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Density Gradient Analysis of Single Polyester Fibers

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ABSTRACT: The densities of single poly(ethylene terephthalate)-based commercial fibers from 14 different yarn bobbins were measured to five significant figures. The densities of three of these fibers were also measured after each of three treatments representing two different laundering methods and one outdoor exposure. The density gradient method was found to be a sensitive tool for discrimination among the yarn types when new as well as after each of the three treatments. In addition, the method was able to discriminate among fibers from the same yarn bobbin but which were in each of the four states examined. Density gradient analysis demonstrated little ability to identify the fiber type of an unknown sample. Consequently, the main value of density gradient analysis of fibers clearly lies in its ability to discriminate among fibers of similar origin.

KEY WORDS: criminalistics, synthetic fibers, physical properties

Measurements of the density of materials have proved useful in many fields, including forensic science as discussed by Kirk [*1,2*]. Methods of measuring density are nearly as numerous as the materials to be examined. Although density of any material is defined as its weight per unit volume, its determination by direct measurements of sample weight and volume is sometimes difficult so that density might better be measured some other way. For example, the density of small, irregularly shaped objects is more conveniently measured indirectly by comparisons with standards of known density; one such method is provided by a density gradient column. The column, a vertical tube containing miscible liquids so mixed that density in the tube changes continuously from top to bottom, is calibrated with standards of known density. An object dropped into the column sinks until it reaches the level corresponding to its own density.

Although Galileo [*3*] clearly described the principle in 1638, the technique was not widely used until its rediscovery in 1937 by Linderstrom-Lang [*4*]. Several methods of preparing density gradient columns have since appeared, and procedures for the most commonly used preparations are available in standard works [*5*]. In addition, methods of column preparation more suitable for some aspects of forensic science analysis have been published [*6-8*].

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Density Gradient Analysis of Fibers

While forensic scientists commonly use density techniques in glass and soil analysis, little use has been made in fiber analysis, as evidenced by the fact that 82, 68, and 0.9% of forensic science laboratories recently reported glass, soil, and fiber analysis, respectively [*9*]. So little use of density analysis by forensic scientists examining fibers is quite surprising because the density gradient method is convenient, inexpensive, nondestructive, and discriminating in the examination of single fibers on a submicrogram level.

Inspection of the literature on fibers reveals that density analysis is used in two different ways. First, when measured to two or three significant figures, fiber density usually can identify the generic class, such as polyester, to which the sample belongs and occasionally identify a particular trade name group, such as Dacron®, of the sample. Various standard works on this subject are readily available [*10–12*]. Second, when measured to four or five significant figures, density has found use in determining the percentage of crystallinity of fibers [*13*], in quantitatively measuring the level of a fiber additive [*14*], and in monitoring polymer degradation of fibers [*15*].

It thus is apparent that if density measurements are made with enough sensitivity, many variables affected by manufacture and consumer use of a textile become demonstrable and can be used to discriminate between fibers of very similar origin. For example, the method is sensitive to the degree of fiber crystallinity, which varies from fiber type to fiber type and may further be altered by consumer use. Similarly, the method may be sensitive to both commercial manufacturing conditions and consumer use that result in varying levels of chemical additions or physical degradation of the fibers. In summary, density gradient analysis offers a means to discriminate between fibers on the basis of a myriad of commercial practices encompassing extrusion, dyeing, and finishing performed under various conditions along with an endless variety of consumer practices including laundering and outdoor exposure.

The objective of this study was to examine variability in fiber density within a given generic class. It was hoped that differences in fiber structure arising from a variability in commercial manufacturing or consumer practices would result in detectable variability in fiber density. The generic class chosen for the study was polyester. The consumer practices chosen for examination were outdoor weather exposure and the laundry techniques of mild low-temperature hand washes and vigorous high-temperature machine washes.

Analysis of Polyester Fibers

The chemical compositions of polyester fibers currently in commercial production fall in two basic groups. The polymer constitution of one group is predominantly poly(1,4-cyclohexylenedimethylene terephthalate), commonly referred to as PCDT (Fig. 1). Some types of Eastman Kodak's Kodel® fibers are well-known representatives of this group. The polymer constitution of the other group is predominantly poly(ethylene terephthalate), commonly referred to as PET (Fig. 2), and PET by far constitutes the greatest majority of polyester fibers commercially produced. Since PCDT-type fibers may easily be distinguished from PET types by a variety of techniques [*16*] and since the vast majority of commercial polyester fibers are PET types, this study was restricted to the latter.

One of the most important decisions that must be made when preparing for a density gradient analysis is the choice of liquids to be used in the column. Criteria necessary for liquid use include lack of chemical interaction, low viscosity, low volatility, additivity by volume, and inertness to the fibers being examined. All of these factors but the last may be easily determined. When considering the last factor, the particular polymer of which the fiber is composed must be taken into account. In the case of PET, several liquid

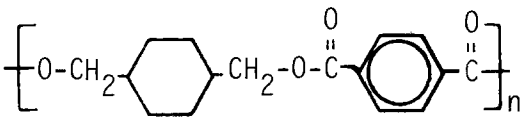

FIG. 1—*Composition of PCDT.*

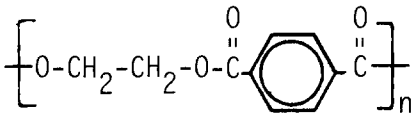

FIG. 2—*Composition of PET.*

systems have been proposed. Carbon tetrachloride/toluene has been used but subsequently abandoned because toluene has been shown to promote crystallization [*17*]. A carbon tetrachloride/ethanol liquid system has also been used in density gradient analysis of PET. It has, however, also been abandoned because, although neither liquid individually promotes crystallization, some of their mixtures have been shown to do so [*18*]. Presently, the most popular liquid system for PET materials is carbon tetrachloride/*n*-heptane. This system has shown no tendency to induce crystallization [*18,19*], and highly oriented PET fibers displayed no shrinkage after three months' immersion the liquids [*20*]. Carbon tetrachloride/*n*-heptane was the liquid system used for this study.

Apparatus and Experimental Procedure

Fourteen commercial PET-type fibers were examined in this study. Yarns from which the fibers were obtained along with their code designations for this study are given in Table 1. The table includes two Encron®, eight Dacron, one Monsanto, one Meyers, and two Fortrel® fibers. Samples from three of these yarn packages—B, G, and J—were subjected to treatment representing 50 low-temperature hand washes according to Test IA of the American Association of Textile Chemists and Colorists (AATCC) Test Method 61-1975 [*21*], while other samples from the same yarn packages were subjected to treatment representing 30 vigorous high-temperature machine washes according to Test IIIA of the same test method [*21*]. In addition, other samples from these yarn packages were subjected to outdoor weather continuously for two months according to exposure conditions as dictated in AATCC Test Method IIIB-1978 [*22*].

Density gradient columns having a sensitivity of 0.0002 $g/cm^3 \cdot mm^{-1}$ were prepared by the reverse stepwise addition method [*5*] using carbon tetrachloride/*n*-heptane in a 500-mL graduated cylinder maintained at 23°C in a constant-temperature bath. Columns were calibrated with commercially prepared glass floats whose densities were known to ± 0.0002 g/cm^3.[2] After a column had been prepared, it was left unaltered for 24 h. Fiber samples previously dried for 24 h over calcium sulfate in a desiccator were cut into lengths of less than 5 mm, agitated in *n*-heptane for 2 min to remove adhered particulate soil, placed under a light vacuum for 2 min for deaeration to remove air trapped on or in the fibers, and then removed with tweezers and placed slightly under the surface of the column liquid. After the fibers had been allowed to settle for 24 h, locations of both floats and fibers were observed through crossed polars and recorded. Locations of the

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TABLE 1—*Fiber types examined.*

Yarn	Code
Encron, Golden Touch	A
Encron, knit-de-knit textured by Burlington Madison Yarn Co.	B
Dacron, Type 52	C
Dacron, Type 55	D
Dacron, Type 56, false-twist stretch textured by Spray Textured Yarns, Inc.	E
Dacron, Type 56, false-twist stretch and stabilized textured by Spray Textured Yarns, Inc.	F
Dacron, Type 56T, false-twist stretch and stabilized textured by Macfield Texturizing, Inc.	G
Dacron, Type 68	H
Dacron, Type 242, false-twist stretch textured, two ply, by Frank IX & Sons, Inc.	I
Dacron, Type 242, false-twist stretch textured, one ply, by Frank IX & Sons, Inc.	J
Monsanto, Type L7A, false-twist stretch and stabilized textured by Macfield Texturizing, Inc.	K
Meyers, false-twist stretch and stabilized textured by Macfield Texturizing, Inc.	L
Fortrel, Type 660, false-twist stretch and stabilized textured by Macfield Texturizing, Inc.	M
Fortrel, Type 296, false-twist stretch and stabilized textured by J. P. Stevens, & Co., Inc.	N

standard floats were used to construct a calibration curve. The density of each fiber in the column was then determined by noting the density on the calibration curve corresponding to fiber locations in the column. The densities of all fibers in Table 2 were determined simultaneously in one column while those of all fibers listed in Table 3 excepting those also included in Table 2 were determined simultaneously in a different but identically prepared column.

Results and Discussion

The density of each untreated fiber is listed in Table 3. One can see from the data presented that little or no discrimination could be made among the fibers if density measurements had been recorded only to two or three significant figures. It is obvious, however, that much discrimination can be made among the fibers if density measurements are recorded to four or five significant figures. The data show that much variability in density exists within any given group of fibers having the same trade names. For example, density values for Dacron vary from 1.3801 g/cm^3 for Type 55 to 1.3916 g/cm^3 for Type 56 textured. Similarly, values for Encron vary from 1.3770 to 1.3835 g/cm^3 and values for Fortrel vary from 1.3880 to 1.3894 g/cm^3. Consequently, density gradient analysis possesses the ability to discriminate among fibers having different trade names as well as among fibers having identical trade names but different type.

On the other hand, the method possesses limited ability in identifying a particular trade name or type of a fiber if unknown. This is especially true in view of the fact that many fiber types are produced in a variety of lusters, including bright, semi-dull, and dull. The various amounts of delusterant used to lower fiber luster will produce various den-

TABLE 2—*Effect of treatments on fiber density.*

Fiber	Untreated	50 Cold Washes	30 Hot Washes	Two Months' Outdoor Exposure
B	1.3835	1.3816	1.3772	1.3845
G	1.3908	1.3837	1.3849	1.3919
J	1.3880	1.3826	1.3860	1.3890

TABLE 3—*Density of untreated fibers.*

Fiber	Density, g/cm^3
A	1.3770
B	1.3835
C	1.3893
D	1.3801
E	1.3914
F	1.3916
G	1.3908
H	1.3914
I	1.3879
J	1.3880
K	1.3881
L	1.3891
M	1.3880
N	1.3894

sities for the same fiber type because the pigment usually used (titanium dioxide) is much more dense than the polymer material it replaces.

Density differences expected from different fiber types override density similarities one might expect from the same texturizing method administered by the same yarn converter to each fiber. For example, each yarn converted by Macfield was imparted a false-twist stretch and stabilized texture, but differences in density arising from the use of different feed yarns are visible in the textured products. On the other hand, reproducibility inherent in modern yarn texturizing is evident by comparison of the two yarns textured by Frank IX (Samples I and J). In each, an identical feed yarn (Dacron, Type 242) was given an identical texture (false-twist stretch) with the result that the measured density of both samples is nearly identical. The plying operation applied to Sample I had little, if any, effect on fiber density, as expected, since it merely involves a mechanical winding operation. It is instructive to compare Samples E and F. While E was given one heat treatment to produce its false-twist stretch texture, F was given the same treatment along with an additional heat application to produce its false-twist stretch and stabilized texture. The additional heat treatment applied to F induced extra crystallization with a resultant increase in density as less dense amorphous material was replaced by more dense crystalline material.

The densities of fibers undergoing laundering and outdoor exposure are provided in Table 2. Interpretation of these data is somewhat difficult because several different processes affecting density may occur during treatment. One process, crystallization, may result in an increase in density, as discussed previously. Crystallization may be induced by heat or solvent action, both of which occur in laundering and the first of which occurs in outdoor exposure. Another process, polymer chain scission, results in a decrease in density as inhomogeneities are introduced along the chain. Chain scission may be introduced by mechanical, thermal, or photochemical action, the first two being present during laundering and the last two being present during outdoor exposure. Other processes involving addition of chemical substances such as soap or fabric softeners to the fibers have a varying effect on measured fiber density.

With all the possible combinations of these processes that may have occurred during sample treatment, interpretation of the treated fiber data becomes an almost hopeless task. To complicate matters further, other aspects of fiber composition may distort data interpretation. For example, the inclusion of a delusterant in the fiber would markedly increase photochemical degradation and alter density with the result that density changes

arising from other processes occurring simultaneously might not be noticed. Even though interpretation on a molecular level is very complex, evaluation of the data still proves instructive. For example, it definitely can be said that the density gradient technique is very sensitive to physical changes in the fiber arising from laundering by either method or from outdoor exposure. The method, therefore, offers a technique of analysis useful in comparing fibers altered by consumer use.

It is important to note that laundering and outdoor exposure produce changes of such magnitude in the density of the new fibers that any attempt to identify the fiber type of an unknown fiber by density analysis would be futile if the fiber had been subjected to consumer use. That is, changes in density arising from these treatments are greater than the differences in density between some fiber types. It is equally important to note, however, that these density changes provide a sensitive means for discrimination among fibers having identical commercial origins but used by different consumers who have different laundering habits or spend different amounts of time outdoors. Although the amount of data representing density changes from laundering and outdoor exposure is limited, it appears that laundering decreased the density of the unlaundered fiber whereas outdoor exposure increased its density.

The use of PET-based polyester fibers, laundering them, and using them outdoors are common among most American and European consumers. Consequently, the data presented in this paper suggest widespread applicability of density gradient analysis in forensic science laboratories. Other fibers in common consumer use would also be expected to demonstrate density differences in an analogous manner. Thus, application of the density gradient method to fiber analysis is expected to yield fruitful information.

Summary

Density gradient analysis of single fibers has been shown to be a discriminating tool in forensic science. The technique may discriminate between fibers within a generic class, fiber types having the same trade name, different fiber types given the same yarn texture, the same fiber type given different yarn textures, the same fiber type given different laundering treatments, or the same fiber type subjected to outdoor exposure. Thus, the method offers a sensitive means to compare fibers of similar origin. It is the author's opinion that density gradient analysis is underutilized by forensic scientists in fiber analysis. A properly performed analysis provides a convenient, simple, inexpensive, and nondestructive method of comparing fibers on a submicrogram level.

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