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**Main journal articles relating to this conference paper:**

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 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

**Other relevant articles:**

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

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## The Role of Molecular Architecture and Length Distribution in the Environmental Stress Cracking of Polystyrene

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This work investigates craze initiation of monodisperse linear and branched, and polydisperse and bimodal linear polystyrene in diethylene glycol through isochoric 3-point bending creep tests. There are two mechanisms for initiation, disentanglement below  $M_n=9M_e$  and chain scission above. Both bimodal blends and polydisperse samples show higher craze initiation stresses than predicted by comparison with linear monodisperse.

### Introduction

Environmental stress cracking is a well known deformation phenomenon of glassy polymers that results from the application of a tensile stress over time in the presence of environmental agents. Crazes appear as long, thin highly deformed wedges of polymer in which voiding occurs and strands of polymer are drawn out from the bulk surfaces. A large body of work has been carried out investigating various aspects of crazing, and several comprehensive reviews are available [1-3].

Craze initiation is an important limiting criterion in the commercial use of clear polymers such as polystyrene (PS). It is also well established that molecular entanglements play a key role in the physical properties of glassy polymers. Kramer has noted that a 'geometrically necessary entanglement loss' is necessary for crazes to form [2]. In general, where chain mobility is reduced, such as in air crazes, or at lower temperatures, the entanglement loss comes from chain scission [4]. Here the craze initiation stress is expected to be essentially independent of molecular weight [3]. Where the mobility is greater, such as in solvent-formed crazes and at higher temperatures and over longer time scales, chain disentanglement is the dominant mechanism [5]. Here molecular weight is a crucial parameter, since a short chain is more mobile and able to disentangle than a long chain.

In this work we investigate craze initiation by isochronal 3-point bending creep experiments. The extent of the crazed region in the specimens is measured using microscopy and the stress at which crazes begin to form is subsequently found from beam theory. We investigate a wide range of linear atactic monodisperse polystyrenes, a selection of bimodal blends of linear polystyrenes, two commercial polydisperse polystyrenes, and a number of monodisperse polystyrenes with carefully controlled molecular architectures such as stars and H-shape molecules. Due to the unusual nature of the materials only a few grams of most have been available, and all experiments have been designed to work with very small samples. This work forms part of a wider study of solid state properties of polymers with tailored molecular architectures and distributions with the aim of optimising the solid state performance of polymers through an understanding of the effects of molecular variables on processing and performance.

### Materials and methods

The materials used in this study are all atactic polystyrenes, and are listed in Table 1. Lian Hutchings, Durham University, has kindly provided a range of special 4-arm stars [6] as well as molecular weight distributions of all materials from size-exclusion chromatography measurements.

Table 1: Polystyrenes used in this study.

	Type and Composition	$M_n$ (g/mol)	$M_w$ (g/mol)	$PD$	Source
A	Linear monodisperse	66,000	67,980	1.03	Durham
B	Linear monodisperse	73,400	75,500	1.02	Durham
C	Linear monodisperse	89,700	94,400	1.05	Durham
D	Linear monodisperse	103,800	108,400	1.04	Durham
E	Linear monodisperse	155,600	160,800	1.03	Durham
F	Linear monodisperse	253,000	263,000	1.04	Durham
G	Linear monodisperse	260,000	267,800	1.03	Durham
H	Linear monodisperse	462,500	525,000	1.13	Durham
I	Linear monodisperse	490,000	499,800	1.02	Durham
J	Linear monodisperse	188,000	193,640	1.03	Dow
K	Linear monodisperse	210,000	216,300	1.03	Dow
L	Linear monodisperse	450,000	463,500	1.03	Dow
M	Linear monodisperse	1,000,000	1,030,000	1.03	Dow
N	Linear monodisperse	1,550,000	1,596,500	1.03	Dow
O	3-arm (145k symmetric) star monodisp.	414,300	435,000	1.05	Durham
P	3-arm (20k-90k-90k) star monodisp.	190,500	200,000	1.05	Durham
Q	H-shape ((30k-70k)-100k-(30k-70k))	295,200	310,000	1.05	Durham
R	4-arm (100k symmetric) star monodisp.	411,600	440,600	1.07	Durham
S	4-arm (133k symmetric) star monodisp.	511,900	541,300	1.06	Durham
T	4-arm (200k symmetric) star monodisp.	797,300	821,300	1.03	Durham
U	4-arm (300k symmetric) star monodisp.	1,122,000	1,148,000	1.02	Durham
V	Bimodal blend 10% A 90% G	196,000	238,800	1.22	Durham
W	Bimodal blend 20% A 80% G	160,900	219,800	1.37	Durham
X	Bimodal blend 10% I 90% G	263,500	282,100	1.07	Durham
Y	Bimodal blend 20% I 80% G	277,700	306,300	1.10	Durham
Z	Bimodal blend 10% A 90% I	298,600	457,200	1.53	Durham
AA	Bimodal blend 20% A 80% I	214,800	414,000	1.93	Durham
AB	Linear polydisperse commercial	97,900	230,000	2.35	Dow
AC	Linear polydisperse commercial	149,000	293,300	1.97	BASF

The materials are pressed into 0.5mm thick discs using picture frame moulds in a Moore heated press. The mould is held at 170°C for 15 minutes and cooled to room temperature at a rate of 15°C/min. Samples are verified as being optically isotropic after pressing. Small beam samples typically 0.5mm x 2mm x 7mm in size are cut from the discs using a custom jig with single bevelled blades and soaked in diethylene glycol (DEG) for a minimum of 1 day prior to testing. Crazes are induced in the beams by subjecting them to 3-point bending at constant load for 300s in DEG as shown in Figure 1. The width of the crazed region under the applied load is then measured within 1 hour of unloading, employing a low power optical microscope exploiting the reflective property of the crazes as shown in Figure 2.

## Results

Simple beam theory is employed to find the stress at the edges of the crazed region,  $\sigma_c$ , from the average of 5 measurements of the length of the region,  $l_c$ , across the width of the sample

$$\sigma_c = \frac{3P(L-l_c)}{2bt^2} \quad (1)$$

where  $P$  is the load applied,  $L$  is the support spacing,  $b$  the breadth and  $t$  the thickness of the beam.

It was not possible to generate stable crazes in the lowest molecular weight PS, sample A. A number of authors have reported that in monodisperse polymers with  $M_n$  close to  $2M_e$ , where the entanglement molecular weight  $M_e=18,700\text{g/mol}$  [7], it is not possible to grow stable crazes [8, 9]. In crazing it is thought that molecules shorter than  $2M_e$  are not coupled to the

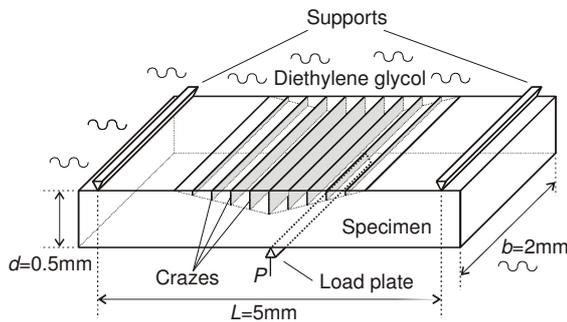


Figure 1 - Schematic representation of a 3-point bending creep crazing test.

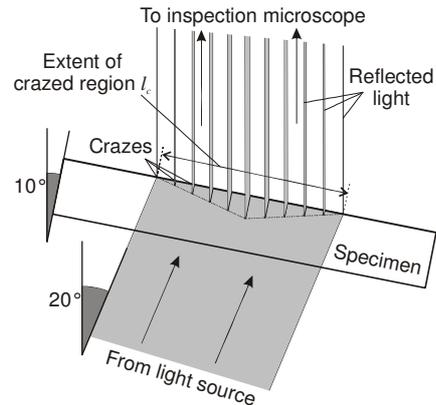


Figure 2 – The use of a microscope for measurement of the extent of crazing.

entanglement network and merely dilute it. For polymer A we have instead established a lower bound for the stress at no craze formation and an upper bound for the stress at which unstable craze propagation leads to fracture.

In order to assess the repeatability of the technique,  $\sigma_c$  is measured on 18 samples of polymer AB and is found to be  $15.8 \pm 1.1$ MPa.  $\sigma_c$  has been measured a minimum of 4 times per material, typically 6-8 times where the material was more plentiful. Values of  $\sigma_c$  are shown with standard error bounds for all monodisperse materials A through to U, and for the 2 polydisperse materials AB and AC as a function of  $1/M_n$ , proportional to the number density of chain ends for linear materials, in Figure 3. Values of  $\sigma_c$  for the bimodal blends V-AA are shown in a ternary plot as functions of the monodisperse constituents A,G and I in Figure 4.

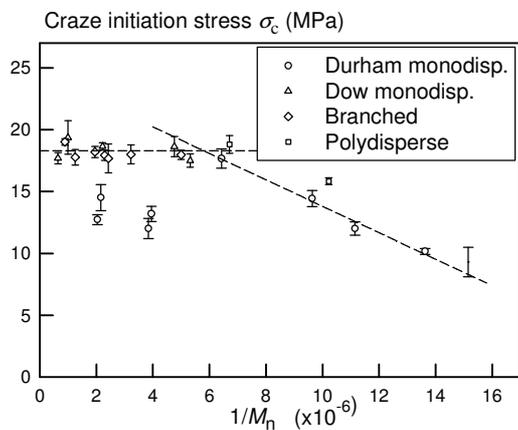


Figure 3 – Craze initiation stress as a function of  $1/M_n$  for linear and branched monodisperse and polydisperse PS.

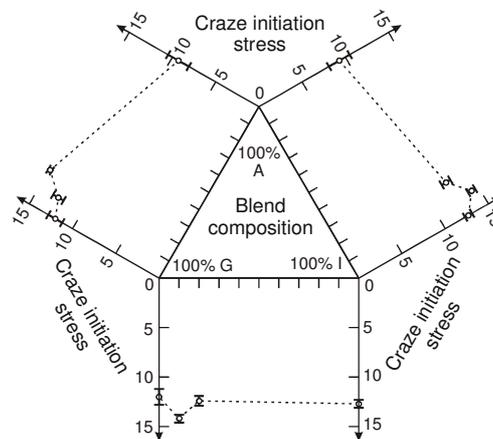


Figure 4 – Ternary plot of craze initiation stress for bimodal blends and their constituents.

### Discussion

If we consider monodisperse linear PS, it is apparent from Figure 3 that there are two regimes of behaviour: below a critical molecular weight  $M_x$  the craze initiation stress  $\sigma_c$  fits a linear function of  $1/M_n$ ; above  $M_x$   $\sigma_c$  becomes approximately constant.

$$\begin{aligned}\sigma_c &= A + b/M_n && \text{for } M_n < M_x \\ \sigma_c &= \sigma_0 && \text{for } M_n > M_x\end{aligned}\quad (2)$$

Fitting these equations to the appropriate data yields  $A=24.5\text{MPa}$ ,  $b=-1.07\times 10^6$ ,  $\sigma_0=18.3\text{MPa}$  and  $M_x=172,600\text{g/mol}$ , or approximately  $9M_e$ . In the regime  $M_n < M_x$  disentanglement is the more energetically favourable mechanism of crazing, shown by the dependence of  $\sigma_c$  on  $1/M_n$ . For molecules longer than  $M_x$  chain scission becomes favourable and the crazing stress is independent of molecular weight. We have as yet no explanation for the outlying points F-I and they have not been included in the parameter fitting procedure.

The 7 branched monodisperse PS all have  $M_n > M_x$  and appear to craze through chain scission. It is probable that branched PS with  $M_n < M_x$  may still craze through chain scission due to the hindrance to disentanglement provided by the added branches. Unfortunately no shorter branched PS samples were available to test this theory.

The 2 commercial polydisperse PS both lie above their equivalent  $M_n$ . This can be explained by considering that in the distribution of lengths, each polymer chain will resist crazing according to its length and the models in equation 2, with long molecules breaking and short molecules disentangling.

The 6 bimodal blends shown in Figure 4 appear to show an increased  $\sigma_c$  compared to both of their components individually, although the data is not conclusive. We may speculate that a small number of shorter molecules act as plasticizers in the vicinity of taught chains and thereby defer chain scission.

## Conclusions

This work has investigated craze initiation of polystyrene in diethylene glycol through isochoric 3-point bending creep experiments in a wide range of monodisperse, bimodal, polydisperse and branched samples. The data indicates that crazing in linear monodisperse PS takes place by disentanglement for  $M_n < 9M_e$  and by chain scission for  $M_n > 9M_e$ . All the branched PS appear to craze by chain scission. Two polydisperse PS have a craze initiation stress greater than their equivalent monodisperse  $M_n$  because of different contributions to resisting craze initiation by different parts of the weight distribution. An examination of bimodal blends of monodisperse PS has indicated that the resistance to craze initiation is higher than both individual components, possibly because of a plasticizing effect of the shorter molecules.

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