Polymer Bulletin 39, 201–208 (1997)

Polymer Bulletin

A new method for determination of fibril volume fraction in polymer crazes by small-angle X-ray scattering

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Received: 3 April 1997/Accepted: 2 June 1997

Summary

A new method for the determination of the volume fraction v_f of fibrils formed inside the crazes in polymers before their brittle fracture has been proposed. The method utilizes small-angle X-ray scattering measured on an absolute scale in combination with the precise measurement of the sample deformation. The method has been applied to the crazes in polystyrene for which the data on v_f are abundant. The result v_f=0.26 is in good agreement with those obtained by other methods ranging v_f=0.21-0.30, which confirms the validity of the proposed method.

Introduction

The structure of crazes grown in various polymers prior to their fracture is essentially different from that of cracks observed for non-polymeric materials; the craze is comprised of fibrillar organization embedded in the void matrix and connecting the opposing craze/bulk interfaces, whereas the crack is merely a slit devoid of material. Because of this structure a craze can support loads, while it can become an embryo of macroscopic fracture of the polymer. Elucidation of the structure of the craze and its change during the fracture process, therefore, is of crucial importance for comprehensive understanding of the fracture mechanism of the polymer. Among various parameters characterizing the craze structure, the volume fraction v_f of the fibrils in the crazes is most interesting, because it can be related to the molecular properties of the polymer, i. e. to the maximum extension ratio of the polymer chains between adjacent entanglement points, through the extension ratio of the fibrils as suggested by Kramer and Berger (1).

A variety of methods to estimate the value of v_f have been proposed. Kambour (2) employed the refractive index of crazes determined from the critical total reflection angle. Doyle (3) has estimated v_f from the thicknesses of the original and the thermally collapsed crazes obtained by the optical measurements of the level differences on the fracture surface. Lauterwasser and Kramer (4) and Brown (5) proposed an elaborate method utilizing the mass thickness contrast on the transmission electron micrographs observed for the crazes grown in thin films. Dettenmaier (6) has proposed a combination of small-angle X-ray scattering measurements (SAXS) on the absolute scale with density measurements of the crazed specimen. This method is useful for the crazes which lead to large density difference between the original and the crazed specimen.

In this paper we present a new method for the determination of fibril volume fraction v_f which utilizes the absolute small-angle X-ray scattering combined with the precise measurement of the sample extension.

Theoretical

Let us suppose that a parallel X-ray beam, the effective width (7) of which is a, is incident on a crazed specimen of thickness t. The craze is considered to comprise uniaxially oriented fibrils embedded in a void slab as illustrated by Brown et al. (8), the axis of the orientation being parallel to the tensile direction. Since the autocorrelation function of the electron density of the fibrils is regarded as cylindrically symmetric, the scattered intensity can be written as $i(s_r, s_z)$ in the electron unit, where s_r and s_z are respectively the radial and the axial components of the scattering vector s with $|s|=(2\sin\theta)/\lambda$, where λ is the wavelength and θ is half of the scattering angle. In terms of the equatorial component $i_p(s_r)$ of $i(s_r, s_z)$ defined by

$$i_p(s_r) = \int_{-\infty}^{\infty} i(s_r, s_z)\,ds_z \qquad (1)$$

the invariant Q, in the electron unit, can be computed by

$$Q = \int_0^{\infty} 2\pi s_r i_p(s_r)\,ds_r \qquad (2)$$

If the craze is regarded as a two-phase system with smooth and distinctive interfaces between the fibril and the void, Q can be related to the volume fraction v_f of the fibrils within the craze through the equation (8, 9)

$$Q = (\Delta\rho)^2 V_{cr} v_f (1 - v_f) \qquad (3)$$

where $\Delta\rho$ is the electron density difference between the fibril and the void, V_{cr} is the irradiated volume of the crazes.

Since we are dealing with brittle fracture, we assume that ductile deformation outside the craze be negligible, and that the cross-sectional dimensions of the specimen remain virtually constant after crazing due to the lateral constrain normal to the stress. The dilation of the specimen owing to the elongation after crazing can then be regarded as associated exclusively with the voids within the crazes. By equating the volume of the irradiated voids and the volume increment, we obtain the relation $V_{cr}(1-v_f)=at\delta$, where δ denotes the elongation of the specimen due to crazing. Substitution of this relation in Equation 3 yields

$$Q = (\Delta\rho)^2 v_f a t \delta \qquad (4)$$

The smeared scattering intensity $\tilde{I}(s_r)$ obtained by slit-collimated experiments is the accumulation along the meridian or the x_3-axis in the detector plane, which corresponds to the integration with respect to the s_z-axis in the reciprocal space. For small scattering angles we can approximate

$$s_z = (2\sin\theta)/\lambda \cong x_3/(\lambda R) \qquad (5)$$

where R is the sample-to-detector distance. Therefore we obtain the following expression for $\tilde{I}(s_r)$ in an absolute scale (6)

$$\tilde{I}(s) = A_e^2 \int_{-\infty}^{\infty} i(s_r, x_3)dx_3 = A_e^2 \lambda R \int_{-\infty}^{\infty} i(s_r, s_z)ds_z = A_e^2 \lambda R i_p(s_r) \qquad (6)$$

where we have used abbreviation s for s_r, and A_e is the scattering amplitude of an electron given by

$$A_e = r_e^2 P / R \qquad (7)$$

The polarization factor has been omitted because of small scattering angles, r_e denotes the classical radius of an electron, and P is the primary beam intensity. The experimental invariant $\tilde{Q}$, which is defined by Equation 2 with substitution of $i_p(s_r)$ by $\tilde{I}(s)$, is therefore related to the theoretical invariant Q through

$$\tilde{Q} = \frac{r_e^2 \lambda P}{R} \cdot Q \qquad (8)$$

Combining Equations 4 and 8 we obtain

$$v_f = \frac{R}{r_e^2 \lambda \cdot \Sigma P \cdot (\Delta\rho)^2 t} \cdot \frac{\tilde{Q}}{\delta} \qquad (9)$$

where ΣP is the primary beam intensity per unit length on the sample plane. The efficiency and the channel or slit width of the detector are canceled out when the scattered intensity and the primary beam intensity are measured on the same detector conditions.

Equation 9 indicates that measurements of the experimental invariant $\tilde{Q}$ and the increment δ of the specimen length enable us to evaluate the volume fraction v_f of fibrils in the crazes, provided that the electron density difference $\Delta\rho$ and other instrumental constants are known.

A few comments on the determination of δ , ΣP and $\tilde{I}(s)$ may be useful to conform with actual experimental conditions. Firstly, in the above discussion, we have assumed that the crazes contributing to the increase δ of the specimen length also contribute to the measured scattering. In reality, however, whereas all the crazes contribute to the increase in the specimen length, not all the crazes grown in the specimen contribute to the scattering because they are not irradiated by the incident beam. To be specific, we consider the following two different typical cases.

Case 1: The length of the specimen is larger than that of the primary beam on the sample plane, and the crazes initiate homogeneously over the entire length of the specimen between the chucks of the tensile machine, as shown in Figure 1 (a). In this case, the value of δ to be inserted in Equation 9 should be reduced by multiplying the total sample extension measured as a movement of the crosshead of the tensile machine by a factor of k_δ= (effective length of primary beam on the sample plane)/(total sample length between chucks).

Case 2: The region of crazing is localized because of the presence of a stress concentrator such as a pair of notches carved on the specimen, so that the length of the primary beam is larger than that of the crazed part of the specimen, as shown in Figure 1 (b). In this case, no correction to the sample extension is necessary to obtain the correct value of δ, since all the crazes contribute to the scattering to be measured on the detector plane (after an appropriate correction by $k_{\tilde{Q}}$; see below). Secondly, for most slit-collimated SAXS cameras, the incident X-rays are not parallel as assumed above but are divergent along the direction of the longitudinal axis of the slits, i. e. the x_3-axis, as is illustrated in Figure 1 (a). As a consequence the primary beam intensity ΣP per unit length on the sample plane is not the same as that on the detector plane; the latter is usually measured experimentally by an appropriate method (10, 11). Therefore, the value of ΣP should be corrected by a factor of $k_{\Sigma P}$=(effective length of the primary beam on the detector plane)/(effective length of the primary beam on the sample plane). This factor is easily estimated either by geometrical consideration or by actual measurements of the profile of the primary beam.

Finally, the above derivation assumes that the detector slit length is long enough to receive all the scattering divergent along the x_3-axis, which is usually not the case in reality. We consider the two typical cases as described above.

Case 1: The correction factor to be multiplied to obtain $\tilde{Q}$ is $k_{\tilde{Q}}$ = (effective length of the primary beam on the detector plane)/(detector slit length or window width of PSPC).

Case 2: Even in this case, the region where the scattering from the crazes can be observed on the detector plane has a certain dimension because of the finite length of the radiation source, as shown in Figure 1 (b). The correction factor to obtain $\tilde{Q}$ is $k_{\tilde{Q}}$=(length of the image of the radiation source on the detector plane)/(detector slit length or window width of PSPC). Note that, in Case 1, the effective lengths of the primary beam on the sample and the detector planes cancel out in the correction by the factor of $k_{\delta}k_{\Sigma P}$, leaving the detector slit length and the distance between the chucks.

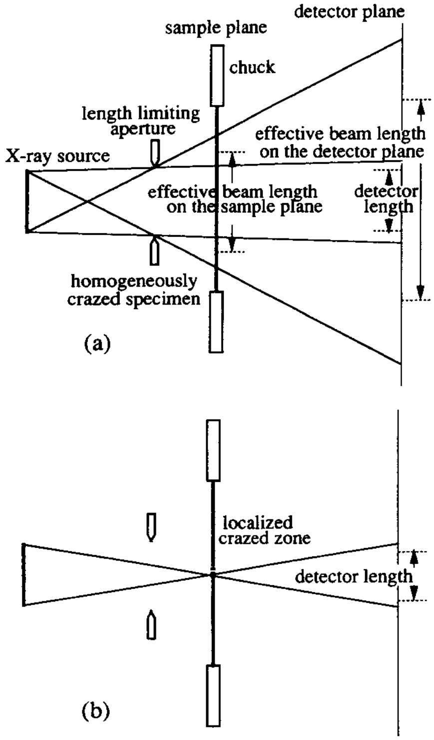

Figure 1: Geometry of slit-collimated small-angle X-ray scattering camera equipped with tensile machine with (a) homogeneously crazed specimen and (b) specimen with localized crazes.

Experimental

Atactic polystyrene was purchased from Wako Pure Chemical Industries, Ltd., Japan. The molecular weight was determined to be 223,000 by gel permeation chromatography. A sheet of 1 mm thick was hotpressed at 230°C under the pressure of 100 kgf/cm^2. Rectangular specimens of size 60 mm long×15 mm wide were cut out from the sheet and used for SAXS experiments.

Measurements of SAXS were made with a Kratky U-slit camera modified in harmony with the detector resolution. A tensile machine was mounted on the camera to stress the specimen in order that SAXS may be measured during the fracture process. The slits of the camera are set parallel to the longitudinal axis of the specimen, and the tensile stress is applied along this direction. A Rigaku one-dimensional position-sensitive proportional counter (1D-PSPC) of delay-line type was used to measure the fibril scattering. The long axis of the PSPC window was placed perpendicularly to the slit direction to measure the scattering pattern normal to the fibrils. The CuK_α radiation from a Rigaku X-ray generator powered by 40 kV and 50 mA was used after filtration with a 10 μm-thick Ni foil to reduce the K_β radiation. The sample was maintained at 50°C during the measurement in a temperature-controlled chamber.

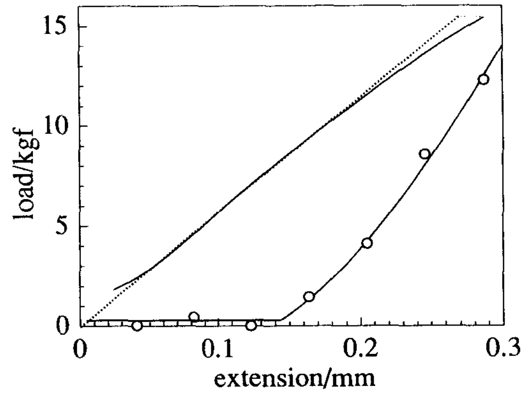

Figure 2: Load-extension curve (solid line) for polystyrene at 50°C, and semi-total excess SAXS intensity measured during extension (open circles).

The primary beam intensity was determined with a reference to the excess scattering from a standard polystyrene of calibrated molecular weight dissolved in cyclohexane at 35°C, the θ-temperature.

The crosshead speed of the tensile machine was 3 μm/s, which corresponds to the nominal strain rate of 8×10^{-5}/s, the original distance between a pair of chucks being 3.8 cm. The scattered intensity was at first accumulated at intervals of 200 s during continuous extension of the specimen in order to monitor the initiation and growth of crazes. Then after an enough number of crazes had been grown, the extension was stopped and the scattering was collected until enough statistics were obtained.

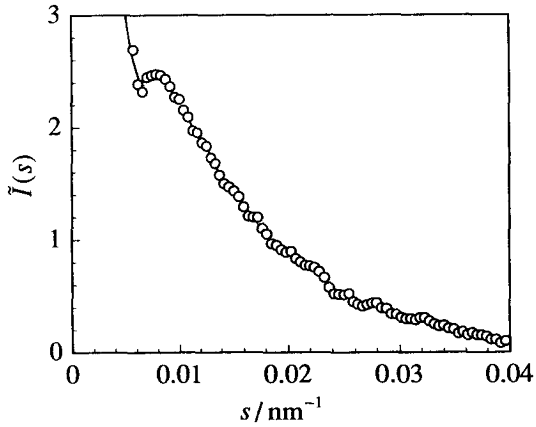

Figure 3: Excess scattered intensity from crazed polystyrene stressed at 50°C.

Results and discussion

The upper solid curve in Figure 2 represents the load-extension relation observed during the SAXS measurement. Hooke's law is obeyed up to the extension of about 150 μm, while deviation due to yielding is observed thereafter, as is typical of a glassy polymer.

Regularly accumulated SAXS intensity can serve as a measure for the initiation and growth of crazes. Scattering observed for the unstrained specimen was regarded as the tentative background to be subtracted from the scattering thereafter to obtain the excess scattering attributable to the crazes alone. The excess scattering was then integrated according to Equation 2 to estimate the semi-total intensity, the integration being terminated at s=0.028 nm^{-1} for simplicity. The results are plotted by the open circles in Figure 2. No appreciable excess scattering is detected until the extension reaches 150 μm, reflecting the structureless feature of a glassy polymer. The excess scattering begins to rise when the extension exceeds this point, indicating the formation of the crazes. The range of no excess scattering is in accordance with the region of Hookean elasticity. The excess scattering afterwards increases with an increase of the deviation from the linearity in the load-extension curve. These observations reconfirm that the non-linearity in the curve is caused by the yield by crazing.

We assume that the elastic component of the extension obeys Hooke's law up to the fracture point with the same elastic modulus as that observed in the small extension region as shown by the dotted line in Figure 2. We further assume that the remaining plastic extension is associated exclusively with the formation of the crazes, as it is prerequisite for the application of Equation 9. We consider these assumptions to be reasonable for brittle fracture in plastics at temperatures well below its glass transition temperature. Their validity can be confirmed by the fact that the uncrazed part of the specimen completely recovers its shape and dimensions immediately after the fracture. The geometrical construction illustrated in Figure 2 leads to the value of 17.4 μm as the plastic component for the total extension of the specimen between the chucks.

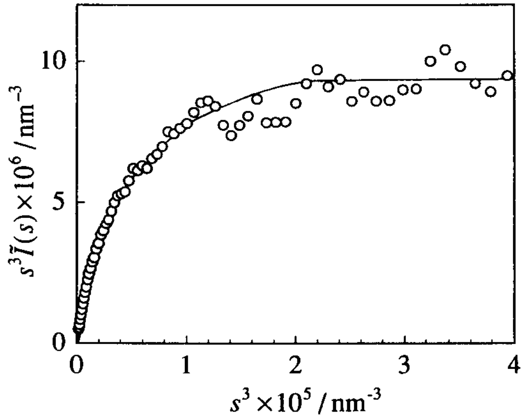

Figure 4: Porod plot for the same data as in Figure 3 for determination of Porod constant k_1.

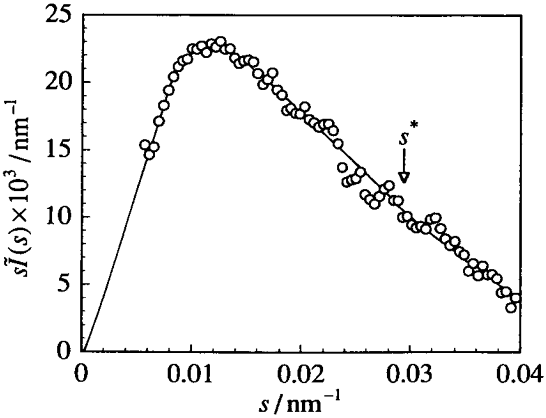

Figure 5: Determination of invariant $\tilde{Q}$.

Figure 3 represents the scattering curve observed at the maximum specimen extension corresponding to the rightmost point in Figure 2. The scattering before crazing has been subtracted as the background. A scattering maximum, indicative of the interference between oriented fibrils, is observed, which is typical of crazes in a glassy polymer.

Since the integration in Equation 2 ranges up to infinity, an accurate

Table 1: Fibril volume fraction v_f in crazes observed for polystyrene by various investigators.

method and investigator	fibril volume fraction v_f in crazes
this work	0.26
refractive indices by Kambour (2)	0.6
level differences on the fracture surface by Doyle (3)	0.30
mass thickness contrast in TEM by Lauterwasser et al. (4)	0.27
the same method as above by Brown (5)	0.24 ± 0.03
the same method as above by Donald et al.(13)	0.26
the same method as above by Yang et al. (14)	0.25

evaluation of the integral requires exact knowledge of the tail end of the scattering curve. For uniaxially oriented rods with smooth and well-defined surface, we can expect Porod's law (12) to be obeyed in the form of $\tilde{I}(s)=k_1/s^3$. Figure 4, in which $s^3\tilde{I}(s)$ is plotted vs. s^3, demonstrates the validity of the law in the range $s>s^*=0.028$ nm^{-1}, and allows the value of k_1 to be evaluated. The contribution from the range $s>s^*$ to the integral was analytically calculated with the value of k_1 as $2\pi k_1/s^*$. The contribution from the smaller angular region $s<s^*$ was determined by the graphical integration in the plot of $sI(s)$ vs. s, as shown in Figure 5. The value of $\tilde{Q}$ thus obtained before correction for geometrical factors is 4.96×10^{11}. The primary beam intensity ΣP is 1.80×10^4. The sample thickness t is 9.62×10^{-2} cm. The width of 1D-PSPC window is 1.0 cm. The electron density difference $\Delta\rho$ between the polymer and the voids is 3.25×10^{23} cm^{-3}. The sample-to-detector distance R is 53.7 cm. The classical radius of an electron r_e is 2.82×10^{-13} cm, and the X-ray wavelength λ is 1.54×10^{-8} cm.

The result of v_f calculated with these parameters is listed in Table 1. The table also includes the values obtained by other methods for comparison. Although Kambour's value (2) based on the measurements of refractive indices seems to be an overestimate, the remaining values show a concentration around v_f=0.21–0.30. We conclude, therefore, that the result v_f=0.26 obtained in this study is in good agreement with these values, and that the validity of the new method is assured.

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7. "Effective length l_e" appearing here and elsewhere in this paper is defined by

$$l_e = \int_{-\infty}^{\infty} f(x)dx \Big/ f(0)$$ for a distribution function $f(x)$ with a maximum at x=0.

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