Static and dynamic properties of monodisperse polystyrenes: influence of molecular weight

In a recent issue of this journal[1], tensile strength values were reported for injection moulded samples of different monodisperse polystyrenes obtained from the Pressure Chemical Co. The authors concluded that the tensile strength increased with increase of molecular weight up to molecular weight values of between 3 x 10^5 and 4 x 10^5 and then became independent of molecular weight.

In our laboratory, we have determined, for compression moulded samples of similar monodisperse polystyrenes, both static tensile strengths and fatigue lifetimes, for various applied stress values, in tension–compression cycling. Some of these data have been reported[2,3]. We find that over the molecular weight range from $\bar{M}_w$ = 1.6 x 10^5 to 2 x 10^6 the static fracture stress continues to rise with increasing molecular weight (albeit more slowly) and fatigue lifetimes to fracture increase even more rapidly, than does the tensile strength.

In view of these apparently different conclusions, it is of interest to present our data and that of Vlachopoulos *et al.*[1] on a common plot. As discussed by Flory[4], Bueche[5] and others[6,7], since chain ends, being less constrained, generate additional free volume and serve as potential sites of weakness and as sources of submicron cracks, we should expect that the fracture stress will be a function of the concentration of chain ends. But chain end density is inversely proportional to the number-average molecular weight. Hence we have elected to plot the static strength data, and the fatigue lifetime data of the polystyrene (PS) fractions as a function of $(\bar{M}_n)^{-1}$. These plots are shown in *Figure 1* for our data on compression moulded samples and for the data of Vlachopoulos *et al.*[1] obtained on injection moulded samples.

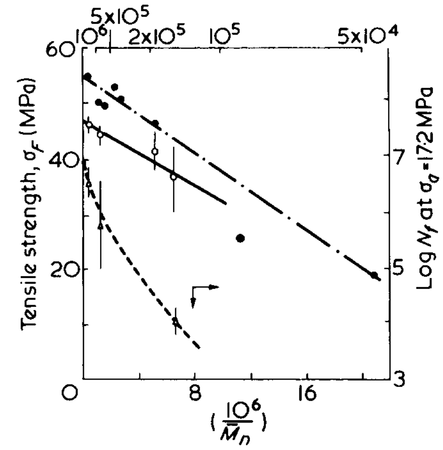

Figure 1 Tensile strength and fatigue lifetime vs. $\bar{M}_n^{-1}$ for a series of monodisperse polystyrenes: ●, σ_f for injection moulded samples (ref 1); ○, σ_f for compression moulded samples; △, log N_f for compression moulded samples

The $\bar{M}_n$ values used for plotting the data points of *Figure 1* are estimated ones, obtained by dividing the reported $\bar{M}_w$ values for the polystyrene fractions by the reported limiting $\bar{M}_w/\bar{M}_n$ ratios. The tensile strength, σ_f, of the compression moulded samples was taken as the maximum stress recorded before fracture in tests conducted at a cross-head speed of 0.84 x 10^{-3} cm/sec. The stress–strain curves were essentially linear up to a stress of about 0.8 of the fracture stress, with some non-linearity developing at higher stresses as surface-initiated crazes became more dense and rapidly propagated across the specimen. In many specimens the stress rose to a maximum value and then fell slightly before fracture occurred. This behaviour is indicative of extensive localized craze yielding and similar behaviour has been noted on testing specimens of a polydisperse commercial heat-resistant polystyrene[8,9]. In both cases, the fracture surface consisted of smooth mica-like facets, indicating that the fracture crack had initiated in and propagated through preformed crazes. This type of behaviour has also been observed in other polystyrenes[10,11], particularly those pretreated to give a low level of styrene monomer and other low molecular weight products.

The open circles represent average σ_f values for the compression moulded samples and the vertical bars give an indication of the spread, usually with 5 samples being tested at each molecular weight. The filled points represent average tensile strength values for the injection moulded samples. Deviations from the average are reported to range up to 15%[1]. These tests were conducted at an elongation rate of 1.5 x 10^{-3} sec^{-1}.

For both sets of samples, the data can be represented (with the exception of one data point) by a linear dependence of the form

$$\sigma_f = A - B/\bar{M}_n \qquad (1)$$

where σ_f is the maximum tensile stress and A and B are constants. The parameter A is the extrapolated tensile strength for infinite molecular weight and the parameter B is a measure of the strength of the molecular weight dependence. A linear dependence of tensile strength on $(\bar{M}_n)^{-1}$ has also been observed to occur in films prepared from cellulose acetate fractions and in vulcanizates prepared from butyl rubbers of different initial $\bar{M}_n$[4]. In polystyrene, a similar relation to that of equation (1) describes the dependence of T_g on molecular weight for both anionically polymerized polymer and for thermally polymerized polymer[12,13].

For the lines shown in *Figure 1* the parameters have the values given in the table below:

Parameter	Injection moulded PS	Compression moulded PS
A	55 MPa	47 MPa
B	1.75 x 10^6	1.45 x 10^6

The higher strength values for the injection moulded specimens are a result of orientation effects and of favourable residual compressive stresses in the surface layer produced by the processing method. Higher strength values for injection moulded samples have also been reported by McCormick *et al.*[14] for samples of both monodisperse PS and of polydisperse polymer.

A continued increase with increase of $\bar{M}_n$, even for molecular weight values above 10^5, has been found in the flexural strength of polystyrene determined at a temperature of −196°C. This is evident from the data of Vincent[6], although the range of molecular weights studied by him was more limited than that covered by the data shown in *Figure 1.*

With regard to fatigue properties rather than static tensile behaviour, the dependence on molecular weight

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is even more striking as may be noted from the broken line of *Figure 1* and from the triangular data points. The fatigue lifetime values, N_f, shown here were obtained under alternating tension–compression at a stress amplitude σ_a, of 17.2 MPa. For the two lower molecular weight samples, the $\log N_f$ values are based on the test data reported by Sauer *et al.*[3] while, for the highest molecular weight polymer, the plotted values are estimated lifetimes based on extrapolation of test data obtained at a higher stress amplitude (20.7 MPa) and at a lower stress amplitude (13.8 MPa).

It is evident from *Figure 1* that the average fatigue lifetime rises by over 3 decades as the molecular weight rises from 10^5 to 2×10^6; this occurs despite the fact that this range of molecular weights is well above the estimated entanglement molecular weight of polystyrene, viz. 35 000 (ref 15). This marked improvement in fatigue performance with increase of molecular weight is attributed primarily to a greater resistance to craze breakdown. Although crazes are less extensive and slower to develop at the lower levels of stress involved in fatigue fracture as compared to static fracture, they nevertheless play an important role in the fracture process[8,16]. Studies of the fatigue fracture surface of polystyrene by scanning electron microscopy show that the fatigue crack invariably initiates in a surface craze which itself developed in response to a high local stress concentration, and then advances and propagates through the process of craze breakdown[3,8]. With increase in chain length and with reduction in the number of chain ends there is a greater degree of chain entanglement and of orientation hardening in the plastically deformed craze microfibrils. If, however, as discussed more fully in a separate publication[17], the increase in molecular weight is produced through crosslinking, and with little change in $\bar{M}_n$ or chain end density, then no improvement in either ultimate strength or in fatigue lifetime is achieved.

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Melt viscosity and thermal properties of poly(ethylene oxide) fractions and blends

Introduction

The temperature dependence of the isothermal growth rate of spherulites and the overall crystallization kinetics of fractions of poly(ethylene oxide) with different molecular weights has recently been studied by one of the authors[1]. In a forthcoming paper we will report a study on the crystallization kinetics of blends of fractions of poly(ethylene oxide)[2].

In this Letter the temperature dependence of the kinematic viscosity of fractions of poly(ethylene oxide) over a range of molecular weight from 1000 to 20 000, and of their relative blends has been studied in order to determine some correlation between molecular and thermodynamic parameters of the melt state and kinetic and thermodynamic quantities normally used in describing the crystallization behaviour of polymers. The present work is preliminary to a more complete and detailed study on crystallization kinetics and thermal and mechanical properties of blends of PEO, which is in progress.

Experimental

Zero shear viscosity (η_0) and density (ρ) were measured on monodisperse melted fractions of poly(ethylene oxide) (PEO) in the range of molecular weight from 10^3 (PEO 1) to 20×10^3 (PEO 20). The PEO samples were produced by Fluka AG. Viscosity was measured by a cone and plate Shirley–Ferranti viscometer at temperatures ranging from 40°–110°C. A quartz plummet suspended from the hook of an analytical balance was immersed in the melted samples to determine the relative densities. In this way it was possible to calculate the density over the same range of temperature. Viscosity and density measurements were also performed on blends of 2×10^3

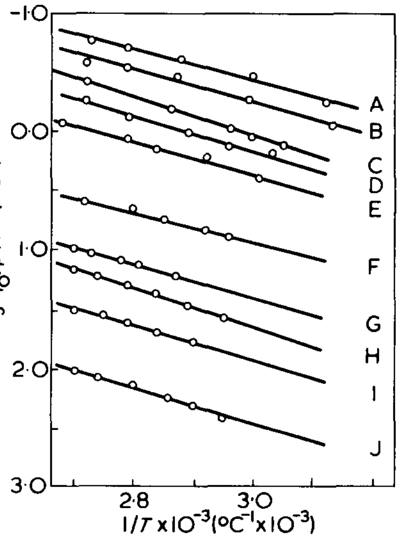

Figure 1 Cologarithm of kinematic viscosity, η_0/ρ, at vanishing shear rate *versus* $1/T$ for different molecular weight fractions of PEO, as indicated: A, 1000; B, 1550; C, 2000; D, 3000; E, 4000; F, 6000; G, 9000; H, 10 000; I, 15 000; J, 20 000

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