X-ray Diffraction Curves for a System of Parallel Cylinders with Liquid-Like Order: A Model for the Diffraction of Crazed Polymers

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Abstract

As a model for the internal structure of polymer crazes, a system of parallel cylinders with liquid-like order is proposed. X-ray diffraction curves were calculated for such a system with Monte Carlo data for the radial distribution function of the two-dimensional hard-disk fluid at different packing densities. A comparison is made between the present calculations and experimental results of crazed polycarbonate showing a very good agreement. A way of evaluating the average craze fibril diameter with the calculations is also discussed.

Introduction

When a glassy polymer is stressed, some localized plastic deformation zones called crazes appear perpendicular to the greatest of the principal stresses (Kambour, 1973). These crazes have an internal structure consisting of thin and highly oriented parallel polymer fibrils separated by empty places, as evidenced by electron microscope studies (Beahan, Bevis & Hull, 1971). In a previous paper (Paredes & Fischer, 1979), a small-angle X-ray study was reported which investigated in a more quantitative manner the structure of the crazes, and a sharp and well pronounced maximum of the scattering intensity was observed in the direction perpendicular to the draw direction. With the assumption that during the craze growth the formation of the fibrils occurs completely at random, a model system consisting of hard parallel cylinders with liquid-like order was proposed for the structure of the polymer crazes. Preliminary calculations of X-ray diffraction curves under this assumed model were also presented.

In the present work we extend these calculations and compare the theoretical curves with typical experimental small-angle X-ray diffraction curves for a crazed polymer.

Calculations and discussion

For a system of parallel identical cylinders with liquid-like order, the diffracted intensity in a plane \( P \) of the reciprocal space normal to the direction of the cylinders is given by (Guinier, 1963; Oster & Riley, 1952)

\[
I(s) = N F^2(s) J(s),
\]

where \( N \) is the number of cylinders and the interference function, \( J(s) \), is expressed as follows:

\[
J(s) = 1 + \frac{2\pi}{\int_0^{\infty} [g(r) - 1] J_0(2\pi sr) r dr}, \tag{2}
\]

where \( s = (2/\lambda \sin \theta) \) is the length of the projection on the plane \( P \) of the usual scattering vector with \( 2\theta \) being the scattering angle, \( g(r) \) is the radial distribution function of the cylinders, \( r \) is the distance in the plane \( P \) between a point and the center of a given cylinder, \( f \) denotes the average surface available for each cylinder in the plane, and \( J_0 \) is the Bessel function of order zero.

The structure factor of the cylinder is given by (Cormack, 1957)

\[
F(s,Z) = q \frac{a^2 \pi \cdot \frac{J_1(nas)}{nas} \cdot \sin(\pi lZ)}{\pi Z}, \tag{3}
\]

where \( q \) is the electron density in the cylinder, \( a \) and \( l \) are the diameter and the length of the cylinders, respectively, \( J_1 \) is the Bessel function of order one, and \( Z \) is the component of the scattering vector on the cylinder axis.

It is usual to make the experimental X-ray measurements with slit collimation, so that the measured intensity is already integrated in the \( Z \) direction. In this case we have for \( F^2(s) \) the following expression:

\[
F^2(s) = q^2 \frac{a^2 \pi^2}{2} \left[ \frac{J_1(nas)}{nas} \right]^2. \tag{4}
\]

The internal structure of the system enters into the equations mentioned above through the radial distribution function. As an approximation the proposed model represents the craze structure as a system of hard parallel cylinders with liquid-like order. The radial distribution function of such a system is identical to that of a two-dimensional hard-disk fluid.

Chae, Ree & Ree (1969) and Uehara, Ree & Ree (1979) carried out Monte Carlo (MC) calculations for the \( NVT \) ensemble and Wood (1970) made similar calculations for the \( NPT \) ensemble of a hard-disk fluid at different densities. Furthermore, those calculations were compared with distribution functions calculated from integral equations; none of those analytical methods gives good agreement with the MC data for the complete range of \( r \) distances. Owing to this behavior we use the MC values reported in the literature, in spite of the fact that these data are available only for finite distances.

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The calculations of the X-ray diffraction curves were carried out for several packing densities \( c \) (defined as the fraction of the total volume occupied by the cylinders, \( i.e. \, c = a^2 \pi / f \)), and with both the \( NVT \)-ensemble and the \( NPT \)-ensemble data.

Fig. 1 shows examples of the obtained interference functions with the characteristic attenuating oscillations around unity. For higher densities smaller sub-oscillations are observed at low \( s \sigma \) values. The sub-oscillations arise mainly from the fact that the function \( g(r) - 1 \) is taken to be zero from the last available distance. The neglected part of this function is more important at higher densities because the radial distribution function deviates more from the assumed unity value. This phenomenon, owing to truncation, becomes less important for higher \( s \sigma \) values because of the nature of the Bessel function \( J_0 \), which decreases the contribution of the neglected part on the interference function, equation (2).

Figs. 2 and 3 show the calculated scattering curves with

\[
I^*(s) = \frac{I(s)}{Nq^2(a^2 \pi/2)^2}.
\]

It is seen that the sub-oscillations discussed in the last paragraph become more pronounced in the scattering curves because the interference function is multiplied by \( F^2(s) \), which is higher for low \( s \sigma \) values. This indicates the need of the radial distribution function calculated for larger distances.

It is also seen that for similar densities the scattering curves calculated with \( NVT \)-ensemble and \( NPT \)-ensemble MC data agree very well. This is more evidence of the agreement reported by Wood (1970) and by Uehara, Ree & Ree (1979).

A magnitude of physical interest is the position of the
main scattering maximum, this gives us information on the mean distance between nearest neighbors. Fig. 4 shows the dependence of the abcissa $s_{max}$ corresponding to the main scattering maximum on the density, and it is observed that with closer packing, i.e. smaller mean distance between cylinders, the position of the maximum moves towards higher $sa$ values. The main maximum peak also becomes sharper with increasing packing density (Figs. 2 and 3) because the fluctuations in the mean distance between cylinders become smaller. The position of the main maximum is also important because in the experimental case of diffraction curves obtained on crazed polymer specimens the average fibril diameter can be obtained by comparing the abcissa $s_{max}$ corresponding to the maximum of the experimental curve with the abcissa $s_{max}$ of the theoretical curve calculated at a density equal to that of the crazes (Paredes & Fischer, 1979). The fibril diameter is a very important structural parameter in the discussion of crazing mechanisms.

Since the position of the main maximum is important for the reasons stated above, calculations were made to test the influence of the truncation of the radial distribution function (r.d.f.) on the calculated diffraction intensities in that region. For that matter, the r.d.f. was truncated at various reasonable points and the resulting intensity was compared with the one calculated with the fully available $g(r)$. As expected from the discussion in an earlier paragraph, the sub-oscillations become more pronounced, but for larger $sa$ values the curves including the maximum position remain virtually unchanged.

Fig. 5 shows an example of an experimental small-angle X-ray scattering curve of a crazed bisphenol A (4,4'-isopropylidenediphenol) polycarbonate specimen. The measurements were done with a Kratky camera and a proportional counter at room temperature. The calculations of the diffracted intensity were described by Paredes & Fischer (1979).

Fig. 4. The position of the main scattering maximum $s_{max}$ as a function of the packing density $c$: $\Delta$ based on the calculations by Wood (1970); $+$ based on the calculations by Chae, Ree & Ree (1969) and Uehara, Ree & Ree (1979).

Fig. 5. A comparison between the experimental scattering of a crazed polycarbonate specimen and the theoretical curve calculated for a packing density $c=0.45$. The points denote the experimental data.
occurring at $a = 1.22$, another method for the evaluation of the fibril diameter, without any assumptions on the packing density, can be devised. Examples of this way of evaluating the average diameter $\bar{a}$ are shown in Table 1 together with the corresponding values obtained from the maximum position by assuming a packing density $c = 0.45$. A very good agreement can be seen from these results, which is an additional confirmation for the proposed model and the assumed packing density of the polycarbonate crazes.

Table 1. Comparison between the average fibril diameter $\bar{a}$ (Å) calculated from the position of the scattering maximum and that obtained from the point 'remnant' of the first zero for polycarbonate specimens crazed at different draw temperatures and rates

| $\bar{a} = 0.76/s_{\text{max}}$ | 146 | 211 | 268 | 322 | 384 | 429 | 543 |
| $\bar{a} = 1.22/s_0$ | 150 | 206 | 285 | 306 | 413 | 440 | 517 |

Conclusions

As a first approximation the proposed model describes qualitatively the scattering behavior of crazed polymers. Similarly, it allows us to obtain information about craze structural parameters like the fibril diameter.

The model, apart from the discussed approximations, makes other assumptions, such as, for example, the parallelism between fibrils, which in the real case have some deviations from the draw direction. In addition, the hard-disk model cannot take into account the dependence of the structure on the temperature and also assumes the impenetrability of the fibrils, which in reality will surely be present to some extent. Further refinements of the inter-fibril potentials should take into account the features described above.

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References


