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The Structural Causes of the Dyeing Variations of Nylon 66 Yarn Subjected to the False-Twist Texturing Process

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Synopsis

The structural variations in nylon 66 caused by heat and the mechanical action of the false-twist texturing process have been studied by measuring dyeing rates with Durazol Blue 2R, the determination of density, x-ray orientation, and lateral order, and also by consideration of x-ray small-angle scattering data. It is concluded that the morphologic units are probably shish-kebabs with straight-chain cores between which the dye penetrates.

INTRODUCTION

Heat setting and texturing are important textile processes with polyamides and polyesters. During these processes, structural changes take place that affect the subsequent dyeing behavior of the treated yarns and fabrics. It is therefore essential to understand and control these structural changes brought about by wet and dry heat if uneven or Barré dyeing are to be avoided.

Earlier work in this field[1,2] investigated the nature of the changes brought about by wet and dry heat but did not offer any detailed structural explanations for the changes. Some attempt at a structural explanation was, however, attempted in previous papers in this series,[3–5] and the view was advanced that changes in void size or content were among the causes of the dyeing differences observed. In the previous work described, the yarns that had been dry heated over the heater of a texturing machine were not subjected to the false-twist process so as to isolate as far as possible the effect of the heat alone. In the present paper, the effect of adding the mechanical action of false twisting to the action of heat is studied for nylon 66. At the same time, further structural details have been investigated by a study of the mechanical properties of the heated yarns; also included is an x-ray small-angle investigation to try to substantiate the theory of voids advanced as an explanation of the cause of the dyeing phenomena.

EXPERIMENTAL

Yarn

Nylon 66 (70/70 Bri-nylon (ICI) Z T100).

Heat Treatment

The yarn under standard humidity conditions of 66% r.h. was passed at 360 ft/min over a 30-in. heater of a Klinger CMG 500 machine (tension feed) under a

tension of 7 g. In one set of experiments, no false twist was applied but a further set of samples was produced under the same conditions with false twist applied (85 tpi). The temperatures of the heater were 180°, 200°, 210°, 220°, 230°, and 240°C.

The dwell time on the heater is not the same for these two sets of samples because of twist contraction in the yarn and to see whether this was a factor a few additional experiments were carried out on another batch of yarn in which the dwell time for plain and textured yarns was the same. This necessitated running the plain yarns over the heater at a slower speed than for the textured yarns, and the correct speed to achieve this was calculated from the known data.

Some steam-heated samples from previous work[4] were also used.

Dyeing Conditions

Pure Durazol Blue 2R (CI Direct Blue 71) was used. The dyebath was 0.5 g dye, 30 cc of 30% acetic acid, made up to 1 liter, 85°C, pH 3.0. The general conditions of preparation of yarn and the dyeing procedure was as previously described.[3]

Dyeing Experiments

Previous work[3] carried out with Durazol Blue 2R and nylon 66 showed that Fick's law was valid for the dyeing process. Under these conditions, it is possible to use the constant $A/\sqrt{t}$, which is proportional to the diffusion coefficient, to characterize the dyeing process. This constant was derived from the slopes of the graphs of A, the absorption in g/100 g, plotted against root time in hours. The data are given on Figure 1.

To check whether the difference in dwell time on the heater could account for the difference in the results between the textured and plain yarns, a separate set of experiments was conducted both on the Scragg CS9 and Klinger texturing machines in which the dwell time was made equal for the textured and plain yarns. As a result of these experiments, it was found that for yarns produced on both machines, $A/\sqrt{t}$ (textured yarns) $> A/\sqrt{t}$ (plain yarns, same speed as textured

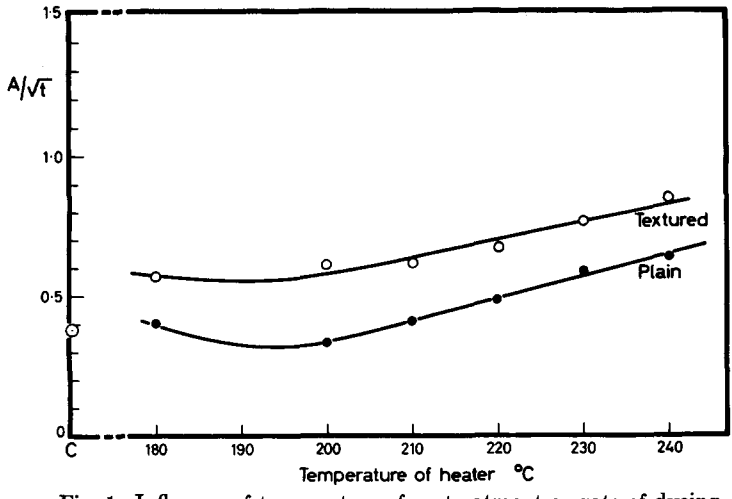

Fig. 1. Influence of temperature of pretreatment on rate of dyeing.

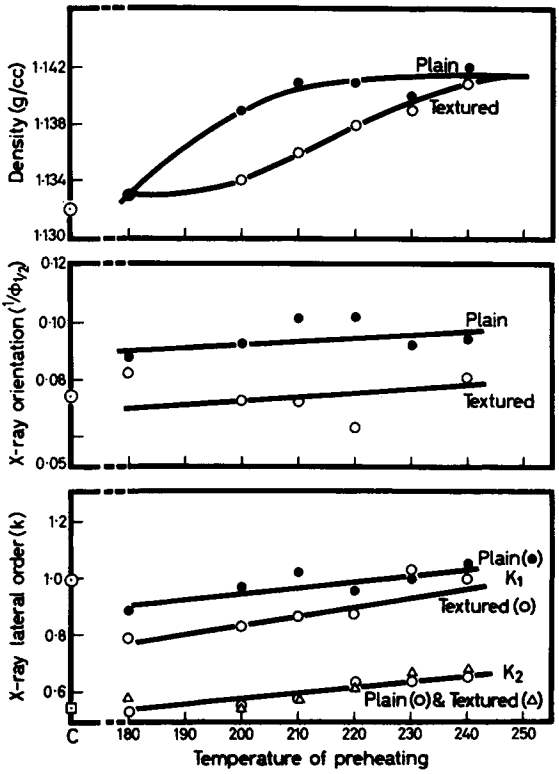

Fig. 2. Effect of temperature of preheating (°C) on (a) overall density (g/cc); (b) x-ray orientation ($1/\phi_{1/2}$); (c) x-ray lateral order (K).

yarns) $> A/\sqrt{t}$ (plain yarns, same dwell time as textured yarns). The difference between $A/\sqrt{t}$ for textured yarns and plain yarns run over the heater at the same speed is, therefore, not due to dwell time but to the mechanical action of texturing.

The result of plotting $A/\sqrt{t}$ against the temperature of pretreatment is shown in Figure 1. It is seen from that figure that the curves for textured and plain yarns run almost parallel; and above 200°C, there is a linear increase of $A/\sqrt{t}$ with the temperature of preheating. The minimum occurs between 180° and 200°C for both curves. To explain these results, it is important to study the structural behavior of nylon 66 preheated between 180° and 240°C.

Structural Measurements

Details of the method for density determination have already been given,[3] and the results are shown in Figure 2.

X-Ray Wide-Angle Determinations

X-Ray Orientation. The method of measuring x-ray orientation by consideration of the azimuthal scan around the two main equatorial reflections of the x-ray fiber diagram given by nylon 66 has been described elsewhere.[3,4,5] As before, the results are expressed as the mean half-breadth ($\phi_{1/2}$) and its reciprocal ($1/\phi_{1/2}$). The latter parameter is useful insofar as it increases with increasing ori-

entation. If allowance is made for experimental errors arising from the preparation of the samples, it is clear from the results (Fig. 2b) that the orientation improves with the treatments.

X-Ray Lateral Order. The method of the measurement of x-ray lateral order was first put forward by Ellis and Warwicker.[6] The essentials of this method are based on the work of Jones[7] who showed that the Cauchy equation is a better choice than the Gaussian to represent the diffraction from a system in which there is a distribution of crystallite sizes. Its development and application to fiber work have been described by Warwicker,[3] and the method used here is essentially the same as that given previously.

The parameter K is related to the reciprocal of the half-breadth and is really an order/size parameter. However, if the assumption is made for a solid system that variations in this parameter reflect changes within the units rather than the growth in size, then K can be taken as a measure of lateral order as shown in Figure 2.

X-Ray Small-Angle Scattering

A Warhurst camera fitted with 0.5-mm pinholes was used with nickel-filtered copper K_α radiation. This camera was modified to take an additional cassette so that a wide-angle pattern could be recorded simultaneously with the small-angle pattern: the wide angle pattern was used for calibration purposes. Film specimen distances were 17 cm (small-angle cassette) and 5 cm (wide-angle cassette).

The x-ray small-angle scattering diagram from nylon 66 consists of a meridional reflection and an equatorial streak either side of the beam stop. It thus superficially appears to be a so-called two-point diagram, but under some conditions an ill-defined four-point diagram can be detected.

In this section is evidence from dry-heated yarns both plain and textured, and also included are some data from steam-heated nylon 66 yarns from samples produced in earlier work.[4]

During the work, it was discovered that there was a residual background scatter produced by the camera without any specimen in the beam. Allowance for this background has been made in all the calculations, but efforts are being directed to discovering its causes with a view to eliminating it. The diagrams produced were not precise enough to yield accurate values of constants, but they are adequate to show up the changes in diffraction caused by structural changes brought about in these experiments. The results, therefore, are likely to be more qualitative than quantitative but adequate to show the trends of changes brought about by heat (dry and wet) and texturing.

Measurements were carried out on the diffraction effects both on the meridian and equator, and an attempt has been made to use these data to indicate the structural changes involved.

Calibration of x-Ray Small-Angle Diagrams. To compare the data from two experiments, it is necessary to calibrate them to a given standard. This was done simply by taking a wide-angle x-ray pattern from the same specimen simultaneously with the small-angle pattern. By so doing, the quantity of material in the beam and the length of exposure is the same for both photographs. The wide-angle photograph was used to determine the integrated density of the (010 + 100) reflection which, when obtained, could then be employed to relate all the

TABLE I
X-Ray Small-Angle Scattering Meridional Data: Dry Heat[a]

Sample heated at, °C	Spacing *A*	Central intensity *I*	Integrated intensity *I*	Type of peak
		Plain Yarn		
Control	87	14	410	S
180	87	36	1156	S
200	94	32	984	D
210	112	20	885	D
220	109	32	1023	D
230	105	34	863	S
240	105	55	1200	S
		Textured Yarn		
180	105	7	243	D
200	131	17	584	S
210	105	17	375	S
220	119	14	295	S
230	131	32	1000	S
240	131	8	167	S

[a] D = Double; S = single; *I* in arbitrary units.

experiments together so that results from x-ray small-angle experiments could be compared after each set of data had been corrected by the calibration factor obtained in this way.

Since the exposure for an x-ray small-angle experiment is much longer than for a wide-angle experiment with the same specimen and conditions, it was necessary to use a sandwich of two films in the wide-angle cassette. The lower film in this cassette was measurable and by reference to an appropriate film factor the integrated intensity of the top film could be derived. An arbitrary standard exposure factor was set at 1000, and all experiments were referred to this standard by means of the integrated intensity of the reflection.

Meridional Reflection Data. The position of the peak intensity maximum was determined on the microdensitometer and a scan taken through it parallel to the equator of the diagram. Two such scans are available per diagram for each meridional arc, and the final scan taken was the mean of the two. The measured intensities were corrected for background and brought on to the calibration scale in the manner described. After correction, the area under the curve was determined and multiplied by the breadth of the peak measured on a scan at right angles to the meridional scan. This gives a measure of the integrated intensity. The intensity at the highest point at the center of the meridional scan was easily determined, and an observation whether the scan was from a single or double peak was made.

The spacing of the meridional peak was determined from the distance of the center point from the middle of the beam stop by reference to the appropriate camera constants in the usual way.

The results are listed in Tables I and II and shown in Figures 3 and 4. An attempt was made to correlate these results with those obtained from the dyeing experiments, and these results are shown on Figures 5 and 6.

Equatorial Scans. The microdensitometer trace along the equator was corrected for background and put on a standard scale.

TABLE II
X-Ray Small-Angle Scattering Meridional Data: Steam Heat

Sample steamed at, °C	Spacing *A*	Central intensity *I*	Integrated intensity *I*	Type of peak	Dye uptake,[a] g/100 kg g/2 hr
Control	87	14	410	S	0.346
100	97	9	202	D	0.394
110	94	14	356	D	0.361
120	—	—	—	—	0.596
130	101	22	442	D	0.784
140	97	24	460	S (D?)	1.15

[a] From J. O. Warwicker, *Brit. Polym. J.*, **3**, 68 (1971).

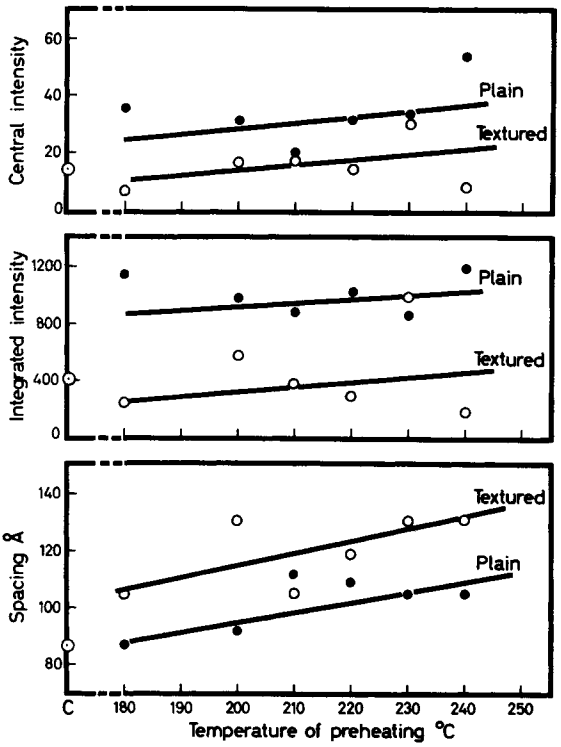

Fig. 3. X-Ray small-angle scattering results meridional data variation with temperature of preheating (dry heat): (a) central intensity; (b) integrated intensity; (c) spacing (Å).

Although an attempt was made to derive values for the specific surface area and other relevant constants by the analysis of Johnson and Tyson,[8] the results were not considered reliable and therefore a more qualitative interpretation of the results had to be made. Similar conclusions were reached with regard to size distribution analysis based on the method of Jelleneck, Solomon, and Fankuchen.[9,10]

The results from the plain yarns suggested that the preheating treatment does not affect the parts of the structure that give rise to the equatorial streak. Since, however, only the outer boundary of the equatorial streak can be recorded, the results of interest may not be revealed unless recording could be made at smaller

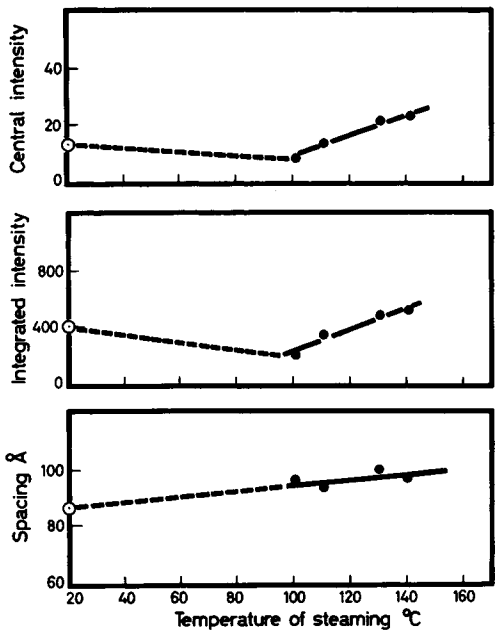

Fig. 4. X-Ray small-angle scattering results. meridional data variation with temperature of preheating (steam heat): (a) central intensity; (b) integrated intensity; (c) spacing (Å).

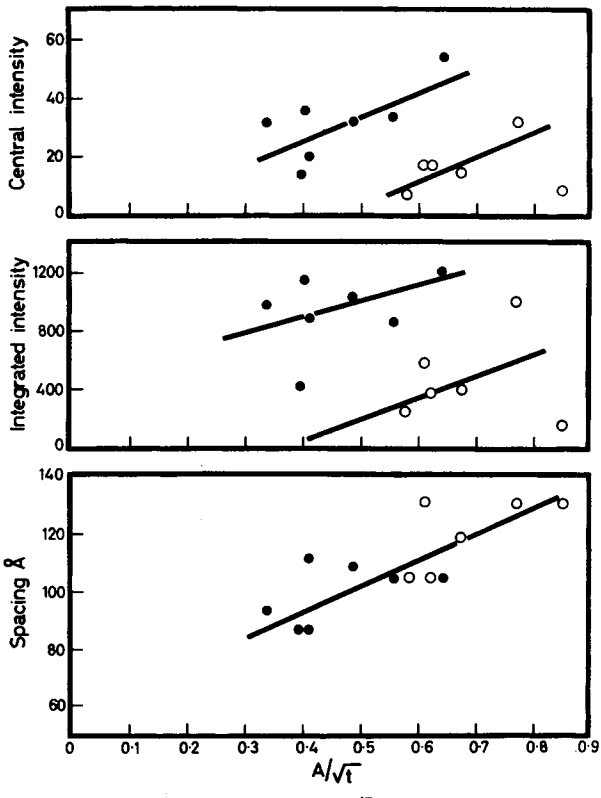

Fig. 5. Correlation of dye uptake constant ($A/\sqrt{t}$) with x-ray small-angle meridional data (dry heat): (a) central intensity; (b) integrated intensity; (c) spacing (Å); (●) plain yarn; (○) textured yarn.

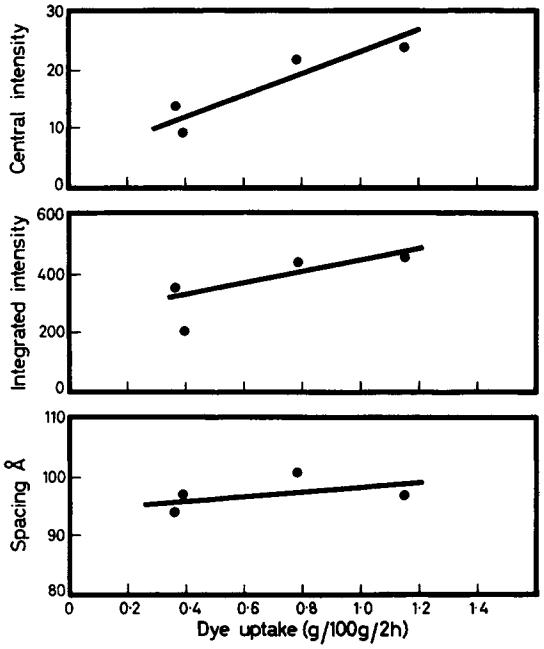

Fig. 6. Correlation of dye uptake constant (g/100 g/2 hr) with x-ray small-angle meridional data (steam heat): (a) central intensity; (b) integrated intensity; (c) spacing (Å); (●) plain yarn; (O) textured yarn.

angles than can be explored by the present system. The general x-ray small-angle scattering pattern is less for textured yarns than for plain yarns, and the equatorial streak is in particular less marked. On consideration of the x-ray small-angle scattering results for steam-heated yarns, it was found that the equatorial streak was difficult to detect at all. Furthermore, it is thus possible that the recorded equatorial scatter is a result of interfilament phonemena and not due to internal structural causes. Hence, caution had to be exercised in interpretations involving equatorial data.

Mechanical Properties

Ten specimens 5.0 cm long were tested for each sample of yarn on the Instron tensile testing machine at a constant rate of 0.5 in./min extension. A mean stress–strain curve was constructed by taking the mean extension for a series of loads read from the individual graphs produced on the testing machine. From this mean curve were derived values of tenacity, breaking extension, and initial modulus (defined as the modulus over the first 1% extension), and the work of rupture was found from the area under the curve. The results are shown in Table III. An attempt was made to correlate these results with those for the dye uptake.

DISCUSSION

The values of the dye uptake constant (*D.U.*) (Fig. 1) for textured yarns are seen to be higher than those for plain yarns at corresponding temperatures of preheating, but the general variation with the temperature is the same for both

TABLE III
Mechanical Properties

Sample heated at, °C	Tenacity, g/Tex	Breaking extension, %	Initial modulus, g/Tex	Work of rupture, g/Tex
		Plain Year		
Control	44	35.5	252	20.9
180	44	34.1	252	10.5
200	42	27.1	293	8.1
210	45	33.8	293	11.0
220	45	28.9	293	8.9
230	45	29.7	293	9.4
240	45	26.7	315	8.2
		Textured Yarn		
180	42	30.2	144	7.8
200	43	29.0	135	7.4
210	43	29.3	135	7.2
220	42	27.6	135	6.7
230	38	22.5	113	4.7
240	34	20.5	72	2.5

sets of results. It can be inferred from this that the mechanical action of false twisting has brought about structural changes that are responsible for this increased uptake of dye. This, then, can be yet another source of dye variation in textured yarns, and it therefore is important to understand its nature.

The density of textured yarns (Fig. 2a) is less than for plain yarns for temperatures of preheating above 180°C, but the values approach one another again at the higher temperatures of treatment. On general grounds, it might be expected that a less dense yarn would permit a greater dye uptake, but density alone cannot account for the dye variations found. Thus, on the one hand, textured and plain yarns of similar density still show a higher dye uptake constant for the textured yarn. On the other hand, the dye uptake constants for both sets of yarns increase as the density increases. Although therefore the structural causes of the dye differences must be in some way related to the juxtaposition or compactness of the morphological units composing the fiber, there must be other factors involved. Since the dye uptake constant relates to speed of dyeing rather than to total capacity of dyeing, the distribution of void size and shape must also play a part as well as the overall density. (To avoid confusion, the term void means space accessible to dye: it is not necessarily a defined hole.)

A somewhat similar situation exists with regard to x-ray orientation (Fig. 2b). It has been found[11] that as the orientation in nylon 66 improves, the dye uptake decreases. Since the textured yarns are less oriented than the plain ones, a superficial explanation of the difference in dye uptake constants could be given in terms of orientation. However, both sets of results show that as the temperature of preheating is raised the orientation improves and at the same time the dye uptake constants also increase, in contradiction with the general rule. Structural factors other than orientation are therefore also operative.

The x-ray lateral order parameter K (Fig. 2c), which is related to the half-width at half-intensity of the corresponding equatorial reflection,[3] indicates imperfections in the morphological units perpendicular to the designated planes. K_2

is the same for both plain and textured yarns and increases as the temperature of preheating increases. A similar increase with temperature is found for K_1, but here the values for the textured yarns are lower than those for the plain yarns. This difference in value suggests that the disorder brought about by mechanical action is between the (100) planes, which implies disorder in the direction of the hydrogen bonds of the structure, an unexpected result, since cleavage might have been imagined to take place more easily in the other direction at right angles, where van der Waals forces operate. Some increase in dyeing might be expected from such disorder, and this difference between the textured and plain yarns might partially explain the dye uptake differences. However, the difference in K_1 tends to disappear for the higher temperatures, and therefore it cannot offer a complete answer to the problem. Furthermore, both constants indicate an increase in lateral order with increase in temperature, and this is accompanied by an increase in dye uptake constants and not a decrease as might be expected.

As in earlier papers,[3-5] the facts so far support the hypothesis that by the morphological units becoming more perfect more space is left between them for dye to enter. This, however, does not explain the mechanical action which also appears to increase the available space for dye to enter. An increase in dye penetration can also be brought about by the lengthening of voids as well as widening them, and it might be here that mechanical action plays a part.

The explanation of the phenomena appears to lie therefore in the size, shape, and distribution of voids between the morphological units in the fiber. Such changes are difficult to study by electronmicroscopy because the preparation of the specimen disturbs the structure. Some information, however, can be derived from x-ray small-angle scattering because the specimen is left undisturbed during the measurements. The available data are limited by the equipment and the large corrections that it is sometimes necessary to apply to the results. However, these results can still show the nature of some of the morphological changes involved.

The essential features of the x-ray small-angle diffraction patterns from these specimens are a meridional two- or four-point diagram and an equatorial streak. There may be interaction between these features, but for the present work a simplifying assumption has been made that they are separately measurable.

The results (Tables I and II) show that the yarns treated with wet or dry heat tend to give four point diagrams, but the textured yarns give two-point diagrams. The latter may, of course, be virtually four-point diagrams where the overlap of the component peaks have not been resolved by the scan. A four-point diagram can arise as reflections along a layer line from a single structure, but since the reflections appear to change in relation to one another as a result of treatments to the specimens, this explanation is probably invalid and the four-point diagram probably arises because of a crossed structure. Such a crossed structure can arise when rows of diffracting centers occur at angles to one another, or from helical morphological units,[12] and at this stage it is difficult to choose between these alternatives. Variation of the four-point diagram toward a two-point diagram can thus be either due to the angular change causing the rows of diffracting units to tend to coincide in angles to the fiber axis, or to a change in pitch of the helix if the morphological units are helical.[12]

The next result to note from the meridional reflections is the intensity. Although the results are somewhat erratic due to the rather large corrections

required, they do nevertheless show up the trend of the results with the heating effect. For both wet- and dry-heated specimens as well as the textured ones, the meridional intensity increases with the temperature of preheating. It is, however, remarkable that the large increases in intensity found by Statton[13] were not observed with these specimens. There is a difference in the conditions of experiment, however, that might explain this difference of result. Statton[13] heated his yarn in oil without tension which it has been shown [14,15] results in core melting. Under such conditions, Statton was dealing with a true two-phase system; the center of the fiber was in the molten condition and the outside, on the other hand, was as the drawn fiber. The present conditions of experiment do not lead to this core melting phenomenon; and, furthermore, the dry-heated specimens were held under tension during heating. The results are therefore more relevant to the fiber structure changes brought about by normal heating processes on textile fibers, without the drastic changes induced by core melting.

According to the conditions for the production of diffraction at small angles, the intensity is a function of the difference in electron density of the components of the system, their weight fractions, and the total volume irradiated. The increase in intensity with heating thus implies a greater difference in electron density between the components of the system, or an increase in weight fraction of one component per unit volume, or both, brought about by heating. Superimposed on this is the fact that the textured yarns show lower meridional intensities than for corresponding dry heated yarns without the use of mechanical action. This implies that the textured yarns have a smaller electron density difference than plain yarns; this difference nevertheless increases as the temperature of preheating is raised. Since mechanical action might be expected to oppose annealing forces, this result might be predicted on the grounds that the fiber is being homogenized to some extent.

The other feature that is found is an increase of meridional spacing, and furthermore than those for the textured yarns are greater than those for the plain yarns. Both sets increase in spacing as the temperature of preheating increases. In terms of the general picture of structure, this means that the rows of diffracting points move further apart on mechanical action and with heat, or, alternatively, the helical angle becomes steeper if the diffraction is from helices.

The changes in structure causing these changes in the x-ray small-angle pattern permit the increase in the rate of dye uptake, and it is of interest to see if there is any correlation between these results and those for dye uptake. In Figures 5 and 6, dye constants have been plotted against the meridional data from the x-ray small-angle scattering experiments. There is a scatter of points; and although there does seem to be some correlation between the two sets of data, it is not certain whether or not this is significant. The structural changes can be of two main types. Either the changes are associated with the achievement of greater lateral order in the morphological units, and thus indirectly with dye uptake by the alteration in disposition of the units, or directly to changes between the units affecting the dye uptake and the x-ray small-angle data. The fact that the textured yarns have a greater rate of dye uptake than plain yarns but have smaller meridional intensities suggests that the intensity data are connected with internal changes in the morphological units. On the other hand, the correlation between the dye uptake constants for the dry-heated yarns and the meridional spacing seems to be the same for both textured and plain yarns.

If dye does not penetrate the units, then these data seem to be connected with the arrangement of units as well as with internal changes in them—probably the latter affecting the former. Before trying to suggest a structure to fit these facts, it is necessary to also consider the equatorial x-ray small-angle scattering.

Data from the equatorial scans can give some indication of the trend in the changes in the lateral dimensions of the units or voids causing them. Of significance is the fact that no equatorial streak is found with steam heated specimens. Since the apparatus cannot detect lateral dimensions greater than 200 Å, this must mean either that these dimensions in these samples are larger or, alternatively, that the lateral arrangement is virtually homogeneous and hence gives rise to no equatorial streak at all. However, accompanying these changes is a larger rate of uptake of dye consistent with a greater accessibility of dye. A tentative solution to these facts is a structure in which there are a few large pores dispersed in a relatively homogeneous material, but without further evidence this can only be put forward as a possibility.

With dry-heated yarns, the equatorial scans did not show any marked changes. This does not vitiate previous attempts to explain the increase in the rate of dye uptake accompanying these changes because the dye phenomena are sensitive to distribution of void sizes and the production of a relatively few larger pores would greatly affect the diffusion of the dye but may not alter the mean pore size sufficiently to make marked changes in the equatorial scans. Furthermore, changes in the length of pores will also affect diffusion results and still remain undetectable in the equatorial scans.

Since the equatorial scans for textured yarns were less intense than for plain yarns, this might be due to larger voids being present and the major portion of the scan thus inaccessible to measurement. In general, such larger voids may be inferred by the mechanical action aiding crystallization and from previous theories,[3,4] thus causing more accessible areas in the fibers. The temperatures of heating are in the region where maximum crystallization rates of nylon are claimed[16] which would thus be consistent with such an explanation, but the reason for the less intense x-ray small-angle scattering phenomena for textured yarns is still obscure.

Mechanical Properties

It is also important to consider the mechanical properties of the yarns before suggesting a fine structure and morphology to account for the data accumulated. In Table III are the parameters measured both for the plain and textured yarns, and Figure 7 shows an attempt at correlating the work of rupture with dye uptake constants. The latter is justified on the grounds that the structural features that influence the dye uptake must also contribute toward the mechanical properties of the fiber.

The tenacity of plain yarns is slightly improved by the heat treatment but the breaking extension is reduced. The initial modulus is improved but the work of rupture is reduced as the temperature of preheating increases. All these properties point to a stiffer and more brittle fiber being produced on heating.

However, on examination of the data from the textured yarns it is found for the same range of temperatures the tenacity and breaking extension are reduced, but the initial modulus is considerably reduced as well as the work of rupture.

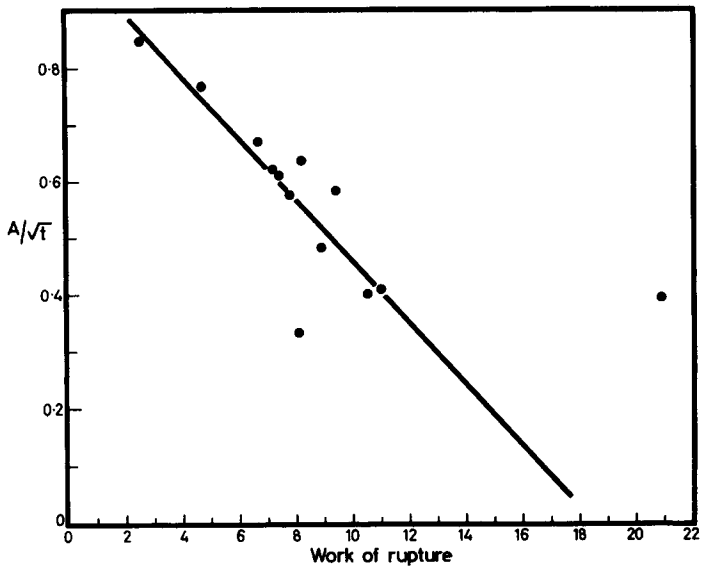

Fig. 7. Dye uptake constant $(A/\sqrt{t})$ vs. work of rupture. Combined results for plain and textured yarns.

This points to a more flexible but considerably weaker yarn being produced by the combined action of heat and false twisting.

Although these mechanical properties are quite consistent with those expected, they are not consistent with current theories of structure. The plain yarns appear to follow the expected course by producing a stronger more brittle yarn as the perfection and alignment of the fibrils are increased, as shown by the structural studies. The textured yarns structurally are similar to the plain yarns but they are considerably weaker. It is clear, therefore, that the production of more perfect fibrils and better alignment of them is not sufficient to account for mechanical properties as often is assumed: there are other more powerful factors involved. The most likely factor that can account for these differences between plain and textured yarns in terms of structure is the adhesion of the morphological units together. Where good adhesion is present, the yarn is strong; but if this adhesion is disturbed by the false-twisting process, then, despite the same type of fibrils being present, the fiber is weaker.

In the attempt to link mechanical with dyeing properties, the best correlation seems to be with the work of rupture. Here, except for the control, there seems to be a direct link between the work of rupture and the dye uptake constant both for plain and textured yarns. If the weakest fiber is the one with the least adhesion between the fibrils, then this also might be expected to be the one to have the highest dye uptake constant because the structural features must include cracks into which the dye can enter.

With the textured yarn, the tenacity, breaking extension, and initial modulus results all point to the same result that, as the adhesion between internal units becomes less, the uptake of dye constants become greater. The results for plain yarns are less easily interpreted: the tenacity and initial modulus remain almost constant over the range of temperatures, but the results for breaking

extension suggest that heat produces less extensible places in the fiber which lead to breakdown before the normal extension of the fiber.

It is therefore interesting to note that the best correlation between dyeing and mechanical properties is with textured yarns where the results suggest that there is a loosening of the internal structure due to the action of false twisting. This again lends support to the concept that the changes brought about by heat are mainly to achieve a higher fibrillar order and alignment with some interfibrillar changes as a result. The mechanical action largely enhances the interfibrillar changes, but insofar as mechanical action can influence ease of crystallization, it probably helps in the achievement of order within the fibrils.

Fine Structure and Morphology

The essential morphology and fine structure given before[3,4] seems to be still valid. The effect of mechanical action is to increase the accessible space between the morphological units either by allowing the lateral dimensions of the morphological units to decrease and/or increasing the length of the pores into which the dye enters.

However, in summarizing the results in this fashion, it is necessary to examine the nature of the morphological units to not only account for the dye results but also to explain the changes in the x-ray small-angle diffraction data. As pointed out above, the x-ray small-angle diffraction data can be explained by fibrils with alternate dense and less dense regions along their length, by a system of fibrils of uneven diameter along their length, or from helical fibrils, in a crossed system.

Attention should be drawn to the theories of Morgan,[12] which basically appear to offer a solution to the structural problem although in details the views may not be acceptable with modern folded-chain concepts. Morgan[12] regards the structure as consisting of three phases, a central core (A) of imperfectly crystalline material in which the chains are oriented in the fiber direction, a second phase

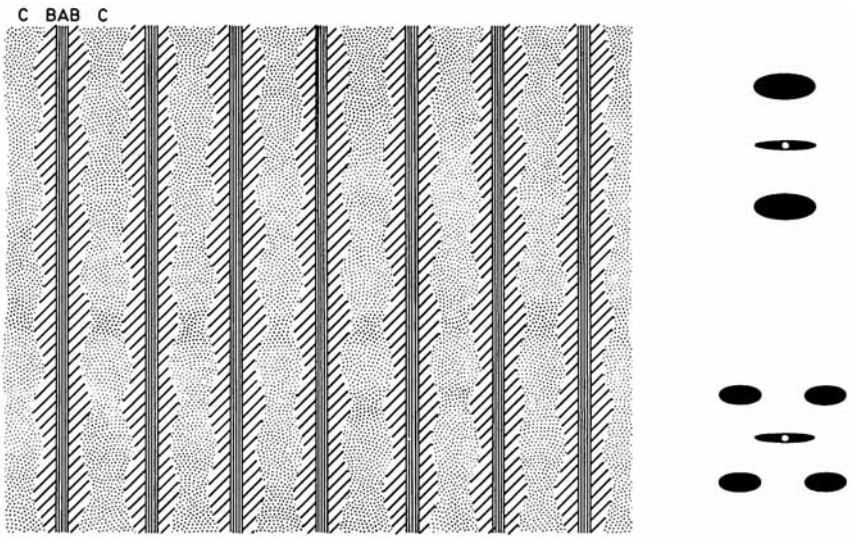

Fig. 8. Suggested structure to account for x-ray small-angle scattering data: (a) suggested structure; (b) two-point diagram; (c) four-point diagram.

(B) of similar crystalline material spiralling around (A), together with an outer noncrystalline phase (C) with chains largely oriented in the draw direction. Generalizing this structure, it is possible to obtain similar x-ray effects by having a core of imperfectly crystalline straight-chain material (Fig. 8, region A) around which is arranged an imperfectly crystalline region with varying diameter (Fig. 8, region B), e.g., a shish-kebab structure. This region can be of folded-chain material, or it can spiral as suggested by Morgan. Such a composite fibril is not inconsistent with the electronmicroscope evidence of Veld, Morris, and Billica[17] who showed nylon 66 to contain fibrils of uneven diameter. Region C (Fig. 8) is noncrystalline and need not be straight-chain material but can contain folded-chain molecules. Indeed, it could be the source of the continuous ring found on all x-ray fiber photographs of nylon 66. If such a structure were perfectly aligned as shown in Figure 8a, then the small-angle x-ray diffraction pattern would be similar to that depicted in Figure 8b; but if the units were at an angle to the fiber axis, a system would be formed which to x-ray analysis would constitute a crossed system giving rise to the four-point diagram depicted in Figure 8c.

This model can be taken as a basis for an explanation of the results. Dye is envisaged as penetrating into phase C, the width of which will depend on the extent to which phase B crystallizes onto phase C owing to heat effects. Furthermore, if phase C is loosened also by mechanical action, then the fall in strength of the polyamide on texturing can also be explained as well as the relations between dyeing, temperature, and mechanical properties. Since it also accords with the x-ray small-angle scattering data, the model thus becomes a reasonable working hypothesis. It should be emphasized, however, that this model was developed to explain results with nylon 66 but it would be unwise to suggest that it was a universal model applicable to all fiber systems.

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