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Oxidative stabilization of acrylic fibres

Part 1 *Oxygen uptake and general model*

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The mechanism of oxidative stabilization of acrylic fibres is characterized by two limiting cases which are determined by the fibre chemistry, the reaction conditions, and the diameter of the filament. These limiting cases correspond to diffusion-limited and reaction-limited kinetic processes. Although the chemistry of stabilization is too complex to specify, the various reactions are separated into two categories: those which occur prior to or concurrently with polymerization of the nitrile groups, called "prefatory reactions"; and those which occur subsequent to nitrile polymerization, called "sequent reactions". Under conditions which allow the prefatory reactions to occur significantly before the sequent reactions, the diffusion of oxygen to reactive sites is limited by previously oxidized material; and the fibre shows a typical two-zone morphology. Under conditions where the prefatory and sequent reactions occur sequentially, the overall stabilization process is limited by the rate of the prefatory reactions; but a skin is established at the fibre surface which acts as an oxygen barrier. Data from a variety of sources, including oxygen analysis, microscopic examination, fibre residue after etching, tension developed in fibres held at constant length, and small-angle X-ray patterns, are cited as evidence for the two limiting cases.

1. Introduction

The conversion of acrylic fibres into carbon or graphite fibres normally requires two or three processing steps: a slow thermal oxidation to stabilize the fibres prior to further treatment, carbonization in an inert atmosphere to eliminate the bulk of the hetero-atoms, and a rapid high-temperature heat treatment in an inert atmosphere to eliminate the remaining hetero-atoms and to develop the final carbon morphology. The high-temperature treatment is carried out either at 1500° C or less to form high strength carbon fibres, or at a temperature approaching 2800° C to form high modulus fibres. The carbonization step is generally used if only a modest degree of stabilization is achieved; with more extensive stabilization, the carbonization step may be omitted. The process of stabilization has been the subject of much study because it is costly and involves a number of chemical reactions which are not well understood.

If an acrylic fibre is rapidly heated to about 300° C – the exact temperature depending on the heating rate, composition, bulk density, heat transfer conditions, environmental conditions (vacuum, inert gas, air) etc. – a destructive exotherm occurs with an attendant loss of weight and the generation of volatile gases, liquids, and waxes. To maintain good high temperature properties and to increase the yield of solid material, the destructive exotherm must be avoided and the chemical reactions controlled so that the properties of the final material are satisfactory. This is accomplished by heating the fibres at moderate temperatures in

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an oxidizing atmosphere, a process carried out under tension to provide desirable mechanical properties in the final product. Detailed studies of the reactions occurring during this oxidative stabilization have been hampered by the fact that the stabilized material cannot be examined by the usually powerful techniques of physical-organic characterization.

Most studies of stabilization have been concerned with the nature of the exotherm [1–12], changes in length which occur as the fibres undergo stabilization [13–15], changes in infra-red absorption [16–19], chemical analysis [20, 21], or microscopic examination [22, 23]. A large variety of structures have been proposed for the stabilized material. These are based largely on the interpretation of rather broad, indistinct infra-red bands. Few confirmatory results, based on alternative techniques or on the similarity of reactions in model systems, are available. The suggested structures, interpretations and processes are discussed in recent reviews [24, 25].

The area of stabilization phenomena is further characterized by a state of confusion and conflicting results because of a lack of characterization of the precursor (co-polymer composition, cross-sectional configuration and area, post-spinning conditions and microstructure) and the variety of process conditions which are employed in stabilization.

Watt and Johnson [22] have recently shown that different phenomena can be observed during stabilization at a given temperature, depending on the co-polymer composition. In particular, a commercial 3-denier ($0.33\,\mathrm{mg\,m^{-1}}$) fibre which contains a weak acid co-monomer exhibits the following phenomena when heat-treated in air at 230° C:

(1) For stabilization times greater than a critical value, the fibre has a cross-section which consists of a dark rim and a cream-coloured core. This is denoted as a two-zone morphology. The radius of the cream-coloured core decreases linearly with the square root of time [26] for nearly all times where a distinct rim-core structure is observed.

(2) The oxygen content of the fibre increases as the square root of time for nearly all times where a distinct rim-core structure is observed.

In contrast, Watt and Johnson showed that a commercial 1.8 denier ($0.2\,\mathrm{mg\,m^{-1}}$) fibre which did not contain a weak acid co-monomer, displayed the following features when subjected to the same heat-treatment conditions:

(1) The fibre gradually increases in coloration throughout the cross-section as the time of stabilization increases. This is denoted as a single zone morphology.

(2) The fibre combines with oxygen more slowly than the fibre containing the weak acid; the oxygen uptake of the fibre appears to speed up slightly with increasing time.

If, however, the fibres free of weak acid are subjected to a heat treatment in an inert atmosphere or vacuum (for, e.g., 6 h at 230° C in vacuum) prior to oxidation in air, the interior morphology and the curve of oxygen uptake versus time both resemble the behaviour of the fibres containing a weak acid.

The dark outer rim of the partially-stabilized fibre containing a weak acid or given a pre-treatment in an inert atmosphere (both treatments being carried out on 3-denier fibres at 230° C) has been suggested to be oxygen-rich [27] or oxidized [22] relative to the core material. Watt draws the conclusions that a ladder polymer is formed prior to oxidation, a conclusion reached by Fitzer and Muller based on DTA measurements [11].

Previous work on oxidative stabilization can be summarized as follows: stabilization of a 3-denier fibres which contain a weak acid co-monomer, carried out in air at between 220 and 230° C, is limited by the diffusive transport of oxygen [21, 22]. Similar fibres which do not contain a weak acid co-monomer, when stabilized under similar conditions, exhibit behaviour limited by reaction rate [22]. These results are, however, expected to change with the denier of the fibre and the temperature of stabilization.

A set of three papers will be presented which provide further insight into the stabilization of acrylic fibres. In the present paper (Part 1), data derived from oxygen analysis, the examination of fibre cross-sections, and examination of solution-etched fibres, as well as the results of the papers to follow, are presented to elucidate the mechanism of stabilization. The second paper describes the dynamics of the behaviour of fibres during oxidative stabilization and follows the variation of tension in the fibres when stabilized at constant length and the instantaneous variations in local fibre velocity as a function of time as a fibre moves continuously and at constant overall velocity through a stabilization furnace. The

TABLE I Acrylic fibre data

Fibre description	Manufacturer	Co-polymer composition	Fibre type
M, N	Monsanto	7% vinyl acetate	drawn experimental fibres
O	Du Pont	6% methyl acrylate	sweater grade, type 42, crimped
D	Bayer	homopolymer	Z twist
C	Courtaulds	6% methyl acrylate 1% itaconic acid	sweater grade, crimped

third paper is concerned with small-angle X-ray scattering and electron microscope studies of stabilization, together with a model of the morphology of acrylic fibres.

2. Experimental procedure

2.1. Materials

Three commercial acrylic fibres and one experimental fibre were employed in this work; their characteristics are summarized in Table I. They are described in these reports by a letter taken either from the trade name or from the supplier. It is not intended to rank these fibres by the relative efficiency of their stabilization, but rather to examine how different compositions and process variables affect stabilization. Only one of the fibres contains an acid co-monomer (fibre C). the other three do not (fibres M, O, and D). Two fibres were prepared by wet spinning (fibres C and M); the other two by dry spinning. Fibre C was spun from an inorganic salt water solution, whereas the others were spun from organic solvents.

2.2. Elemental analysis

The oxygen contents of fibres were determined by neutron activation analysis. Fibre samples were wrapped around a brass U-frame and then heat-treated for various times in a circulating air oven. The material near to the frame was discarded, and the remaining fibre was flushed for two days with dry forming gas (5% hydrogen, 95% nitrogen) at 20° C and then sealed in ampoules supplied by the analysts. Care was taken to exclude air and moisture from the ampoules.

2.3. Examination of fibre cross-sections

Heat-treated fibres were mounted in a thermosetting polyester, cut to 1 to 5 μm sections with an LKB ultra-microtome, immersed in oil, and examined under a Zeiss Universal Research Microscope using transmitted light. Whenever a two-zone morphology was observed, the thickness of the oxidized zone was measured with a Filar eyepiece.

2.4. Acrylic solvents

To examine the effects of heat treatment, fibre samples were immersed either in 50 wt% aqueous sulphuric acid solution at reflux for 24 h or in boiling dimethyl formamide (DMF) for 3 min. On removal from the etching liquids, the fibres were washed in distilled water, allowed to dry in air, coated with a conductive layer of gold, and examined in a Cambridge Stereoscan scanning electron microscope (SEM).

These etching conditions were chosen because previous work [28] indicated that the sulphuric acid treatment would erode both the untreated virgin acylic fibres and fibres heat treated in an inert atmosphere, but sulphuric acid would not attack material which was completely stabilized in air. DMF, on the other hand, will readily dissolve virgin acrylic material, but not material heat-treated for prolonged times in either air or vacuum.

3. Results

The oxygen contents of 1.2 denier (0.13 mg m^{-1}) fibre M and 3.8 denier (0.42 mg m^{-1}) fibre C are shown in Fig. 1 as a function of heat treatment time in air at 220° C. The oxygen uptake of fibre C has a parabolic time dependence, whereas the oxygen uptake of fibre M is much slower, increasing linearly with time.

Examination of the fibre cross-sections shows that 3.8 denier fibre C, heat-treated in air at 230° C, is characterized by a two-zone mor-

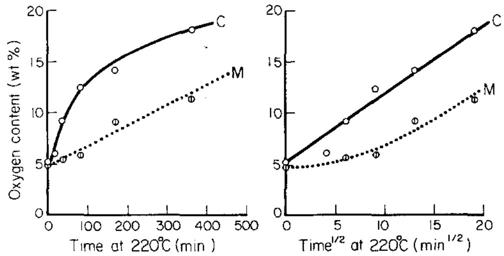

Figure 1 Oxygen uptake of fibre M and fibre C as a function of time at 220° C.

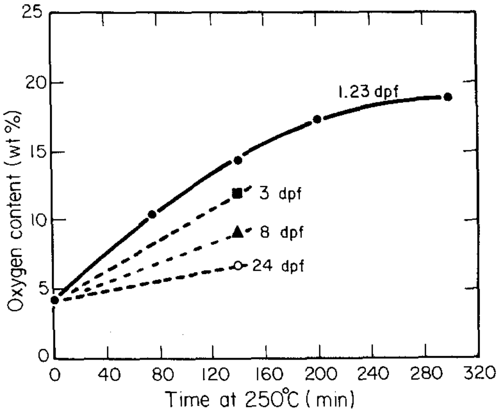

Figure 2 Oxygen uptake of various deniers of fibre N (obtained by varying the draw ratio) as a function of time at 250° C.

phology for times ranging from about 8 min to about 1400 min. For times shorter than 8 min, no evidence of a two-zone structure is seen. At about 8 min such a structure becomes visible, with the boundary between the zones located at about half the fibre radius. For the next 600 min, the mantle (outer-zone) thickness increases approxiately linearly with the square root of time. This suggests that diffusive transport of oxygen is rate-controlling.

Examination of the other fibres (M, O and D), with sizes in the 1 to 4 denier range shows that the fibres uniformly darken – from the original white, through yellow, orange, brown, and eventually to black – with increasing heat-treatment time in air at between 220 and 230° C. This, coupled with the linear rate of increase of oxygen content, suggests that the stabilization process is reaction-rate limited, at least for the temperature and fibre deniers considered – but could simply reflect the morphological characteristics of the fibres [34].

When the fibre denier and/or the reaction temperature is varied, the behaviour can be changed for any of the four fibres. For example, 3-denier fibre C at 180° C is typified by a single-zone cross-section, while 3-denier fibre O at 260° C and 8-denier (0.89 mg m^{-1}) fibre M at 250° C are characterized by the two-zone morphology. The effect of denier on the uptake of oxygen is illustrated by the data in Fig. 2 on fibre N at 250° C. The data indicate that the oxygen concentration in the fibres after a given time of treatment decreases with increasing denier.

A scanning electron micrograph of a section of 3-denier fibre C following partial stabilization at 230° C and sulphuric acid etching is shown in Fig. 3a. A hollow tube of stabilized material is present; the inner core of material has been eroded. Fig. 3b shows a corresponding micrograph of partially stabilized (again, 230° C) and etched 3-denier fibre M. In this case, the bulk of the fibre has been attacked at various points distributed uniformly across the cross-section, and the surface or skin of the fibre has remained intact, indicating that its composition is that of stabilized material.

4. Discussion

As indicated above, a plethora of reactions and reaction products have been suggested by various

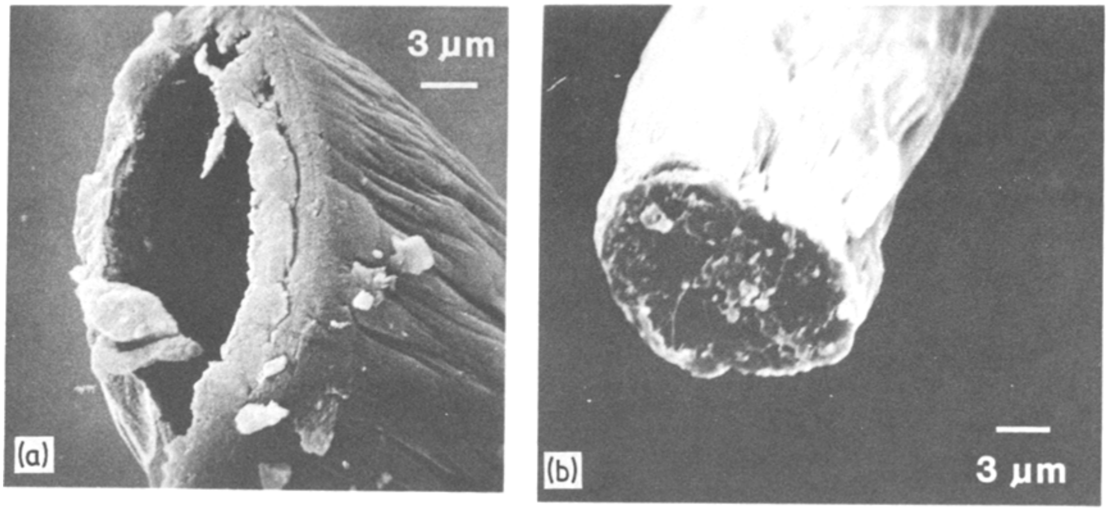

Figure 3 Scanning electron micrographs of fibres C (a) and M (b) after stabilization in air at 240° C for 80 min, then etched in aqueous sulphuric acid at reflux.

authors as occurring during the stabilization process. Since it is not yet possible to establish in detail which reactions occur in the various stages of stabilization, it is proposed to divide the stabilization, process into two stages, much like Fitzer [11] and Watt [22]. The two stages will be used to explain the different cross-section morphologies observed for fibres C and M when stabilized under similar conditions.

The first group of reactions are called "prefatory" and those that follow "sequent". In this context, prefatory reactions are those which are involved in the initiation and polymerization of nitrile groups to form a reddish-brown chromophore. Oxidative reactions may be involved in the production of hydroperoxides, carboxylates, and other active groups – all of which act as initiators for nitrile polymerization. Nitrile polymerization can form a polyamine chain of the type suggested by Grassie [16], or the polyimine chain of the type proposed by Johnson *et al.* [10]. Whatever combination of chemical species are present at the end of the prefatory stage (if sequent reactions do not occur simultaneously), the material is coloured reddish-brown rather than black, is etched by sulphuric acid, and will burn in air when exposed to the flame of a match. Sequent reactions (also exothermic) occur when the products of the prefatory reactions are exposed to oxygen: the reddish-brown colour rapidly changes to black; the black material is not etched by sulphuric acid, and will not burn when exposed to the flame of a match. These two stages of the overall stabilization process are designated prefatory and sequent, and are used to describe the stage of stabilization without specifying in detail the underlying chemistry.

The basic thesis advanced here is that the fundamental processes involved in stabilization are similar for all acrylic fibres – but that the details of the process and the characteristics of the fibres at various stages of partial stabilization depend upon factors such as the temperature, fibre denier and fibre chemistry. This thesis has significant implications for processing acrylic fibres of various types, and will be supported by examples which illustrate the limiting cases of stabilization behaviour.

When 3-denier fibre C, which contains a weak acid co-monomer, is heated in air at 230° C, the prefatory reactions occur quite rapidly throughout the fibre, since an initiator for nitrile polymerization is already present in the fibre. In the zone near the exterior of the fibre at treatment times of less than 8 min, the prefatory reactions occur in a region where oxygen can readily diffuse into the fibre, and sequent reactions start to occur simultaneously. Near the centre of the fibre, prefatory reactions occur essentially in the absence of oxygen (save that which was dissolved or trapped in the fibre interior). Once the sequent reactions have occurred in the outer reaction zone, the diffusion of oxygen is further limited and the slow movement of the outer zone toward the fibre centre is a result of oxygen diffusing through the reacted zone and reacting at an advancing front. If this explanation is correct, there should be distinct chemical differences between the core material and that near the fibre surfaces. Fig. 3a shows that the inner core of partially stabilized material which exhibits the two-zone morphology is removed by treatment in hot sulphuric acid.

Love *et al.* [27] examined by electron microprobe analysis a 3-denier sample of fibre O which had been heated for 1 h in air at 230° C after preliminary heat treatment in vacuum at 230° C for 1 h. The fibre displayed a two-zone morphology; and the oxygen content was found to be higher in the dark-coloured exterior of the fibre than in the cream-coloured interior zone. In contrast, a similar sample of fibre O treated only in air for 1 h at 240° C displayed a fairly uniform coloration over the entire cross-section. For the latter fibre, no significant differences in oxygen concentration (without the large scatter in the data) were found between the central region and the near-surface region.

As indicated above, when the outer dark mantle is first perceived in fibres undergoing diffusion-limited reactions, it occupies some 40 or 50 per cent of the radius. The classic diffusion-limited ($t^{1/2}$) kinetics are observed for times when the dark mantle is advancing toward the centre of the fibre. During the initial period when the mantle is formed, the outer region darkens progressively with little or no apparent change in dimension. In cases where the diameter of the fibre is less than the first-seen thickness of the outer mantle, diffusion-limited kinetics should not be observed even at temperatures where such behaviour is seen for larger fibres. The thickness of the first-seen outer mantle provides a measure of the scale on which the overall reaction becomes diffusion-controlled. It depends on both the diffusion coefficient of oxygen (which itself depends on the extent of reaction) and the kinetics of the slowest reactions (which very likely depend on the extent and kinetics of prior reactions).

Grassie and McGuchan [6] have shown that weak acid co-monomers have a strong initiating effect on nitrile polymerization, with polymers containing such co-monomers undergoing the exothermic reaction and developing dark colours at lower reaction temperatures or at faster rates at a given temperature than polymers without the weak acid. Pre-treatment in an inert atmosphere allows the prefatory reactions to get underway before exposure to oxygen, which takes part in the sequent reactions. Thus when the two-zone texture is observed, the prefatory reactions are well established prior to the initiation of the sequent reactions. In this case, the rate of the overall stabilization process is limited by the transport of oxygen into the interior of the fibre and the process is termed diffusion-limited.

The measurements of Watt and Johnson [26] on the rate of thickening of the outer zone of 3-denier fibre C heated in air at 220° C may be used together with a treatment of the sequent reactions as a tarnishing process [30] to estimate the diffusion coefficient of oxygen through the reacted material. This treatment, together with the assumptions employed therein, is outlined in Appendix 1. The results indicate a diffusion coefficient, D_{RM}:

$$D_{\mathrm{RM}} \approx 2 \times 10^{-12}\ \mathrm{cm}^2\ \mathrm{sec}^{-1} \tag{1}$$

This value is appreciably smaller than the diffusion coefficient of oxygen in PAN fibres reported by Allen [31]. Allen obtained, for a temperature of 50° C:

$$D_{\mathrm{PAN}} \approx 6 \times 10^{-10}\ \mathrm{cm}^2\ \mathrm{sec}^{-1} \tag{2}$$

Since the diffusion coefficient in the reacted material at 50° C is expected to be appreciably smaller than its value at 220° C, the difference between reacted material and precursor fibre is larger than the indicated factor of 300. In this light, since PAN itself has notably good resistance to oxygen transport, the reacted material must be regarded as having outstanding barrier properties.

When 3-denier acrylic fibres which do not contain a catalyst for the prefatory reactions are heated in air at 230° C, the prefatory and sequent reactions seem to occur sequentially and simultaneously throughout the interior of the fibre; the overall rate of stabilization is limited by the rate of the prefatory reactions. This may be termed a reaction-limited process.

The two limiting cases of the stabilization process – diffusion-controlled and reaction-controlled – are observed in all types of acrylic fibre. The observation of a particular limiting case depends upon temperature, time, fibre chemistry and denier. For example, small denier, low temperatures, and the absence of a weak acid co-monomer favour observation of reaction-controlled kinetics. In contrast, diffusion-controlled kinetics are favoured by large denier, high temperatures and the presence of catalyst for prefatory reactions. Diffusion-controlled kinetics can also be observed by heat-treating fibres not containing a catalyst for prefatory reactions under inert conditions prior to their treatment under oxidizing conditions.

The rate of stabilization cannot be completely explained by the two extremes of diffusion-limited and reaction-limited kinetics. Under conditions where the single-zone morphology is observed there remains a decrease in the rate of oxygen uptake with fibre diameter, Fig. 2, which suggests a process that limits the flux of oxygen into the fibre. Re-examination of the acid-etched fibre, Fig. 3b, indicates that although the interior of the fibre has been eroded, the exterior or skin is intact. The skin has resisted the sulphuric acid treatment, indicating that it may be composed of stabilized material which acts as an oxygen barrier. If this is correct, then the rate of oxygen uptake should vary directly with the surface-to-volume ratio. That is, the rate of oxygen uptake should be proportional to the surface area per unit volume, and hence to $(\mathrm{denier})^{-1/2}$. A test of this relation is provided by the data in Fig. 4, which indicates reasonable agreement with the suggested relation.

From the data in Fig. 4, a rough estimate of the

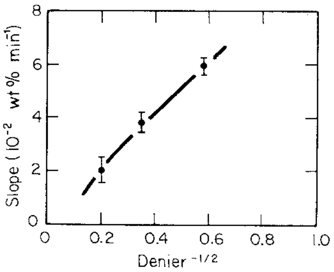

Figure 4 Oxygen uptake rate of fibre N at 250° C as a function of surface-to-volume ratio expressed as $(\mathrm{denier})^{-1/2}$

skin thickness, l, can be obtained. From Fick's first law:

$$J = D(C_s - C_i)/l \qquad (3)$$

where J is the flux of oxygen into the fibre, and equals the rate of oxygen uptake (obtained from Fig. 1) divided by the cross-sectional area of the fibre; C_s is the oxygen concentration at the surface as defined in the Appendix; C_i is the free oxygen concentration inside the fibre which is assumed to be negligible; and D is the diffusion coefficient of oxygen through the skin. With these approximations, and taking D as the value obtained for the diffusion of oxygen through oxidized fibre C (Equation 1 above), l is calculated as approximately 1 μm. This value for l is in reasonable agreement with that measured from Fig. 3b, about 0.4 μm.

The origin of the skin is unclear. Because of the high concentration of oxygen at the surface of the fibre, prefatory and sequent reactions may occur at an accelerated rate, thus establishing a barrier to the transport of oxygen into the fibre. Alternately, the surface regions of uncollapsed wet-spun acrylic fibres are known to be more dense than the cores of the fibres [32, 33], and this material may form the skin observed in the stabilized fibres.

If the density of acrylic fibers at different stages of the stabilization process differs from that of the starting material, and if the reactions take place at a large number of individual sites, then their occurrence should produce an increase in the small angle X-ray scattering (SAXS) from the fibres. Three such SAXS studies of acrylic fibres undergoing stabilization have been carried out previously [29, 35, 36]. The results indicate the development and subsequent annihilation of an intense SAXS peak in the course of stabilization. This peak can be associated with the presence of many heterogeneities distributed throughout the fibre interior. Heterogeneities associated with prefatory reactions are expected to be distributed throughout the fibre. When the two-zone morphology is present under diffusion-limited kinetics, the heterogeneities associated with the sequent reactions might be viewed as occurring primarily in a relatively narrow region at the zonal interface. During the intitial formation of the outer mantle, however, heterogeneities associated with sequent reactions should also be distributed throughout a sizeable volume of the fibre.

SAXS studies of fibre C treated under conditions of diffusion-controlled stabilization exhibit a transitory maximum in scattering similar to that observed for fibre M treated under conditions of reaction-controlled stabilization. In both cases, the angular location of the maximum in intensity corresponds to a Bragg law spacing of about 100 Å. The times of appearance and disappearance of the SAXS maximum are, however, much shorter in the case of fibre C. The transitory maximum is also observed in fibre C when it is heat-treated in an inert atmosphere.

Part 3 of the present series of papers [34] considers the SAXS in more detail to suggest that the fibrils in polyacrylonitrile fibres consist of ordered rods which form a amphiphilic middle phase liquid crystal – i.e., layers of more ordered rods interspersed with layers of less-ordered amorphous material. It is suggested that the prefatory reactions occur more rapidly in one of these phases (very likely the amorphous phase), thereby establishing the regions differing considerably in electron density. The dimensions of the suggested structural inhomogeneities are consistent with those inferred from the angular position of the SAXS maximum. Once the reactions occur to an appreciable extent in the second phase, the density difference between different regions in the fibres will decrease and the SAXS will show a corresponding decrease.

When fibres are stabilized at constant length, the tension developed in the fibres changes as a function of time. By altering the atmosphere in the stabilization oven the prefatory reactions can be separated from the sequent reactions: the latter do not occur in the absence of oxygen, and the fibre tension increases slowly with time. When oxygen is present, the characteristics of the development of tension vary with the nature of the stabilization process. Part 2 of the present series of papers [37] shows that fibres undergoing diffusion-limited stabilization develop tension as soon as the fibres reach the reaction temperature (approximately 10 min), whereas fibres undergoing reaction-limited stabilization develop tension far more slowly.

5. Conclusions

Two different limiting conditions of stabilization, designated diffusion-limited and reaction-limited, have been noted to occur in the heat treatment of acrylic fibres. The role of oxygen uptake, the texture of the fibre cross-section, the fibre residue after etching, the tension developed in fibres held at constant length, and the small-angle X-ray scattering pattern are characteristics which can be used to differentiate between the two limiting conditions.

The reactions which fibres undergo during stabilization have been classified into two groups: Those that lead up to and include polymerization of the nitrile groups are called prefatory reactions; and those that involve the reaction of polymerized nitrile groups with oxygen are called sequent reactions.

The diffusion-limited condition is illustrated by the formation of a two-zone morphology in the fibre: a dark outer mantle surrounding a light-coloured core. During stabilization, the interface between mantle and core moves toward the fibre centre. In this case, prefatory reactions preceed the sequent reactions, and the movement of the interface is associated with diffusion of oxygen through already-stabilized material to the interface where sequent reactions occur. The uptake of oxygen varies linearly with the square root of time from the time when a distinct mantle–core boundary is first observed.

Under reaction-limited stabilization conditions, prefatory reactions occur rapidly at the fibre surface and less rapidly at selected but uniformly distributed locations throughout the fibre interior. A skin is formed on the fibre surface which limits the flux of oxygen into the fibre, but once oxygen has permeated the skin, it is relatively free to diffuse in the unreacted regions and to initiate the prefatory and sequent reactions. The uptake of oxygen is linear with time.

Appendix 1

Evaluation of the diffusion coefficient of oxygen through stabilized material

The analyses of Crank [30] for tarnishing reactions can be used to estimate the diffusion coefficient of oxygen through stabilized material. According to this analysis, the diffusion coefficient can be expressed:

$$D = \left(\frac{1}{2\alpha} \cdot \frac{X}{t^{1/2}}\right)^2 \qquad (4)$$

where α is a dimensionless variable related directly to $g = C_\epsilon / W\xi$, (see [30]), in which ξ is the density of the oxidized material, W is the mass fraction of oxygen in the stabilized material, and C_s is the concentration of oxygen adsorbed onto the surface in grams per volume of oxide. Based on published data [17, 26], W is about 0.20; and approximating the molecular weight of the stabilized material as 120 g mol^{-1} based on the Watt model [22] of the stabilized fibre, $C_6H_4N_2O$,.g is estimated as about 0.26. Using this value of g with Crank's analysis, $\alpha \cong 0.39$. Applying Equation 4 with $\alpha = 0.39$ to the data of Watt and Johnson [26] on oxygen pickup in fibres of type C at 220° C, one obtains:

$$D \simeq 2 \times 10^{-12}\ \text{cm}^2\ \text{sec}^{-1}$$

In making this calculation, the following assumptions and approximations have been made: (1) Fickian diffusion through a homogeneous medium; (2) a diffusion coefficient independent of concentration; and (3) C_s approximately equal to the concentration of oxygen in air.

Acknowledgements

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