EFFECT OF HEAT TREATMENT ON DYEABILITY, GLASS TRANSITION TEMPERATURE, AND TENSILE PROPERTIES OF POLYACRYLONITRILE FIBERS (ORLON 42)

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(ABSTRACT)

Acrylic filament fibers (DuPont Orlon 42 Tow) were subjected to a series of heat treatments consisting of dry heat at 110° C and 150° C and to saturated steam at 110° C for periods of 5 minutes; samples were exposed both under tension of 0.025 grams/denier and slack (no tension). Following the heat treatments, physical and chemical properties of fibers were determined.

Deniers of treated and untreated fibers were determined and the results were used in calculations of tenacity and initial modulus. Tensile properties were measured on a constant-rate-of-extension machine. Shrinkage of treated and untreated fibers were measured after they were boiled in water for 15 min. The glass transition temperatures (Tg) were obtained by differential scanning calorimetry. The ratio of the intensities of the CN/CH stretching bands were found by infrared spectroscopy, using the KBr method.

Dye uptake was measured spectrophotometrically, using filtered solutions of fiber which had been dyed with C. I. Basic Red 18 from an infinite dyebath for 15 minutes at the boil.

Physical properties (tenacity, elongation, initial modulus and shrinkage) were found to be affected primarily by the presence or absence of tension during heat treatment. That is, the temperature of dry heat and the presence or absence of moisture at 110° C had less effect. Chemical properties (Tg and dye uptake) responded to treatment in a less clearcut fashion. Heat treatment with moisture at 110° C, both slack and under tension, produced the highest values of Tg. Moist heat at 110° C, slack, gave the highest dye uptake while treatment at 150° C, dry under tension, produced the lowest dye uptake. Nitrile group association was found to be statistically unaffected by treatment, but the values found correlated well with Tg and dye uptake results. These results were interpreted as supporting the theory that both free volume and pore mechanisms are operative in the dyeing of acrylic fibers.

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Chapter I

INTRODUCTION

The introduction of man-made fibers was one of the most significant events in the history of the textile industry. Initially, these fibers had very little affinity for dyes used on natural cellulose or protein fibers. However, the unique physical and chemical properties of these fibers and the increasing demand for textile goods led scientists to develop a vast selection of dyestuffs suitable for them. Still, research related to morphology and dyeing of synthetic fibers would be useful for both the textile industry and consumer because of the potential for increased efficiency and reduced costs in dyeing and for improved consumer properties in dyed textiles. Most man-made fibers such as nylon and polyester are thermoplastic. This means their dimensional stability and their resistance to permanent deformation can be improved by heat setting under certain conditions. In this process, structural changes take place in the fiber, which affect the physical and dyeing properties of the treated substrate (16,17,24,75). Morton and Hearle (53) have stated that the breaking of interchain bonds between the molecules due to high temperature, and the reformation of interchain bonds in the new configuration is responsible for the change in the physical properties of the polymer. The application of saturated steam under a pressure of 5 to 45 lb/in^2 at 108-143° C for about 10-30 min is probably the method which is most

often used (16) for heat setting. However the new trend is toward shorter heat setting times and higher temperatures. An autoclave is still commonly used to achieve the desired temperature, pressure, and needed steam for heat setting. There is a great deal of literature on the heat setting of nylon and polyester and the effects of heat on physical and chemical properties, but there is relatively little information on acrylic fibers. Literature exists on the effects of heat on fiber structure and on the dyeing of acrylics, but few studies combine the two subjects. Therefore, the purpose of this study is to investigate the effect of heat treatment upon the morphology, physical properties, and dyeability of polyacrylonitrile (PAN) fibers.

Chapter II

REVIEW OF LITERATURE

Recent literature pertaining to the broad subject of the effect of heat treatment on the properties of polyacrylonitrile fibers was reviewed, and is reported under the following headings: preparation of acrylic fibers, morphology of polyacrylonitrile fibers, thermosetting of polyacrylonitrile fibers, infrared spectroscopy, infrared analysis of morphology, thermal analysis techniques, and dyeing of polyacrylonitrile fibers.

Preparation of Acrylic Fibers

The Textile Fiber Products Identification Act (46) has defined acrylic as "a manufactured fiber in which the fiber forming substance is any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile units $(-CH_2-\underset{\underset{CN}{|}}{CH}-)$."

Most acrylic fibers are made of copolymers. Table 1 lists some of the typical comonomers used along with the acrylonitrile. These comonomers have specific functions; for example, comonomers such as vinylpyridine or methylvinylpyridine which contain a tertiary or quaternary nitrogen in their molecular structure, impart affinity for acid dyes (20).

TABLE 1. Typical Monomers Copolymerizable with Acrylonitrile

1. Hydrocarbons
   - Styrene
   - α-Methylstyrene
   - Isobutylene

2. Alcohols
   - Allyl alcohol
   - Methallyl alcohol
   - α-Hydroxymethylacrylonitrile

3. Ethers
   - Vinyl methyl ether
   - Allyl ethers of amino alcohols
   - Vinyl ethers of amino alcohols
   - Allyl glycidyl ether

4. Halides
   - Vinyl chloride

5. Amines
   - 2-Vinylpyridine
   - 2-Methyl-5-vinylpyridine
   - Allyldimethylamine
   - 2-Vinylquinoline

6. Amides
   - Acrylamide
   - N-Dimethyacrylamide
   - N-Dimethylaminopropylacrylamide
   - N-(2-Hydroxyethyl)acrylamide

7. Acids
   - Acrylic acid
   - Methacrylic acid
   - Itaconic acid

8. Ketones
   - Vinyl methyl ketone
   - α-Acetoxystyrene
   - Allyloxyethanol

9. Acrylates
   - Methyl acrylate
   - Methyl methacrylate
   - N-Dimethylaminoethyl acrylate
   - Methyl-acetaminoacrylate
   - Methoxyethyl acrylate
   - Methyl-chloracrylate

10. Vinyl esters
    - Vinyl acetate
    - Vinyl chloroacetate

11. Miscellaneous
    - Allypyridinium chloride
    - N-vinyl-N,O-diethyl isourea

(Reproduced from reference 45)

Acrylic polymers can be made by solution, suspension or emulsion polymerization (14,20). Fibers can be manufactured by either a dry or wet spinning process. In general, the solution method has the advantage that the polymerization solvent can be used as the spinning solvent (14). In suspension polymerization the monomers, dissolved or in the form of small globules, depending on the concentration used, are dispersed by agitation throughout an aqueous solution of the catalyst and polymerized at suitable temperatures. Some of the common catalysts are water-soluble compounds such as hydrogen peroxide, peroxy salts such as ammonium or alkali metal peroxydisulfates, and redox catalysts such as potassium peroxydisulfate and a bisulfite at concentrations ranging from 0.1 to 5.0% of the total monomers (20). The suspension which includes the monomers and catalyst is held at 30-70° C to form the polymer. This polymer is insoluble in the aqueous medium of the reaction. The polymer is then filtered from the aqueous reaction medium and rinsed to remove impurities (20). Brubaker (11) has patented a method of emulsion polymerization for production of acrylonitrile. In general emulsion polymerization has the following recipe (11,49):

1. monomer
2. water (as heat transfer medium)
3. surfactants (anionic and/or nonionic as emulsifier)
4. buffer
5. initiator

McGrath (49) has stated that, compared to other processes, emulsion polymerization has the advantage of providing a fast rate of polymerization while allowing for a high molecular weight. Some of the emulsifying agents are compounds such as salts of higher fatty acids, for example soap, sodium or potassium stearate or palmitate, and salts of higher fatty alcohol sulfates such as sodium or potassium cetyl sulfate (20).

The spinning dopes or polymer solutions are extensively degassed and filtered, then converted by a wet-spinning or dry-spinning technique to tow. In the wet-spinning process, spinning dope is extruded through a multi-holed jet (spinneret) into a coagulating bath. In order to decrease recovery problems, the coagulation bath normally is made of an aqueous solution of the same solvent as that in the spinning dope. When coagulation is complete, the fiber tow is washed thoroughly to remove the spinning solvent. Wet spinning is done commercially from inorganic or organic solvents. The following are some of the patented spinning solvents: nitric acid, sodium and calcium thiocyanates, zinc chloride (20), dimethylformamide (DMF), dimethylacetamide (40,48); N,N-dimethylcyanoacetamide (41), Σ-capralactam (31), succinonitrile (58), and tetraethylenesulfone (31). Dry spinning is done from an organic solvent, usually dimethylformamide (20). The spinning dope is extruded into a heated chamber where solvent is removed by vaporization; thereby solidified filaments are formed. Further heating is required to remove residual

solvent. Two examples of dry spinning have been patented by Latham (39) and Houtz (29).

Preparation of Orlon Fibers

Moncrieff (52) describes the following procedure for the production of Orlon fibers; Ammonium persulfate as catalyst and sodium bisulfite as an activator are dissolved in distilled water at 40° C. Thereafter, a mixture containing 90% acrylonitrile and 10% of other monomers (which have not yet been disclosed) are added with constant stirring. In the presence of a peroxy catalyst, the mixture would result in a modified polyacrylonitrile polymer with a molecular weight of about 60,000. Then the polymer is filtered, rinsed, and dried. The dried polymer is then dissolved in a proper solvent such as DMF. The solution is heated and extruded into a heated spinning cell and dry spun in hot air or nitrogen to remove the solvent. Sometimes steam is used instead of air or nitrogen in the spinning process. The extruded filaments are hot drawn to several times their original length. Orlon fiber type 42, which is used in this study as tow, is presented to the market as staple fibers, which have a tenacity of about 2.3 g/den and 28% elongation (52). Thus Orlon 42 appears to be a dry-spun fiber with the copolymer prepared by redox initiation, and having both sulfate end groups and sulfonic acid groups along the chain to serve as receptors for cationic dyes.

Morphology of Polyacrylonitrile Fiber

The structure of polyacrylonitrile fibers is still under investigation. However there are two schools of thought, both of which are debatable. Some researchers such as Brandrup and Immergut (8) have presented evidence which indicates acrylic fibers have a two-phase structure. The existence of a glass transition temperature, which is characteristic of an amorphous phase, is one of the pieces of evidence that has been reported by many workers in this area. Gupta and Chand (21) have presented X-ray diffraction patterns which show sharp reflection superimposed over diffuse scattering. They stated that this is characteristic of crystalline and amorphous regions of semi-crystalline polymers. The second theory suggests a one phase paracrystalline structure for acrylic. However, it is generally agreed that different acrylic fibers have different structures. This is due to the influence of (up to 15%) comonomers. Hearle and Greer (27) have stated that the acrylonitrile molecule when polymerized alone ($-CH_2-CH.CN$) gives a flexible rod-like molecule. However, due to the bulky dipolar -CN side group, the molecule would take a helical form. Due to the electrical dipolar forces the rod-like molecules would be attracted to each other strongly. This would finally generate a pseudo crystalline structure. Acrylic polymer molecules, like most fiber forming molecules are not capable of sorting themselves out completely. This would cause some polarization distribution between regions of high and low order (27). Van Veld et al. (72) have studied the structure of acrylic fibers by peeling the drawn fibers. They

reported that their study confirms the open fibrillar structure suggested by other workers, based on the X-ray analysis of fibers.

Hearle and Greer (27) stated that although the chain flexibility of polyacrylonitrile polymer results in a significant degree of freedom in the system at room temperature, relative chain mobility is restricted because of electrical attractive forces. The lowest transition temperature for acrylic fiber is around 80° C. It is at this temperature that the freedom for relative mobility develops in the disordered regions. The next transition temperature is around 150° C. At this temperature a breakdown starts in the ordered region. However, due to the presence of electrical attractive forces and chain stiffness which still affect the system, the polyacrylonitrile fibers stay solid. The morphology of acrylic fibers, like that of most man-made fibers, may be directly related to the spinning and stretching conditions. Bell and Dumbelton (6) have investigated the effects of these conditions. They reported that the coagulated, uncollapsed, unoriented wet-spun acrylic fibers produced a network with more voids compared to dry-spun fibers. They also found that lowering the coagulation temperature resulted in a tighter network (more dense structure), and dry-spun fibers had a more fibrillar structure.

Thermosetting of Polyacrylonitrile Fibers

The dimensional stability of thermoplastic fibers and their resistance to permanent deformation can be improved by heat setting under certain conditions. It is believed that heat setting causes structural changes which might affect the physical and dyeing properties of treated fibers (16,17,24,75). Gupta and co-workers (21,22,23,26) have investigated the glass transition temperature (Tg) and dielectric relaxation of polyacrylonitrile fibers. Gupta and Singhal (22) heat treated acrylic fibers for 24 hours at two temperatures, one (120° C) slightly above the Tg and the other (160° C) much above the Tg; then the dielectric relaxation of heat treated and untreated fibers was measured and compared. Their study showed that the heat treatment at 120° C generated a greater change in the dielectric relaxation than that at 160° C. They also used infrared spectroscopy to study the change in the intensity of the CN stretching band measured at 2240 cm^{-1}, relative to the CH stretching band at 2990 cm^{-1}. Their comparison of untreated and heat treated samples showed the lowest intensity of CN stretching bands for samples heat treated at 120° C followed by samples heat treated at 160° C. There are also other studies (16,21,22,23,25,26) which indicate no change or little change on some selected properties of acrylic fibers treated at temperatures higher than 125° C. Since lower intensity of the CN band means a lower number of free nitrile groups, Gupta (23) concluded that heat treatment at 120° C produced a higher degree of bound nitrile groups in the structure. The increase in the number of bound nitrile

groups would limit the polymer's segmental mobility which might affect dyeing and other properties of this fiber.

Dawson (16) heat treated acrylic fibers for 5, 10, and 20 minutes at 108° C and 125° C. He reported that hot aqueous dyeing of polyacrylonitrile fibers removed the heat setting effect. This is due to the dyeing of fibers above their second-order transition temperature. Therefore, he suggested that fibers be heat set after they have been dyed with dyes which are stable at the heat setting temperature. Although he has reported that structural changes due to heat setting are reversible by dyeing at high temperatures, he did report some changes in dyeing caused by heat treatment. His study revealed that Acrilan (Type A 71 W) and Courtelle (Type S) polyacrylonitrile fibers behaved differently after heat treatment. In the case of Acrilan, a 16% decrease in dye uptake was observed when fibers were treated at 108° C. The same treatment caused a 16% increase in dye uptake by Courtelle fibers. Both fibers were dyed with C.I. Basic Orange 24. Further investigation showed that heat treatment at 125° C caused 7% decrease in dye uptake for Acrilan. The increase in dye uptake for Courtelle was more than 1000% using the same dye at the same temperature. These results were in agreement with the data obtained from dyeing both fibers with C.I. Basic Blue 41. However, when C.I. Basic Blue 22 was used, heat treated Acrilan did not show any significant change in its dye uptake contrary to Courtelle which showed a 35% increase at 108° C and a 500% increase at 125° C.

Therefore, it can be concluded that the effect of heat setting on dye uptake might be both dye and fiber dependent.

Dynamic mechanical properties, IR spectroscopy and wide angle X-ray diffraction of heat treated polyacrylonitrile fibers were also studied by Gupta and Maiti (24). This study showed that heat treatment at 110° C and 150° C resulted in some changes in nitrile bound groups. Although this study did not show a significant difference between the two temperatures, the magnitude of the changes were higher for samples treated at 110° C.

Manocha and Bahl (47) have studied the role of oxygen during thermal stabilization of PAN fibers which are used to make carbon fibers. They reported that a sharp change in strength and shrinkage would occur within the first 30 minutes. After that the changes are gradual with time, and changes are practically insignificant after 200 min. For example, the shrinkage at 200 min was about 21% compared with 24% after 800 min for PAN copolymer fibers treated at 215° C in the presence of air. However, these temperatures are far above the useful range for textile processing.

Layden (43) studied the dimensional changes and tension generated by PAN filaments under load as a function of time. His study revealed that the significant change would occur within the first 10 minutes at temperatures up to 150° C. Then the changes started to be reversed when both time and temperature were increased at the same time.

Stoyanov (68) has investigated the influence of thermosetting in the presence of steam at 100° C and drying on shrinkage, tenacity and

elongation of acrylic fibers. He measured the shrinkage of the fibers after each heat treatment, and the residual shrinkage after boiling the fibers in water for 15 min. He found that thermosetting in steam produces greater shrinkage than drying at 125° C. He attributed this to increased segmental mobility in the presence of water molecules, which also results in a tension free fiber. At a high temperature and in the presence of steam, the supermolecular structure becomes more mobile resulting in significant axial shrinkage. He also found that elimination of tension in heat treatment increases the elongation and compactness of the fibers after drying.

Infrared Spectroscopy

Introduction

Infrared radiation was discovered in the early 1800's. The infrared region of the spectrum extends from the long wavelength end of the visible region at 13000 cm^{-1} out to the microwave region at about 25 cm^{-1}.

However, the region between 4000 and 250 cm^{-1} has received much attention compared to other wavelengths. This is due to the fact that vibrational frequencies of most molecules lie in this region (66). A lot of information about the structure of a compound can be obtained from its infrared spectrum because many of the individual bands occurring in the infrared spectrum are characteristic of specific pairs or groups of atoms.

Experimental Techniques

KBr Disk Technique. Berni et al. (9) give the following method for this technique. The potassium bromide (KBr) disk method is the most useful method to obtain infrared absorption spectra of textiles. For example, a cotton specimen is cut in a Wiley mill fine enough to pass through a 20-mesh screen. Then 350 mg potassium bromide is mixed with about 2 mg of the specimen. After the materials are thoroughly mixed, 300 mg of the mixture is placed in a die. The die is then evacuated for two minutes and then a pressure of 18,000 to 20,000 Psi is applied to the specimen while being evacuated for two more minutes. In this way, uniform clear disks with good transmission are produced. These disks, when matched against reference KBr disks, show no interference from absorbed water. Then a double-beam infrared instrument is set at 100% transmittance at 2000 cm^{-1} with a blank KBr disk in each beam. These blank disks are made with 300 mg KBr in the same way that the specimen disk was prepared. Then the specimen is measured against a blank KBr disk in the reference beam. This procedure results in excellent qualitative spectra and also provides a precise and accurate way of measuring band intensities quantitatively. An advantage of this method is that it requires a small amount of textile material. Also, disks can be stored for months with a desiccant. The method is very useful in infrared analysis of all cellulosic fibers. Some modifications are needed for those synthetic fibers in which the refractive index does not match well with KBr. The problem can be solved either by fine grinding of the specimen or by using other halides with a refractive

index closer to that of the specimen. Some of these halides are NaCl, KI, CsBr or TlI.

Pressed Fiber Films. Knight et al. (36) used short staple natural or synthetic fibers to prepare a thin pressed film of parallel fibers for infrared analysis. This method eliminates cutting, grinding or adding any extraneous material.

Berni and Morris (9) reported that Rousselle and Nelson wetted a thin layer of parallel fibers with hexachlorobutadiene (HCBD) to decrease the amount of scattered light. Then the treated specimen is sandwiched between two plates of window material. In order to compensate for the effect of HCBD bands, a thin layer of HCBD is placed between reference plates.

Microtechniques. Carlsson et al. (12) introduced a simple technique for the measurement of transmission infrared spectra on a 1-2 cm length of a single monofilament. Utilizing this method, a useful spectrum for whole filaments was recorded on a conventional grating infrared spectrophotometer without recourse to an infrared microscope. However, the technique was limited to fibers with diameters smaller than 100 microns, and to fibers of low inherent infrared absorption such as polyolefins. Fibers such as polyethylene terephthalate (PET), or nylons absorb too intensely to give useful spectra even as single 100-micron diameter filaments.

Film from Solution or Suspension. These techniques are based on the preparation of the films cast on glass plates. The techniques have many limitations such as:

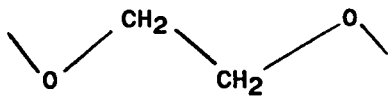
a). difficulty in obtaining a uniform film, resulting in the absorption intensities being dependent upon the particular area tested;

b). difficulty finding a solvent or suspending system for some textile fibers.

Results obtained by casting films from solution or suspension are not generally satisfactory.

Infrared Study of Morphology

As mentioned, infrared spectroscopy is a useful tool for measuring differences in the configuration and environment of polymers. Bands assigned to stereoisomers in polymers are well known. For instance, Ward (73) has reported that main differences in the infrared spectra of PET are not due to the presence of crystallinity per se but to configurational changes in the amorphous material which affects the



groups. X-ray analysis has shown that in crystalline regions the configuration of these groups is trans.

Koenig and Hannon (38) stated that hydrogen bonding and crystallinity are environmental effects in polymers which show differences in their infrared spectra. Ordering of similar rotational isomers or a unique conformation in the polymer fold may cause some changes in the infrared spectra. The regularity of the fold may promote spectral coupling of the rotational isomers. This coupling effect, if it is significant, may result in a change in the vibrational frequency, the absorption coefficient, or both. It has been

experimentally proven that consecutive gauche units in polyethylene folds produce a difference in the extinction coefficient for the 1304 and 1350 cm^{-1} bands. Therefore, it is possible to measure the relative amounts of folded and amorphous material in a polyethylene sample from their contribution to the 1304 and 1350 cm^{-1} bands (38). Also it is possible that the fold is formed by a unique conformation, which could be detected if it made a sufficient shift in frequency of the spectra.

According to Koenig and Hannon (38), the infrared bands associated with fold conformation in the semi-crystalline polymer will show the following characteristics:

a). Their intensities in the solid phase are proportional to the amount of folding. This intensity will disappear on melting.

b). They appear if crystallization from the glass occurs, by the folded chain mechanism.

c). They decrease in intensity during annealing when annealing causes unfolding of polymers in the folded area.

d). They disappear rapidly and irreversibly during chemical attack.

Koenig and Hannon (38) stated that folds constitute accessible lamellar surfaces and due to the energetic nature of the conformation, they are chemically more reactive. Also, they have pointed out that the unique fold band will appear only when the fold introduces a characteristic conformation having resolvable energy differences from conformations in the disordered regions. No unique fold band will appear when the fold conformation arises from a combination of ordinary

rotational isomers. A good example of this appears in polyethylene, in which no spectral difference between a fold band and a crystallizable type can be found. Thus the fold contribution is included in the intensity of crystallizable bands.

Thermal Analysis Techniques

The most frequently used thermal analysis techniques in the textile industry are: thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). TG measures the mass change; DTA measures (T_s - T_r) where T_s and T_r are the temperatures of the sample and reference as both are heated at a constant rate; and DSC measures dH/dt, the difference between the heat input to the sample and that to the reference per unit time, while maintaining both at the same temperature (50).

Differential Thermal Analysis

A typical DTA apparatus generally consists of (a) a furnace or heating device, (b) a sample holder, (c) a low-level dc amplifier, (d) a differential temperature detector, (e) a furnace with temperature programmer, (f) a recorder, and (g) control equipment for maintaining proper atmosphere in the furnace and sample holder. There has been a great deal of improvement in DTA systems. It is now possible to obtain DTA curves of samples in the temperature range from -190° to 2400° C (71).

Sample containers for DTA/DSC

The sample container used depends upon the nature and quantity of the sample and on the maximum temperature to be studied. Sample

containers have been made of alumina, zirconia, borosilicate glass, vycor glass, fused quartz, beryllia, boron nitride, graphite, stainless steel, nickel, aluminum, platinum or platinum alloys, silver, copper, tungsten and many other materials (71). McNaughton and Mortimer (50) stated that the contact surface between pan and sample should be maximized in order to obtain optimum peak sharpness and resolution. Therefore, using a thin disc, or film, or fine granules is recommended.

Experimental Aspects of DTA/DSC

The application of DTA/DSC to fibers can be put in three broad categories (71):

a). the evaluation of physical transitions such as the glass transition temperature,

b). the evaluation of chemical reactions such as decomposition,

c). kinetic studies of either physical or chemical phenomena.

DTA allows only the study of temperatures associated with these events, while utilizing DSC enables one to evaluate both the temperature and the energetics of the processes. One should bear in mind that heating rate, sample size and atmosphere have significant effects on the resulting thermograms. A typical heating rate is 20° C/min for both DSC and DTA. A sample size of 5-10 mg is suggested for DSC, and 75-150 mg for DTA.

In older instruments, fibers were either cut into short lengths or were coiled by carefully winding the necessary fiber length around

instruments such as tweezer tips. In some new DTA/DSC apparatuses, samples can be wound on the outside of a grooved aluminum cylinder. One should remember to secure the fibers in the pan by crimping the pan lids to prevent variation due to the movement of the sample in the pan. Also if the sample is to be tested under a special atmosphere, lids with holes should be used or lids may be made from aluminum or gold screening.

Figure 1 shows a typical fiber thermogram of a spun PET yarn heated at 20° C/min. Part a of these thermograms (which were reproduced from reference 71) is useful to monitor the glass transition temperature, the exotherm associated with cold "crystallization" (crystallization on heating from the glass), and the melting endotherm. Figure 1b shows the crystallization from the melt. Figure 1c shows that cold crystallization is absent. The high temperature endothermic peak in Figure 1c is an indication of decomposition of the polymer. Therefore, from these thermographs the following parameters of a polymer can be monitored:

a). Glass transition temperature (Tg),

b). The peak temperatures of melting and crystallization (Tm, T_{xcold}, T_{xmelt}),

c). The enthalpies of melting and crystallization (H_m, H_{xcold}, H_{xmelt}),

d). The peak temperature and enthalpy of decomposition (T_D, H_D).

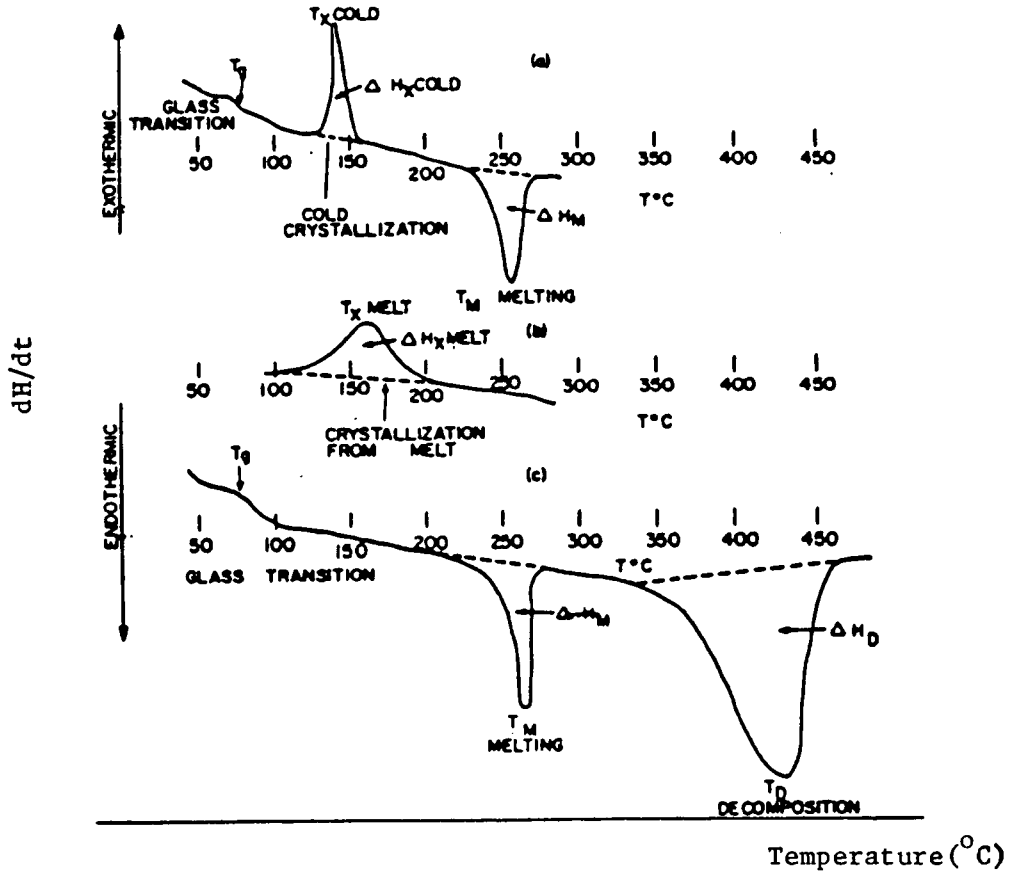


Figure 1 Typical DSC thermograms of as-spun poly(ethylene terephthalate) fiber: (a) first heating, (b) first cooling, (c) second heating. 0.9IV PET, low-speed spinning conditions. Perkin-Elmer DSC-II, 8mg sample weight, coiled sample, N_2 atmosphere, 2 min hold at 280° C between heating and cooling, 20° C/min heating and cooling rate. (Courtesy of B. Morris, Celanese Reseach Company)

It is believed that in semicrystalline polymers Tg would increase with an increase of crystallinity. This is true for most fibers such as nylon and polyester. But the effect of crystallinity on Tg is not significant in isotactic polypropylene. This suggests that the Tg of polymers having large crystallites show a minimum or no dependence on the degree of crystallinity. Therefore, determination of Tg in semicrystalline polymers can be achieved for low crystallinity fibers. As the degree of crystallinity increases, the Tg becomes more difficult to detect by direct measurement. It is also shown that increase in degree of order by drawing, for example, affects the physical properties of polymers. These effects are partly due to the orientation of the amorphous phase. Glass transition is one property that could be affected. For instance, it was noted that the Tg of PET decreases when drawn at a draw ratio of 1.5, increases to a maximum at a draw ratio of 2, and decreases at higher draw ratios (70). The decrease of Tg at the beginning of drawing may be due to the increase of configurational entropy, whereas at draw ratio above 2.0 the decrease in the Tg might be due to the increase of entropy associated with intermolecular interactions (71).

DTA/DSC Analysis of Acrylic Fibers

Most of the literature on thermal analysis of acrylic fibers is on pyrolysis of these fibers. However, Tg has also received some attention. Turi (71) has stated that Tg is a strong function of residual solvent and annealing conditions. Yarns which contained residual DMF have shown Tg's at 55°, 71°, 115°, and 140° C. However, in

the absence of residual solvent only two Tg's, 84° and 140° C, were observed. Annealing at temperatures around 140° C or higher changed the Tg's of all acrylic fibers (with or without residual solvent) to have a similar Tg of 71° to 73° C and suppressed the 140° C transition (71). Turi has also stated that Dunn and Ennis have used a fast heating DTA/DSC experiment as an effective characterization tool for identifying different acrylic fibers (71) as shown in Figure 2.

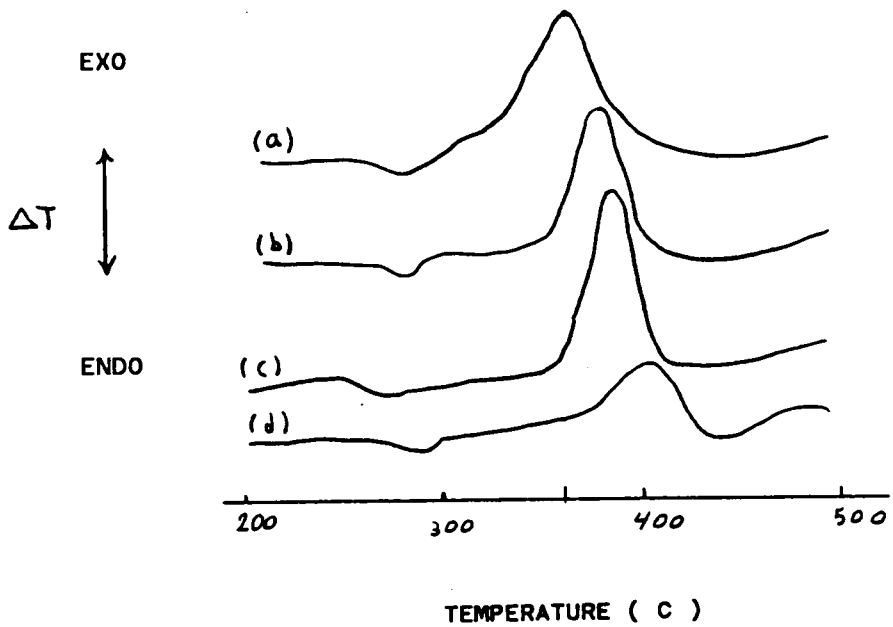


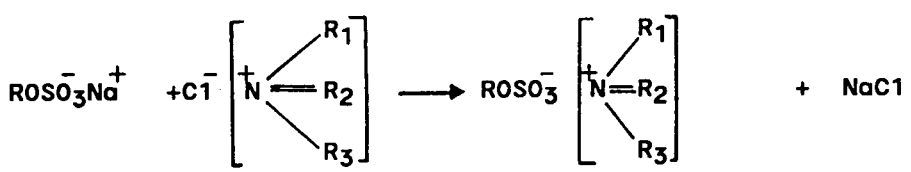
Figure 2 DSC thermograms of various acrylic fibers showing the melting region: (a) Orlon, (b) Cashmilion, (c) Creslan 61B, (d) Acrilan 16. Du Pont DSC, chopped fibers encapsulated sample (2-3 mg). Air atmosphere, 100° C/min heating rate.

Dyeing of Polyacrylonitrile Fibers

Dyeing in general is done from a liquid which in most cases is water. Dye is dissolved or dispersed in a proper liquor. Depending on the type of dye and the substrate to be dyed, usually other chemicals such as salts, dispersing agents, retardants or some organic or inorganic compounds are added to the dye liquor to facilitate dyeing or exhaustion.

It has been found that there are three steps in dyeing. First, the dye is transferred from the bulk of solution to the surface of fibers. The second step is sorption of dye at the fiber surface. The last step is penetration of dye in the fiber and fixation of dye within the fiber.

Emserman (19) has stated that, for acrylic fibers in the third stage fiber anion and dye cation form a salt-like bond which fixes the dye in fiber as shown below:



The chemical composition and structure of fibers are very important in the penetration and fixation stage. Since acrylic fibers have a variety of chemical and fiber structures, and due to the fact that there is a wide range of cationic dyes with different chemical structures, a generalized dyeing method may not be very practical. However the following points are common in most acrylic dyeing procedures:

a). For most cationic dyes the optimum pH has been reported to be somewhere between 4 and 6 (18,32,56,60,64). This can be obtained with acetic acid and sodium acetate. Acidic pH prevents possible decomposition of the dye.

b). Dyeing starts at about 50° to 60° C in the presence of a proper retarder. Then the temperature is raised to 85° C at a rate of 3° C/min and from 85° C to boil at a rate of 1° C/min. Thereafter dyeing is continued at boil for 1.5 to 2 h.

c). The dyebath is cooled slowly to 50° C in order to avoid formation of creases and crack marks on textile goods.

d). The dyed goods are then rinsed and scoured in a solution containing 1 g/l surfactant, and 1 to 2 g/l acetic acid (56%). This is followed by warm and cold rinses.

It should be noted that addition of cationic retarder would increase the levelness of dyeing but also the dyeing time. It is believed that retarders diffuse into the fiber at a speed equal to or higher than that of the dye molecules. Therefore, by occupying some of the sites, they significantly reduce the dyeing rate. However, they are slowly replaced by the dye molecules, ensuring level dyeing.

Role of Fiber Structure in Dyeing

McGregor and Peters (51) have reviewed literature with regard to the relationship between dyeing and fiber structure. They reported that, in general, nonionic dyes are used for those fibers which have very low moisture absorption and do not swell significantly. These dyes have

little effect on hydrophilic fibers which show a sizable swelling. However, water soluble dyes produce satisfactory results on hydrophilic fibers such as protein and natural cellulosic fibers. Fibers which are classified as intermediate fibers can be dyed with both ionic and nonionic dyes. McGregor and Peters (51) have also divided the dye fiber systems into: 1) non-ionic systems and 2) ionic systems. The ionic systems were subdivided based on electrical charge on the dye ion and the electrical charge on the ionizable groups in the fiber which gives the following classes: 2a) ionic systems with like electrical charges, and 2b) ionic systems with opposite charges. They have reported a simplified classification of some dyeing systems which is reproduced here as Table 2.

As Table 2 indicates, acrylic fibers have acidic dye sites such as $-SO_3H$ or $-OSO_3H$; these sites were introduced to the polyacrylonitrile polymer by copolymerization using redox initiators (10). These acid groups would impart cationic dyeablity to the fiber. Other groups such as basic vinyl groups which have affinity for anionic dyes have been used also as comonomers (67).

Silkstone (67) has reviewed studies related to the morphology and dyeing of fibers. The highlights of his review of acrylic fibers are stated as follows: Acrylic fibers are made either by a wet or dry spun method. Wet-spun fibers dye more rapidly due to the presence of a more porous structure than the dry-spun acrylic fibers. The study of changes in structure of wet spun PAN fibers has shown that the structure of fibers treated under no tension with saturated steam consists of large

TABLE 2

Simplified Classification of Some Dyeing Systems

Fibre	Groups present in significant amount and which may ionise at an appropriate pH	Regain at 21°C and 65% r.h.	Swelling in water (%)	Main types of dye used	Class of system
Wool	$-COOH$, $-NH_2$	17	32–38	Water-soluble anionic dyes (acid, milling acid and metal-complex dyes)	2*b*
Silk	$-COOH$, $-NH_2$	11	30–41	As for wool Also water-soluble cationic dyes (basic dyes)	2*b*
Viscose rayon	$-COOH$, $-OH$†	11·5–16·6	45–82	Water-soluble anionic dyes (direct dyes) Vat dyes Azoic dyes*	2*a*
Cotton	$-OH$†	8·5	44–49	Water-soluble anionic dyes (direct dyes) Vat dyes Azoic dyes*	2*a*
Nylon	$-COOH$, $-NH_2$	4–4·5	2	Water-soluble anionic dyes (acid, metal-complex and direct dyes) Non-ionic dyes (disperse dyes)	2*b* and 1
Acrylic	$-COOH$, $-SO_3H$, $-OSO_3H$	ca 1–2		Water-soluble cationic dyes (basic dyes) Non-ionic dyes (disperse dyes)	2*b* and 1
Secondary cellulose acetate	$-OH$†	6·4	6–30	Water-soluble anionic dyes [acid dyes, e.g. the Solacet range (ICI)] Non-ionic dyes (disperse dyes)	2*a* and 1
Cellulose triacetate		<4·0		Non-ionic dyes (disperse dyes)	1
Poly(ethylene terephthalate)		0·4		Non-ionic dyes (disperse dyes)	1

*Classification based on sorption of azoic coupling component

†Only at high pH

(Reproduced from reference 51)

radial pores. However, when superheated steam (140° C) was used to treat fibers, a microporous layered structure was formed which greatly accelerated the kinetics of dyeing.

Knudsen has investigated the effect of coagulation temperature on acrylic fiber structure. His work, as reported by Hearle and Greer (27), indicated that electron microscopy has clearly shown a fine pore and fibrillar network structure.

Silkstone (67) reported that, despite the above evidence for the porosity model of PAN structure, some workers such as Hoffman prefer a free volume model, and they emphasize the role of the glass transition temperature, plasticization and segmental mobility in dyeing. Silkstone (67) also reported that Falkai et al. made three different acrylic fibers which contained 0.0 , 6.7 and 8.8% comonomer, and then subjected them to dry heat and saturated steam. Their study was based on the concept of a two-phase structure, one phase being less ordered than the other. It was found that both dry heat and steam increased the degree of order in all three polymers, but that the magnitude of changes was larger for fibers treated with steam.

Free Volume Model

In the free volume model, the assumption is made that the thermal motion of atoms creates spaces which are not occupied by the constituent atoms of the polymer. Therefore, an increase in the polymer temperature increases the unoccupied space or free volume within a fiber.

A dye molecule moves within a fiber by jumping from one space to another. This is only possible if segmental mobility next to the dye molecule generates a free volume larger than the volume of the dye molecule.

Below Tg, the polymer chains are frozen in position and no bond rotation is observed. Bond rotation starts only when sufficient energy in the form of heat is given to the polymer to overcome the interchain forces (57). At this point a whole segment of polymer chain between two simultaneously rotating bonds changes its position by rotation until stopped from further motion by other polymer molecules. These segmental jumps generate free volume which can accommodate another segment of the polymer or dye molecules.

Peters and Ingamells (57) reported that Williams, Landel and Ferry (WLF) developed the following equation showing the relationship between temperature and dye diffusion based on free volume theory:

$$\log \left(\frac{D_T}{D_{Tg}}\right) = \log \left(\frac{\eta_{Tg}}{\eta_T}\right) = \log \left(\frac{1}{a_T}\right)$$

where

D_T = diffusion coefficient at temperature T

D_{Tg} = diffusion coefficient at glass transition temperature, Tg

η = the value of any property of the polymer which is dependent on segmental mobility at temperature T.

a_T = shift factor of the WLF equation

where:

$$\log a_T = \frac{-A(T - Tg)}{B + (T - Tg)}$$

where A and B are constants.

The shift factor explains the amount by which the viscoelastic properties are changed when polymer temperature changes from Tg to the temperature T.

Rosenbaum (61) has successfully used the WLF equation to explain the relationship between the diffusion coefficients of a cationic dye in acrylic fibers and the variation in the physical properties with temperature. He found the values of 17.44 and 51.6 for constants A and B respectively, where a_T was considered as the ratio of the relaxation times.

Pore Model

This is a mechanical model which considers a fiber to be a network of interconnecting channels or pores. In a dye bath, these capillary channels fill with water, and dye molecules diffuse through them and are simultaneously absorbed on the wall of the pore (56,57). The pore model offers an explanation of the diffusion of dye into hydrophilic fibers such as cotton, rayon and wool which swell significantly in water. Peters and Ingamells (56,57) noted that it is possible that the path taken by a water soluble dye into the interior of a hydrophilic fiber is the same path as that of water which causes the swelling of the fiber. However, the diameter of the pores may differ for different fibers. For instance, cotton absorbs direct dye easier than rayon does, which may be due to the larger pore size of cotton.

Combination of the Pore and the Free Volume Model

The pore model does not explain the increase of dye uptake with the increase in the temperature of dyeing. Furthermore the pore model

assumes that the dye molecule diffuses without hindrance down the tortuous capillary channels (56). On the other hand, free volume is more applicable to synthetic fibers. In practice, however, both models may contribute to the theory of dyeing. Hori, et al. (28) combined both of these models to desire an equation applicable for both natural and synthetic fibers which is as follows:

$$\ln\left(\frac{D_T}{D_{Tg}}\right) = \ln\left(\frac{T}{Tg}\right) + \left(\frac{\Delta H_D + \Delta H_H}{R}\right)\left(\frac{T - Tg}{TTg}\right) + \frac{A(T - Tg)}{B + (T-Tg)}$$

where:

A, B, T, Tg, D_T, and D_{Tg} are defined as in the WLF equation,

ΔH_H is the enthalpy change necessary to form a hole,

ΔH_D is the enthalpy change necessary to allow a dye molecule to free itself from adsorption forces.

$R = 1.38054 \times 10^{-23}\ JK^{-1}$

Rohner and Zollinger (59) investigated the dyeing kinetics of cationic dyes on two commercial acrylic fibers which were not significantly different in their chemical structures, but were different in the volume percentage of permanent pores and pore size distribution. Their research showed that neither the pore model nor the free volume model alone explains all aspects of the mechanism of dyeing acrylic with cationic dyes above Tg. Therefore, they suggested that pore diffusion and matrix diffusion contribute to dyeing of acrylic fibers simultaneously. However, the amount of their contribution depends on the fiber type.

One of the most important implications of these three models is that when the values of A and B are found, the results at one temperature

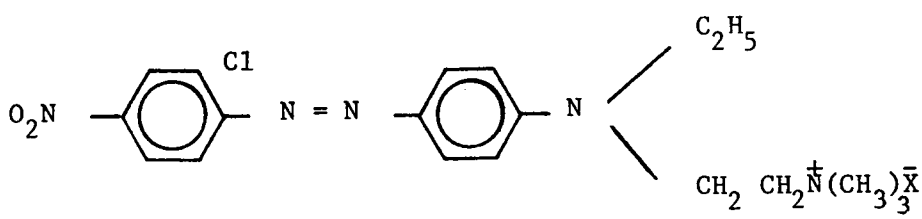
acrylic fibers simultaneously. However, the amount of their contribution depends on the fiber type.

One of the most important implications of these three models is that when the values of A and B are found, the results at one temperature can be used to calculate the results for another temperature by multiplying the appropriate value of the shift factor.

Cationic Dyes

Cationic or basic dyes were the earliest group of synthetic dyes and have a wide range of use from natural fibers like wool and silk to synthetic fibers such as polacrylonitrile fibers. They are referred to as cationic dyes since the chromophoric system carries a positive charge (1). Cationic dyes are usually salts of organic compounds (19). They can be classified as follows (1,15,19):

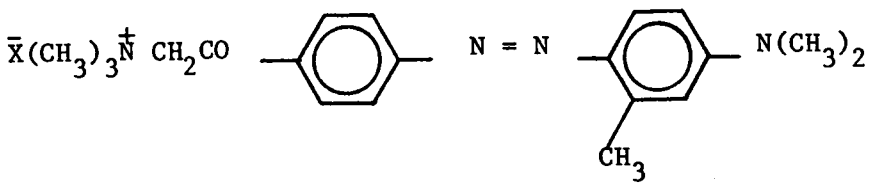
a). Azo dyes, which have the chromophoric azo group (-N=N-) attached to one or two aromatic rings, (15) for example:



I

C.I. Basic Red 18

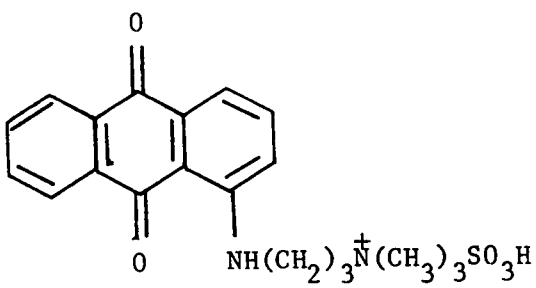
and



II

C.I. Basic Red 14

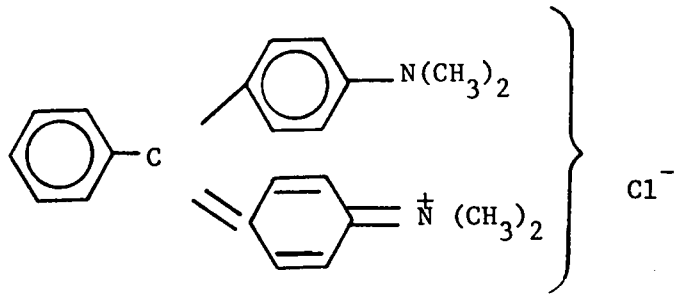
b). Anthroquinone, the characteristic feature of these dyes being one or more carbonyl groups (-C=O) in association with a conjugated system (1). An example of these dyes is (56);



III

C.I. Basic Blue 22

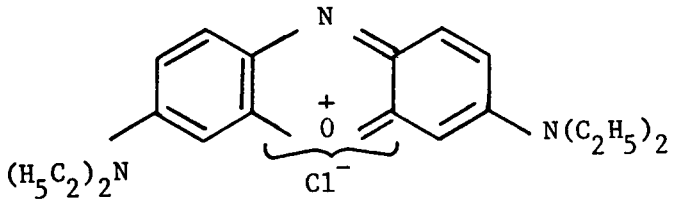
c). Triarylmethane, an example of this group is (15);



IV

C.I. Basic Green 4

d). Oxazine, for example (15):



V

C.I Basic Blue 3

Quantitative Determination of Cationic Dyes in PAN Fibers

There are two well known methods of measuring the amount of dyes in textile goods. One way is to find a good solvent which dissolves both fiber and dye. This method is fast, easy, and more accurate if a proper solvent can be found. The other method is determining the amount of dye by extraction. This method may be more time consuming, and a few extractions may be needed to insure complete removal of dye from material. Pacifici and Irick (55) have used a solvent containing 50% chlorobenzene and 50% acetic acid to extract disperse dyes from acrylic fibers. Kissa (34) has reported that increasing the mobility of polymer chains by thermal energy and or by using a solvent which swells and plasticizes the fiber would increase the extraction rate. To select a good solvent for extraction, the concept of the solubility parameter is a great help. Maximum swelling is obtained when the solubility parameters of solvent and polymer are equal (34). The solubility parameters are also used to find whether or not a particular solvent can dissolve a particular dye.

As indicated above, dissolving both polymer and dye in a solvent is the more convenient method of determining the amount of dye in a substrate. Kissa (34) has suggested the use of dimethylformamide (DMF) or dimethylsulfoxide (DMSO), which are good solvents both for cationic dyes and acrylic fibers. He placed 0.1 g of a fabric dyed with cationic dyes in a 100-ml volumetric flask and covered the material with 50 ml of either of the following solvents;

a). DMSO, MP 18.3° C, containing less than 0.20% water.

b). N,N-Dimethylacetamide (DMAC), spectrograde, UV cutoff 268 nm, pH 7.0 (as 10% solution in water).

c). N,N-Dimethylformamide (DMF), ACS spectrograde.

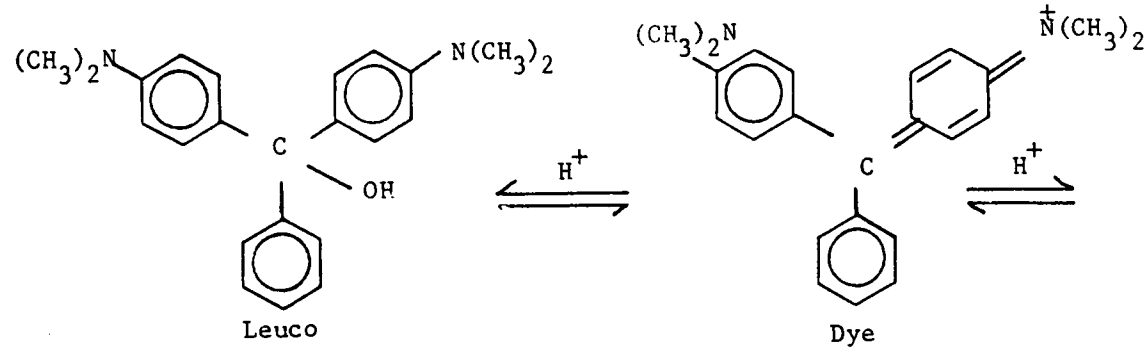
Then the pH of the solution was adjusted to 3.2 by p-Toluenesulfonic acid, $CH_3\ C_6H_4\ SO_3H.H_2O$, Mp 104-105° C. The flask was shaken from time to time until the sample was completely dissolved. Then the volume was increased to 100 ml with the prepared solvent. He then dissolved 0.1 g of undyed fiber in fresh solvent and used it as the reference solution to measure the maximum absorbtion using a spectrophotometer. He found that some dyes are not very stable in the above mentioned solvents. Kissa (33) suggested that the following might be responsible for loss of color of cationic dyes:

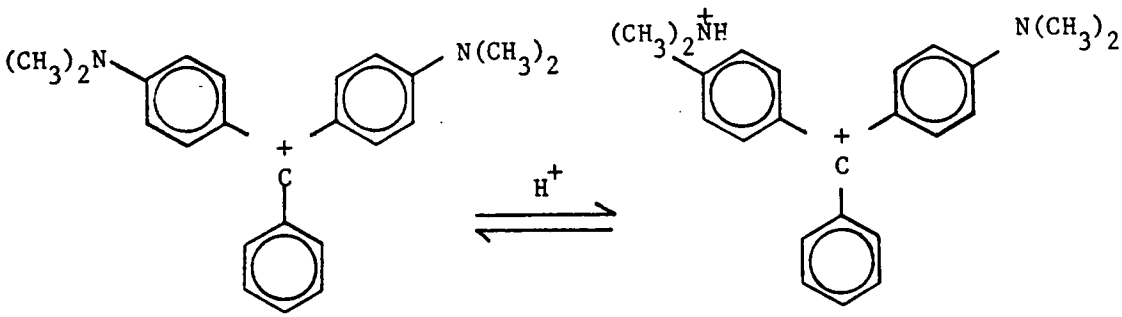
a). loss of a proton or conversion of dye to a leuco base due to change in the pH of solution,

b). nonphotolytic degradation of the dye, or

c). photochemical degradation of the dye.

He has stated that the presence of even a small amount of water will speed up fading of cationic dye in DMSO or DMF. The following fading equilibria was proposed by Kissa for C.I. Basic Green 4 in aqueous acid solution:





Kissa (35) in part III of the series of papers on quantitative determination of dyes in textile fibers recommended a solution containing:

a). 54.5 g (0.4M) of dry granular zinc chloride, A.C.S. reagent grade,

b). 8 ml concentrated hydrochloric acid,

c). 20 g of 2,6-di-t-butyl-4-methylphenol (DBMP)

d). add DMF to bring the volume to 1 liter.

This mixture is colorless if pure DBMP is used. The disadvantage of using DMF instead of DMSO is that the former dissolves acrylic fibers slower than the latter, however, it can be heated to accelerate dissolution of the sample. Kissa has stated that using the above mixture prevents fading of cationic dyes in DMSO or DMF.

Chapter III

STATEMENT OF PROBLEM

Theoretical Framework

Textile fibers or their polymer precursors respond to heat treatment in a wide spectrum of physical and chemical phenomena which reveal some important information about their molecular structure. Therefore information about the Tg and Tm of these polymers is essential in fiber research and its progress. Previous studies of the effect of heat on thermoplastic fibers have shown that dimensional stability and resistance to permanent deformation of these fibers can be improved by heat setting under certain conditions. In this process structural changes take place in the fiber which affect the physical and dyeing properties of the treated substrate (16,17,24,66). Physical properties likely to be affected include modulus, tenacity, elongation (17,27,75), and shrinkage (43,68).

The study of dimensional changes and tension generated by PAN filaments under load as a function of time revealed that the significant changes would occur within the first 10 minutes of heat treatment at temperatures up to 150° C. Then the changes started to be reversed when both time and temperature were increased simultaneously (43).

Thermosetting in steam produces greater shrinkage than dry heat does (68). This is due to increased segmental mobility in the presence of water molecules, which also results in a tension free fiber (68). At a high temperature and in the presence of steam, the supermolecular

structure becomes more mobile resulting in significant axial shrinkage. Empirical results also indicate that heat treatment under tension decreases the elongation and increases the initial modulus and tenacity of the treated fibers (68).

Dyeing is related to the chemical composition and structure of fiber, accessibility of dye sites, chemical structure of dye, and dyeing conditions such as pH, time, and temperature of dye bath (18,32,56,60,64). Accessibility of dye sites is related to interchain bonding. Changes in the interchain bonding, which can be studied utilizing infrared spectroscopy, affect the chemical and physical properties of fibers.

The infrared study of treated and untreated PAN fibers (22) showed the lowest intensity of CN stretching bands for samples heat treated at 120° C followed by samples heat treated at 160° C. Since lower intensity of CN band means a lower number of free nitrile groups, Gupta (22) drew the conclusion that heat treatment at 120° C produced a higher degree of bound nitrile groups in the structure. The increase in the number of bound nitrile groups would limit the segmental mobility and increase the Tg which affects dyeing and other properties of acrylic fibers.

Free-volume theory and pore theory have both been developed to account for dyeing behavior. Recently a combination theory has been advanced (57). The design of this study is based on the combination model. As was stated earlier, in this theory, both pores and the thermal motion of atoms contribute to dyeing of acrylic fiber.

Experimental Design

There are three independent variables in this study: temperature, tension, and moisture. Type of fiber, denier, time of heat treatment, and cooling rate were held constant. Each of the independent variables had two levels as follows: temperature, 110° C and 150° C; tension, 0 and 0.025g per denier; moisture: saturated steam and dry.

Figure 3 shows the experimental design for this research. One way analysis of variance was used to detect if at least one of the means of the six different treatments was significantly different from the others. Where ANOVA indicated a significant difference between the means, Fisher's Least Significant Difference (LSD) was used to make pairwise comparisons among the means. The criterion for the statistical significance of pairwise comparisons was calculated to be 0.0025.

The following dependent variables were tested: tenacity, elongation, initial modulus, fiber shrinkage, dye uptake, Tg, and the ratio of the intensities of the CN and CH stretching bands.

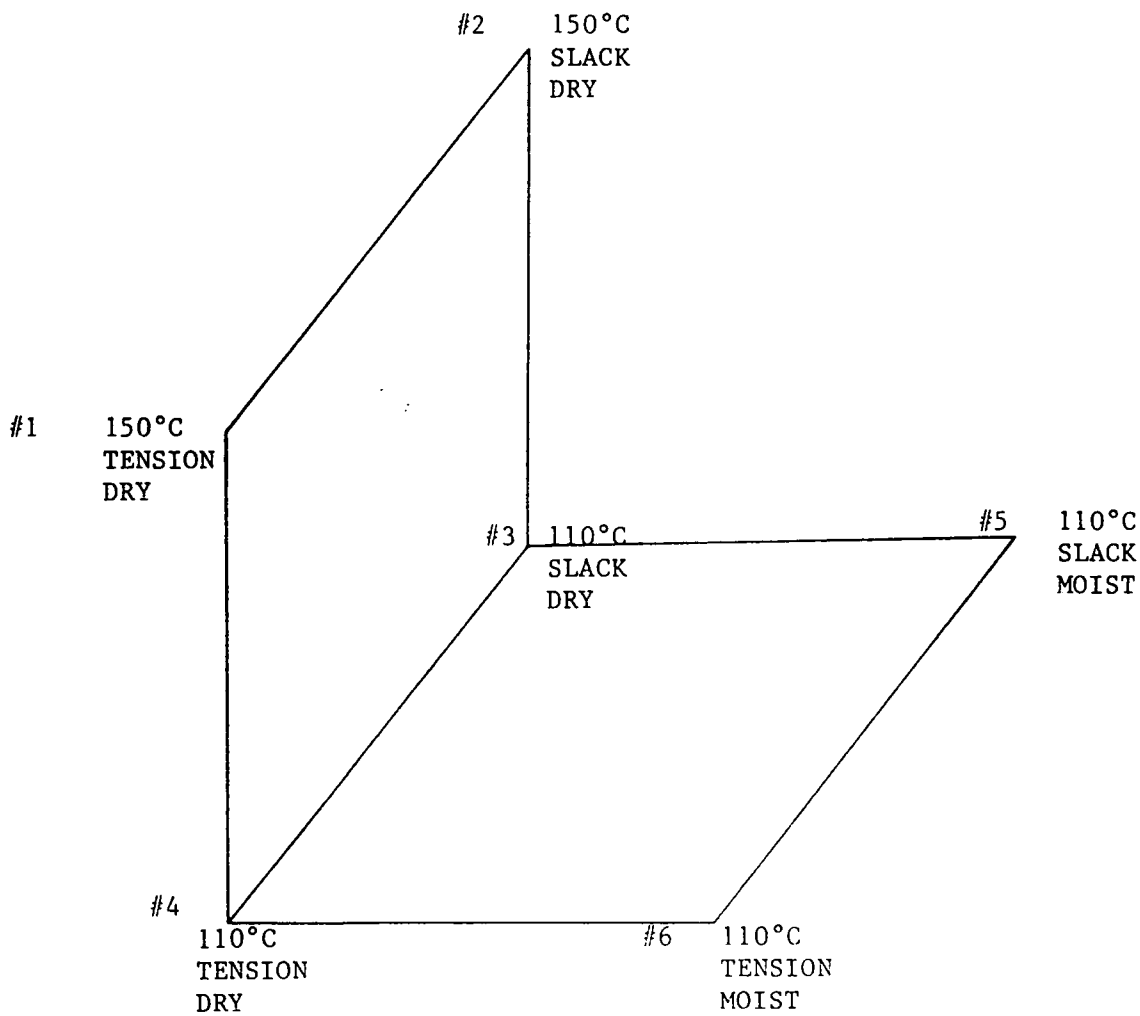


Figure 3 Experimental Design

Objectives

1. To determine the effect of dry heat (110° and 150° C) on selected properties of polyacrylonitrile fibers (Orlon Type 42), under tension and slack, specifically tenacity, elongation, initial modulus, shrinkage, glass transition temperature, nitrile group association, and dye uptake.
2. To determine the effect of heat (110° C) in the presence or absence of moisture on selected properties of polyacrylonitrile fibers (Orlon type 42) under tension and slack, specifically tenacity, elongation, initial modulus, shrinkage, glass transition temperature, nitrile group association, and dye uptake.

Limitations

1. Only one type of acrylic fiber (Orlon type 42) was heat treated and tested. This fiber was selected because it is readily available and is one of the major acrylic fibers in the U.S. market.
2. Only one cationic dye, C.I. Basic Red 18, was used to dye untreated and heat treated samples.
4. Only three different time periods, 5, 15, and 30 minutes were used in a preliminary study to heat treat fibers in order to find the time period in which treated fibers showed the greatest change in the selected properties. This time period was used to heat treat all samples.
5. Only two temperatures (110° and 150° C) were used to heat treat samples. These temperatures were selected because 110° C is slightly above the Tg and 150° C is well above the Tg of acrylic fibers.
6. Only 110° C was used to heat treat samples in the presence of moisture.
7. Only the composition of about 90% (by weight) of the monomers in Orlon 42 are known to be acrylonitrile units. The composition of the other 10% has not been disclosed by the manufacturer.

Assumptions

The following assumptions are made for the purpose of this study:

1. The thermal history of all the polyacrylonitrile fibers in the tow used is uniform.
2. In this study all samples were heat treated uniformly.
3. The instruments used to obtain data were reliable and accurate.
4. The rate of heating of oven or autoclave is assumed to remain constant through the research period.

Chapter IV

METHODOLOGY

This chapter includes operational definitions, research hypotheses, and procedures for heat treatment, physical testing, scouring, dyeing, dye uptake measurement, glass transition temperature measurement, and infrared measurement of CN and CH bands.

Operational Definitions

Breaking Tenacity.

The tensile stress at rupture of a specimen, expressed as grams per denier (44).

Breaking Elongation.

The increase in length, expressed as a percentage of original length of material, at breaking load (42).

Initial Modulus.

In a load-elongation curve, the slope of the initial straight portion of the curve. Mathematically, the modulus is the ratio of the change in stress, expressed in grams per denier, to the change in strain, expressed as a fraction of the original length (42).

Standard Atmosphere.

The air conditioned to 65 $\pm$ 2% relative humidity and 70° $\pm$ 2° F (21° $\pm$ 1° C) temperature (4).

Shrinkage.

The change in fiber length after 15 minutes boiling in water, expressed as a percentage of the original length (4).

Dye Uptake.

The amount of dye taken up by fibers in 15 minutes at the boil with a liquor ratio of about 1:2333 (150 mg fibers in 350 ml dyebath), expressed as a percentage of the weight of dyed fiber.

Research Hypotheses

1. Fibers heat treated at 110° C in the presence of saturated steam will have higher tenacity, higher initial modulus, higher glass transition temperature, and higher dye uptake, but lower elongation, lower shrinkage, and lower nitrile group association than fibers heat treated at 110° C dry.
2. Fibers heat treated under an applied tension of 0.025 gram/denier will have higher tenacity, higher initial modulus, higher shrinkage and higher glass transiton temperature but lower elongation, lower nitrile group association, and lower dye uptake than fibers heat treated without applied tension.
3. Fibers heat treated with dry heat at 110° C will have higher tenacity, higher initial modulus, and higher glass transition temperature, but lower elongation, lower shrinkage, lower nitrile group association, and lower dye uptake than fibers heat treated with dry heat at 150° C.

Heat Treatment Methods

Samples for heat treatments were prepared in the following manner: Acrylic fibers (Orlon 42) in the form of tow were placed flat on a large piece of brown paper. Then the tow was pulled carefully by hand to remove as much crimp as possible without elongating the fibers. A sample consisting of one meter long parallel fibers and weighing 6 g was knotted on a wooden rod in a way that the two ends of the sample hung freely. To generate a tension of 0.025 grams per denier, a 1350-g weight was attached to one of the ends. This tension was low enough to not have any significant effect on the stress-strain curve of fibers and was high enough to remove the crimp introduced in the manufacturing processes. Then the wooden rod carrying the fibers, both hanging free and hanging under 0.025 g/den tension, was placed on a wooden stand designed for this study. Appendix 1A shows a drawing of the frame with fiber.

The oven was preheated to the desired temperature. When the oven temperature was stable, the wooden stand was placed in the oven for the designated time. Samples were heat treated at two temperatures, 110° and 150° C for 5 minutes, the time period found in a preliminary study. Each treatment was replicated three times.

The Amsco Autoclave was used to heat treat samples in the presence of saturated steam, using the same frame and tension arrangement as for the dry heat treatment. A temperature of 110° C was used for this treatment; the equipment was not capable of attaining 150° C.

Physical Testing

Sample Preparation

Specimens for all physical tests were conditioned for at least 24 hours at 70° ±2° F and relative humidity of 65 ± 2% (3,4).

Fiber Denier Measurement

Morton and Hearle (53) have discussed several cutting and weighing methods for fiber-length measurement. ASTM (5) has also published Standard Test Method, D1577, which has been adopted for this study. The method is based on calculating the average linear density of single fibers in a bundle from mass and length measurements on the bundle and number of single fibers in the bundle. The specimens chosen from treated fibers were in two forms:

a). Those which were heat treated under tension which, due to the application of a load approximately equal to 0.025g per denier, did not have any crimp in them.

b). Those which were heat treated slack having the crimp introduced by the manufacturing company.

In order to remove most of the crimp from fibers heat treated slack, a 56g weight was applied to a bundle of parallel fibers for 5 min. While the fibers were under load, the upper and lower parts of the bundle were taped and the distance between the tapes was accurately measured. Then the weight of the fibers located between the two tapes was measured by cutting the fibers at the inside edge of the tapes, and weighing the fibers on an analytical balance. Using tweezers, the

number of fibers was determined by removing and counting fibers from the accurately weighed bundle. Fiber denier was calculated by:

Denier = (9000 X W)/(L X N)

where:

W = weight of the bundle (mg),

N = number of fibers in the bundle and

L = length of fibers (mm),

The denier of samples heat treated under tension was calculated the same way. However, due to the absence of crimp on the fibers, the application of the 56g load for 5 minutes was not necessary.

Fiber Tensile Testing

The number of fibers needed to be used for tensile properties was calculated with the following equation suggested by ASTM (5) Standard Test Method D3822-82

$$N = 0.169V^2$$

where;

N = number of specimens and

V = reliable estimate of the coefficient for variation of individual observation for tenacity of untreated fibers.

The coefficient of variation of 45 untreated fibers was calculated and used as the value of V in the above formula. Therefore, the minimum number of specimens needed was found to be 7.14. However, in order to

make sure that sample size was large enough, a minimum of 12 fibers were tested to determine the tensile properties of treated fibers.

A table model Instron testing machine with special fiber clamps and a 50 gram load cell was used. A crosshead speed of 0.5 inch per minute (1.27cm/min), a chart speed of 10 inch per minute (25.4cm/min), and a gauge length of 0.5 inch (1.27cm) were used to break individual fiber specimens by directly mounting the fiber into the clamps. The system was calibrated using a 50 g calibration weight.

Breaking load, elongation at break,and initial modulus were calculated using the following equations suggested by ASTM (5) Standard Test Method D3822. However, instead of tex, denier was used in this study.

a). Breaking tenacity gf/den = M/D

where:

M = breaking load in grams-force and

D = linear density in denier

b). Breaking elongation % = 100 X (B/C)

where;

B = fiber elongation in cm and

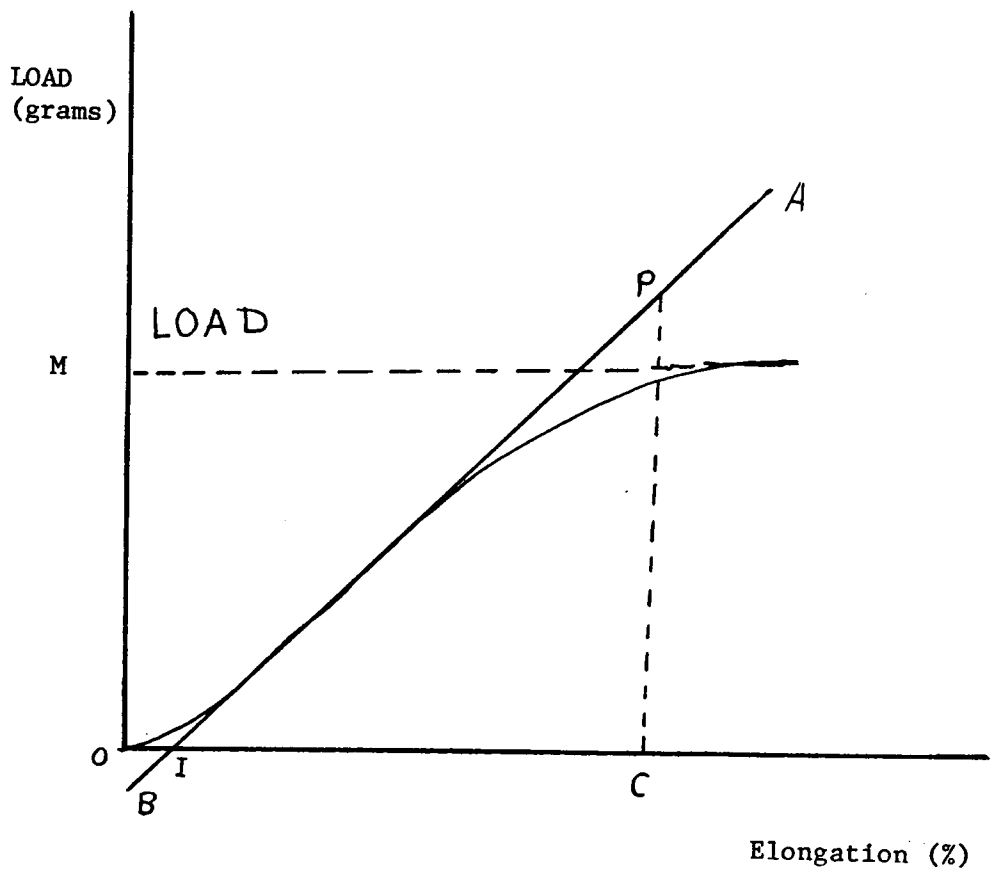
C = effective specimen length (1.27 cm).

c). Initial modulus

The tenacity in grams-force per denier corresponding to P on the line AB was calculated (see Figure 4). Then the line PC was drawn perpendicular to zero load axis.

The elongation corresponding to IC was calculated by dividing the distance IC by effective specimen length. Then initial modulus was obtained by dividing the tenacity at point P by the corresponding fractional elongation. The following equation has been suggested by Ko (35) for calculating initial modulus.

$$\text{Initial modulus(g/den)} = \frac{\text{load (g/den)}}{\dfrac{\text{elongation(in)}}{\text{gauge length(in)}} \times \dfrac{\text{crosshead speed (in/min)}}{\text{chart speed(in/min)}}}$$



Elongation

Figure 4 Load-Elongation curve with superimposed Initial Modulus AB

Fiber Shrinkage

A uniform parallel bundle of fibers was selected. Then the upper and the lower parts of the bundle were each marked by a knot. The distance between these two knots was carefully measured in standard atmosphere and the bundle was loosely run through a galvanized screen with 1/2 inch openings. The ends of the bundle were secured to the screen in a way that the distance between the two knots would be long enough to allow at least 20% shrinkage. Then the screen was placed in a water bath and was boiled for 15 minutes. The bundle then was cooled and reconditioned in standard atmosphere, and the distance between the knots was measured.

The following equation was used to calculate percent shrinkage;

$\% \text{ Shrinkage} = [(L - S)/L] \times 100$

where:

L = initial distance between the knots

S = the distance between the knots after boil.

Using the screen helped to prevent entanglement of fibers. A galvanized screen was used to prevent a rust effect on the fibers.

Scouring

A bundle of fibers weighing 0.150 g was scoured with 350 ml of a solution containing 1 g/l nonionic surfactant (Triton X100) and 3 g/l tetrasodium pyrophosphate (TSPP) for 20 min at 150° F (65° C). Then the scoured goods were rinsed thoroughly with distilled water.

Dyeing

C.I. Basic Red 18 was used in this study. This dye was selected because a preliminary study showed it is completely soluble in water and DMF; it is widely used; and its chemical structure is known. Other dyes tested, such as C.I. Basic Yellow 11, C.I. Basic Orange 21, C.I. Basic Blue 3, and C.I. Basic Violet 16, left some crystal residue at the bottom of the flask when 0.1 g of dye was dissolved in 100 ml DMF.

A 0.25g portion of dye was pasted with 0.75 ml acetic acid (56%) and 1 drop of Triton X100. The paste then was dissolved in boiling distilled water. The dissolved paste was quantitatively transferred to a 1000 ml. volumetric flask, cooled, and brought to the mark with distilled water. A bundle of scoured fibers weighing 0.150 g was dyed in 350 ml of a solution containing 0.1 g/l Triton X100 and 20 ml of the prepared dye solution. The temperature of the Ahiba dye bath was raised to the boil then the scoured fibers were entered into the dye bath. Dyeing at the boil proceeded for 15 min. The dyed samples then were removed and rinsed thoroughly with distilled water and scoured with 350 ml of a solution containing 2 g/l acetic acid (56%) and 1 g/l Triton X100 at 55° C. The scouring was performed to remove unbound dyes from the surface of the dyed fibers. Finally, the dyed and scoured fibers were rinsed thoroughly with distilled water and air dried.

Dye Uptake Measurement

A DMF mixture solution was prepared in the following manner (35);

a). 54.5g (0.4 M) of dry granular Zinc Chloride, A.C.S. reagent grade,

b). 8 ml concentrated Hydrochloric Acid, and

c). 20g of 2,6-di-t-butyl-4-methylphenol (DBMP), C.P. grade was placed in a volumetric flask and volume was raised to 1000 ml with N,N-dimethylformamide, spectral grade(DMF).

Then a weighed bundle (0.15g) of dyed fiber was dissolved in 25 ml of the DMF mixture. The dissolved fibers were filtered using a fine sintered-glass filter and suction to remove TiO_2 and any other insoluble particles. A drawing of the modified volumetric flash is shown in Appendix 1A. Then the volume of the solution was raised to 50 ml by adding DMF mix. Thereafter, the absorbance of the filtered solution was measured using a Bausch and Lomb Spectronic 2000 with a filtered solution of undyed fibers in the same solvent as the reference. The wave length corresponding to maximum absorption was found (495 $\pm$ 1nm) and all absorbances were read at this wave length.

The standard curve (Figure 5) for dyed fibers was made by dissolving 0.100 g dye in 100 ml of the above DMF mix containing 3 g per liter untreated fibers. Eight different dilutions from each one of the above solutions were made in order to obtain enough data to construct Beer's Law plots.

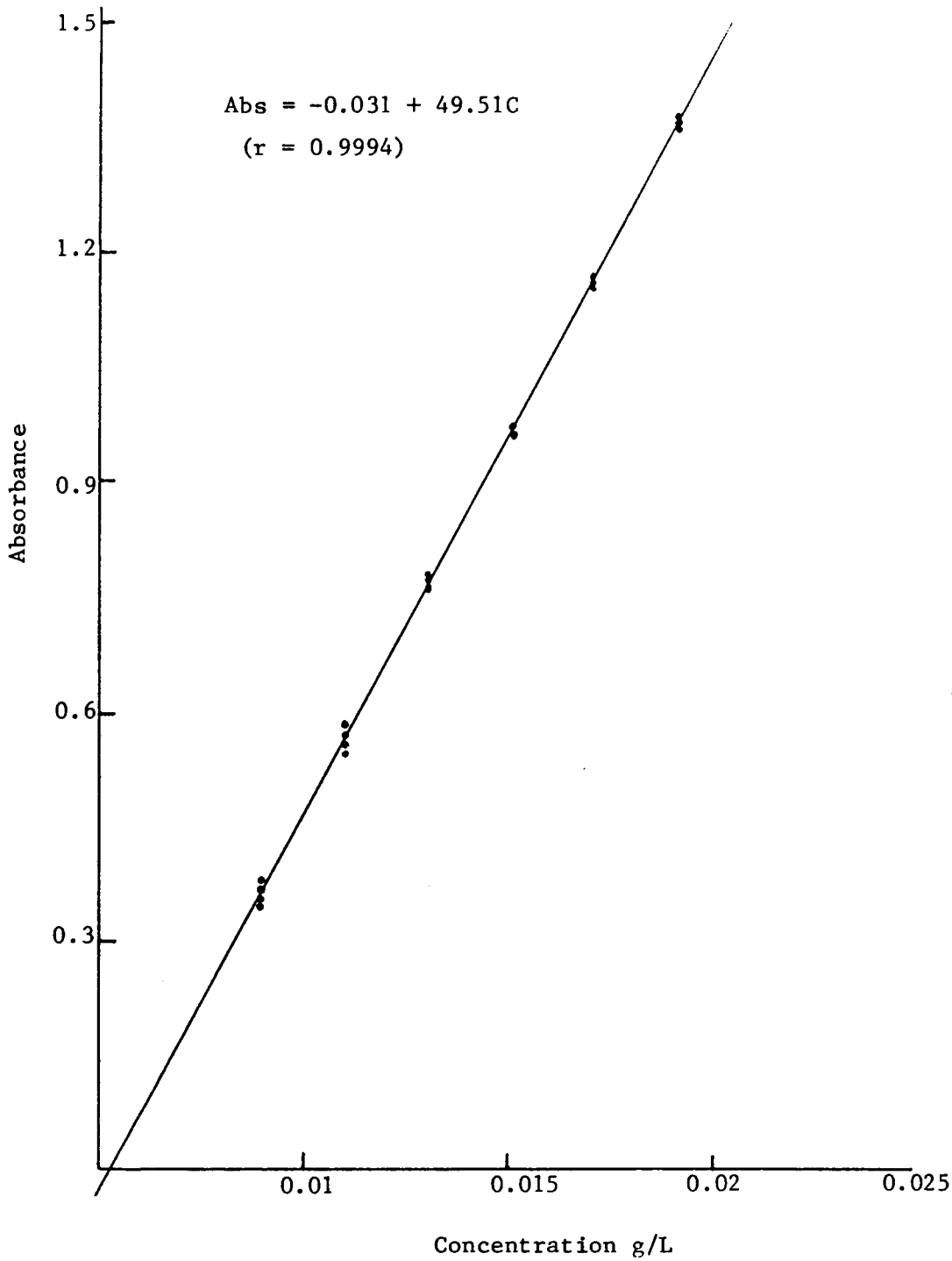


Figure 5 Concentration vs Absorbance curve of C.I. Basic Red 18 in DMF Mix with Polymer

Glass Transition Temperature Measurement

The Perkin Elmer DSC-4 was used for all Tg measurements. Test fibers were cut very fine using a razor blade. This helped to obtain a close packing and maximum contact surface between the DSC pan and sample. In this study 4-6 mg of the finely cut fibers were placed in an aluminum pan. In order to keep the fibers inside the pan, the lid of the pan was crimped using a special lid-crimping device.

A heating rate of 10° C per minute was used to heat the pan to 155° C. The Tg of acrylic fibers is different from type to type. However, most studies show a range of temperatures between 80° and 95° C. Acrylic fibers decompose before true melting, therefore most studies have reported Tg and not Tm.

Infrared Measurement of CN and CH Bands

The absorbance of the CN stretching band (at 2240 cm^{-1}) and of the CH stretching band (at 2900 cm^{-1}) was measured using the KBr IR technique. An IBM-Model 32 Fourier Transform Infrared Spectrophotometer equipped with a MCT detector was used to obtain the spectra. Then the ratio of the absorbance of the CN stretching band to the absorbance of the CH stretching band was calculated.

Chapter V

RESULTS AND DISCUSSION

The results of this research are presented and discussed in three sections. The first section covers the results of the preliminary series of experiments which led to the selection of treatment time for the main research effort. The second section covers the effect of heat treatment on the physical properties of the acrylic fiber (tenacity, elongation, initial modulus, and shrinkage). The final section covers the effect of heat treatment on the chemical properties of the fiber (glass transition temperature, nitrile group association as indicated by measurement of the ratio of the absorbances of the CN/CH stretching bands in the infrared, and dye uptake).

Preliminary Studies

Acrylic filament fibers (Du Pont Orlon 42 tow) were subjected to a series of heat treatments consisting of exposure to dry heat at 110° C and 150° C and to moist heat at 110° C for periods of 5, 15, and 30 minutes. In all exposures samples were exposed both under a tension of 0.025 grams/denier, and slack (under no tension). Following the heat treatments, physical and chemical properties of the fibers were determined. The results of the testing are shown in Table 3, which also contains the corresponding properties of the untreated control. Examination of these results leads to the following conclusions:

1) The properties of denier, tenacity, elongation and initial modulus are primarily affected by tension during heat treatment, and to a lesser extent by the duration of the heat treatment, the

TABLE 3

Summary of Results of Preliminary Experiments

TREATMENT CONDITIONS				FIBER PROPERTIES						
TEMPERATURE °C	MOISTURE	TENSION	TIME min	DENIER	TENACITY g/den	ELONGATION %	INITIAL MODULUS g/den	Tg °C	CN/CH	DYE UPTAKE %
110	Dry	Slack	5	10.35	2.78	44.3	37.9	103.0	1.73	0.412
110	Dry	Tension	5	9.25	3.16	35.6	53.3	107.2	1.76	0.413
110	Moist	Slack	5	10.17	2.86	43.3	43.3	106.2	1.90	0.372
110	Moist	Tension	5	9.30	3.12	30.6	57.1	107.0	1.88	0.348
150	Dry	Slack	5	10.32	2.89	41.7	55.2	102.0	1.75	0.380
150	Dry	Tension	5	9.18	3.28	29.3	58.1	101.6	1.70	0.356
110	Dry	Slack	15	10.11	2.96	41.8	47.3	104.6	1.72	0.377
110	Dry	Tension	15	9.30	3.21	34.8	52.1	105.6	1.73	0.395
110	Moist	Slack	15	10.28	2.80	38.5	40.9	107.4	1.87	0.405
110	Moist	Tension	15	9.29	3.36	29.3	64.3	107.6	1.87	0.368
150	Dry	Slack	15	10.22	3.09	40.4	45.1	100.8	1.65	0.360
150	Dry	Tension	15	9.31	3.29	32.4	73.1	102.0	1.64	0.348
110	Dry	Slack	30	10.40	2.83	41.8	39.8	102.8	1.81	0.402
110	Dry	Tension	30	9.27	3.09	37.8	57.7	104.8	1.78	0.384
110	Moist	Slack	30	10.33	2.82	44.6	49.1	108.0	1.76	0.402
110	Moist	Tension	30	9.41	3.12	35.1	49.1	108.0	1.84	0.376
150	Dry	Slack	30	10.28	2.85	39.6	45.9	99.2	1.81	0.328
150	Dry	Tension	30	9.17	3.21	36.3	51.8	103.6	1.77	0.415
CONTROL - AS RECEIVED - NO TREATMENT				10.24	2.89	45.6	43.5	101.3	1.69	0.415

temperature of dry heat treatment, or the presence or absence of moisture during 110° C heat treatment. Fibers heat treated under tension had lower denier, higher tenacity, lower elongation, and higher initial modulus than did samples heat treated in the absence of applied tension. Fibers heat treated without tension had properties similar to those of the untreated controls. Duration of exposure in particular seemed to have little influence on any of these properties.

2) The properties of glass transition temperature, nitrile group association, and dye uptake were affected only slightly by the presence or absence of applied tension during heat treatment, and almost not at all by duration of heat treatment. Temperature of dry heat treatment and the presence or absence of moisture during 110° C heat treatment appeared to have greater effects on these three properties.

Based on these results, it was decided to conduct the heat treatments for the rest of the study for a time of five minutes only, since there appeared to be little systematic further change in any property with prolonged exposure time.

Effect of Heat Treatment on Physical Properties

Acrylic filament fibers (Du Pont Orlon 42 tow) were subjected to a series of heat treatments consisting of exposure to dry heat at 110° C and 150° C and to moist heat at 110° C. All exposures were five minutes in duration; samples were exposed both under a tension of 0.025 gram/denier, and slack (under no tension). All heat treatments were

replicated three times. Following the heat treatments, denier, tenacity, elongation, initial modulus, and shrinkage (in boiling water for fifteen minutes) were measured. The results of these measurements are presented in Table 4. Results for the untreated control fiber are also given in this table.

Separate one-way analyses of variance (ANOVA) were run to test for differences in tenacity, elongation, initial modulus, and shrinkage with treatments. In each case the ANOVA's indicated the existence of a highly significant difference between means associated with treatments, therefore Fisher's Least Significant Difference (LSD) Analysis was used for making pairwise comparisons between the means. The results of these LSD analyses are presented in Table 5 and are discussed in the following paragraphs.

Effect of Heat Treatment on Tenacity

LSD analysis of the mean values of tenacity associated with the six heat treatments and the untreated control shows that these values fall into two distinct groups (Table 5, A). Tenacities associated with Treatment 3 (110° C, Dry, Slack), Treatment 5 (110° C, Moist, Slack) and Treatment 2 (150° C, Dry, Slack) were not significantly different from each other nor from the tenacity of the untreated control. Tenacities associated with Treatment 4 (110° C, Dry, Tension), Treatment 1 (150° C, Dry, Tension) and Treatment 6 (110° C, Moist, Tension) were not significantly different from each other, but were significantly different from the first group. The factor responsible for the difference is the tension applied during heat treatment.

TABLE 4

Physical Properties of Heat Treated Fibers

Treatment Conditions			Treat-	Fiber Properties[a]				
Temp.	Moisture	Tension	ment	Denier	Tenacity	Elongation	InitialModulus	Shrinkage
°C			#		g/den	%	g/den	%
110	Dry	Slack	3	10.32	2.84	45.7	43.9	0.09
110	Dry	Tension	4	9.21	3.16	40.6	55.3	3.61
110	Moist	Slack	5	10.22	2.87	43.1	45.4	0.22
110	Moist	Tension	6	9.22	3.26	31.2	62.2	3.54
150	Dry	Slack	2	10.35	2.90	41.9	45.6	-0.03
150	Dry	Tension	1	9.25	3.22	30.6	65.2	3.83
Control - As Received - No Treatment			C	10.24	2.89	45.6	41.6	0.33

[a]Number of Specimens = 6 for Denier, 36 for Tenacity, Elongation, and Initial Modulus, and 9 for Shrinkage

TABLE 5

LSD, Pairwise Comparisons Between

Means on Physical Properties

Physical Properties		Treatment Means						
	Treatment	3	5	C	2	4	1	6
A	Tenacity g/d	2.841	2.870	2.891	2.903	3.163	3.222	3.260
	Treatment	1	6	4	2	5	C	3
B	Elongation %	30.56	31.17	40.62	41.88	43.11	45.59	45.67
	Treatment	C	3	5	2	4	6	1
C	Modulus g/d	41.65	43.90	45.37	45.61	55.26	62.25	65.25
	Treatment	1	4	6	C	5	3	2
D	Shrinkage (% Gain/Loss)	-3.830	-3.606	-3.538	-0.329	-0.223	-0.086	-0.033

Treatment

1. 150° C, Dry, Tension
2. 150° C, Dry, Slack
3. 110° C, Dry, Slack
4. 110° C, Dry, Tension
5. 110° C, Moist, Slack
6. 110° C, Moist, Tension

C. Control, no treatment3

Fibers heat treated under tension had significantly higher tenacities than fibers heat treated without applied tension or not heat treated at all. Figure 6 shows that the tenacity of fibers heated at 110° C with either dry heat or saturated steam responded to applied tension in the same manner, and that the tenacity of fibers exposed to dry heat at either 110° C or 150° C responded to applied tension in the same way. Tenacities of fibers heated at 110° C with steam were slightly higher than tenacities of fibers heated dry at 110° C, and tenacities of fibers heated dry at 150° C were slightly higher than tenacities of fibers heated dry at 110° C, but the differences were not statistically significant.

Effect of Heat Treatment on Elongation

LSD analysis of the mean values of elongation associated with the six heat treatments and the untreated control shows that these values fall into five groups, four of which show overlap (Table 5, B). Elongations associated with Treatment 1 (150° C, Dry, Tension) and Treatment 6 (110° C, Moist, Tension) were not significantly different from each other and were significantly lower than all other treatments and the untreated control. Elongations associated with Treatment 4 (110° C, Dry, Tension) and Treatment 2 (150° C, Dry, Slack) were not statistically different from each other. Elongations of fibers from Treatment 2 were statistically equivalent to those of fibers from Treatment 5 (110° C, Moist, Slack) but those from Treatment 4 were significantly lower than those from Treatment 5. Elongations of fibers from Treatment 5 were statistically equivalent to those of the

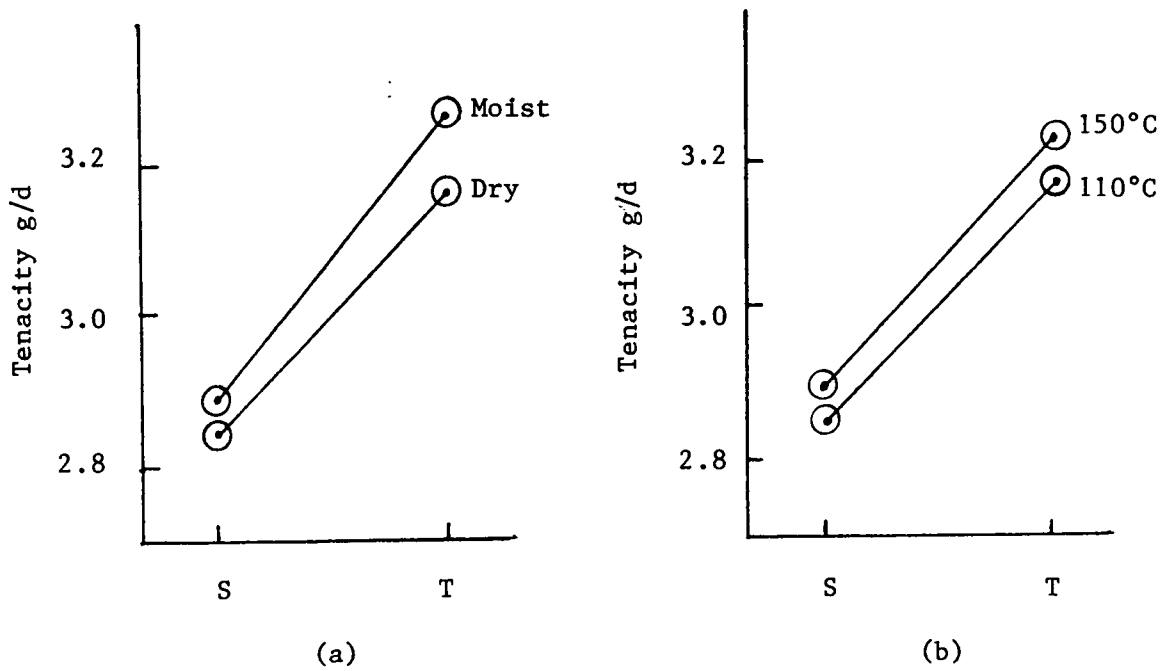


Figure 6 Effect of Moisture at 110°C and Temperature of Dry Heat on Tenacity of Heat Treated Acrylic Fiber:
(a) 110°C Moisture Vs. Tension, (b) Temperature Vs. Tension

untreated control, but those from Treatment 2 were significantly lower than those from the untreated control. Finally, the elongations of fibers from the untreated control were statistically equivalent to those from Treatment 3 (110° C, Dry, Slack) but those from Treatment 5 were significantly lower than those from Treatment 3. As in the case of tenacity, the tension applied during heat treatment appears to be the factor most responsible for changes in elongation, but moisture at 110° C and temperature of dry heat appeared to play a more important role in this case. Figure 7 shows that elongation was affected by applied tension to a greater extent with moist air compared to dry heat at 110° C, and that elongation was affected by applied tension to a greater extent with 150° C dry heat compared to 110° C dry heat. Elongation was reduced to a greater extent with either moist heat at 110° C or dry heat at 150° C compared to dry heat at 110° C. The differences in response of elongation to applied tension account for the overlaps noted in the LSD analysis.

Effect of Heat Treatment on Initial Modulus

LSD analysis of the mean values of initial modulus associated with the six heat treatments and the untreated control (Table 5, C) shows that these values of initial modulus associated with the untreated control, with Treatment 3 (110° C, Dry, Slack), with Treatment 5 (110° C, Moist, Slack) and with Treatment 2 (150° C, Dry, Slack) were not significantly different from each other, but were significantly lower than those from the other three treatments. Values of initial modulus associated with Treatment 4 (110° C, Dry, Tension) were

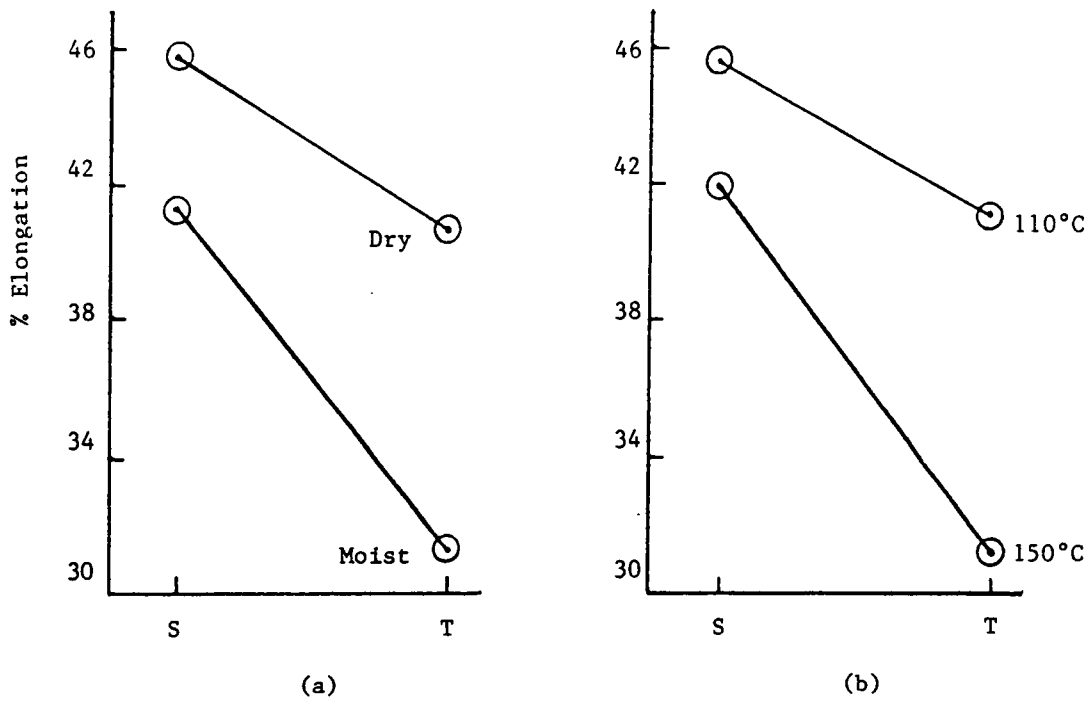


Figure 7 Effect of Moisture at 110°C and Temperature of Dry Heat on Elongation of Heat Treated Acrylic Fiber: (a) 110°C Moisture Vs. Tension, (b) Dry, Temperature Vs. Tension

significantly higher than those of the untreated control and Treatments 3, 5, and 2, but were significantly lower than those from Treatment 6 (110° C, Moist, Tension) and Treatment 1 (150° C, Dry, Tension). Values of initial modulus associated with Treatments 6 and 1 were statistically equivalent, and were higher than those from all other treatments and the untreated control. As in the case of tenacity, the factor most responsible for the difference was the tension applied during heat treatment. Fibers heat treated under tension had significantly higher initial modulus than did fibers heat treated without applied tension or not heat treated at all. Figure 8 shows that the presence of moisture during heat treatment at 110° C and that dry heat at 150° C both had a greater effect on the response of initial modulus to applied tension than does dry heat at 110° C, but this was less pronounced than in the case of elongation so the overlaps seen in the LSD analysis there were not seen for the case of initial modulus.

Effect of Heat Treatment on Shrinkage

LSD analysis of the mean values of shrinkage associated with the six heat treatments and the untreated control show that these values fell into two distinct groups (Table 5, D). Values of shrinkage associated with Treatment 1 (150° C, Dry, Tension), with Treatment 4 (110° C, Dry, Tension) and with Treatment 6 (110° C, Moist, Tension) were not significantly different from each other, but were significantly lower than those values of shrinkage associated with the untreated control, with Treatment 5 (110° C, Moist, Slack), with

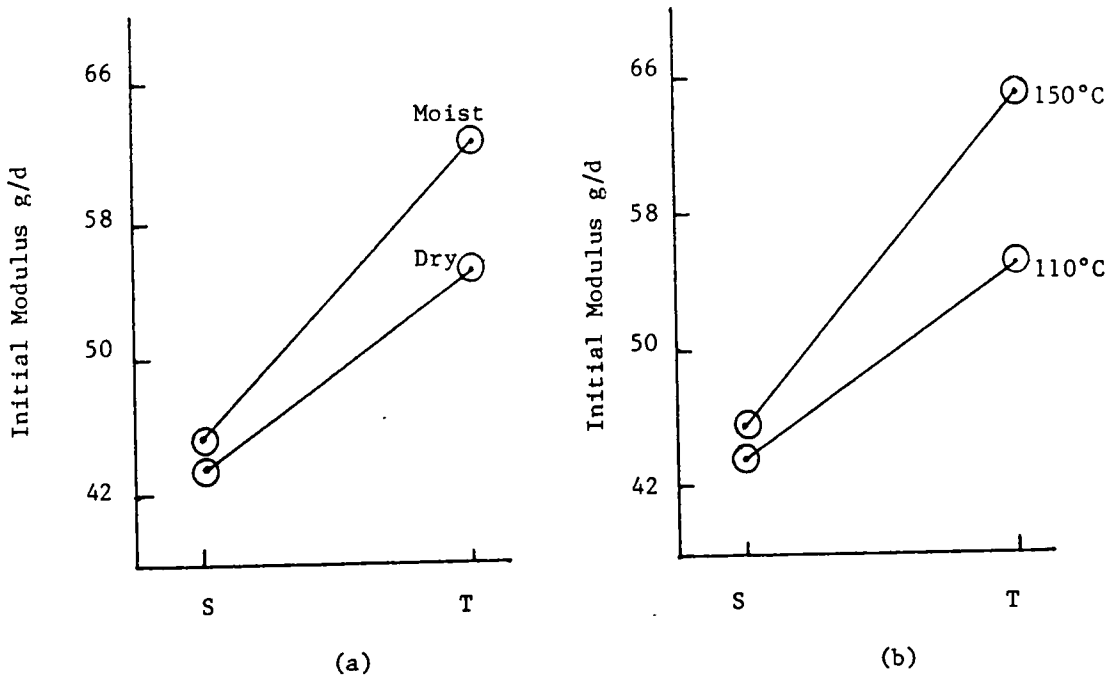


Figure 8 Effect of Moisture at 110°C and Temperature of Dry Heat on Initial Modulus of Heat Treated Acrylic Fiber: (a), 110°C Moisture Vs. Tension, (b), Dry Temperature Vs. Tension

treatment 3 (110° C, Dry, Slack) and with Treatment 2 (150° C, Dry, Slack). Values of shrinkage associated with the untreated control, and with Treatments 5, 3, 2 were not significantly different from each other. As in the case of tenacity, the factor responsible for the difference was the tension applied during heat treatment. Figure 9 shows that the shrinkage of fibers exposed to either dry or moist heat at 110° C responded to applied tension in the same manner, and that the shrinkage of fibers exposed to dry heat at either 110° C or 150° C responded to applied tension in the same way.

In summary, the tenacity, elongation, initial modulus, and shrinkage of heat treated acrylic filament fibers (Du Pont Orlon 42 tow) were primarily affected by the presence of applied tension during heat treatment. Fibers heat treated under a tension of 0.025 gram/denier had higher tenacities, lower elongations, higher initial moduli and higher shrinkages than fibers heat treated slack or not heat treated at all. Box plots showing these results are given in Appendix E. The presence or absence of moisture during heat treatment at 110° C, and the use of 110° C or 150° C dry heat treatment had no appreciable effect on either tenacity or shrinkage, but had a moderate effect on initial modulus and a somewhat greater effect on elongation. For both initial modulus and elongation, the response to applied tension was greater with both moist heat at 110° C and dry heat at 150° C, compared to dry heat at 110° C.

Table 4 also contains denier values for each heat treatment and the untreated control. The denier values can be used to calculate

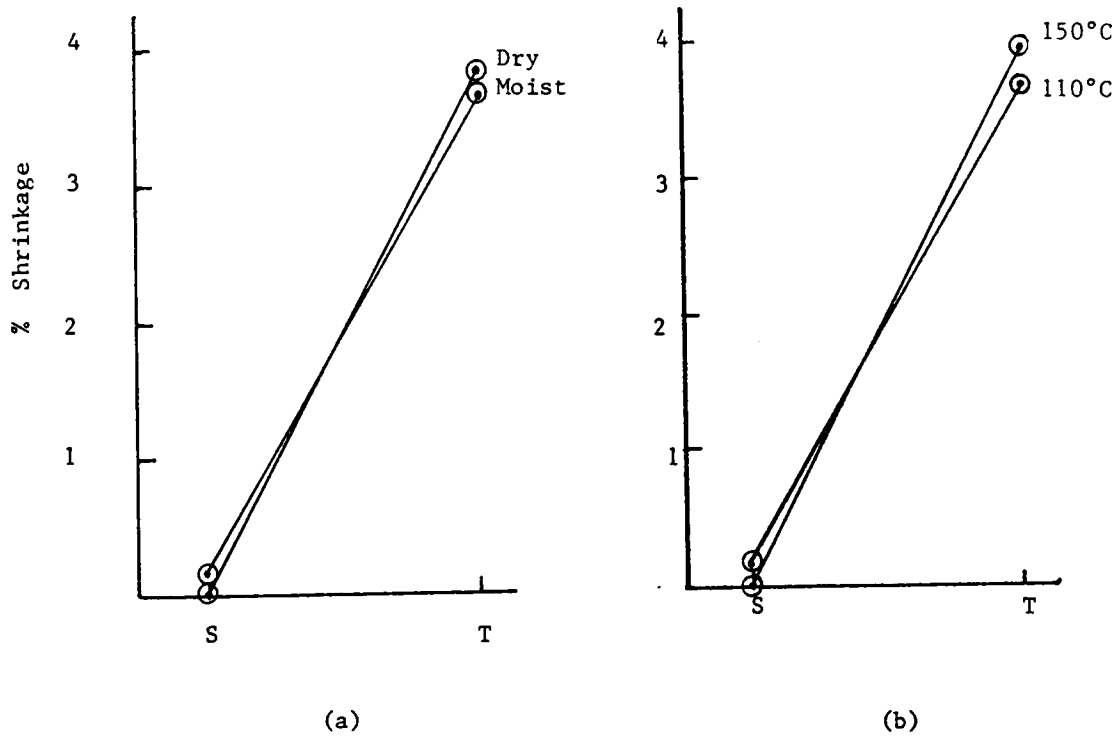


Figure 9 Effect of Moisture at 110°C and Temperature of Dry Heat on Shrinkage of Heat Treated Acrylic Fiber: (a) 110°C Moisture Vs. Tension, (b) Dry, Temperature Vs. Tension

equivalent length changes associated with the heat treatments. The shrinkages values given in Table 4 can be used to calculate a final equivalent length after heat treatment and boiling for fifteen minutes. The results of these calculations are given in Table 6. Treatment 2 (150° C, Dry, Slack) caused fibers to undergo a shrinkage during heat treatment of about 1.07%. These heat treated fibers grew slightly during boil-off, so the final heat-treated, boiled off sample showed 1.03% shrinkage relative to its original 9000 meter length. Treatment 3 (110° C, Dry, Slack) caused fibers to undergo an 0.78% shrinkage during heat treatment; an additional slight shrinkage during boil-off was observed, giving a final 0.87% shrinkage relative to its original length. Treatment 5 (110° C, Moist, Slack) grew slightly during heat treatment (0.20%) even though no tension was applied; shrinkage after boil-off offset the growth so that a final shrinkage of only 0.02% was observed relative to its original length. The untreated control shrinkage on boil-off was 0.33%, so the fibers heat treated in the absence of applied tension all showed slight shrinkages ranging from 0.10 to 1.03%, relative to the original length following boil-off. The three treatments including applied tension all gave considerable increases in length after heat treatment, ranging from 10.7% for Treatment 1 (150° C, Dry, Tension), through 11.1% for Treatment 6 (110° C, Moist, Tension), to 11.2% for Treatment 4 (110° C, Dry, Tension). However, these length increases were not completely stable to boiling water, and increases in length after heat treatment and

TABLE 6

Length Equivalents for Heat Treated and Boiled-Off Samples

	Denier	Treated [a] Equivalent Length(M)	Boiled-Off[b] Equivalent Length(M)
Treatment 2 (150° C, Dry, Slack)	10.35	8904	8907
Treatment 3 (110° C, Dry, Slack)	10.32	8930	8922
Untreated Control	10.24	(9000)	8970
Treatment 5 (110° C, Moist, Slack)	10.22	9018	8998
Treatment 1 (150° C, Dry, Tension)	9.25	9963	9581
Treatment 6 (110° C, Moist, Tension)	9.22	9996	9642
Treatment 4 (110° C, Dry, Tension)	9.21	10007	9646

(a) Calculated from denier
(b) Calculated from denier changes and shrinkages

boil-off were 6.5% from Treatment 1, 7.1% for Treatment 6, and 7.2% for Treatment 4. These data suggest that filament acrylic fibers cannot be heat-set under tension to improve dimensional stability, at least not for tensions of the order of 0.025 gram/denier.

Effect of Heat Treatment on Chemical Properties

Besides the physical testing described above, the heat treated acrylic filament fibers (Du Pont Orlon 42 tow) and the untreated controls were also evaluated to determine chemical properties. Glass transition temperatures (Tg) were determined by Differential Scanning Calorimetry (DSC). Nitrile group associations were measured using Fourier Transform Infrared Spectroscopy (FTIR); absorbance of the peaks associated with the CN stretching mode and the CH stretching mode were measured and the ratios of CN absorbance to CH absorbance were calculated. Dye uptake was measured by immersing the fibers in infinite dye baths at the boil for fifteen minutes, then determining the absorbance of filtered solutions of dyed fibers by visible spectrophotometry. Results of these determinations are given in Table 7.

Separate one-way analyses of variance (ANOVA) were run to test for differences in these properties with treatments. In the cases of glass transition temperature and dye uptake the ANOVA's indicated the existence of a highly significant difference between the means associated with treatments, therefore Fisher's Least Significant Difference (LSD) Analysis was used for making pairwise comparisons

TABLE 7

Chemical Properties of Heat Treated Fibers

Treatment Conditions			Treatment	Fiber Properties[a]		
Temp. °C	Moisture	Tension	#	Tg °C	CN/CH	Dye Uptake %
110°	Dry	Slack	3	102.2	1.833	0.406
110°	Dry	Tension	4	106.1	1.803	0.406
110°	Moist	Slack	5	108.6	1.781	0.449
110°	Moist	Tension	6	109.2	1.794	0.393
150°	Dry	Slack	2	106.1	1.807	0.397
150°	Dry	Tension	1	103.5	1.808	0.373
Control - As Received - No Treatment			C	98.9	1.828	0.415

[a]Number of Specimens = 9 for Tg and CN/CH, and 3 for Dye Uptake, except for control, where 7 determinations of dye uptake were made.

between the means. The ANOVA for nitrile group association was not found to be significant with treatments; LSD analysis was run to check this. The results of these LSD analyses are presented in Table 8 and are discussed in the following paragraphs.

Effect of Heat Treatment on Glass Transition Temperature

LSD analysis of the mean values of glass transition temperature associated with the six heat treatments and the untreated control showed that these values fell into four different groups with no overlap (Table 8, A). The value of Tg associated with the untreated control was significantly lower than the Tg values associated with all six heat treatments. The Tg values associated with Treatment 3 (110° C, Dry, Slack) and Treatment 1 (150° C, Dry, Tension) were not significantly different from each other, but were significantly lower than the Tg values associated with the remaining four heat treatments. The Tg values associated with Treatment 2 (150° C, Dry, Slack) and Treatment 4 (110° C, Dry, Tension) were statistically equivalent and were significantly lower than the Tg values associated with Treatment 5 (110° C, Moist, Slack) and Treatment 6 (110° C, Moist, Tension). The Tg values associated with Treatments 5 and 6 were not significantly different from each other, and were significantly higher than the Tg values associated with all the other heat treatments and with the untreated control. The highest Tg values were obtained in heat treatment at 110° C with saturated steam; the presence of applied tension had almost no effect. At 110° C with dry heat, applied tension caused a significant increase in Tg compared to treatment with no

TABLE 8

LSD, Pairwise Comparisons Between Means of Chemical Properties

A	Treatment	Control	3	1	2	4	5	6
	Tg °C	98.86	102.19	103.48	106.13	106.13	108.62	109.20
B	Treatment	5	6	4	2	1	Control	3
	CN/CH	1.781	1.794	1.803	1.807	1.808	1.828	1.833
	Treatment	1	6	2	4	3	Control	5
C	Dye Uptake	0.3732	0.3930	0.3969	0.4060	0.4061	0.4154	0.4487

Treatment

1	150° C Dry, Tension
2	150° C Dry, Slack
3	110° C Dry, Slack
4	110° C Dry, Tension
5	110° C Moist, Slack
6	110° C Moist, Tension
C	Control, No Treatment

applied tension, but the opposite effect was observed at 150° C with dry heat. In this case, fibers treated with applied tension had lower Tg values than fibers treated without applied tension. These effects are shown graphically in Figure 10.

Effect of Heat Treatment on Nitrile Group Association

LSD analysis of the mean values of the nitrile group association measurements (the ratios of absorbancies of the CN and CH bands) associated with the six heat treatments and the untreated control showed that these values all fell into one group (Table 7, B). There was no statistically significant difference between any pair of CN/CH ratio values. Given that the pairwise differences were not statistically significant different, the values were associated with treatments in a manner which is consistent with the way that the Tg values were associated with treatments. A low value of the CN/CH ratio means that the relative number of CN groups not engaged in dipole-dipole interaction is down, hence, there is a greater degree of nitrile-nitrile interaction, suggesting a higher value of Tg. The two treatments which gave the highest Tg values also gave the lowest CN/CH ratios (Treatments 5 and 6 - both at 110° C with saturated steam). The two treatments which gave the lowest values of Tg, next to the untreated control, also gave the highest values of the CN/CH ratios, except for the untreated control (Treatment 3 - 110° C, Dry, Slack and Treatment 1 - 150° C, Dry, Tension). The untreated control had the lowest Tg value and the second highest CN/CH ratio. Further,

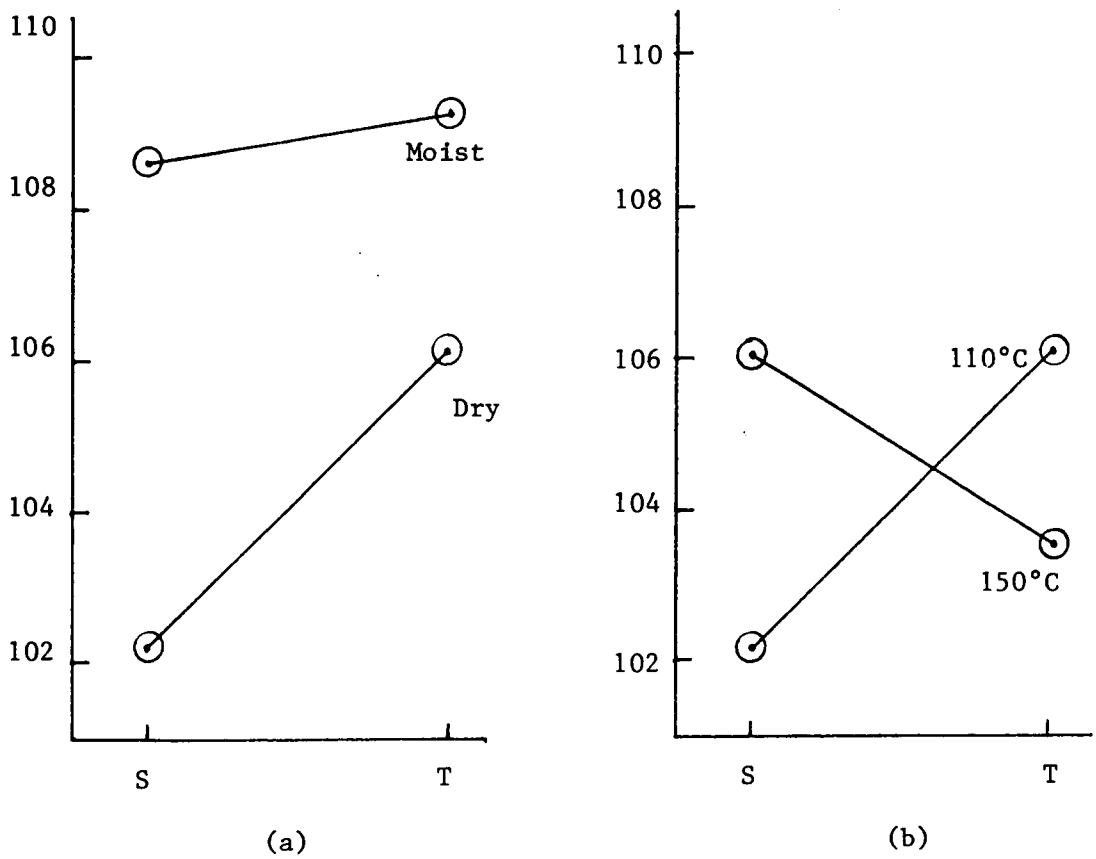


Figure 10 Effect of Moisture at 110°C and Temperature of Dry Heat on Glass Transition Temperature of Heat Treated Acrylic Fiber: (a) 110°C Moisture Vs. Tension, (b) Dry, Temperature Vs. Tension

Figure 11 shows that the response of the CN/CH ratio to applied tension for fibers heated at 110° C in the presence or absence of moisture showed the exact opposite behavior as the response of Tg to applied tension for these samples, and that the response of the CN/CH ratio to applied tension for fibers heat treated with dry heat showed a temperature-tension interaction similar to that shown for the response of Tg, but in the opposite sense, as would be predicted. Even though the CN/CH ratios were not statistically significantly different from each other, their association with treatments agreed with what would be expected from Tg data.

Effect of Heat Treatment on Dye Uptake

LSD analysis of the mean values of dye uptake associated with the six heat treatments and the untreated control show that these values fell into four groups with considerable overlap (Table 7, C). The values of dye uptake associated with Treatment 1 (150° C, Dry, Tension) and Treatment 6 (110° C, Moist, Tension) were statistically equivalent. The value of dye uptake associated with Treatment 6 was statistically equivalent to the values associated with Treatment 2 (150° C, Dry, Slack), Treatment 4 (110° C, Dry, Tension), and Treatment 3 (110° C, Dry, Slack), but those values associated with Treatment 1 were statistically different from the values associated with Treatments 2, 4, and 3. The dye uptake values associated with Treatments 4 and 3 were statistically equivalent to the dye uptake value associated with the untreated control, but those values associated with Treatments 2 and 6 were significantly different from the value for the untreated

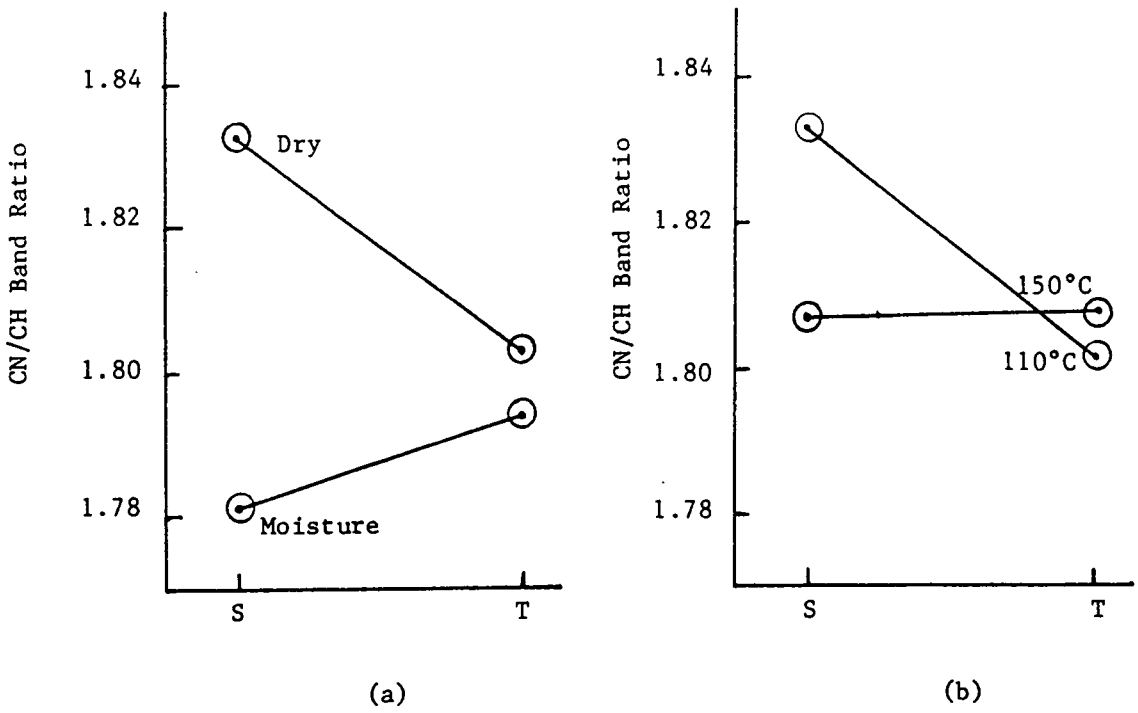


Figure 11 Effect of Moisture at 110°C and Temperature of Dry Heat on CN/CH Band Ratio of Heat Treated Acrylic Fiber;
(a) Moisture Vs. Tension, (b) Temperature Vs. Tension

control. The dye uptake value associated with Treatment 5 (110° C, Moist, Slack) was significantly higher than the dye uptake values associated with all the other heat treatments and the untreated control. Figure 12 shows that the response of dye uptake to applied tension was flat for the fibers heat treated at 110° C with dry heat. With moist heat at 110° C, tension applied during heat treatment was associated with low dye uptake while fibers so treated without tension showed high dye uptake. With dry heat at 150° C, fibers exposed with applied tension had significantly lower dye uptake than did fibers exposed without applied tension.

In summary, the glass transition temperature, nitrile group association, and dye uptake of heat treated acrylic filament fibers (Du Pont Orlon 42 tow) were not affected by the presence or absence of applied tension during heat treatment as were the physical properties discussed earlier. Box plots showing these results are given in Appendix E. Glass transition temperature was increased relative to the untreated control by all heat treatments; moist heat at 110° C had the largest effect and this was independent of applied tension during heat treatment. For dry heat treatment at 110° C, the Tg was higher for the fibers exposed with applied tension than for fibers exposed slack but for dry heat treatment at 150° C, the Tg was higher for fibers exposed slack than for fibers exposed with applied tension. Nitrile group association as measured by the ratio of absorbances of the CN and CH stretching bands was, statistically at least, unaffected by heat treatment. However, high values of the CN/CH ratio were associated

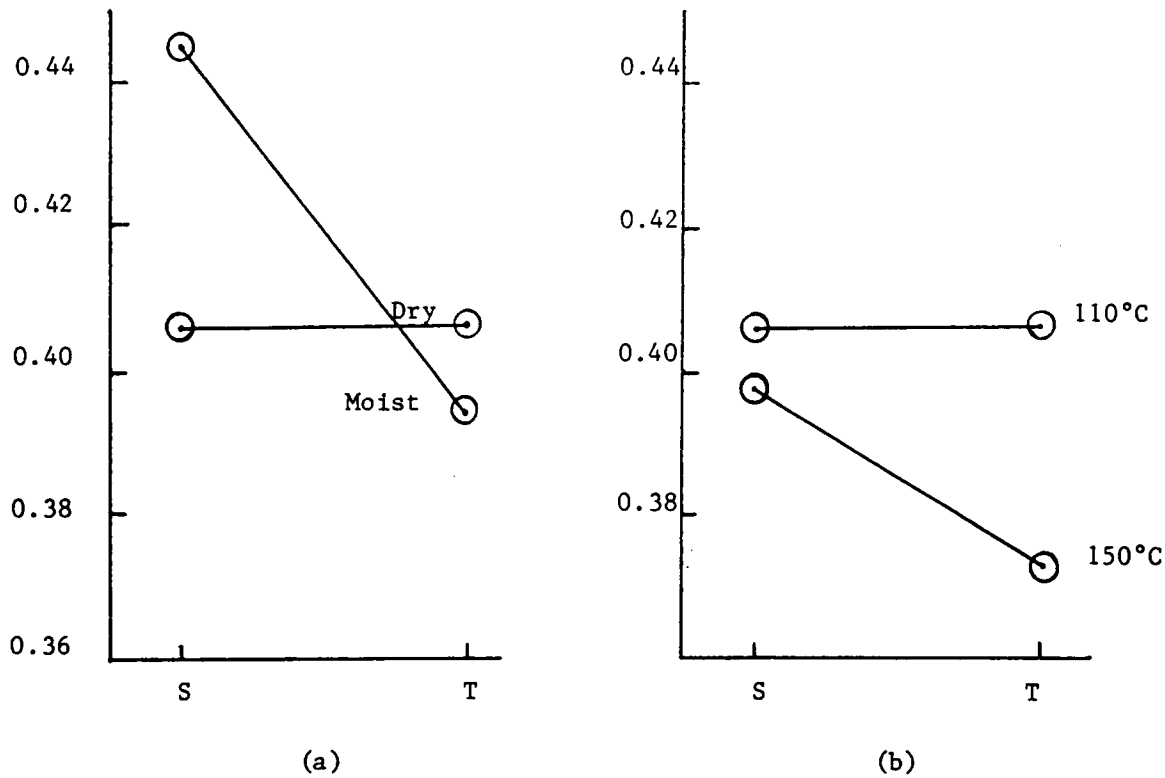


Figure 12 Effect of Moisture at 110°C and Temperature of Dry Heat on Dye Uptake of Heat Treated Acrylic Fiber;
(a) 110 Moisture Vs. Tension, (b) Dry Temperature Vs. Tension

with low values of Tg. Since this ratio is a measure of the relative concentration of free or unassociated nitrile groups in the fiber polymer, high values of the ratio would be expected with low Tg and low values of the ratio with high Tg. Figure 13 shows the relationship between Tg and the CN/CH ratio; the correlation coefficient (-0.8906) indicates a fairly strong relationship between the two and the direction is as expected. Dye uptake was highest for the fiber heat treated slack at 110° C saturated steam and lowest for the fiber heat treated with dry heat at 150° under tension. If dyeing is proceeding strictly according to a free volume mechanism, then dye uptake would be expected to decrease with increase in Tg and conversely to increase with increase in the CN/CH ratio (i.e., with increase in unassociated nitrile groups). If however, a pore mechanism is operative in conjunction with the free volume model, then the relationship between dye uptake and either Tg or CN/CH ratio might not be so clear cut. Figure 14 shows the relationship between dye uptake and Tg, and Figure 15 shows the relationship between dye uptake and CN/CH ratio. Five of the seven points in Figure 14 appear to suggest a linear relationship in the expected direction for the free volume mechanism, dye uptake decreases as Tg increases. These five points correspond to the untreated control and four of the heat treatments; the correlation coefficient (r=-0.9138) suggests a strong relationship between Tg and dye uptake for these conditions. One point lies well above the straight line and the other lies well below. The point lying well above the line corresponds to Treatment 5 (110° C, Moist, Slack) and

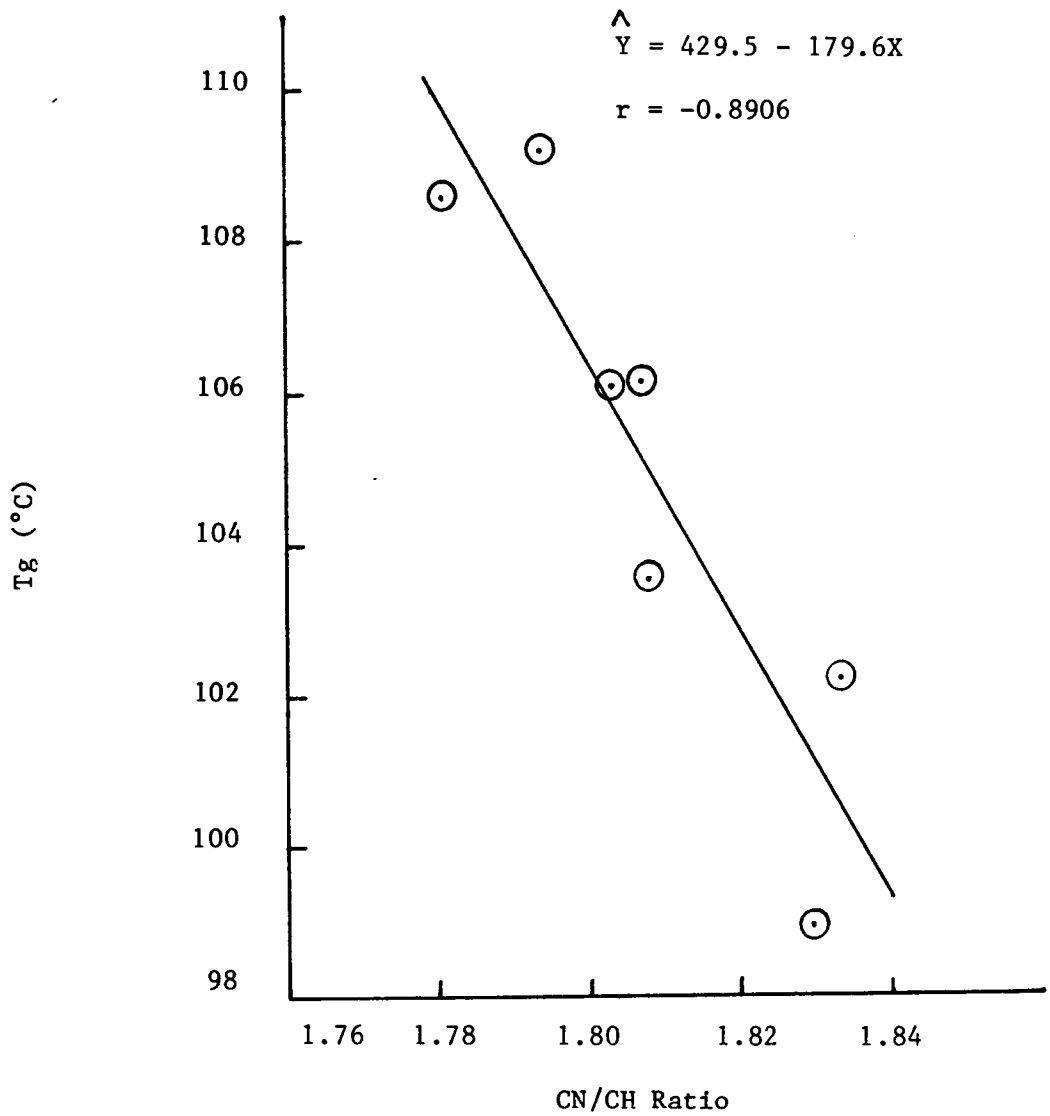


Figure 13 Tg Vs. CN/CH Ratio for all Treatments and Control

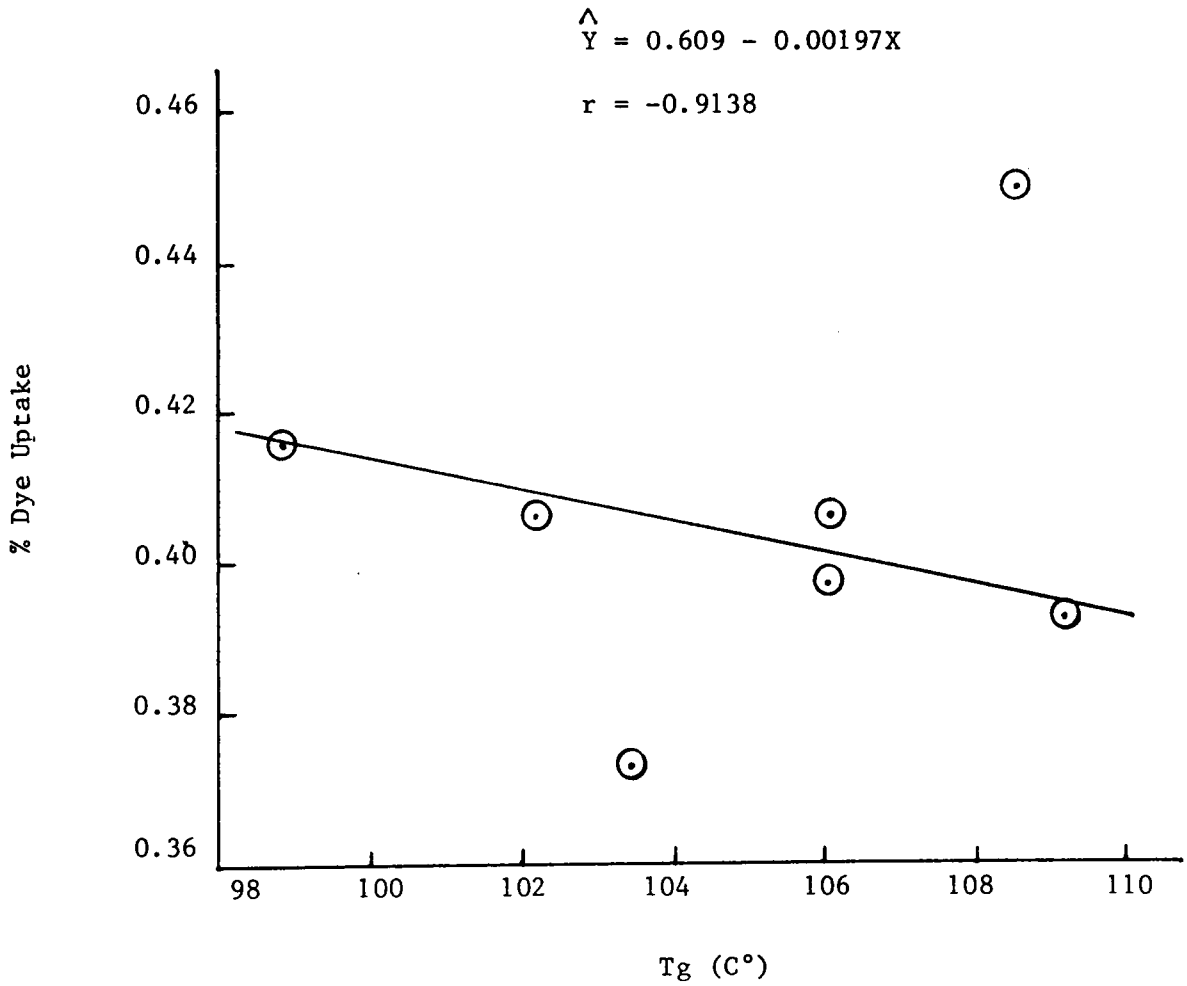


Figure 14 Dye Uptake Vs. Tg

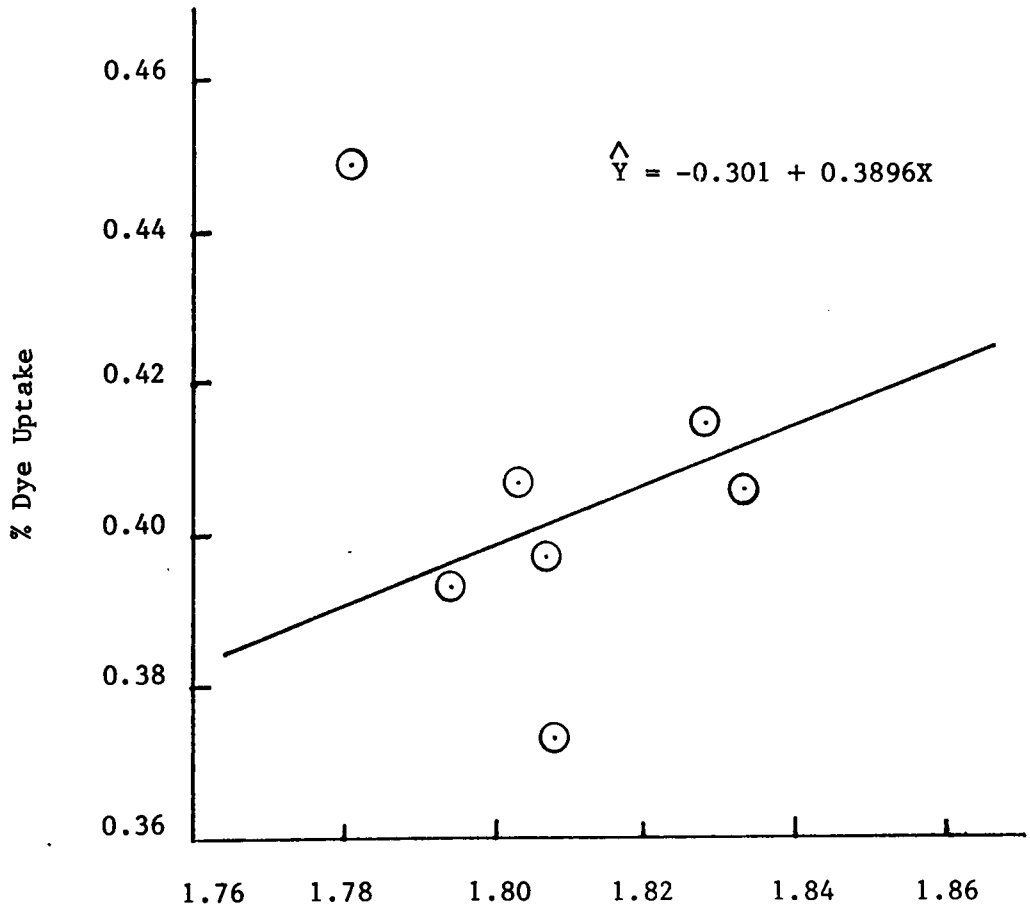


Figure 15 Dye Uptake Vs. CN/CH Ratio

the point lying well below the line corresponds to Treatment 1 (150° C, Dry, Tension). The two heat treatments which provided the extreme values of dye uptake correspond to the extreme opposite ends of the experimental design. If any treatment would be expected to collapse any pore structure present in the fiber, it would be Treatment 1. If any treatment would be expected to enhance any pore structure present in the fiber it would be Treatment 5. Using the equation for the straight line in Figure 14 to calculate predicted values for dye uptake for Treatment 1 (Tg = 103.5° C) and for Treatment 5 (Tg = 108.6° C), the values of 0.405% and 0.395% were obtained. The actual dye uptake obtained for Treatment 1 was 0.373%; this value is 0.032% lower than the predicted value (7.9% below predicted). The actual value obtained for dye uptake for Treatment 5 was 0.449%; this value is 0.054% higher than the predicted value (13.7% above predicted). These results suggest that both a free volume and pore mechanism are operative for the dyeing of this acrylic fiber. Similar results are obtained when dye uptake is plotted against CN/CH ratio (Figure 15). A straight line can be fitted to the same five points; the correlation coefficient (r = 0.7550) suggests a fairly strong relationship in the expected direction. The points corresponding to Treatment 5 and to Treatment 1 lie well above and well below the line, respectively. Using the equation of this straight line to calculate predicted values for dye uptake for Treatment 1 (CN/CH = 1.808) and for Treatment 5 (CN/CH = 1.781), the values of 0.401% and 0.391% were obtained. The actual value of dye uptake for Treatment 1 was 0.373%; this value is 0.028%

lower than the predicted value (7.0% below predicted). The actual value of dye uptake for Treatment 5 was 0.449%; this value is 0.058% higher than the predicted value (14.8% above predicted). As before, these data suggest that both a free volume and pore mechanism are operative for the dyeing of this acrylic fiber.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary

Following a series of preliminary experiments to establish a time for heat treatments, acrylic filament fibers (Du Pont Orlon 42 tow) were subjected to a series of dry heat treatments at 110° C and 150° C and heat treatments with saturated steam at 110° C. Each heat treatment was of five minutes duration and provided fiber treated under an applied tension of 0.025 gram/denier as well as fiber treated without applied tension. Each heat treatment was repeated three times. Following heat treatments, the treated fibers and untreated controls were extensively characterized. Tenacity, elongation, and initial modulus were measured using an Instron tester; shrinkage upon exposure to boiling water for fifteen minutes was measured; glass transition temperature was measured by differential scanning calorimetry; nitrile group association was measured by Fourier Transfrom Infrared Spectrophotometry; and dye uptake was measured by dissolving fiber dyed in an infinite dye bath in a suitable solvent and measuring the absorbance of the filtered solution by visible spectrophotometry. Because of equipment limitations, the experimental design did not provide for exposure to moist heat at 150° C, so three way analyses of variance involving the variables temperature, tension, and moisture could not be run. Therefore one way analyses of variance were run for each dependent variable against treatment. Fisher's Least Significant

Difference Analyses (LSD) were run to obtain pairwise comparisons between treatments. Physical properties (tenacity, elongation, initial modulus, and shrinkage) were found to be affected primarily by the presence or absence of applied tension during heat treatment; temperature of dry heat and the presence or absence of moisture at 110° C had less effect. Chemical properties (Tg and dye uptake) responded to treatment variables in a less clearcut fashion; the presence of moisture at 110° C produced the highest values of Tg, while treatment at 110° C, moist, slack gave the highest dye uptake. Nitrile group association was found to be unaffected by treatment, statistically, but the values found correlated well with values of Tg. Dye uptake was related to both Tg and nitrile group association; the results were interpreted as supporting the theory that both free volume and pore mechanism are operative in the dyeing of this fiber.

Fibers heat treated under tension had higher tenacity and initial modulus and lower elongation than fibers heat treated without applied tension. The denier of fibers heat treated under tension was also lower than the denier of fibers heat treated without applied tension. The lower denier indicates that the fibers elongated during heating under the applied tension; the higher tenacity and initial modulus and lower elongation of these fibers suggests a greater degree of molecular orientation for the tension treated fibers. To check this, samples were examined by wide angle x-ray scattering (WAXS) and the increased orientation of the tension treated fibers was confirmed as shown in Appendix D. Shrinkage measurements on the fibers treated with and

without applied tension showed that the length increase induced by heating under tension was not completely stable; only about 63% of the length increase was retained after fifteen minutes in boiling water.

Dye uptake was found to increase linearly with nitrile group association over four of the heat treatments and the untreated control, and to decrease linearly with glass transition temperature for the same conditions; regressions showed strong relationships in both cases. Two heat treatments did not fit the linear relationships; treatment at 110° C slack with saturated steam gave much higher dye uptake than the linear relationships would predict and treatment with dry heat at 150° C under tension gave much lower dye uptake than predicted by the linear relationships. The treatment giving the higher dye uptake would be expected to enhance any pore structure present in the fiber; saturated steam would allow greater chain mobility and permit more nitrile-nitrile association (lower CN/CH ratio) and the increased nitrile-nitrile association would result in higher interchain interaction (higher Tg). The absence of tension prevents length contraction so the more compact chain structure in the same fiber length results in enhancement of porosity, leading to higher dye uptake than the Tg or CN/CH would predict. The treatment giving the lower dye uptake would be expected to minimize any pore structure present in the fiber; the high temperature would permit chain mobility but the applied tension causes the fibers to elongate during heat treatment. The elongated fiber has enhanced molecular orientation as shown by WAXS, but the nitrile group association is very close to that of the

untreated control and to the slack treated fiber. The Tg is increased only slightly compared to control and not as much as the slack treated fiber. Since the Tg and CN/CH indicated little increase in interchain interaction while the length increases and denier decreases, a similar polymer structure is present in a smaller volume suggesting reduction of porosity, and lower than expected dye uptake.

CONCLUSIONS

Three research hypotheses were set forth earlier. The first dealt with the effects of moisture during heat treatment at 110° C in fiber properties, the second with the effect of applied tension during heat treatment on fiber properties, and the third with the effect of temperature during dry heat treatment on fiber properties. The expected directions of property changes were based on the literature review. Table 9 summarizes the results of pairwise comparisons of treatments based on Fisher's LSD analyses. Treatment conditions are shown in order of ascending values of the means of the property indicated. The mean values of the properties are not included in this table as they already have been given in Tables 5 and 8. Treatment conditions underlined with a common line are not significantly different from each other at the 0.0025 probability level; this level was selected as it represents the 0.05 probability level partitioned among twenty treatment, replicate combinations. This information in Table 9 can be used to test the research hypotheses.

Since pairwise comparisons were obtained in the data analysis, it was decided to break down the research hypotheses according to treatment conditions for hypothesis testing. A summary of hypothesis testing results is given in Table 10. As indicated in this table, Research Hypothesis 1 was tested separately for slack and tension during heat treatment, Research Hypothesis 2 was tested separately for 110° C - Dry, 110° C - Moist, and 150° C - Dry heat treatments, and

TABLE 9

Effect of Treatment Conditions on Fiber Properties

as Indicated by Least Significant Difference Analyses

Property	Treatment Conditions[a,b,c]						
Tenacity	110 D S	110 M S	C C C	150 D S	110 D T	150 D T	110 M T
Elongation	150 D T	110 M T	110 D T	150 D S	110 M S	C C C	110 D S
Initial Modulus	C C C	110 D S	110 M S	150 D S	110 D T	110 M T	150 D T
Shrinkage	150 D T	110 D T	110 M T	C C C	110 M S	110 D S	150 D S
Tg	C C C	110 D S	150 D T	150 D S	110 D T	110 M S	110 M T
CN/CH	110 M S	110 M T	110 D T	150 D S	150 D T	C C C	110 D S
Dye Uptake	150 D T	110 M T	150 D S	110 D T	110 D S	C C C	110 M S

[a]Arranged in order of increasing mean value of the property.
[b]Conditions underlined with a common line have property means which are not significantly different at the 0.0025 probability level.
[c]110 and 150 are temperatures (°C), M and D are moist and dry heat, S and T are slack and tension, and C is untreated control.

TABLE 10

Summary of Hypothesis Testing

Research Hypothesis	Effect	Fiber Property[a] Tenacity	Elong	Init Mod	Shrink	Tg	CN/CH	Dye
1	Moisture at 110°C							
	Slack	R_e	A	R_e	R_e	A	R_e	A
	Tension	R_e	A	A	R_e	A	R_e	R_e
2	Tension							
	110°C, Dry	A	A	A	A	A	R_e	R_e
	110°C, Moist	A	A	A	A	R_e	R_e	A
	150°C, Dry	A	A	A	A	R_o	R_e	A
3	Temp. of Dry Heat							
	Slack	R_e	R_o	R_e	R_e	R_o	R_e	R_e
	Tension	R_e	R_o	R_e	R_e	A	R_e	R_o

[a]A - Research hypothesis accepted; expected effect was observed.
R_e - Research hypothesis rejected; properties were not significantly different.
R_o - Research hypothesis rejected; opposite effect was observed.

Research Hypothesis 3 was tested separately for slack and tension during heat treatment. Research hypotheses were accepted for a given fiber property if there was a significant difference between values of the properties obtained at the two treatment conditions and this difference was in the direction specified in the research hypothesis. Research hypotheses were rejected for a given fiber property either because the values of the properties obtained for the two treatments were not significantly different (designated Re in the table), or were significantly different but in the opposite direction to that hypothesized (designated Ro in the table).

Research Hypothesis 1 states that fibers heat treated at 110° C in the presence of saturated steam will have higher tenacity, higher initial modulus, higher glass transition temperature and higher dye uptake but lower elongation, lower shrinkage, and lower nitrile group association than fibers heat treated at 110° C, dry.

For this Research Hypothesis, there were fourteen possible acceptances or rejections. Six hypotheses were accepted and eight were rejected, but all eight rejections were because the paired comparisons were statistically equivalent; there were no opposite effects observed. Thus the results of this study are fairly consistent with published information concerning the effect of moisture during heat treatment on the properties of acrylic fibers.

Research Hypothesis 2 states that fibers heat treated under an applied tension of 0.025 gram/denier will have higher tenacity, higher initial modulus, higher shrinkage and higher glass transition

temperature, but lower elongation, lower nitrile group association, and lower dye uptake than fibers heat treated without applied tension. For this Research Hypothesis, there were twenty one possible acceptances or rejections. Fifteen hypotheses were accepted and six rejected; of the six rejected, five were because the paired comparisons were statistically equivalent and only one because the opposite effect to that expected was observed. Literature would have predicted a higher glass transition temperature for fiber treated at 150° C, dry, under tension than for fiber treated at 150° C, dry, slack. Values obtained were 103.5° C for the fiber treated under tension and 106.1° C for the fiber treated slack. The reason for this difference is possibly related to the rapid extension under tension during heat treatment. In general the results of this work are quite consistent with published results concerning the effect of tension during heat treatment.

Research Hypothesis 3 states that fibers heat treated with dry heat at 110° C will have higher tenacity, higher initial modulus, and higher glass transition temperature, but lower elongation, lower shrinkage, lower nitrile group association, and lower dye uptake than fibers heat treated with dry heat at 150° C. For this Research Hypothesis, there were fourteen possible acceptances or rejections. Only one hypothesis was accepted, nine were rejected because the paired comparisons were statistically equivalent, and four were rejected because the observed effect was opposite to that expected. The four cases where opposite effects were observed were elongation, from heat treatments both slack and under tension, glass transition temperature

for heat treatment slack, and dye uptake for heat treatment under tension. Lower elongations were obtained at 150° C, dry, slack than for 110° C, dry, slack (41.9% vs. 45.7%) and for 150° C, dry, tension than for 110° C, dry, tension (30.6% vs. 40.6%). Lower elongation is usually associated with higher tenacity and higher molecular orientation. Higher tenacities and higher initial moduli were actually observed for the 150° C treatments compared to the 110° C treatments, but the differences were not statistically significant, so the hypotheses regarding tenacity and initial modulus were rejected for statistical equivalency rather than for the indicated opposite effect. The results of this study thus are internally consistent, but different from published results. The research hypothesis that dry heat at 110° C would give a higher glass transition temperature than dry heat at 150° C was accepted for fibers heat treated under tension but rejected for fibers heat treated slack, because the Tg at 150° C, dry, slack was higher than the Tg at 110° C, dry, slack (106.1° C at 150° C vs. 102.2° at 110° C). The research hypothesis regarding dye uptake was also rejected for 150° C vs. 110° C, dry and under tension as the opposite effect to that expected according to literature that was observed. The postulated reason for the low dye uptake for this treatment is that the pore structure would be adversely affected by high temperature under tension. The suggested rapid collapse of the fiber upon treatment would also account for the lower Tg value. The results of this study are not in complete agreement with published

results concerning the effect of dry heat treatment temperature. This study tends to suggest stronger effects at the higher temperature (150° C) than at the lower temperature (110° C).

This Research Hypothesis indicating that treatments at 110° C would have a greater effect on properties than treatments at 150° C was based largely on the work of Gupta, et al (21-26). However Gupta's heat treatments were 24 hours in duration, while this study used only five minutes. In the short exposures here, the opposite effects to those predicted by Gupta's work were observed; perhaps the long duration of exposure in his work reversed the trends observed here.

The results of this study generally are in agreement with the literature concerning the effects of moisture and tension during heat treatment on the properties of acrylic fibers. The results are not in agreement with some published work concerning the effect of temperature of dry heat on these properties. Differences may be due to the different comonomers in the fibers in the different studies, and may also be related to the short time exposures used in this study. Dye uptake was found to vary with both Tg and nitrile group association in a manner consistent with the free volume theory for four heat treatments and the untreated control, but two heat treatments gave results which could only be interpreted in terms of the pore model. Thus, it is felt that the results are consistent with the idea that both models are operative in the dyeing of acrylic fibers. The relative contribution of both models could not be estimated from the data obtained.

Implications For Further Study

The results of this study indicate a need for the study of the pore structure of fibers utilizing the electron microscope. An in-depth investigation of the degree of order and crystallinity which affect the physical and chemical properties, especially tensile properties and dye uptake, will also be very informative. Dye uptake of acrylic fibers might be affected by the molecular size of the dye used. Therefore, an investigation of dye uptake in treated and untreated fibers using dyes of different chemical structure, size and bulk will be very helpful in understanding acrylic dyeing behavior. This study revealed that physical properties (tenacity, elongation, initial modulus and shrinkage) were affected primarily by the presence of applied tension during the heat treatment. Therefore, an investigation of the effects using differing amounts of tension is highly recommended.

Boiling of the heat-treated fibers in water may reverse the effect of heat treatment to some degree. Therefore, a study of structural changes which might take place during boiling (for instance in dyeing) can greatly contribute to an understanding of the physical and chemical properties of the fiber under investigation. This study would include an analysis of the relationship between Tg as measured by DSC on dry fiber, Tg as measured in a dyeing experiment where the fiber is immersed in a dyebath (T_D), and CN/CH band ratio before and after heat treatment and after boiling in water.

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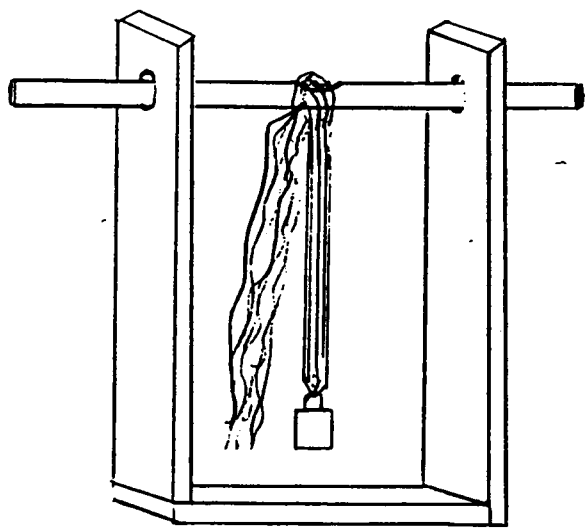
APPENDIX A

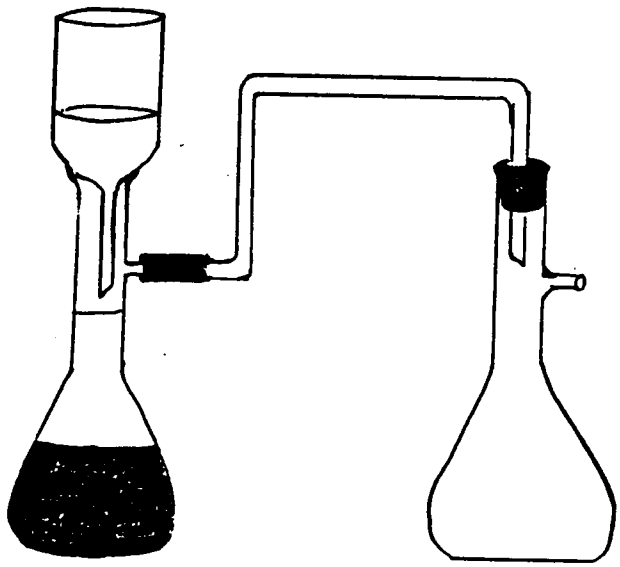
Appendix 1A

Drawing of the Wooden Frame with Fibers



Appendix 2A

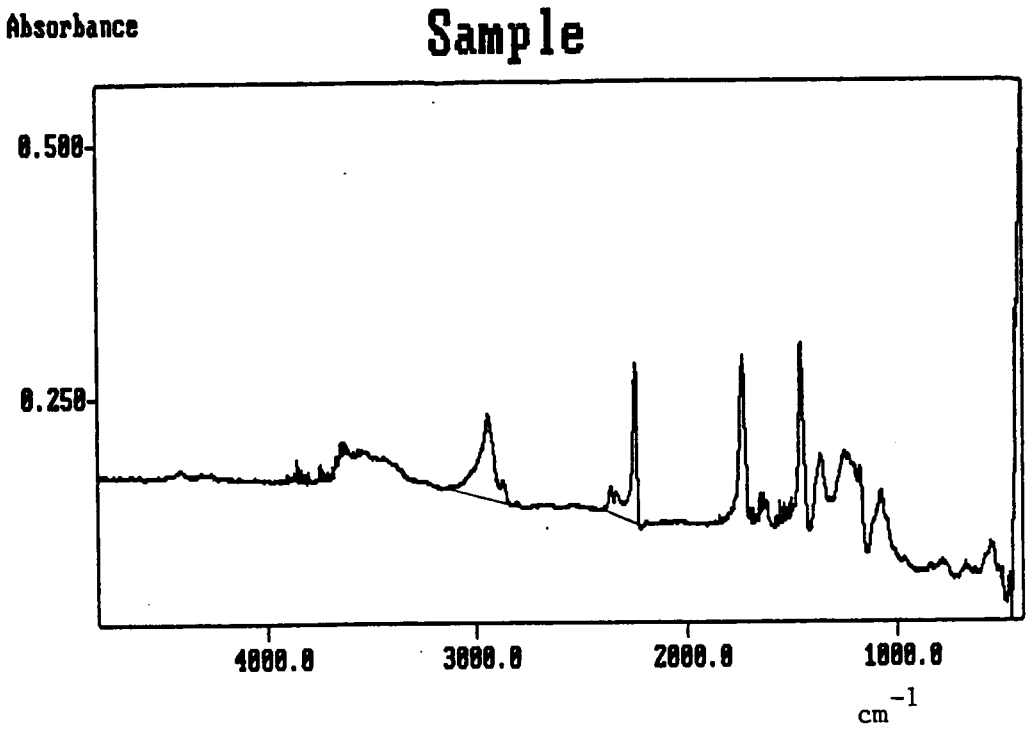
Drawing of the filtration Apparatus



APPENDIX B

Appendix B

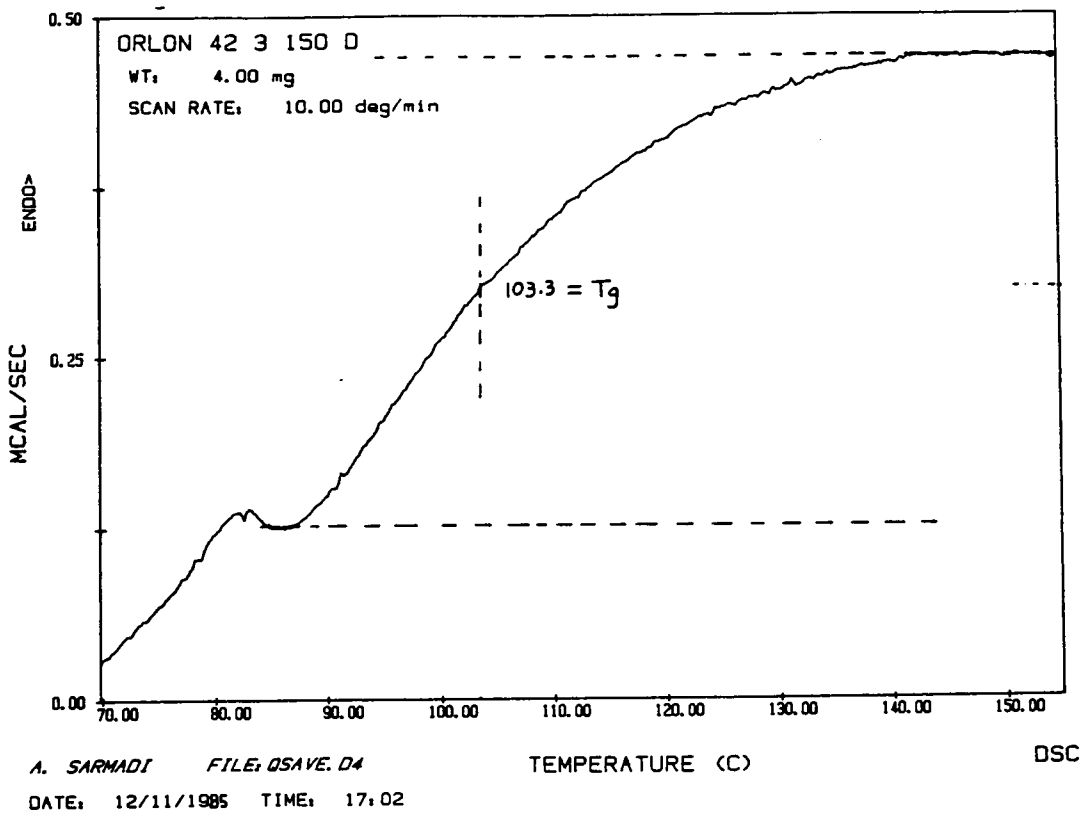
Sample of Infrared Spectrum for Untreated Acrylic Fiber



APPENDIX C

Appendix C

Tg of Heat Treated Fiber at 150° C for 15 Minutes

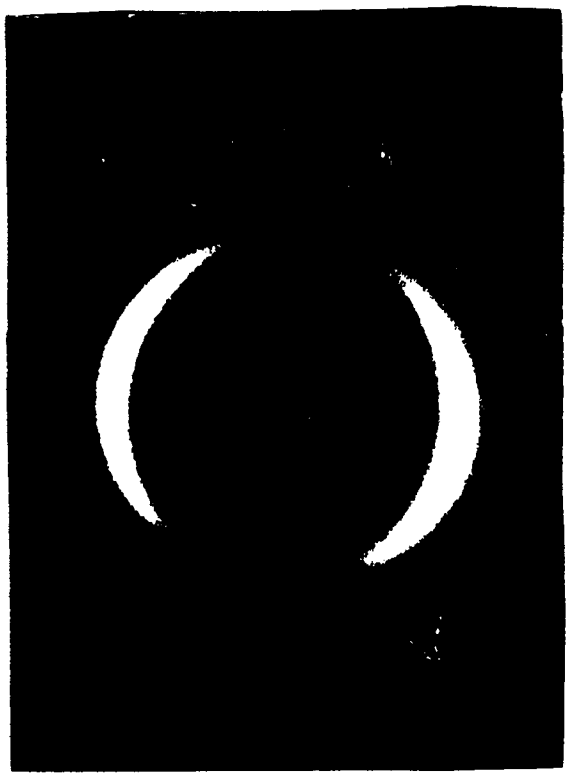


APPENDIX D

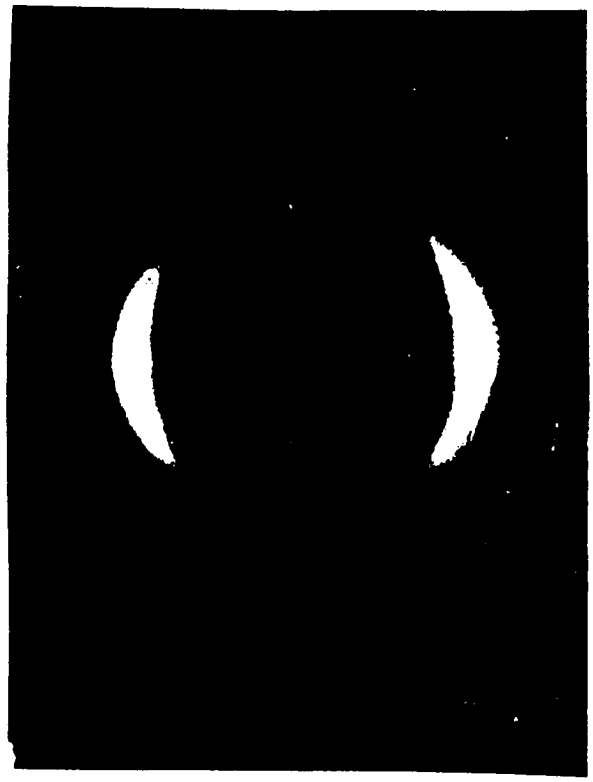
Appendix D

Samples of X-Ray Photograph of Acrylic Fibers:

(a) Untreated Fibers, (b) Fibers Treated at 110° C Under Tension in the Presence of Saturated Steam



(a)

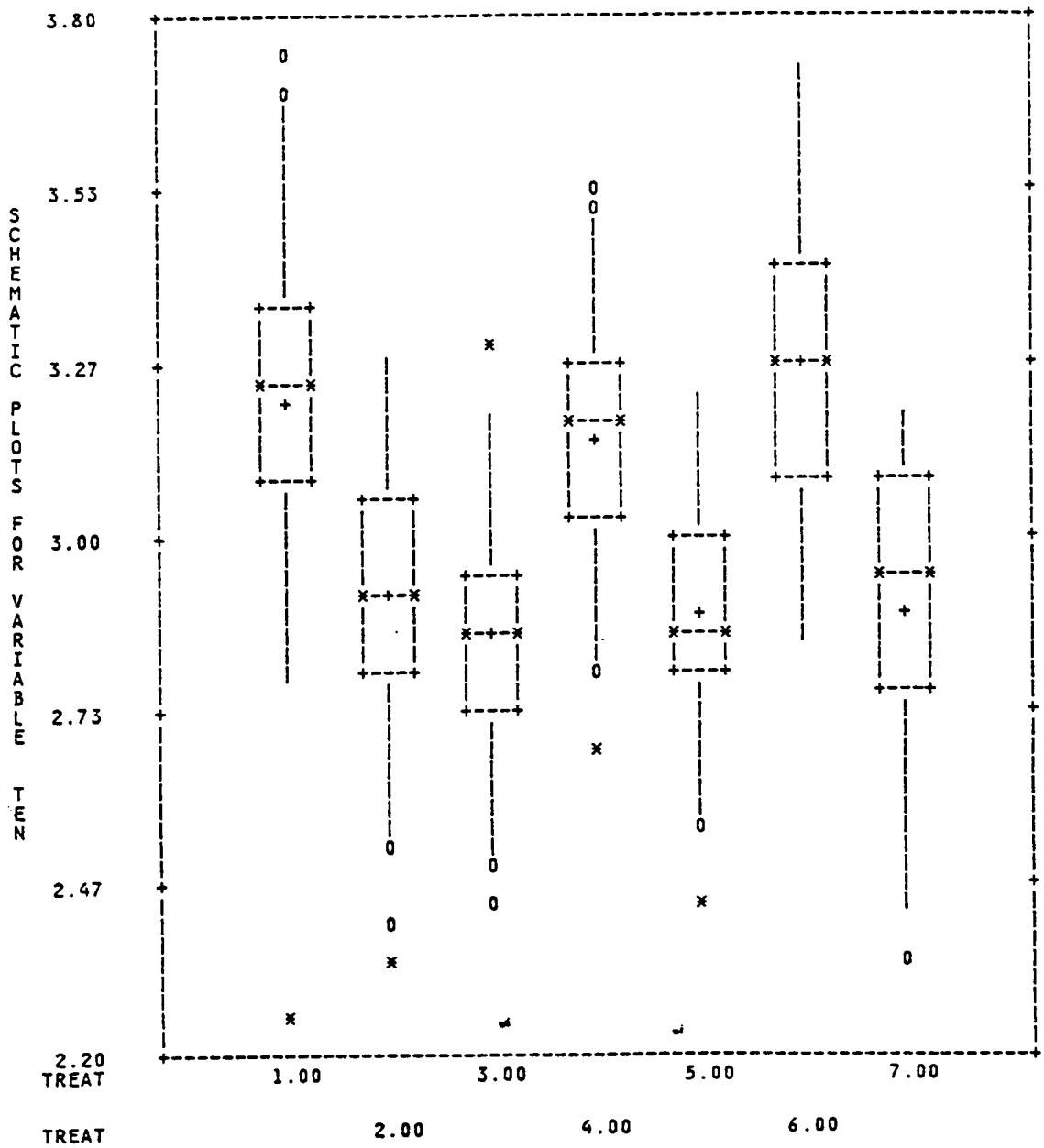


(b)

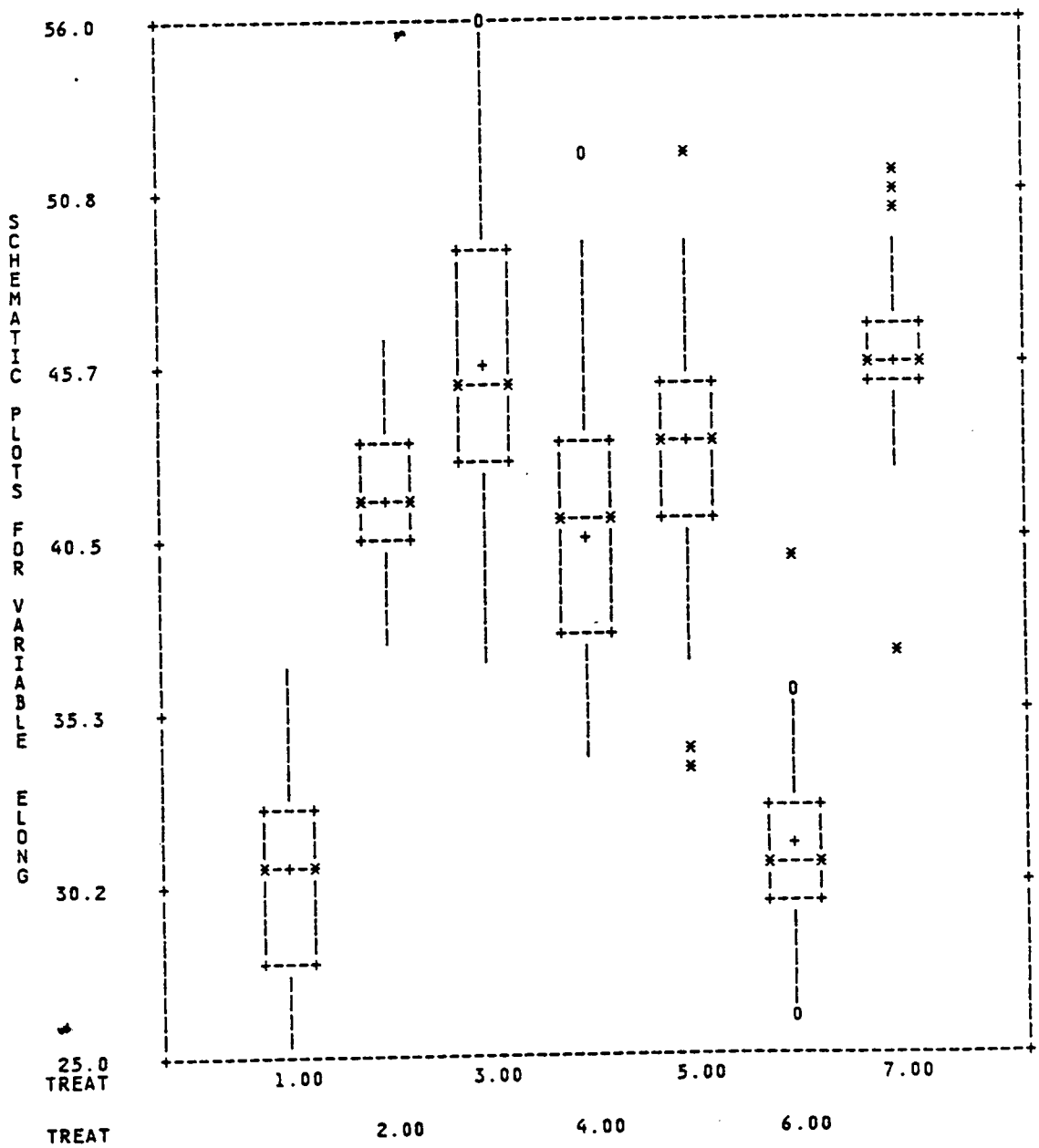
APPENDIX E

Box Plots of the Results for Each Treatment

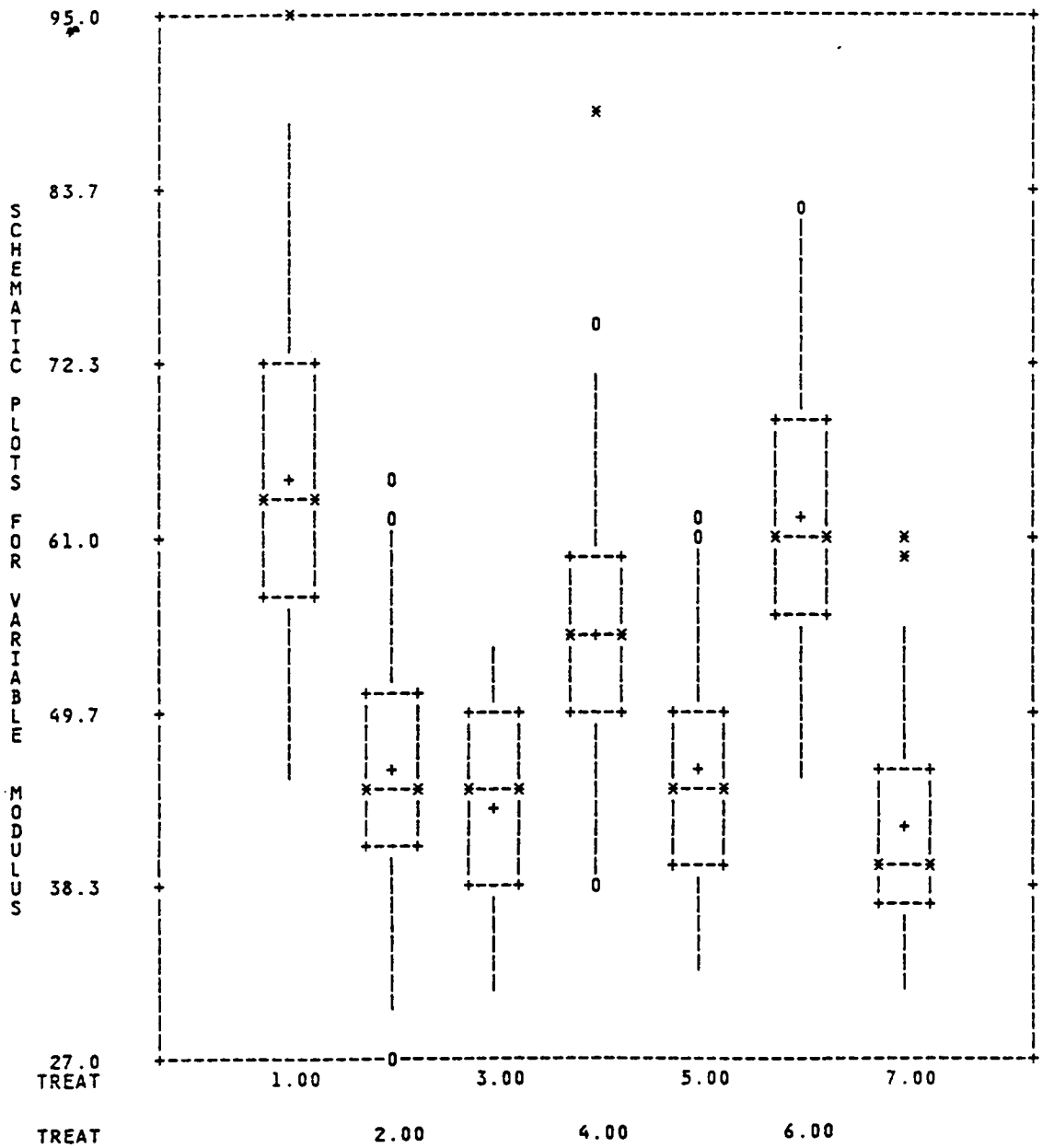
STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOT OF TENACITY BY TREATMENT



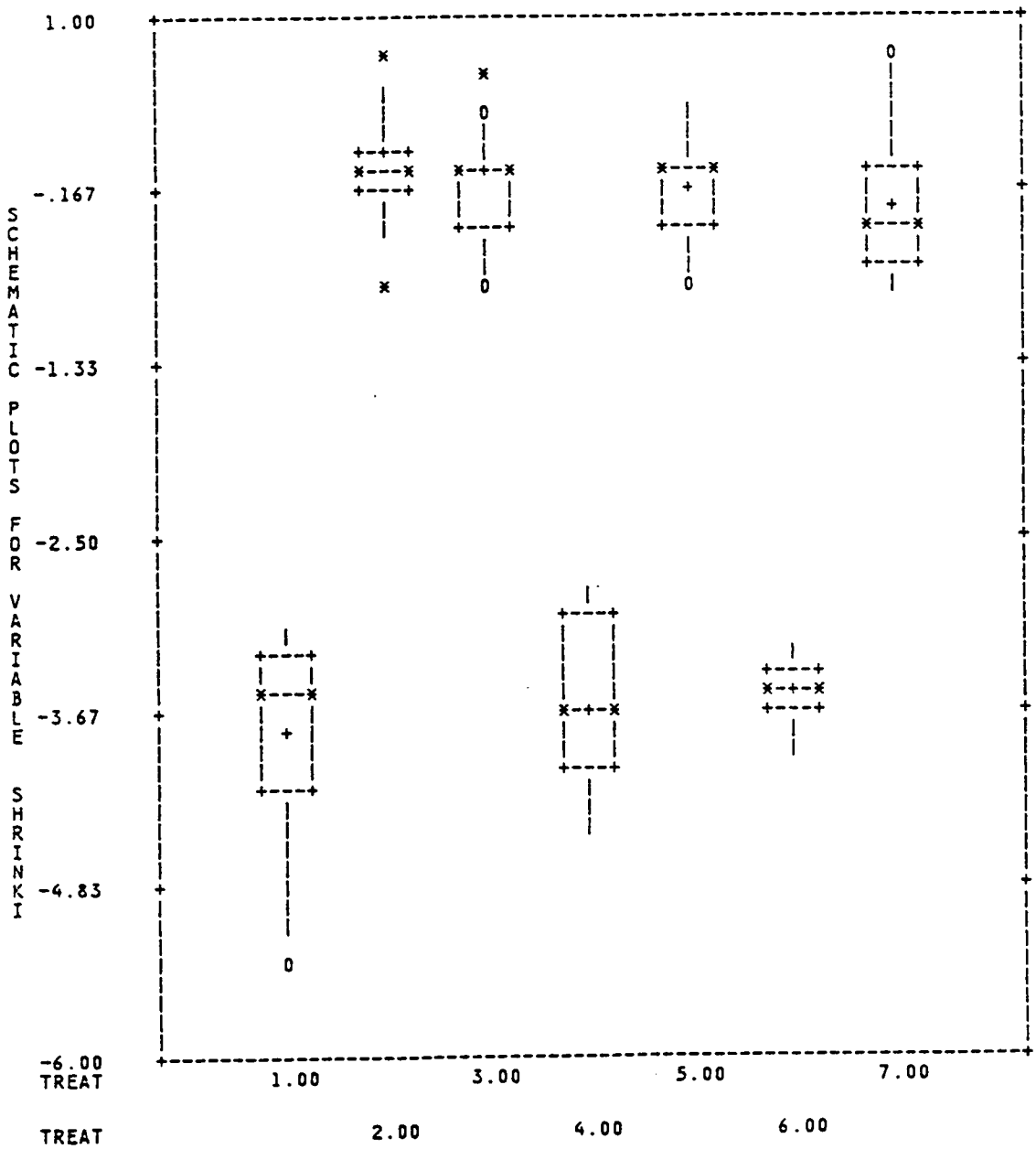
STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOT OF ELONGATION BY TREATMENT



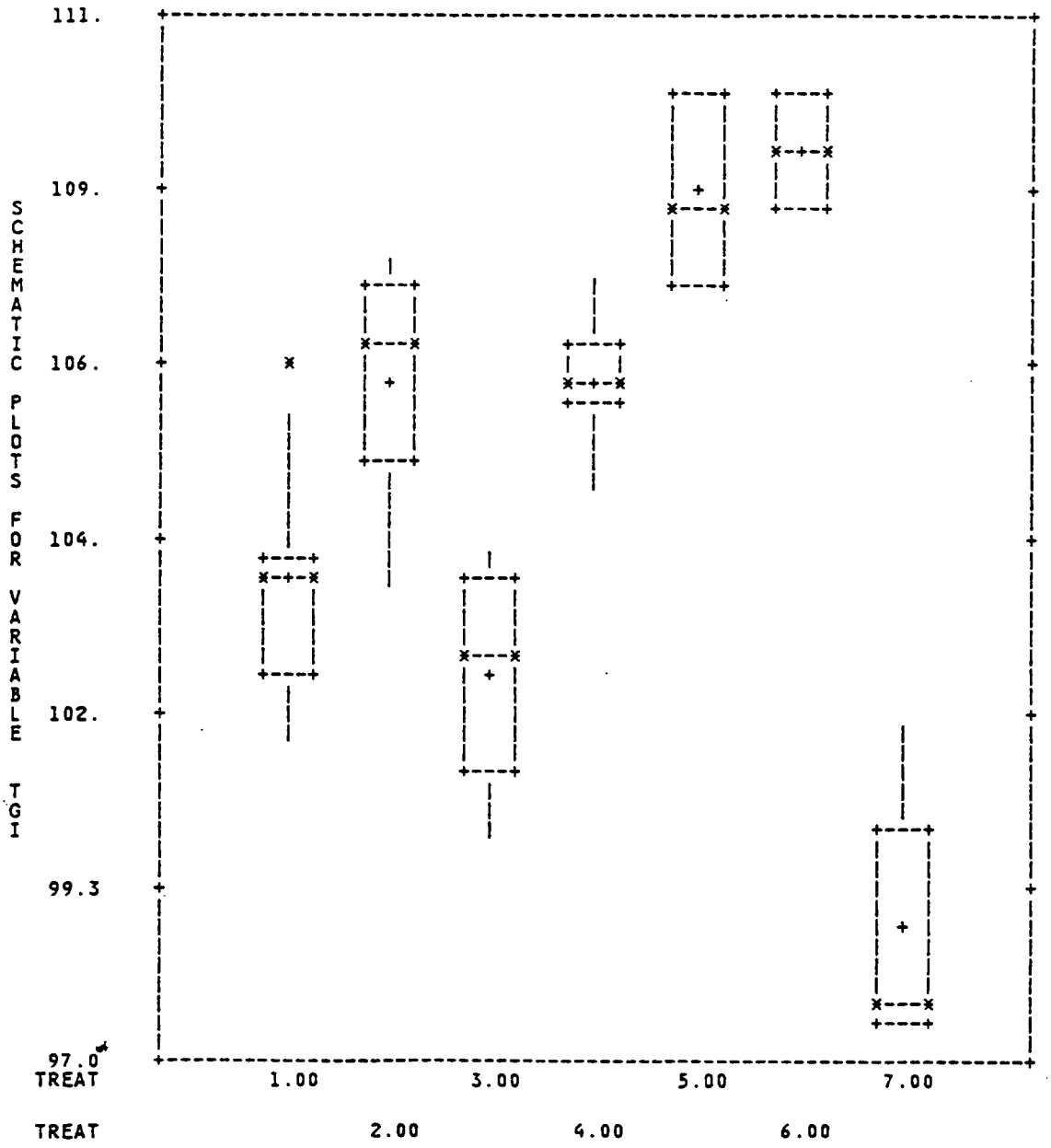
STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOT OF MODULUS BY TREATMENT



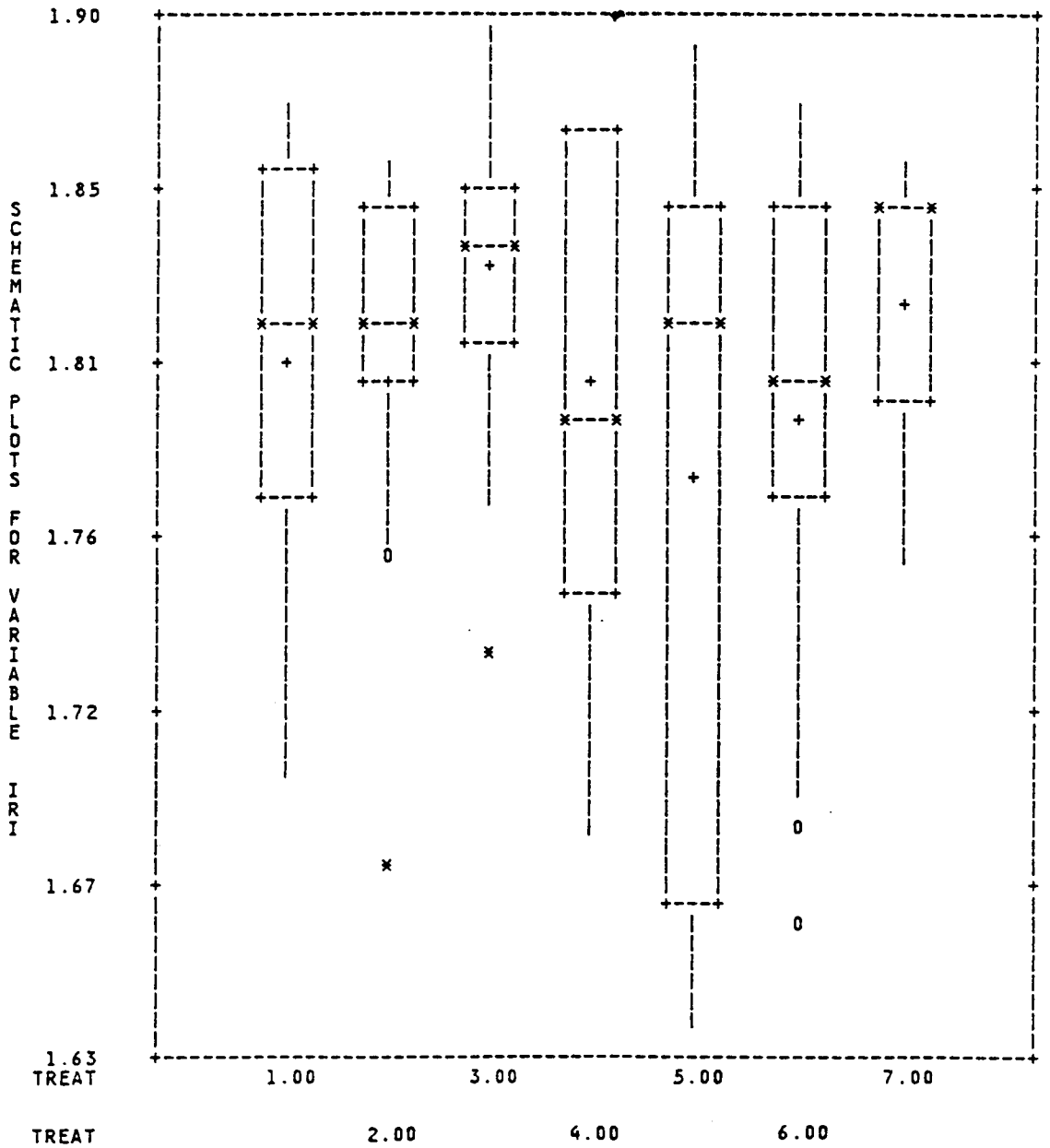
STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOTS OF THE SHRINK DATA BY TREATMENT



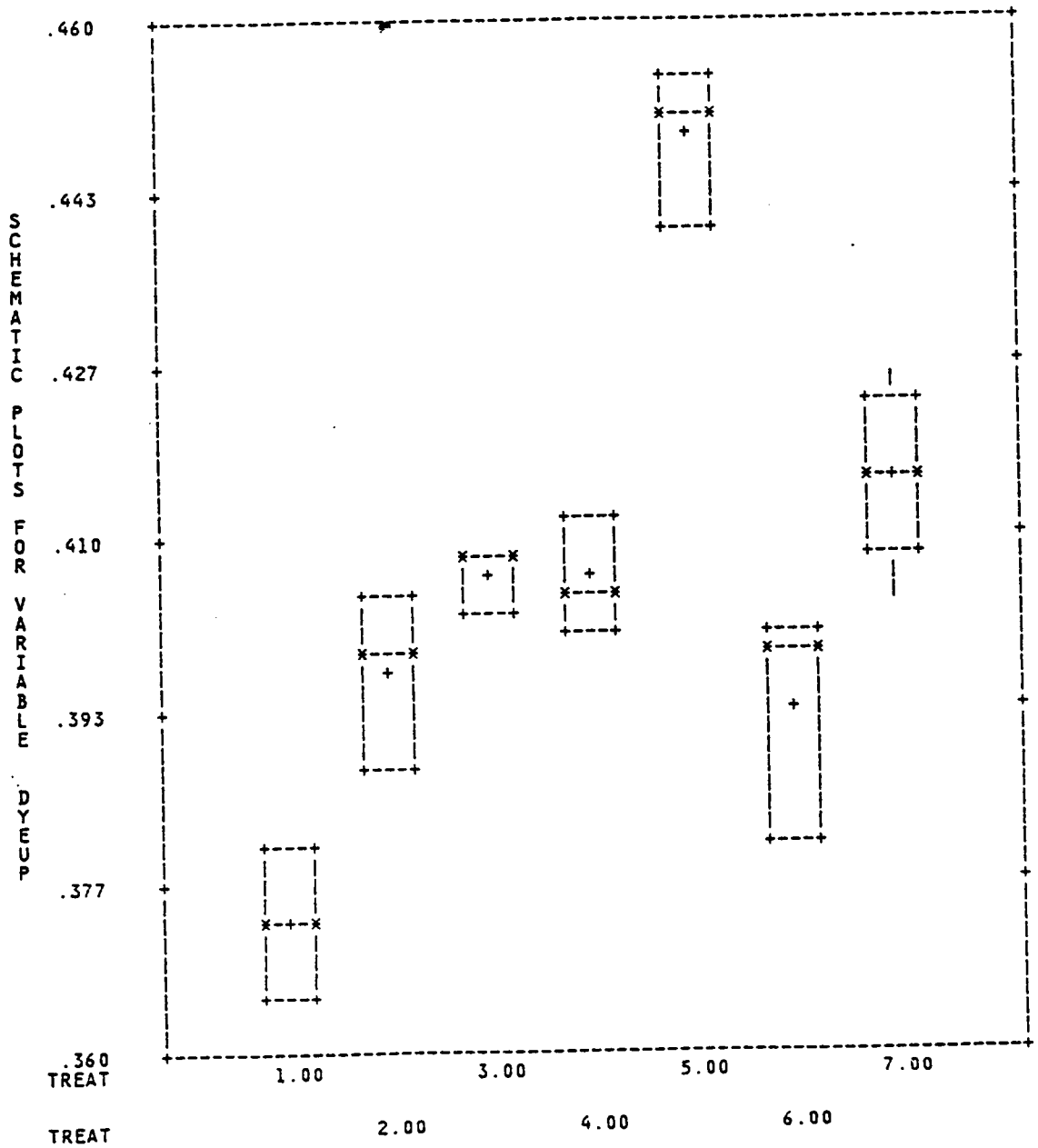
STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOTS OF THE TG DATA BY TREATMENT



STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOTS OF THE IR DATA BY TREATMENT



STATISTICAL ANALYSIS OF DISSERTATION DATA
BOX PLOTS OF THE DYE DATA BY TREATMENT



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