.J. Groves, A.E. Likhtman, T.M. Nicholson, O.G. Harlen, T.C.B. McLeish, L.R. Hutchings, C.M. Fernyhough, and R.N. Young, *Constriction flows of monodisperse linear entangled polymers: Multiscale modeling and flow visualization*, Journal of Rheology, **49(2)**, 501-522 (2005)