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The Identification of Acrylic Fibers by Polymer Composition as Determined by Infared Spectroscopy and Physical Characteristics

Acrylic fibers are now regularly encountered in the investigation of crime mainly due to their widespread use in the manufacture of outer clothing and carpets. Although acrylic fibers are easily recognized as a group, making a specific identification is particularly difficult. The sample available for identification and comparison in forensic science laboratories may be restricted to a few single fibers, a condition which imposes severe limitations on the value of existing identification schemes for acrylic fibers.

A reference collection of 40 different acrylic fibers was obtained from the world's manufacturers. The infrared spectrum for each specimen as a KCl pellet was recorded using a Unicam SP 200 spectrophotometer. The resulting spectra were interpreted and divided into groups so that each group corresponded to a particular polymer type. The physical characteristics determined for each sample were surface appearance and cross-sectional shape. Samples which were similar in qualitative composition and physical characteristics were further compared using quantitative infrared spectroscopy.

The results have been recorded in tabular form so that an identification scheme is directly provided for acrylic fibers. The scheme is shown to be effective with a wide range of sample sizes from bulk samples to single dyed fibers.

Definition

The United States Federal Trade Commission defines an acrylic fiber as one in which the fiber forming substance is any long chain synthetic polymer composed of at least 85 percent by weight of acrylonitrile units.

Chemical Identification

Commercial production of acrylic fiber began at Camden, South Carolina in 1950 when Du Pont produced 100 percent acrylonitrile filaments under the name "Orlon". Although these filaments were strong and resistant to a wide range of chemicals they could be dyed to only pale shades with basic dyes. Since then Orlon and most other acrylic fibers have been modified with small amounts of other vinyl monomers to overcome this difficulty. Acrylic fiber plants have now appeared all over the world, but compositions and manufacturing details have not been released by the industry. Therefore, some divergence of opinion over process details is evident in the literature. The most useful information

concerning polymer compositions and process details has been collected and published by Sanders [1].

Although polyacrylonitrile might appear to be a linear polymer, it in fact shows only lateral order [2], negative optical birefringence, and is highly insoluble. Saum [3] has shown that the association of CN groups in pairs by dipole interactions is more important for organic nitriles than hydrogen bonding. The magnitude of the CN dipole interaction energy in commercial fibers depends on the concentration of interacting CN groups. As the concentration in the structure decreases, the fiber becomes more readily soluble in a given solvent. The Textile Institute scheme for the identification of acrylic fibers uses solubility in nitromethane, dimethyl nitrosamine, and dimethyl formamide at various temperatures. The Shirley Institute scheme makes use of solubility in 70 percent nitric acid, dimethyl formamide, and dimethyl sulphoxide for various periods of time. Solubility tests tend to be inconclusive, and they are also affected to some extent by the physical condition of the fiber.

Vinyl comonomers containing basic or acidic functional groups can provide sites for anionic and cationic dyes. Ester comonomers disrupt the structure of polyacrylonitrile and, therefore, allow easier penetration of basic dyes. Mixed stains containing an acid dye, a disperse dye, and a basic dye form the basis of both published identification schemes for acrylic fibers. The colour obtained depends on the quantity and proportion of each dyestuff taken up. The Textile Institute scheme [4] uses Meldrum's Stain and the Shirley Institute scheme [5], Shirlastain E. Relatively large samples are necessary for staining tests, and great difficulties arise with samples which are already deeply coloured.

Textile fibers in general [6] and acrylic fibers in particular [7] may be characterized by pyrolysis gas chromatography. Although very small samples may be analyzed, the multiplicity of pyrolyser units, pyrolysis temperatures, and column packings employed, almost inevitably leads to poor interlaboratory agreement.

Acrylic fibers may also be characterized by their infrared spectra [5,8]. However, no systematic scheme based on infrared spectroscopy is available at the present time although spectra for a number of acrylonitrile copolymers have been published. The structure and infrared spectrum of polyacrylonitrile has been discussed in detail by Krimm and Liang [9]. Infrared spectra of copolymers of acrylonitrile with α-methyl styrene and vinyl acetate have been published by Hummel [10]; those with acrylic acid, methyl acrylate, and methyl methacrylate by Gentilhomme et al [11], and that with styrene by Haslam and Willis [12].

Although solvent cast films produce good quality spectra, they are tedious to produce and require relatively large samples. Pelleting techniques are generally rapid and qualitatively reliable. Quantitative measurements using absorbance ratios are still possible using pelleted samples. A wide range of sample sizes can be successfully pelleted, commercial dies being available for samples weighing between a few milligrams and a few micrograms. The infrared spectrum of a polymer depends to a large extent on the functional groups present. This is a distinct advantage over other methods such as staining and solubility tests which are influenced by physical form.

Gentilhomme et al [11] have shown that dimethyl formamide (DMF) persists in the polymer produced from DMF solution even after drying at 80°C for 85 hours. The primary amide band for the residual solvent is at 1672 cm^{-1}; whereas the band for liquid DMF is at 1688 cm^{-1}. This displacement indicates a molecular association with the polymer chain and explains why residual DMF is so difficult to remove. A gas-chromatographic method for the determination of residual DMF in acrylic fibers has been published by Nestler and Mai [13].
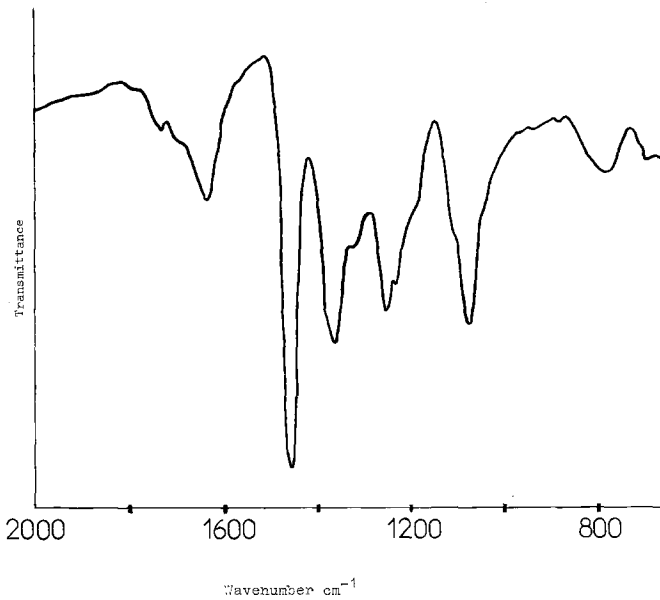
FIG. 1—*Infrared spectrum of polyacrylonitrile.*

Physical Characteristics

The physical characteristic normally used in identification schemes is cross-sectional shape. Since there is a considerable variation in the spinning processes used for the manufacture of acrylic fibers, it was decided to investigate the possibility that the surface appearance would also be of value for identification purposes.

Experimental Procedure

Infrared Spectroscopy

Pellets of KCl 13 mm in diameter for infrared spectroscopy were prepared using a Beckman–RIIC DO1 evacuable die.[2] One polished metal pellet was placed in the die body, and this was covered with a layer of dry powdered KCl. A tuft of fiber weighing a few milligrams was held over the assembly and cut into short lengths with scissors. The pieces were allowed to fall evenly on the KCl powder. The fiber was lightly covered with further KCl powder, and the die was assembled using the second polished metal pellet and the metal plunger. The assembly was then pressed at 10 tons under vacuum for 2 minutes. The resulting KCl pellet was examined, using a Unicam SP 200 spectrophotometer in the fast scan mode, from 650 to 5,000 cm^{-1}.

For each sample the qualitative polymer composition was determined using the standard infrared spectra in Figs. 1 to 6. The result was recorded numerically using the code shown in Table 1.

[2] Beckman-RIIC Limited, Sunley House, 4, Bedford Park, Croydon CR9 3LG, Surrey, England.
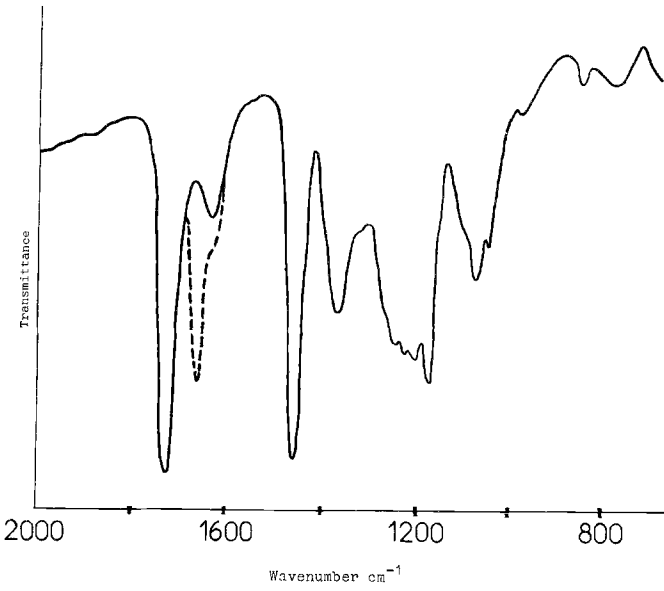
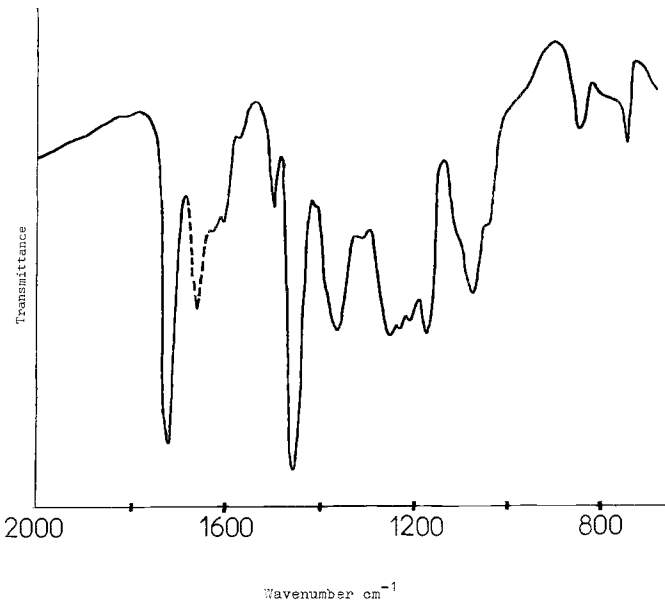FIG. 2—*Infrared spectrum of an acrylonitrile/methyl acrylate copolymer.*

FIG. 3—*Infrared spectrum of an acrylonitrile/methyl acrylate/methyl vinyl pyridine terpolymer.*
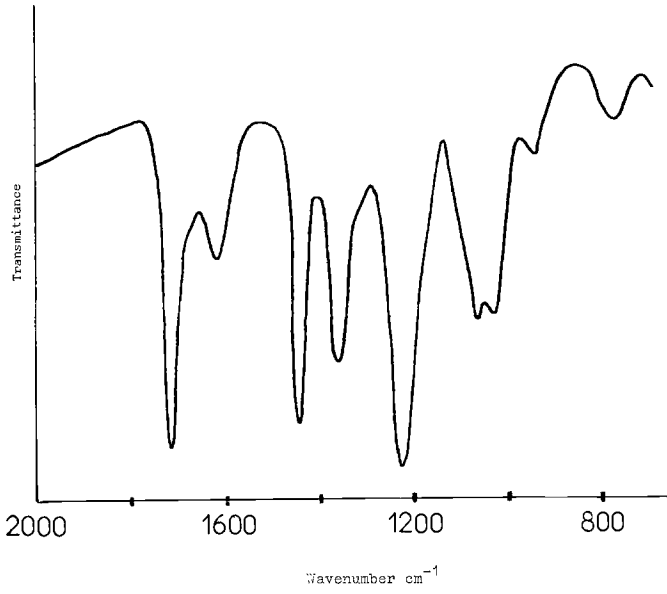
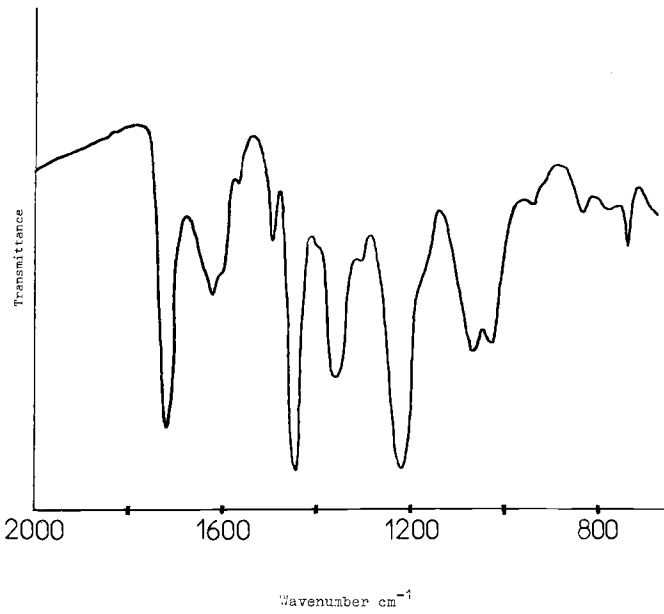FIG. 4—*Infrared spectrum of an acrylonitrile/vinyl acetate copolymer.*

FIG. 5—*Infrared spectrum of an acrylonitrile/vinyl acetate/methyl vinyl pyridine terpolymer.*
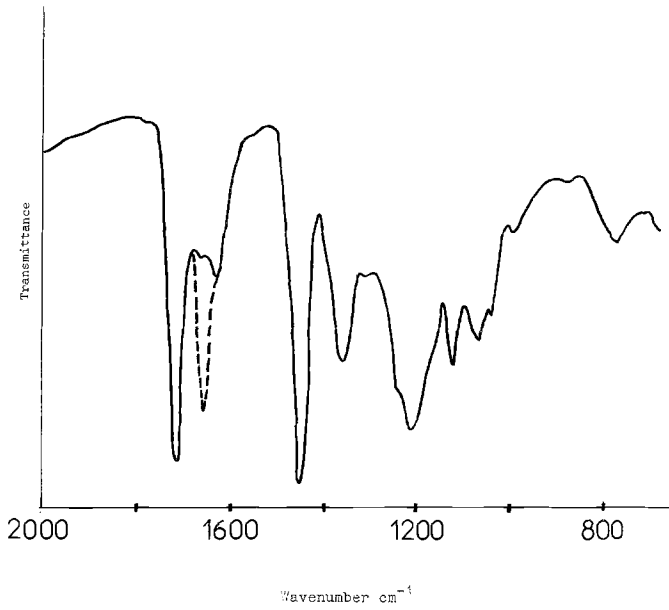
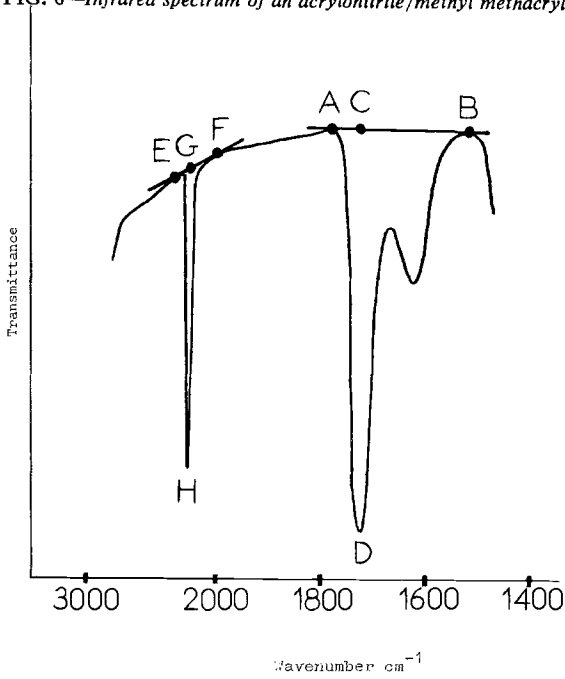FIG. 6—Infrared spectrum of an acrylonitrile/methyl methacrylate copolymer.

FIG. 7—The construction of quantitative baselines.

TABLE 1—*A numerical code for polymer composition, surface appearance, and cross-sectional shape.*

Polymer Composition	Surface Appearance	Cross-sectional Shape
1. Acrylonitrile	1. Long striations	1. Round
2. Acrylonitrile/methyl acrylate	2. Short striations	2. Bean
3. Acrylonitrile/methylacrylate/methyl vinyl pyridine	3. Irregular	3. Peanut
4. Acrylonitrile/vinyl acetate	4. Relatively smooth	4. Lobed
5. Acrylonitrile/vinyl acetate/methyl vinyl pyridine		5. Acorn
6. Acrylonitrile/methyl methacrylate		6. Mixed peanut and bean
7. Acrylonitrile/any other monomer(s)		

Absorbance ratios of $C=O$ (stretching):$C\equiv N$ (stretching) were calculated, at slow scan speed and minimum slit width, using the target baseline constructions AB and EF shown in Fig. 7. Before each spectrum was recorded, the gain control was set at 2150 cm^{-1} so that the recorder pen returned from 50 percent full scale deflection with an overshoot of approximately 2 percent. The absorbance ratio (R) was then calculated by dividing the absorbance CD by GH.

A number of dyed and delustred samples were examined in order to determine the effect of dyestuffs and delustrants on the identification scheme. Small samples were examined by the lead disc technique of Cleverley [14] and single fibers by the method of Fox and Schuetzman [15] to determine the limits of infrared spectroscopy in terms of sample size.

Physical Characteristics

A temporary mount of each fiber sample was prepared on microscope slides under transparent adhesive tape. This mount provides a large difference in refractive index between fiber and mountant so that surface features predominate. Transparent adhesive tape is routinely used for the collection of surface fibers in our laboratory. The samples were examined in transmitted light using a Zeiss Student Research Microscope at a magnification of $\times 500$. Standard photographs, prepared by using the stereoscan Electron Microscope for the four distinct types observed, are shown in Fig. 8. The result of each examination was recorded numerically using the code shown in Table 1.

Cross sections were also prepared for each sample and the results were again coded numerically as shown in Table 1.

Results and Discussion

The results recorded for 40 samples are shown in Table 2 in a form which directly provides an identification scheme for acrylic fibers.

Polymer Compositions

Approximately 50 percent of the fibers examined contained methyl acrylate, 12 percent contained vinyl acetate, 10 percent contained methyl methacrylate, and 5 percent contained acrylonitrile only. Two fibers containing methyl acrylate and five containing vinyl acetate also contained the basic termonomer methyl vinyl pyridine. According to Bellamy [16], substitution in pyridine ring systems may be determined by treating the heterocyclic nitrogen atom as a ring substituent. On this basis the termonomer would appear to be 3–methyl–5–vinyl pyridine.

TABLE 2—*Data for the identification of acrylic fibers.*

Polymer Composition	Surface Appearance	Cross-sectional Shape	Absorbance Ratio (R)	Name	Manufacturer	Additional Comments
1	1	4	...	Wolpryla	Friedrich Engels	Wet DMF[a] process reported. Dope dyed.
1	3	1	...	Zefkrome	Dow Chemicals	Dope dyed.
2	1	1	1.17	Tacryl	Stockholme Superfosfats	Wet DMF[a] process reported.
2	1	1	1.24	Courtelle Latent Crimp	Courtaulds	Bicomponent. Target baseline slopes downwards from A to B. Residual solvent peak near 1675 cm^{-1}
2	1	1	1.249±0.016	Courtelle	Courtaulds	Target baseline slopes downwards from A to B.
2	1	1	1.34	Tacryl N	Stockholme Superfosfats	
2	1	1	1.68	Beslon	Toho Rayon	
2	1	1	1.69	Euroacril	A.N.I.C.	
2	1	1	1.73	Cashmilon A	Asahi Chemicals	
2	1	1	1.79	Zefran II	Dow Chemicals	
2	1	1	1.82	Exlan L	Japan Exlan	
2	1	2	1.32	Velicren	Snia Viscosa	Residual solvent peak near 1672 cm^{-1}
2	1	2	1.67	Toraylon 20	Toyo Rayon	
2	2	3	1.09	Nymcrylon	Nyma	Residual solvent peak near 1672 cm^{-1}
2	2	3	1.18	Dralon	Bayer	Residual solvent peak near 1672 cm^{-1}
2	2	3	1.27	Redon F	Phrix-Werke	Residual solvent peak near 1672 cm^{-1}. Minor bands near 700, 725, and 1538 cm^{-1}
2	2	3	1.31	Orlon 42	Du Pont	Residual solvent peak near 1672 cm^{-1}
2	2	3	1.312±0.075	Orlon 72	Du Pont	Non uniform sample. Residual solvent peak near 1672 cm^{-1}
2	2	3	1.42	Orlon 75	Du Pont	Residual solvent peak near 1672 cm^{-1}
2	4	5	...	Orlon 23	Du Pont	Bicomponent. Residual solvent peak near 1672 cm^{-1}
2	4	6	...	Dolan 25	Suddentsche Chemifaser	} Residual solvent peak near 1672 cm^{-1}
3	2	3	1.26	Orlon 44	Du Pont	
3	2	3	1.28	Orlon 28	Du Pont	
4	1	2 (small deniers may be 1)	1.38	Acrilan 16	Chemstrand	
4	1	2	...	Acrilan	Monsanto U.K.	} All made by the same Chemstrand processes. DMA[b] reported as solvent
4	1	2	...	Acrilan A16	Israeli Chemicals	
4	1	2	...	Leacril 16	A.C.S.A.	
4	1	2	...	Vonnel	Mitsubishi Rayon	
4	1	2	1.41	Acrilan 57	Monsanto	Bicomponent
5	1	1	1.29	Creslan 58	Cyanamid	} Both made by the same Cyanamid processes.
5	1	1	...	Exlan	Japan Exlan	

(Continued)

TABLE 2—Continued.

Polymer Composition	Surface Appearance	Cross-sectional Shape	Absorbance Ratio (R)	Name	Manufacturer	Additional Comments
5	1	2 (small deniers may be 1)	1.15	Acrilan 36	Chemstrand	}Both made by the same Chemstrand processes. DMA[b]
5	1	2	...	Leacril N	A.C.S.A.	} reported as solvent.
5	1	2	1.23	Acrilan 41	Chemstrand	DMA[b] reported as solvent.
6	1	1	...	Creslan 61	Cyanamid	}Both made by the same Cyanamid processes.
6	1	1	...	Crilenka	Cyanenka	}
6	1	2	...	Acribel	U.C.B. Fabelta	DMF[a] reported as solvent.
6	1	4	...	Crylor	Rhodiacéta	Residual solvent peak near 1672 cm^{-1}
7	3	1	..	Zefran	Dow Chemicals	Graft copolymer of polyvinylpyrrolidone
7	4	5	...	Orlon 21	Du Pont	Bicomponent

[a] DMF = Dimethyl formamide
[b] DMA = Dimethyl acetamide

Only two fibers were in the unclassified group by polymer type. Dow Chemical's Zefran acrylic fiber is reported to be a graft copolymer of polyvinylpyrrolidone [1]. The composition of Du Pont's Orlon 21 bicomponent fiber is unknown.
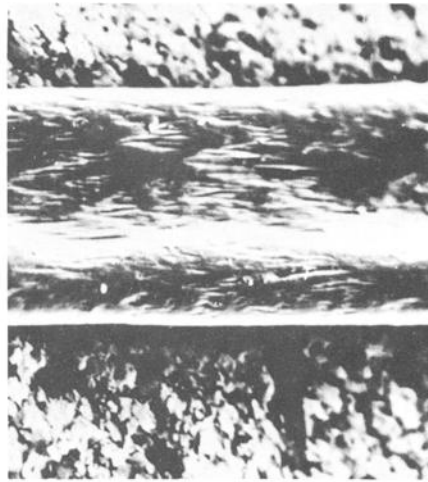
Absorbance ratios (R) were calculated for those fibers which were otherwise similar and the results are shown in Table 2. Each result is the mean of at least two separate determinations. In order to estimate the standard error in the measurement of an absorbance ratio, ten separate halide discs containing Courtelle were examined. The mean result obtained was 1.249 ± 0.016. Sanders [1] reports that Courtelle contains 6 percent methyl acrylate by weight. Thus, assuming a linear relationship between R and comonomer content, the above standard error represents approximately ±0.08 percent in terms of the methyl acrylate content by weight.

As work progressed, it became clear that some samples could produce much higher standard errors than Courtelle. For example, ten determinations of the absorbance ratio for Orlon 72 using separate discs gave a mean of 1.312 ± 0.075. Each individual disc, however, gave more reproducible results. It was also clear from examination of individual spectra that there was a true variation in copolymer composition for this particular sample of Orlon 72. Therefore, before valid quantitative comparisons between "crime" and "control" samples of acrylic fibers can be made, the mean and standard error of the control sample must be estimated using the same infrared procedures as for the "crime" sample.
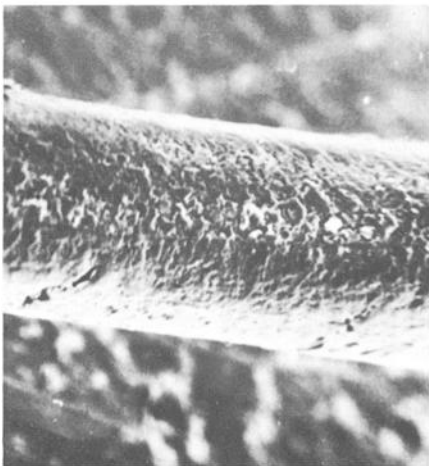
It was also noted that both Courtelle and Courtelle Latent Crimp produced a target baseline which clearly sloped downwards from A to B. This was in contrast to all the other fibers examined which produced almost ideal horizontal target baselines. The origin of this effect is not known, although it appeared in all the Courtelle samples examined.
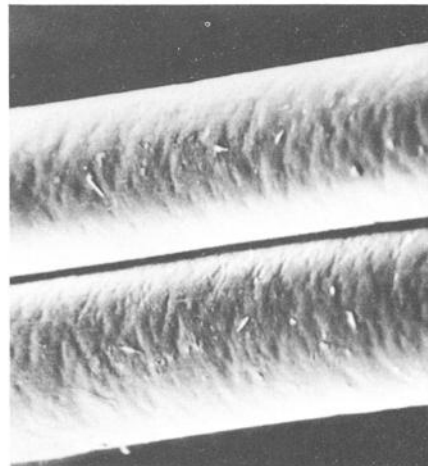
LONG   STRIATIONS   SHORT   STRIATIONS

IRREGULAR   RELATIVELY SMOOTH

FIG. 8—*The surface appearance of acrylic fibres at ×1500 using the Stereoscan Electron Microscope.*

Residual Solvents

A number of samples which are reported to be spun using DMF as solvent [1] possessed a distinct absorption near 1672 cm⁻¹. For dry spun fibers this was often one of the strongest absorptions in the infrared spectrum. The wavenumber 1672 cm⁻¹ is reported by Gentil-homme et al [11] for the primary amide band in associated DMF. The relative intensity of this band varied from batch to batch for the same fiber and decreased markedly when test samples were boiled for 3 h in water. The band which may appear, due to residual DMF,

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in the infrared spectra of acrylic fibers is shown as a broken line in Figs. 2, 3, and 6. Notes have also been made in Table 2 to indicate those samples for which a residual DMF peak was found. Other fibers which are reported to be manufactured using DMF as solvent [1] are also indicated in Table 2.

Most samples from clothing encountered in casework have been worn and washed. This would probably result in loss of most, if not all, residual solvent. However, if residual solvent were found, it would obviously provide a useful feature for comparison purposes.

A peak of variable intensity which decreased on boiling was also found in samples of vinyl acetate/acrylonitrile polymers near 1640 cm⁻¹. This could be due to residual dimethyl acetamide which is reported to be used as spinning solvent in the manufacture of these fibers by Chemstrand processes [1].

These results suggest that in the future, infrared spectra should be recorded both for fibers as received from the manufacturers and also for the same samples after boiling for a few hours in water. The persistence of residual solvents in acrylic fibers clearly merits further investigation.

Dyestuffs and Delustrants

The dyed samples examined often produced spectra which were virtually indentical to those for raw-white fibers of the same type. Even when bands were produced by the dyestuffs, the interference was never sufficient to obscure the basic polymer composition. This result is in agreement with the conclusions of other authors [15,17]. The normal delustrant used in acrylic fibers is titanium dioxide. This produces a very broad band near 650 cm⁻¹ and, therefore, does not interfere with the identification of acrylic fibers.

Small Samples

The lead disc technique of Cleverley [14] gave satisfactory infrared spectra for samples weighing between one and twenty micrograms. The micro pellet technique of Fox and Schuetzman [15] was successfully used for single fibers weighing between twenty micrograms and one microgram.

Physical Characteristics

Correlations were noted between physical characteristics and the manufacturing process. Dry spun fibers tend to be peanut or lobed in cross section and have short striations on the surface of the fibers. Wet spun fibers tend to be round or bean in cross section and have long striations on the surface of the fibers. Zefkrome and Zefran from the Dow Chemical Company have an irregular surface appearance and are reported to be manufactured using an aqueous solution of zinc chloride [1].

Bicomponent Fibers

The bicomponent fibers manufactured by Du Pont, such as Orlon 23, are easily recognized from their acorn cross sections. More recent bicomponents from Courtaulds and Monsanto have the same cross-sectional shapes as the regular fiber; and their average compositions, as shown by the absorbance ratios in Table 2, are also indistinguishable from the regular fiber. It is therefore necessary to use alternative procedures for these bicomponents. The staining of cross sections with a suitable dye would possibly reveal the bicomponent structure. For a sample which is already dyed, the bicomponent structure may already be apparent when cross sections are cut.

General Discussion

Acrylic fibers are easily recognized as a group from the $C \equiv N$ stretching vibration near 2250 cm^{-1}. Modacrylic fibers also contain acrylonitrile, but each of them has a unique infrared spectrum [18]. A polyvinylidine dinitrile fiber named "Darvan" could also be confused as an acrylic, but at present this fiber would not appear to be in commercial production.

Since the identification procedure uses polymer types and physical characteristics, the dangers of attempting the identification of a fiber by tradename is avoided. For example, Courtelle would be identified in the scheme by the numerical representation of polymer composition, surface appearance, cross-sectional shape, and absorbance ratio (R) in sequence, namely, 2:1:1:1.25.

The identification scheme proposed does not depend on a precise match of the infrared spectrum with one in a reference collection; and therefore, even very small dyed samples can be correctly classified by qualitative polymer composition and physical characteristics. Final comparison of samples should include minor peaks, due to traces of additional fiber components or dyestuffs, and measurement of the absorbance ratio (R) whenever possible. A collection of spectra for standard samples recorded on the analyst's own particular spectrophotometer, together with a collection of mounted samples for microscopy, would obviously be advantageous.

Summary

An identification procedure is presented for acrylic fibers which employs polymer compositions and physical characteristics. The scheme has been designed so that raw-white bulk samples or single dyed fibers can be identified by the same procedure. Qualitative and quantitative polymer compositions are determined by infrared spectroscopy using KCl discs. The physical characteristics used are surface appearance and cross-sectional shape. The 40 fibers examined were divisible into 15 groups by qualitative composition and physical characteristics. When quantitative compositions were determined in addition, the samples were divided into approximately 25 groups. The principal monomers used for fiber production are shown to be methyl acrylate, methyl methacrylate, vinyl acetate, and 3–methyl-5-vinyl pyridine. The presence of residual solvent in fibers which are spun from dimethyl formamide and dimethyl acetamide solutions is discussed. The difficulties involved in acrylic fiber identification by tradename are stressed and an alternative schematic procedure is suggested.

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