

The Structural Causes of the Dyeing Variations of Terylene Subjected to the False-Twist Texturing Process

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Synopsis

An examination of the effect of the false-twist process on structure and dyeing behavior of Terylene is described. It was found that if dyed without tension, textured yarns had a higher rate of dyeing than when dyed under tension. However, the textured yarns dyed under tension had a lower rate of dyeing than corresponding flat yarns prepared without the application of the false-twist process. An explanation of these results is given in terms of a structure that on heating leads to a higher lateral order of the morphologic units and thence to an increased formation of voids, but superimposed on which is a system of gross elongated cracks brought about by the false-twist process.

INTRODUCTION

A recent paper¹ described an investigation into the action of the false-twist texturing process on the structure and dyeing properties of a nylon 66 yarn. Since polyester is of increasing importance as a textured fiber, a similar investigation has been carried out with it. Preliminary studies of the action of heat on Terylene yarn passed over the heaters of a texturing machine but without the application of the false-twist process has already been published.² An extension of this work to investigate the effect of the mechanical action applied at the same time as heat on the false-twist process has now been carried out. This paper describes how the application of the false-twist process modifies the dyeing behavior of the polyester and discusses these variations in terms of possible structural models.

EXPERIMENTAL

Heat Treatment

The Yarn, Terylene 150/30, was passed over the heater (2 ft long) of a Scragg-Shirley CS9 Minibulk machine in an ambient humidity of 66% R.H. and under a tension of 7 g. Samples were prepared with and without false twist being applied. When false twist was applied, the speed of the yarn was adjusted to give the same dwell time (0.05 S) on the heater as with plain yarns; textured yarns also were set by being passed over a second heater at 180°C. The temperatures

of the first heater for both sets of yarns were 190°, 200°, 210°, 220°, and 230°C.

Dyeing Conditions

As in previous experiments, Duranol Blue G (C.I. Disperse Blue 26) was used. Commercial dye was used for the dyeing experiments, but calibration of dye was in terms of purified dyes. The dyeing conditions were such that dyeing took place virtually from an infinite dyebath. The dyebath was as follows: 0.5 g Duranol Blue G, 0.75 g Atexal DA-AC, 10 cc 30% acetic acid, and 1 liter water, 95°C.

Two types of dyeing experiment were carried out. In one, the dye was wound on frames under a tension of 10 g (0.067 g/den) or 20 g (0.13 g/den). The other, for dyeing completely free from tension, was done on small tufts of Terylene held submerged in the dyebath by stainless steel weights.

Before dyeing, the prepared yarn samples were given a brief scouring treatment. The yarn samples were boiled for 15 minutes in 2.0 g sodium carbonate ("soda ash"), 1 cc Lissapol ND, and 1 liter water, then washed, given a brief acid wash in 1 cc 30% acetic acid per liter, rewashed, and then left in distilled water until required.

Dyeing was carried out in liter-flasks with vigorous stirring applied during dyeing. After dyeing for the prearranged times, the frames were removed and the yarn washed, given standard reduction-clear and soaping treatments, washed, and dried in the air.

The dye was extracted from a weighed portion of dyed yarn by dimethyl-formamide at a temperature sufficient to extract the dye and then estimated spectrophotometrically. Each result is the mean of duplicates.

Dye Uptake Parameters

The final dye results were expressed as a rate of dyeing given by the parameter A/\sqrt{t} , which is the slope of the straight line passing through the origin obtained by plotting the uptake (A , g dye/100 g fiber) against the square root of the time (\sqrt{t} , hr). This relation was found to be valid for all the experiments. Results are shown in Table I and plotted in Figure 1.

TABLE I
Rate of Uptake (A/\sqrt{t}) of Duranol Blue G by Terylene

Sample	A/\sqrt{t}^b					
	Control	190° C	200° C	210° C	220° C	230° C
Flat, 10-g tension ^a	0.114	0.107	0.093	0.097	0.118	0.206
Textured, no tension ^a	0.227	0.210	0.197	0.166	0.144	0.148
	(flat)					
Textured, 10-g tension ^a	—	0.081	0.092	0.085	0.105	0.120
Textured, 20-g tension ^a	—	0.103	—	0.122	—	0.184

^a Tension during dyeing.

^b A = Dye, in g, per 100 g fiber; t in hours.

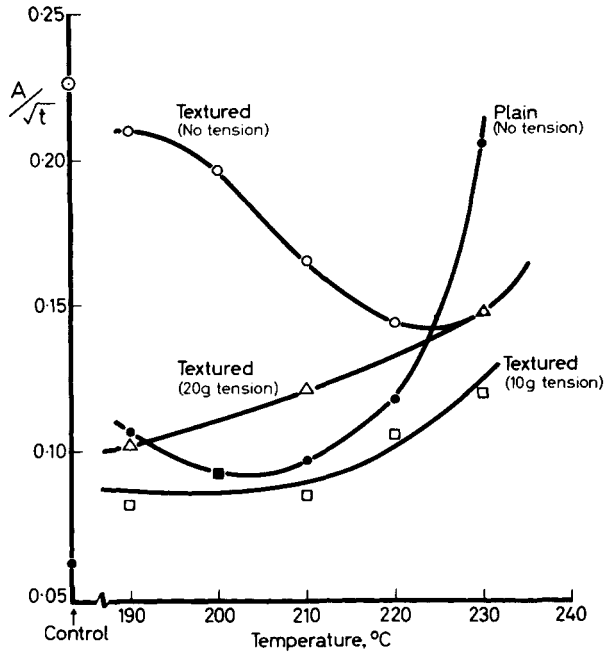


Fig. 1. Rate of uptake (A/\sqrt{t}) of Duranol Blue G by Terylene.

Density

Density determinations were carried out with a density gradient column. At first, this was done with a mixture of methylene dichloride and trichlorethylene, both liquids thought to be inert toward polyester and calibrated with glass beads of known density. The resultant densities (Table II) were consistent among themselves but appeared higher than expected for polyester. Confirmation of this finding was found by Winkler et al.³ who showed that the density depends

TABLE II
Densities of Samples at 25°C^a

Sample temp., °C	Density in methylene dichloride + triklone, g/cc	Density in heptane + carbon tetrachloride, g/cc
Control	1.4170	1.3766
Flat yarns		
190	1.4181	1.3824
200	1.4185	1.3840
210	1.4194	1.3846
220	1.4197	1.3862
230	1.4249	1.3914
Textured yarns		
190	1.4172	1.3816
200	1.4175	1.3820
210	1.4183	1.3830
220	1.4193	1.3848
230	1.4204	1.3870

^a Crystal density, 1.455 g/cc.

on the pair of liquids used. According to these authors, heptane and carbon tetrachloride should give correct densities, so a redetermination of the densities was carried out with these liquids, also calibrated by the same glass beads of known density, which were also checked. The result was a consistent set of data, but of an overall lower value than previously found (Table II). Further comment on the correctness of density determinations will be made later in the section on discussion.

X-Ray Measurements

It has already been shown² that Terylene improves in lateral order when heated without the false-twist process. Inspection of x-ray diagrams showed that this was also true for this series of experiments with and without the addition of the false-twist process. Actual measurement of lateral order was, therefore, not carried out but an effort was made to discover factors associated with the size, shape, and disposition of the morphologic units from measurements of x-ray small-angle scattering.

X-Ray Small-Angle Scattering

The essentials of this method have already been described.¹ A Warhurst camera fitted with 0.5-mm pinholes was used with nickel-filtered copper K_{α} radiation. As before, an additional cassette to record a wide-angle calibration pattern was included. The film specimen distance for the small-angle experiments was 17 cm, and the calibration cassette distance was 5 cm.

Residual scatter as reported previously was eliminated, and measurements could be made on the films without background corrections being applied except for the general background due to the film itself. Calibration was carried out essentially as previously described¹ by reference to the intensity of the wide-angle pattern. X-Ray orientation of the wide-angle patterns, carried out as part of

TABLE III
X-Ray Small-Angle Scattering Data

Sample temp., °C	Meridional intensity, arbitrary units	Spacing, Å
Control	697	114
Flat yarns		
190	421	109
200	674	116 ^a
210	547	116
220	661	116 ^a
230	884	122 ^a
Textured yarns		
190	274	109
200	235	109
210	262	109
220	206	109
230	281	116

^a Distinct four-point diagrams; the rest are fused four-point diagrams.

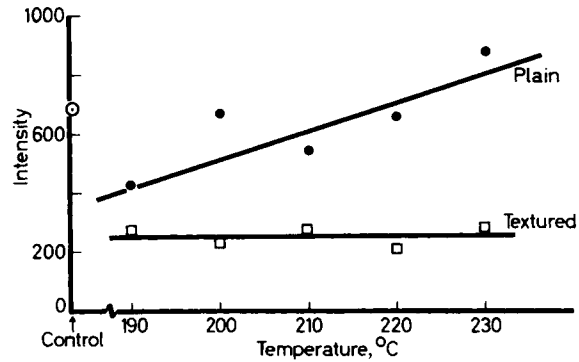


Fig. 2. Relation between the meridional intensity of the x-ray small-angle diagram and the temperature of preparation.

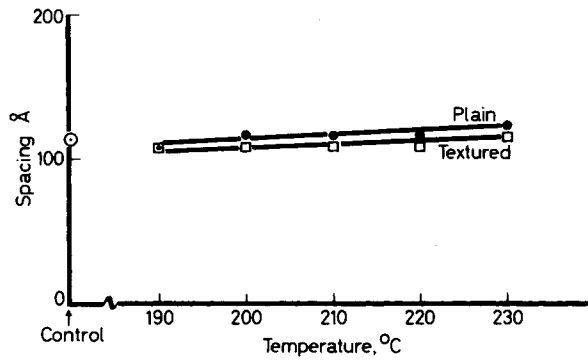


Fig. 3. Relation between the meridional spacing of the x-ray small-angle diagram and the temperature of preparation.

TABLE IV
Mechanical Properties

Sample temp., °C	Tex/denier	Breaking load, g	Tenacity, g/den	Extension at break, %	Initial modulus, g/den	Work of rupture, g/den
Flat Yarns						
Control	17.10/153.91	678.7	4.41	22.3	104.5	0.378
190	18.56/167.03	657.0	3.93	29.1	77.1	0.358
200	18.44/166.00	682.2	4.14	30.3	83.9	0.406
210	18.54/166.82	676.2	4.05	29.9	80.9	0.387
220	18.54/166.82	685.6	4.11	29.7	79.7	0.393
230	18.53/156.79	693.2	4.42	30.5	82.9	0.412
Textured Yarns						
190	18.03/162.27	567.9	3.50	16.1	54.4	0.175
200	17.96/161.61	579.1	3.58	16.2	51.7	0.177
210	17.96/161.61	574.8	3.56	15.9	46.9	0.169
220	17.65/158.85	565.9	3.56	15.2	47.6	0.162
230	17.70/159.31	574.9	3.61	15.7	46.6	0.167

the calibration procedure, showed that little, if any, loss of orientation was suffered for any of the specimens.

Terylene gives essentially four-point diagrams in most experiments; and, therefore, the integrated intensity of the meridional streaks was recorded as well as the spacing of them. No attempt was made to measure the equatorial streaks since, in general, they were either not recorded at all with this equipment or too short to make accurate measurement difficult and hence unreliable. Results are given in Table III and Figure 2.

A simple measurement of the distance apart of the meridional streaks was used to calculate the spacing of these layers by the application of Bragg's law. These results are given in Table III and in Figure 3.

Mechanical Properties

The mechanical properties were measured with an Instron textile testing machine at a cross-head speed of 2 in./min (5.0 cm/min) with a test length of 50 cm. The results are shown in Table IV and in Figure 4a-d.

DISCUSSION

The chemical nature of the polyester fibers is such that it plays no direct part in the uptake of disperse dyes. Thus, explanations for shade variations in dyeing must be sought mainly in terms of structural changes. Furthermore, previous results² showed that variations in moisture regain were not related to the observed variations in dyeing and did not give any indication for the essential changes taking place. Because of this, moisture regain was not further considered in this series of experiments.

Density measurements, however, can give information on structural changes. Initially, the densities of the samples were measured in a density column containing trichloroethylene and methylene dichloride calibrated by glass beads of known density. Redetermination was carried out with heptane and carbon tetrachloride calibrated with the same glass beads whose densities were independently checked. As a result, consistent but lower densities were recorded for the samples than were found with the first column. Such a result can only be caused by some penetration or interaction between the liquids used in the column and the terylene. Winkler et al.,³ in an investigation of Lanon polyester fiber, showed that densities could range from 1.514 to 1.371 g/cc according to the pair of liquids used in the determination. Since the crystal density can be calculated to be 1.455 g/cc, the density of 1.514 is clearly too high and is attributed to the formation of complexes with ethylene dibromide, one of the liquids used.

This raises the question of what is the right density for polyester, since there is still a range of values reported in the expected region. Winkler gives eight different values between 1.371 and 1.397. The lowest value, i.e., 1.371 reported by Winkler, cannot be automatically taken as the correct value because this could arise as a result of complex formation with the lowest density liquid used in the determination. Hence, in this work, two sets of values are given, one set which appears to be too high in general value, and the other set determined in a pair of liquids known to give the lowest values of density. Clearly, with this uncer-

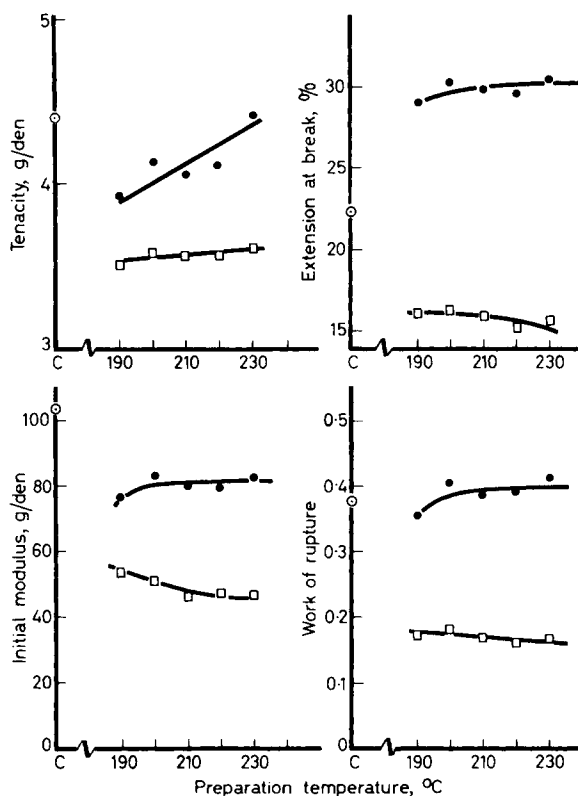


Fig. 4. Variation of the mechanical properties and the preparation temperature: (a) tenacity; (b) extension at break; (c) initial modulus; (d) work of rupture; (●) flat yarns; (□) textured yarns.

tainty about the correct density, there must be a corresponding uncertainty about accessibility values derived from density measurements reported in the literature.

What is of importance, however, is the trend of the density values, and this fortunately is the same whichever set of values is taken as correct (Table II). There is a steady increase in density as the temperature of the preparation is raised, both for flat and textured yarns. For dyeing of textured yarns without tension (see Fig. 1), this result is in accordance with expectation; i.e., as the density increases, the rate of dyeing (A/\sqrt{t}) decreases. But for most of the data obtained from dyeing under tension (see Fig. 1), and increase in density is associated with an increase in the rate of dyeing. Such a result can be explained if there are cracks and fissures in the textured terylene that can be closed by the application of tension, thus allowing a greater access to dye in the free state than under tension. To be in accordance with the results, such extraneous fissuring must be greater per unit volume the lower the preparation temperature. Under tension, therefore, the mechanism already discussed in a previous paper² comes into play, viz., heat tends to form voids, whereas tension during dyeing partially eliminates the effect of the tortuosity of these voids; and in this way the increase in the rate of dyeing with an increase in the density can be explained as previously.

The state of crystalline order can be assessed from wide-angle x-ray diagrams. In a previous paper,² it was shown that this increased as the preparation temperature of the yarns increased for flat Terylene yarns. The wide-angle x-ray diagrams included in the determination of the x-ray small-angle scattering parameters showed clearly that this was also true for both flat and textured yarns in the present series of experiments, but the changes were not quantified.

Considering the x-ray small-angle diagrams in relation to the fundamental morphology of the fibers, reference to Table III and Figure 2 shows that the integrated meridional intensity of the x-ray small-angle diagram increased for flat yarns but not for textured yarns. The meridional spacing increased only slightly both for flat and textured yarns. As an increase in meridional intensity corresponds to an increase in electron density differences within the fiber, the increase in meridional intensity for flat yarns must, therefore, correspond to a compacting of the morphologic units as the temperature of preparation increased for flat yarns. But since virtually no change is shown for textured yarns, then such compacting has been prevented by the application of the false-twist process. It seems unlikely that mechanical action would prevent the compacting within morphologic units, but it seems feasible that it could prevent compacting between units. Hence, these data suggest that aggregation of morphologic units takes place with flat yarns but not with textured yarns as the preparation temperature is raised.

The nature of the diagram does not change, i.e., it remains a four-point diagram throughout, and there is little change in the meridional spacing, which suggests that there is little change in relative disposition of the units both for flat and textured yarns. A four-point diagram can be given by structures that include helices, shish-kebabs,¹ or tilted lamellae, but there is insufficient evidence to make a positive choice between these alternatives. Choice is made more difficult when it is realized that when first spun, Terylene, as well as other polyesters, give an amorphous-type x-ray diagram that does not change to the familiar crystalline-type diagram until a hot-drawing process has been subsequently applied to the yarn. Thus, the formation of crystalline units takes place after spinning; and hence stress crystallization, which can lead to the formation of shish-kebabs, may not be part of the crystallization mechanism. However, the speed of spinning⁴ can have a profound effect upon the properties of the subsequent yarn produced by hot-drawing, and, therefore, stress cannot be entirely ruled out as part of the mechanism for predisposing the formation of one type of morphologic unit over another. Unfortunately, the final form of the morphologic unit cannot be determined by the present data and, therefore, must be left an open question.

Further structural information can be obtained from consideration of the mechanical properties. The tenacity for flat yarns is reduced more than that of the control as a result of heating, but it progressively improves as the temperature of preparation is increased. This is consistent with a compacting of the morphologic units in the fiber as suggested by the density considerations and the x-ray small-angle results. On the other hand, the tenacity of textured samples, although smaller than that of the control, does not vary appreciably as the temperature of the preparation is raised. This is again consistent with the x-ray small-angle scattering results, which suggest a more uniform product. In fact, if the tenacity is plotted versus the meridional intensity, quite a rea-

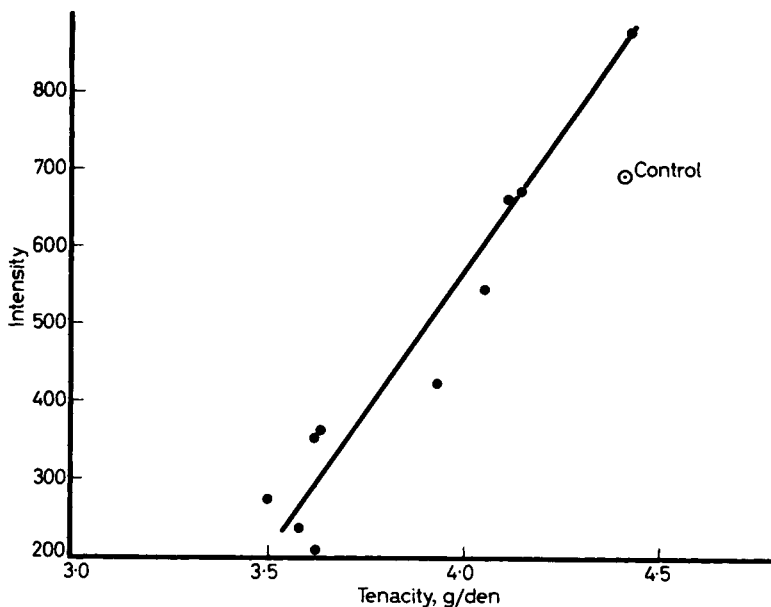


Fig. 5. Relation between the meridional intensity of the x-ray small-angle diagram and the tenacity.

sonable straight line correlation is given (Fig. 5). Other mechanical properties such as breaking extension, initial modulus and work of rupture correlate with x-ray small-angle scattering data but not in a linear manner.

Thus, there is a tendency for the breaking extension to be higher, the initial modulus to be higher, and the work of rupture to be higher with greater values for the meridional intensity of the small-angle x-ray diagrams. These effects can be partly explained on the assumption that a greater openness of morphology can result from structural changes that increase the electron density of the morphologic units at the expense of the surrounding regions. No doubt, this is an oversimplification, and other more complex factors also come into play. Such an explanation also accords with the concept of void formation as a result of temperature treatments, which improves the lateral order of the morphologic units faster than annealing forces can compact the fiber as a whole thus leaving voids or accessible volumes.⁵

Correlation with dye uptake data was also sought. One effect of the change of density and tex is to alter the specific surface area presented to the dye and, therefore, to affect the rate of dyeing. It can easily be shown that the surface area A is given by a simple formula for a cylindrical yarn, viz.,

$$A = 2 \sqrt{\pi l} \sqrt{\frac{tex}{\rho}}$$

On a simple assumption that the yarns are cylindrical, or if not cylindrical the surface area is proportional to $(tex/\rho)^{1/2}$, it can be shown that the changes brought about by heating have only a small and virtually negligible effect on the dyeing results. The main changes in the rate of dye uptake found cannot, therefore, be attributed to changes in surface area brought about by the heating processes.

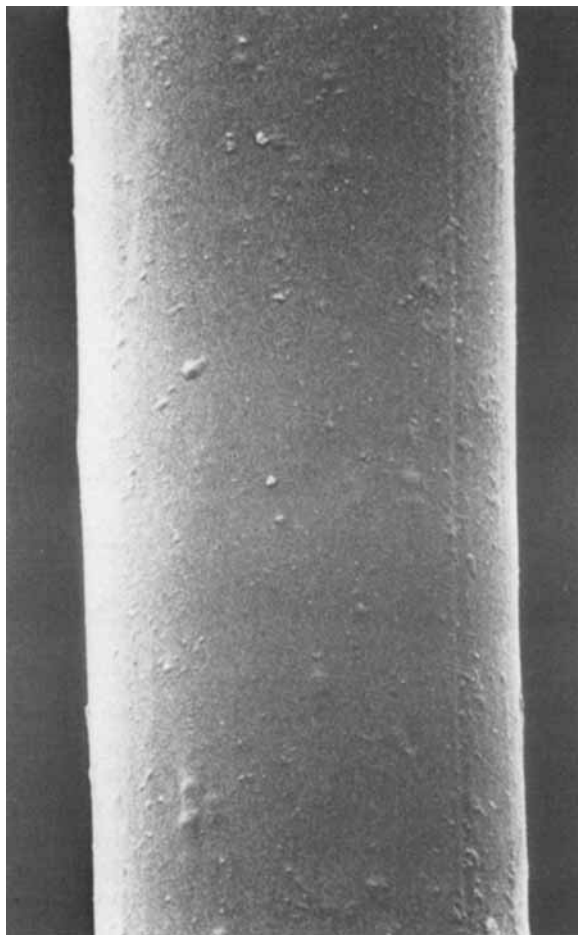


Fig. 6. Scanning electron microscope picture of flat terylene yarn drawn over the heater at 210°C (3500X).

No clear correlations were found between any of the other mechanical properties and dyeing rate; the expected¹ correlation with work of rupture was not evident. Correlation of the rate of dyeing with x-ray small-angle scattering results was qualitative, the higher rate of dyeing results being associated with higher meridional intensities. If the higher intensities are attributed to compacting of the morphologic units with an attendant increase in less electron-dense regions, then qualitatively this might be expected to lead to greater rates of dyeing. The mechanical action associated with the false-twist process causes the meridional intensities of textured yarns to be less than for flat yarns and not to vary appreciably with preparation temperature. At the same time, when dyed under tension, the rate of dyeing of textured yarns is less than that of the corresponding flat yarns, and the variation with preparation temperature is not as great as for flat yarns.

There is thus a qualitative correlation between the x-ray small-angle results and the dyeing results so that in explanation it would appear that the mechanical action is bringing about a more uniform structure. Furthermore, since the rate

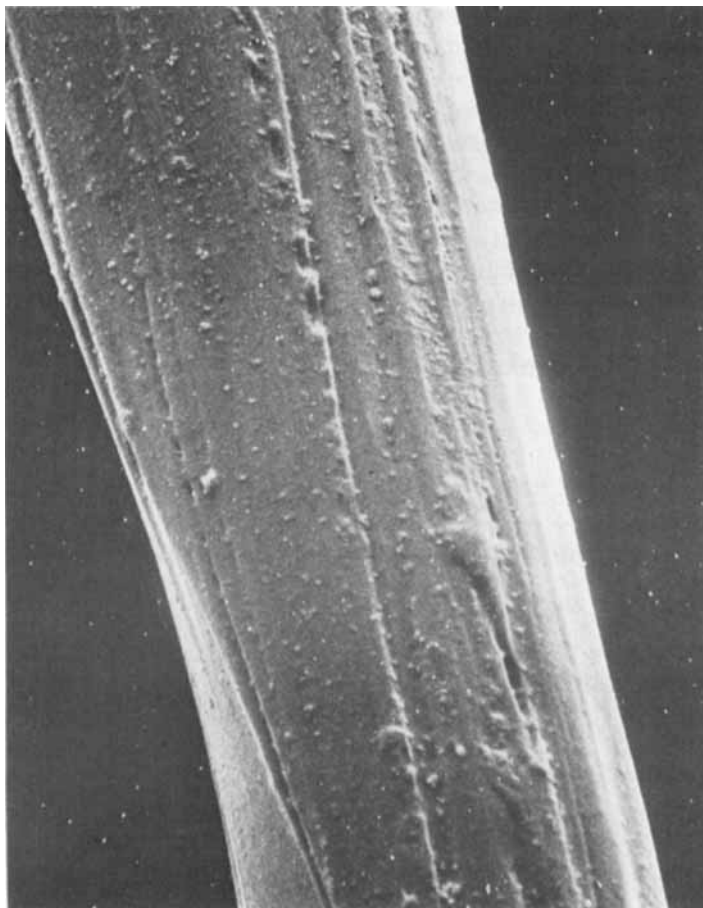


Fig. 7. Scanning electron microscope picture of textured terylene yarn drawn over the heater at 210° (3500 \times).

of dyeing is lower for textured yarns than for corresponding flat yarns when dyed under tension, it can be inferred that at the same time the mechanical action leads to more tortuous channels and hence limits the rate of dyeing. It is significant that raising the tension during dyeing causes the rate of dyeing to increase, which would support this concept. The apparently anomalous results of a higher rate of dyeing when no tension is applied during dyeing of textured yarns can be explained by the superimposition of gross fissures on the structure just discussed, with such fissures being partly or fully closed by tension during the dyeing process. Such gross fissures would not contribute to the x-ray small-angle data being too great to produce coherent diffraction effects.

To obtain further evidence for such gross cracks and fissures, Mr. S. C. Simmens of these laboratories explored the surface of the samples with a scanning electron microscope, having first lightly coated the surface with gold. All the flat samples showed typically smooth surfaces except for the adhering oligomer crystals, which is common for polyester surfaces (Fig. 6). The textured samples all showed distortion and cracking of the surface (Fig. 7), thus confirming the general thesis.

The model of structure that emerges from this discussion, therefore, is one of morphologic units that build up a structure with accessible regions between them. These accessible regions are probably elongated and tortuous and are increased in volume by the application of heat, but at the same time made more tortuous if false-twist processes are applied during heating. Superimposed on such a structure for textured yarns are gross elongated fissures and cracks that probably extend into the interior of the fiber, although supporting evidence for the interior of the fiber is not available at the moment. Unfortunately, the nature of the morphologic units cannot yet be decided but they must be such as to cause a four-point diagram in the x-ray small-angle results, and among possible units are those that are helical, shish-kebabs, or tilted lamellae, but the data available do not allow a distinction to be made.

References

1. J. O. Warwick, *J. Appl. Polym. Sci.*, **19**, 1147 (1975).
2. J. O. Warwick *J. Soc. Dyers Colour.*, **88**, 142 (1972).
3. F. Winkler, G. Homann, and W. Götze, *Faserforsch. Textiltech.*, **20**, 80 (1969).
4. E. Liska, *Chemiefasern Textil. Ind.*, **23.75**, 818 (1973).
5. J. O. Warwick, *J. Soc. Dyers Colour.*, **86**, 303 (1970).

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