Fiber Structures: A Fresh Look from Metallography

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Synopsis

The parallel between fibers and metals is discussed in terms of their behavior upon heat treatment, crystallite size and orientation, and diffusion of atoms and molecules. It is pointed out that the degree of crystallinity employed to interpret the x-ray diffraction patterns of fibers is not an important physical parameter. The need for critical study of the mechanism of the growth of primary and secondary walls is stressed for a better understanding of the physical properties of fibers. Reference is made to Hosemann's theory of paracrystals which will help to resolve the "open" problems in polymer physics.

Introduction

The resemblance of an x-ray diffraction pattern for a drawn metal wire to that for a fiber is well known. The purpose of this note is to emphasize the possibility of obtaining further clarifications on fibrous materials by an extension of the analogy from metal physics. Reference will be made here to the concepts of crystallinity, preferred orientation, crystallite size, and resolution of line profiles.

Crystallinity

The degree of crystallinity is a term especially coined for studies on high polymers, although they are not the only substances to exhibit a non-crystalline character: liquid mercury,[1] amorphous carbon, fibrous sulfur,[2] etc. do give rise to very diffuse reflections or amorphous halos. The role of crystalline–amorphous ratio estimated by Hermans and Weidinger[3,4] from x-ray study has been exaggerated.[5,6] Ruland's work[7] does endow the concept of degree of crystallinity with some physical meaning, but its arbitrary character is not eliminated.

The concept of degree of crystallinity has not been evoked in metal physics, since no difficulty is experienced in differentiating the crystalline reflections from the background scatter, even without applying any corrections for specimen absorption, incoherent scatter, etc. In the case of many nonmetals also, e.g., silicon (Fig. 1) with its characteristic diamond-type structure, interpretation of x-ray diffraction data is quite simple, not involving the degree of crystallinity. When the necessary corrections are made for a diagram obtained from a high polymer, e.g., Ashmouni cotton fibers (Fig. 2), there is still a very considerable overlapping of reflections,
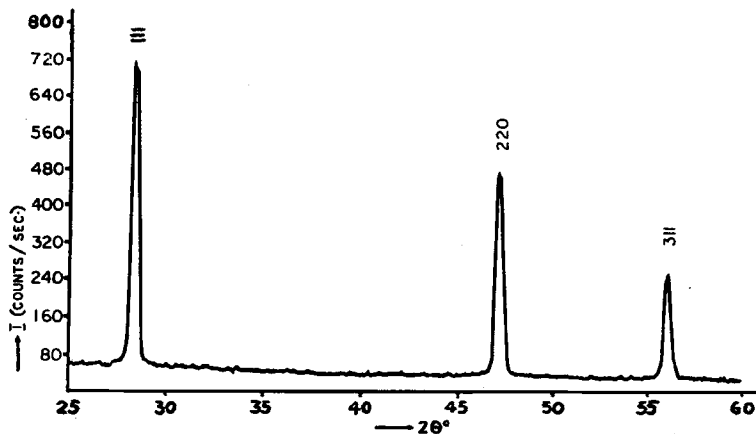
Fig. 1.   Diffractogram for silicon.   Texture goniometer used.   Reflection geometry;
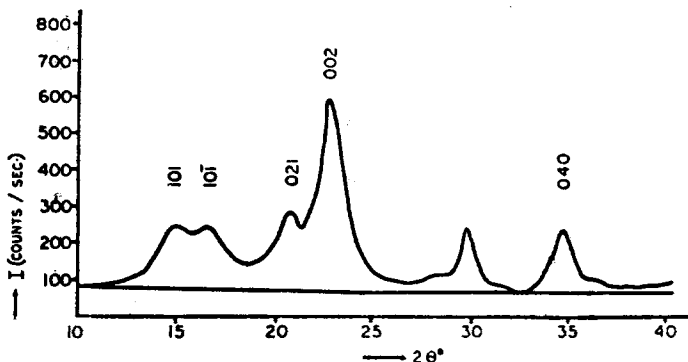Ni-filtered Cu radiation;   32 kv., 10 ma.;   Geiger counter scanning.

Fig. 2.   Diffractogram for unoriented Ashmouni cotton fibers.   Transmission geometry;   texture goniometer adapted for fiber studies.[8]   Ni-filtered Cu radiation;   40 kv., 18 ma., Geiger counter scanning.

and hence the concept of degree of crystallinity is introduced.   Nevertheless, there is other information contained in the x-ray diffraction[9] which is more important than degree of crystallinity.

Orientation

In vacuum deposition of thin metallic films,[10] it is often observed that the crystal structure of these films depends on the nature of the metal, the substrate on which deposition takes place, and the conditions thereof. The noncrystalline or amorphous structure that one observes quite often at room temperature soon disappears on annealing at higher temperature.[11] Sharp reflections with their characteristic orientations are also obtained when the metals are evaporated directly onto cleavage faces of single crystals.[12]   This phenomenon is easily understood in terms of diffusion of atoms.   Diffusion depends both on the size of atoms (or molecules) and

on the temperature. Relative intensities of crystalline peaks naturally vary with the preferred orientation and consequently with the conditions of deposition.

Similar considerations apply to polymers as well. For instance, cottons with no growth rings have been produced by maintaining constant temperature and humidity with an alternation of light intensity and the physical properties of these cottons have been recently investigated.[13,14] Again, studying the fibers from aromatic polyamides, Sprague and Singleton[15] found that annealing at high temperatures or boiling in water increased the degree of crystallinity of the fiber when shrinkage was not allowed and that further boil-off without constraint resulted in considerable reduction in crystallite orientation. Also a hot after-drawing of nylon 6-T increased both degree of crystallinity and orientation markedly. Thus annealing of polymers is seen to give rise to sharper reflections. At very high temperatures the fiber structures also break down just as metals do. The behavior of polyurethane[16] on heat-treatment, for instance, is reminiscent of metals and is reversible with temperature.

Though all cottons are made of cellulose, the relative intensities of reflections vary. Ashmouni cotton shows a prominent peak near $2\theta = 30°$, whereas this reflection is present only as a bump in the background for other cottons, in different degrees though. Simultaneously, there is a reduction in the intensity of (002) peak. This lends support to an hypothesis of variations in the conditions of natural deposition of cellulose on the inner surface of the primary wall of the cotton fibers. This situation may especially arise from differences in the structure of the primary wall whose inner surface constitutes the base on which long-chain molecules of cellulose are laid in a spiralling manner.

It is interesting to recall here Preston's observation[17] that "it seems rather likely that the proteins of the cytoplasm form an organized system which is responsible for the orientation, as well as the construction, of the cellulose chains." Further investigations, reviewed by Roelofsen[18] have thrown much light on the structure of the primary wall of various plant cells, including cotton, but within the same species no discrepancies seem to have been anticipated. Further electron microscopic and cytological investigations on the cell walls may make an exact description possible of the mechanism of orientation and growth of secondary wall thickening in different cottons.

Crystallite Sizes

Then arises the question of crystallite sizes. Whatever the method of estimation, the crystallites in fibers are scarcely larger than the order of 100 A., though occasionally the well-defined nature of reflections from fibrous materials is confused with sharp lines corresponding to large sizes. Quite naturally, therefore, the resolution of adjacent peaks becomes nearly impossible. This situation is, however, not unique in fiber physics, for Piggott[19] has shown that the (111)–(200) reflections from any face-centered

cubic structure will merge into one if the crystal size is only of the order of $4a_0$, a_0 being the unit cell dimension. In other words, a spherical particle of 64 cells will give rise to an amorphous "halo."

The consistently small values for the crystallite sizes in fibrous materials is easily understood, when one refers back to the aspects of diffusion of atoms in the structure. The high polymers which may linearly extend to fractions of a micron—compared to only a few Angstroms for metal atoms—can hardly be expected to attain the crystallite thickness of the order of 1000–10,000 A. quite common in metal physics. The handicaps for the formation of large crystallites are further accentuated by a folded molecular-chain structure proposed for cotton cellulose, for instance, by Ellefsen and Kringstad[20] and reconciled by Peterlin[21] with fringed-micelle theory.

Resolution of Line Profiles

Before a correct estimate of the crystallite sizes can be made, in most cases of polymers, a resolution of the successive reflections must first be carried out. For the purpose different methods have been proposed. Kast[22] employed a simple geometrical method, in which the true peaks were supposed to be undisturbed. An iterative process of resolution first given by Dumond and Kirkpatrick[23] has been favored by some workers, while others preferred to estimate the crystallite sizes by assuming certain characteristic intensity distribution functions for the line profile. Cauchy and Gauss expressions are most frequently referred to in this context. Ruland,[24] however, has suggested that the two may be considered as limiting cases of one and the same observed intensity profile. Mitra,[25,26] from his considerations of the cumulative intensity distribution of the line profiles of cold-worked copper concluded that it was difficult to decide which of the two types was a better fit and that both were perhaps equally unlikely.

In all the above cases, the symmetry of a line profile was presupposed. From their study on cold-worked silver–cadmium alloys Sen Gupta and Quader[27] have shown recently how twinstacking faults may give rise to a peak asymmetry. The important thing to note here, however, is that in high polymers the situation is exactly identical, except that the finding of a solution is rendered more difficult by the introduction of concept of degree of crystallinity, by the arbitrary character of background estimation, and by the fewer reflections, usually not more than five or six, in the case of fibrous materials.

The Fresh Look

Theory of paracrystals first developed by Hosemann[28] and extended recently by him and his co-workers[29–31] on considerations of lattice defects and distortions, may help solve the structural mysteries, not only in metals but also in fibers, for, from the foregoing, the total analogy between the two fields is obvious. The mechanism of growth of cellulose crystals in fibers has been only imperfectly understood so far. Further studies in

this direction will be very valuable in understanding fiber structures and their influence on gross fiber characteristics.

References

1. A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, D. Van Nostrand, New York, 1935, p. 182.

2. F. Tunistra, *Acta Cryst.*, **20**, 341 (1966).

3. P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 135 (1949).

4. P. H. Hermans and A. Weidinger, *Textile Res. J.*, **31**, 558 (1961).

5. A. Viswanathan, *Textile Res. J.*, **36**, 387 (1966).

6. H. Ruck, *Norelco Reptr.*, **7**, 76 (1960).

7. W. Ruland, *Acta Cryst.*, **14**, 1180 (1961).

8. A. Viswanathan and V. Venkatakrishnan, *Norelco Reptr.*, **13**, 48 (1966).

9. L. G. Roldan, F. Rahl, and A. R. Paterson, in *Analysis and Fractionation of Polymers (J. Polymer Sci. C, 8)*, J. Mitchell, Jr. and F. W. Billmeyer, Jr., Eds., Interscience, New York, 1965, pp. 145–158.

10. L. Holland, *Vacuum Deposition of Thin Films*, Chapman and Hall, London, 1956.

11. N. Takahashi, J. J. Trillat, and A. Saulnier, *Métaux, Corrosion, Inds.*, **28**, No. 333, 185 (1953).

12. A. Viswanathan, Thesis, University of Paris, 1956.

13. J. N. Grant, R. S. Orr, R. D. Powell, *Textile Res. J.*, **36**, 432 (1966).

14. L. P. Berriman, *Textile Res. J.*, **36**, 272 (1966).

15. B. S. Sprague and R. W. Singleton, *Textile Res. J.*, **35**, 999 (1965).

16. H. G. Kilian and E. Jenckel, *Z. Elektrochem.*, **63**, 951 (1959).

17. R. D. Preston, *The Molecular Architecture of Plant Cell Walls*, Chapman and Hall, London, 1952, p. 198.

18. A. Roelofsen, *The Plant Cell Wall*, Gebruder Borntraeger, Berlin, 1959, Chap. 2.

19. M. R. Piggott, *J. Appl. Phys.*, **37**, 2927 (1966).

20. Ø. Ellefsen and K. Kringstad, *Faserforsch. Textiltech.*, **15**, 582 (1964).

21. A. Peterlin, in *Structure and Properties of Polymers (J. Polymer Sci. C, 9)*, A. V. Tobolsky, Ed., Interscience, New York, 1965, p. 61.

22. W. Kast, *Forschungsber. Wirkschafts- Verkehrsministeriums Nordrhein-Westfalen*, No. **261**, 42, 1956.

23. J. W. M. Dumond and H. A. Kirkpatrick, *Phys. Rev.*, **37**, 136 (1931).

24. W. Ruland, *Acta Cryst.*, **18**, 581 (1965).

25. G. B. Mitra, *Acta Cryst.*, **18**, 293 (1965).

26. G. B. Mitra, *Acta Cryst.*, **16**, 429 (1963).

27. S. P. Sengupta and M. A. Quader, *Acta Cryst.*, **20**, 798 (1966).

28. R. Hosemann, *Z. Physik.*, **128**, 1 (1950); *ibid.*, **128**, 465 (1950).

29. R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter*, North Holland, Amsterdam (1962).

30. P. H. Lindenmeyer and R. Hosemann, *J. Appl. Phys.*, **34**, 42 (1963).

31. R. Hosemann, F. J. Balta Caleja, and W. Wilke, *Makromol. Chem.*, **92**, 25, (1966).

Résumé

Le parallélisme entre les fibres et les métaux est discuté sur la base de leur comportement par traitement à la chaleur, la grandeur des cristallites et leur orientation; et la diffusion des atomes et molécules. On note que le degré de cristallinité utilisé pour interpréter les diagrammes de diffraction aux rayons-X des fibres n'est pas un paramètre physique important. Le caractère indispensable d'une étude critique du mécanisme de croissance des parois primaires et secondaires est souligné en vue d'obtenir une meilleure compréhension des propriétés physiques des fibres. On se réfere à la théorie de Hose-

mann concernant les paracristaux qui aident à résoudre les problèmes non résolus de la physique des polymères.

Zusammenfassung

Die Parallelen zwischen Fasern und Metallen werden an ihrem Verhalten bei Hitzebehandlung, an Kristallitgrösse und -orientierung und an der Diffusion von Atomen und Molekülen diskutiert. Es wird gezeigt, dass der zur Interpretation der Röntgendiagramme von Fasern verwendete Kristallinitätsgrad kein wichtiger physikalischer Parameter ist. Die Notwendigkeit einer kritischen Untersuchung des Wachstumsmechanismus primärer und sekundärer Wände für ein besseres Verständnis der physikalischen Eigenschaften von Fasern wird betont. Die Hosemann'sche Theorie der Parakristalle sollte eine wertvolle Hilfe bei der Lösung der "offenen" Probleme der Polymerphysik leisten.