19. OTHER EXPERIMENTAL TECHNIQUES

considered individually when calculating such composite intensities.

19.5.4. Fibre preparation

Natural fibre specimens may require only the selection of fibres or regions of fibres in which the polymers are well oriented, but many other fibres must be made in the laboratory, and orientation can often be improved by a wide variety of laboratory procedures.

Orientation often requires controlled conditions of relative humidity and temperature during the preparation of the fibre; in many cases, these conditions must be maintained during data collection. In some cases, tension must be applied to the fibres; in an increasing number of cases, magnetic fields have been found to improve orientation. Fibres may be drawn directly from concentrated polymer solutions or made by stretching gels, using weights to stretch strips of polymer films cast on Teflon blocks or applying radial heating while forming polymer films (Arnott, Guss *et al.*, 1974; Chandrasekaran, Radha, Lee & Zhang, 1994). A drop of concentrated polymer solution may simply be dried while suspended between two supports. Magnetic fields have dramatically improved the orientation in dried fibres of polymers having significant dipole moments (Torbet, 1987).

Oriented sols, generally enclosed in glass capillaries, are usually made using shearing forces, either by moving the sol in the capillary (Gregory & Holmes, 1965) or by centrifugation (Cohen *et al.*, 1971). Again, magnetic fields can greatly improve orientation, sometimes in combination with centrifugation (Yamashita, Suzuki, & Namba, 1998).

Any of these stretching or orienting processes might facilitate the growth of long microcrystallites along the fibre axis. Crystallization in general and lateral organization in particular are achieved primarily by careful choice of solution conditions, including solvent, pH, additives, relative humidity and temperature. In both crystalline and noncrystalline specimens, annealing processes are often important to both crystallization and orientation.

19.5.5. Data collection

Fibre-diffraction data have generally been collected using laboratory X-ray sources and photographic film. However, synchrotron sources are increasingly being used (Shotton *et al.*, 1998), taking advantage of reduced exposure time, the potential for time-resolved studies and the fact that many fibres (or the well oriented regions of fibres) are too small for laboratory data collection. Imaging-plate systems and charge-coupled device (CCD) cameras are replacing film as detectors (Yamashita *et al.*, 1995; Okuyama *et al.*, 1996; Shotton *et al.*, 1998). Pinhole cameras, mirror-monochromator optics and double-mirror optics are used in different applications. Diffraction by most fibres is inherently weak, and very long repeat spacings often require long distances between the specimen and the detector, so fibre cameras are often flushed with helium to reduce air scatter. Constant relative humidity is often required and is achieved by bubbling the helium stream through a saturated salt solution followed by a salt trap.

The X-ray beam commonly strikes a stationary fibre perpendicular to the fibre axis. Because of the cylindrical averaging of the data, this procedure allows most of the diffraction pattern to be collected in a single exposure. There is, however, a 'blind region' around the meridian, where the Ewald sphere does not intersect the diffraction pattern (Fraser *et al.*, 1976). Data in this region are collected by tilting the fibre.

19.5.6. Data processing

19.5.6.1. *Coordinate transformation*

Data must be transformed from detector space into reciprocal space (Fraser *et al.*, 1976). Transformation of coordinates requires determination of the origin of the diffraction pattern in detector space, the fibre tilt angle β, the twist angle (often called in-plane tilt, the inclination of the projection of Z along the beam to the detector coordinate system) and the specimen-to-detector distance. It may also require determination of the detector mis-setting angles (the deviation of the normal to the detector plane from the beam). All of these parameters can be determined by comparing equivalent reflections in the diffraction pattern.

Most data-processing programs determine the transformation parameters by some form of minimization of the deviation from equivalence in the positions of well resolved equivalent reflections. The tilt was traditionally determined by comparing the apparent Z values of equivalent reflections, but the apparent value of R for near-meridional reflections is much more sensitive to tilt. The minimization set should therefore include some near-meridional reflections if the tilt value is to be determined accurately. The helical repeat distance and, for polycrystalline fibres, the unit-cell parameters must also be determined at this time, but helical repeat distance and specimen-to-detector distance are so highly correlated that it is not often practical to refine both.

19.5.6.2. *Intensity correction*

Data intensities must be corrected for geometric and polarization effects (Fraser *et al.*, 1976; Millane & Arnott, 1986). The geometric correction has two components: a factor due to the geometry of the intersection between the diffraction pattern in reciprocal space and the sphere of reflection, and a factor due to the angle of incidence of the diffracted beam on the detector. The first factor is analogous to the Lorentz factor in crystallography, which arises because of the time taken for a reflection from a moving sample to pass through the Ewald sphere. The geometric correction can be applied to each data point as a single correction (Fraser *et al.*, 1976); this is the simpler procedure for diffraction from noncrystalline fibres. For crystalline fibres, it is often convenient to apply Lorentz and polarization corrections to each data point, to integrate the intensities within each reflection, and then to apply the remaining geometric corrections (Millane & Arnott, 1986). The Lorentz correction is

$$1/L = 2\pi \sin\theta [\cos^2\theta \cos^2\beta - (\cos\sigma - \sin\theta \sin\beta)^2]^{1/2}, \quad (19.5.6.1)$$

where θ is the Bragg angle and $\tan\sigma = R/Z$ (Millane & Arnott, 1986). The polarization correction is

$$p = (1 + \cos^2 2\theta)/2. \quad (19.5.6.2)$$

Intensities should be divided by Lp. Intensities may also be corrected for nonlinearity of detector response and for absorption by the specimen and by detector components.

19.5.6.3. *Background subtraction*

The background can be very high in fibre-diffraction data because of long exposure times and scattering from amorphous material. Because of specimen disorientation, fibre-diffraction data often contain large regions where there is no space between layer lines, so local-background-fitting methods are rarely useful. The background may be determined by fitting an analytical function to intensities at points between reflections (Millane & Arnott, 1985; Lorenz & Holmes, 1993), or by fitting a function that includes both signal and background components to the reflection data. This type of profile fitting has been described for individual reflections (Fraser *et al.*, 1976), for data in concentric rings about the centre of the

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