

EFFECT OF HEAT TREATMENT
ON TENSILE PROPERTIES, DYEABILITY AND CRYSTALLINITY
OF NYLON AND POLYESTER FILAMENT YARNS

by

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Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Clothing and Textiles

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June, 1984
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(ABSTRACT)

Changes in nylon 6.6 and polyester filament yarns were determined after heat treatment with dry heat at various temperatures under constant length conditions. An attempt was made to relate structural changes and changes in physical properties due to heat setting.

Density, obtained by the density gradient column technique, was used to calculate the degree of crystallinity as a structural parameter. Filament tensile strength and elongation at break were measured on a constant-rate-of-extension machine, and then toughness of the sample was obtained from the load elongation curve. The amount of dye uptake was estimated spectrophotometrically.

Degree of crystallinity increased significantly as temperature increased for both nylon 6.6 and polyester fibers. Tenacity decreased substantially for nylon 6.6 and increased marginally for polyester. Elongation and toughness at break decreased for both nylon 6.6 and polyester.

Tenacity of nylon 6.6 decreased despite an increase in degree of crystallinity. This suggests degradation of the fibers. Therefore, degree of crystallinity appeared to be of little importance as a contributor to change in tensile strength for degraded nylon 6.6. Tenacity of polyester was well predicted by degree of crystallinity. As crystallinity increased, tenacity of polyester increased. Elongation and toughness of both nylon 6.6 and polyester decreased as degree of crystallinity increased, but the relationship to crystallinity for polyester was not significant. Dyeability of both nylon 6.6 and polyester was well predicted by degree of crystallinity. In both cases, the amount of dye uptake decreased as crystallinity increased.

This research suggests that determinations for structural changes such as degradation and orientation might be utilized in addition to crystallinity to predict tenacity of nylon 6.6 and elongation and toughness of polyester.

ACKNOWLEDGMENTS

The author wishes to express her sincere gratitude and appreciation to her advisor, Dr. Barbara E. Densmore, Professor of Clothing and Textiles, for her advice and encouragement given so generously throughout the study. Appreciation and thanks are extended to the other members of the graduate committee: Dr. Michael L. McGilliard, Associate Professor of Dairy Science, Dr. Charles J. Noel, Professor of Clothing and Textiles, Dr. Marjorie J. Norton, Assistant Professor of Clothing and Textiles, and Dr. Mary Ann Zentner, Associate Professor of Clothing and Textiles.

For their interest and advice in this study, thanks are extended to Dr. Ronald A.F. Moore, Senior Staff Scientist of the Textile Research Institute, Dr. H.-D. Weigmann, Associate Director of Research at the Textile Research Institute, and Dr. Garth L. Wilkes, Fred W. Bull Professor of Chemical Engineering at Virginia Polytechnic Institute and State University.

Special acknowledgment is extended to the E.I. du Pont de Nemours & Company, Inc., Wilmington, Delaware, for providing the yarns, and to the Crompton & Knowles Corporation, Charlotte, North Carolina, for supplying the dyestuff used in this investigation.

The writer would like to thank Dr. Michael A. Ogliauso, Professor of Chemistry and Mr. Robert L. Eagan, graduate student in Chemistry, for their assistance in the distillation of a solvent used for this research.

Grateful acknowledgment is given to her colleagues for their encouragement.

The support and encouragement by the author's family have been deeply appreciated and have made this study possible.

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Chapter I

INTRODUCTION

Heat setting of textile materials has developed in importance since the introduction of synthetic fibers. When thermoplastic fibers such as nylon and polyester are heat set, they become dimensionally stable and resist permanent deformation; thus the resulting fabric or garment will retain its shape and keep the creases which have been put in. This process, accordingly, has been stimulated by the demand for easy care textile items by consumers (24,47).

It is well known (10,59,63,64,65,66,67) that, during the heat setting processes, structural changes take place which affect the subsequent dyeing behavior and the tensile properties of the treated yarns and fabrics. These processes change the molecular arrangement within fibers and consequently bring about altered physical properties, dyeability as well as dimensional stability (24).

The simplest form of heat setting consists of heating an assembly of filaments so as to relax the stresses incurred during the manufacturing processes and to establish a new equilibrium state for the fiber assembly (3). At an elevated temperature, the cross links between the molecules

in the fiber break and reform in the equilibrium positions for the new configuration, and then remain in the structure and tend to bring the fiber back to the same form (47).

However, improper heat setting brings about certain undesirable results such as wrinkles introduced during the washing and drying processes. If fabrics which are improperly heat treated are washed at temperatures above or even close to the glass transition temperature, wrinkles develop throughout. These wrinkles do not disappear on drying and the fabrics require ironing to improve their appearance; thus the easy care properties which synthetic fabrics ought to possess are not realized in practice.

With the increasing use of man-made fibers, especially nylon and polyester, the need for proper heat treatment to impart desirable physical properties and dyeabilities to the treated yarns and fabrics has become very important. Therefore, it is essential to understand and control the structural changes which are brought about by the heat treatment of fibers and highly related with the physical properties of the fibers. In addition, it is useful to consider the heat setting behavior of nylon and polyester fibers together since they are similar in general characteristics.

The purpose of this research was to investigate the effect of heat setting on the tensile properties and the dyeability of nylon 6.6 and polyester filament yarns. The yarns were treated at varying high temperatures with dry heat while in the constant length condition, a treatment analogous to some setting treatments. Furthermore, by obtaining the degree of crystallinity by density measurements, it aimed to relate the tensile properties and the dyeability to the structural changes caused by the heat treatment.

Chapter II

LITERATURE REVIEW

The literature reviewed for this study is divided into four areas which include: structure and heat setting, crystallinity in relation to heat setting, tensile properties in relation to heat setting, and dyeability in relation to heat setting.

Structure and Heat Setting

Man-made fibers such as nylon and polyester are composed of straight long-chain molecules. The structure of nylon 6.6 has alternating segments along the polymer chain, where the $-\text{CH}_2-$ segments are expected to be flexible and the $-\text{CO.NH}-$ groups are associated with one another by hydrogen bonding (6). On the other hand, a polyester, polyethylene terephthalate, consists of alternating units of flexible inert segments and stiff interactive benzene rings (23). As Hearle and Greer (23) pointed out, it is from this that the similarities and differences between nylon and polyester arise.

A typical drawn nylon 6.6 fiber has a possible structure where the chains are essentially extended and more

or less folded (9). The model of the drawn fiber, shown in Figure 1 A, is characterized by relatively randomized dots which represent hydrogen bond positions placed along the chains. When such a drawn fiber is heat treated at higher temperatures under unconstrained conditions, more stable intermolecular bonds are formed and the local order (crystallinity) increases by allowing a recrystallization of folded chains to occur. Thus the number of folded chain segments will increase. This refolding of the chains provides the retractive force producing significant shrinkage in the fiber (9,31).

The model of the heat treated yarn is shown in Figure 1 B. The characteristics of this model include:

- (a) increased crystal perfection,
- (b) many chain-folded sites which increase the porosity of the fiber and would affect dye diffusion,
- (c) relatively few molecules which pass continuously through the structure, thereby reducing the load-bearing ability and lowering the fiber's breaking strength,
- (d) many more defect sites which give rise to fluid-like motion, and
- (e) high orientation of the whole system (24).

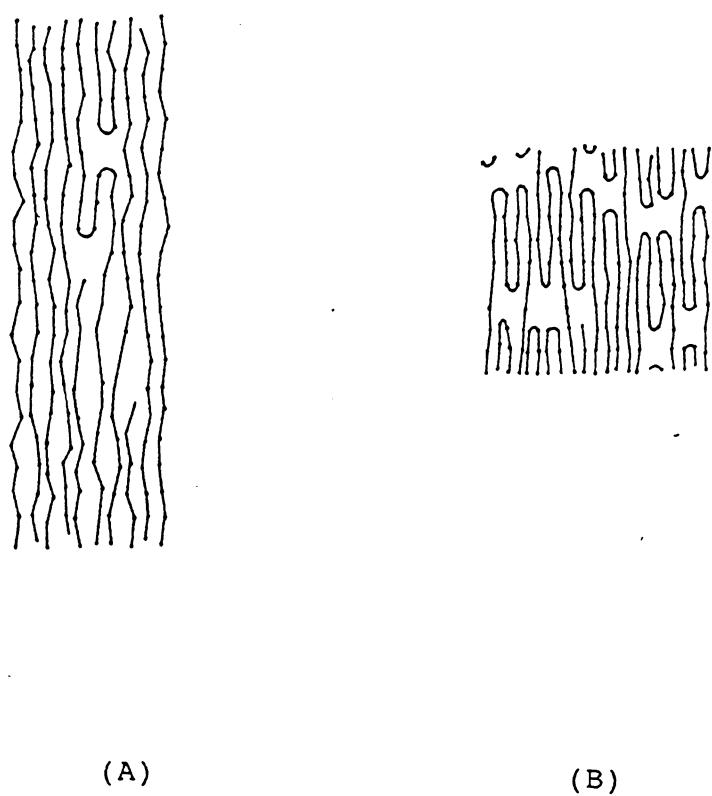


Figure 1: Models of Drawn (A) and heat treated (B) nylon 6.6 yarns

The models for nylon 6.6 shown in Figure 1 are found to be applicable to polyethylene terephthalate from many structural and physical property measurements. As the result of many studies with polyester fibers, there is now little doubt that high temperature treatments cause refolding of chains (24). However, the extent of tension on the fiber during the heat treatment process can greatly alter the amount of refolding. Generally, tension inhibits the refolding process (31).

The structural parameter changes in nylon 6.6 are analogous to those measured for polyester. The main structural difference between nylon and polyester is that the quenched polyester fiber is noncrystalline; crystallization in polyester fibers occurs only on drawing. However, there is no evidence to indicate that the drawn polyester fibers show structural differences when compared with the drawn nylon ones (23).

The structure of the man-made fibers transformed during the drawing process is reformed to give better-defined crystalline regions by subsequent heat treatments. And the treatments presumably have a similar effect on both nylon 6.6 and polyester fibers (23,44,45,46).

According to Venkatesh et al. (63), optimum heat setting involves proper control of four basic factors: the initial high temperature to which the material has to be

raised, the length of time for heat setting, the tension on the material and the rate of cooling. The importance of each of these factors can not be underestimated.

When high temperatures are applied, the molecules of the polymer, which are immobile and lie roughly parallel to the fiber axis, become active and tend to change their configuration. This freedom of movement begins at about 150°C and becomes more pronounced with increasing temperatures. The use of excessive temperatures, however, causes a decrease in fiber strength. Heat setting temperatures greater than 215°C should be used with caution (37).

The time of heat setting can be optimized by considering productivity and the fiber mass. Once an entire fiber mass arrives at a given temperature it is heat set in less than a second. But because it is impossible to tell when the fiber mass has attained the desired temperature, an overall dwell time of 45 seconds to 1 minute or slightly longer time is recommended for hot-air heat treatment (61). However, too long a duration of setting results in lower production rates and a harsh fabric hand (63).

The tension on the material and the rate of cooling are also important. Too much tension or cooling too rapidly results in poor dimensional stability and unsatisfactory

appearance after washing. A cooling process which is too slow, on the other hand, would lower production rates (63).

The literature on heat setting treatments illustrates that the materials are usually heat set in the slack condition (5,9,10,18,21,25,28,50,58,63,68), under constant tension (3,12,63,64,65,66,67) or at a constant length (18,21,63,68) to vary the amount of tension given. If refolding and shrinkage are permitted during the heat treatment, subsequent shrinkage forces are greatly reduced. And, when greater tension is applied, careful heat setting process control is needed.

Heat setting of polyester can be done by the use of steam or dry heat. If steam is used, some hydrolysis of the ester groups within the polyester fiber can occur resulting in a possible loss of strength. Therefore, dry heat setting is nearly always used for polyester (37).

Nylon can be heat set by either wet or dry heat, and the choice is important to the properties of the finished fabric (61). Dry heat setting can result in a decrease in amine end-group content through oxidation at temperatures above about 200°C (50). Therefore, heat treatment of nylon with dry heat over 200°C should be applied carefully.

The effect of steam on polyamide fibers is commonly explained by the concept that water acts like a plasticizer

and thus increasing the segment mobility of the polymer molecules. Steaming also opens the structure and provides for better dye uptake and diffusion.

Crystallinity in Relation to Heat Setting

Polymer molecules in the solid state have a tendency to aggregate into a semicrystalline state. The crystallizing ability is determined by the chemical configuration and the regularity of the structure, by the presence of active groups able to form secondary interlinkages such as hydrogen bonds and by the molecular flexibility (35,52).

The presence of crystallinity in polymers strongly influences their properties. Since the polymer chains are more tightly packed in the crystalline areas than in the amorphous areas and are in close and regular contact over relatively long distances in the crystallites, the net forces holding them together are far greater than in the amorphous areas. Thus crystallinity can significantly increase the strength and rigidity of a polymer (33).

If thermoplastic fibers are heat set they experience such effects as variation in crystallinity, orientation, fluid-like segmental motion and sonic modulus. The degree of crystallinity can be investigated by various methods, such as density measurements, X-ray diffraction techniques,

infrared spectroscopy and thermal analyses. The orientation changes can be detected by methods such as birefringence measurements and X-ray measurements. The segmental motion that exists in a fiber when it is thermally activated can be measured by the NMR (Nuclear Magnetic Resonance) technique. Sonic modulus methods are used to find defect sites in the structure (4,27,38,41,47,51,63).

Changes in the degree of crystallinity of nylon and polyester yarns have been investigated by the various methods mentioned above (5,9,12,16,18,19,25,43,57,65). High temperature heat treatments, in general, increase the crystallinity whenever synthetic fibers are heat treated at temperatures above that of their previous treatment (24).

Density is the most basic macroscopic quantity of a crystalline material (69), and in fact a convenient measure of the degree of crystallinity (52). Both nylon and polyester increase in density when heated; thus extent of crystallinity also increases with density (18,33,65). This suggests that a more closely packed fine structure is formed as the result of heat setting. Density yields an immediate correlation with the structural morphology and conformational array of the polymeric molecules (23). Polymers used in fibers usually have regions that are well ordered and others that are not. Areas of high order are

generally considered to be in stabilized lattices. Disordered regions are not as stable. The more stabilized lattice has a higher density than the disordered region. Heat treated yarns have a larger portion of the stabilized area than the untreated ones. Therefore, a density measurement will serve as an indication of the degree of crystallinity (23).

It is assumed that a semi-crystalline polymer consists of two separate and distinct phases: a purely amorphous phase and a purely crystalline phase. Experimental values of the densities of semi-crystalline polymers lie somewhere between the crystalline and amorphous densities (69).

On the basis of the two-phase assumption, semi-crystalline density can be expressed as the sum of contributions from each phase in proportion to its weight fraction. The simple derivation can be written as follows (69):

$$\text{Total volume} = W_t/\rho_t = W_a/\rho_a + W_c/\rho_c$$

$$\text{Partial weights: } \beta_a = W_a/W_t \text{ and } \beta_c = W_c/W_t$$

$$\text{then } 1/\rho_t = (1 - \beta_c)/\rho_a + \beta_c/\rho_c$$

$$\text{or } \beta_c = \frac{\rho_c (\rho_t - \rho_a)}{\rho_t (\rho_c - \rho_a)}$$

Thus the weight fraction percent crystallinity can be expressed as:

$$\frac{\rho_c (\rho_t - \rho_a)}{\rho_t (\rho_c - \rho_a)} \times 100$$

where ρ_t = density of sample

ρ_c = density of 100% crystalline material

ρ_a = density of 100% amorphous material.

Crystallinity is, as illustrated in the above equation, an increasing function of density.

Gupta and Kumar (18) obtained the degree of crystallinity from density by using the foregoing equation. They reported that the crystallinity of polyester increased with an elevation of the heat setting temperature. Moore and Weigmann (43) also calculated the sample crystallinity by the density-crystallinity equation. Warwicker (65), however, obtained the percent crystallinity by utilizing different density-crystallinity relationships. But he also observed that the crystallinity increased with an increase in the heat setting temperature.

Venkatesh et al. (63) state that heat setting may result in a decrease in the orientation of the molecular

chains in the amorphous region of the fibrous material, but this is accompanied by a significant increase in the total crystallinity of the sample, irrespective of the conditions under which it is heat set.

In other research the crystallinity of nylon 6 filaments was measured using wide angle X-ray diffraction and infrared spectroscopy (19). The authors found that crystallinity increased as the heat treatment temperature rose.

Thermal analysis techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermomechanical analysis used to obtain the quantity of crystallinity are described in several references (25,30,57). However, they are not directly related to the heat treatment of fibers.

Heuvel and Huisman (25) studied the effect of winding speed on the structural changes of polymer fibers. The authors concluded from DTA measurements that the physical structure of the fibers changed from amorphous to semicrystalline with increasing winding speeds, but the amount of crystallinity could not be obtained from the DTA measurements because of the uncertainties with respect to the course of the baseline.

Simpson, Southern and Ballman (57), studying nylon 6.6 fiber properties as a function of morphology, utilized the DSC technique. Several samples were selected which had quite different tenacity and elongation values. In spite of this, they found that the crystalline contents were not significantly different for the limited range of samples available.

Tensile Properties in Relation to Heat Setting

A two-way relationship exists between physical properties and structure. In other words, the physical properties can be regarded either as evidence in determining the structure or when the structure is known, as being explained by it (22,23,38,47).

Factors influencing tensile properties may include crystallinity, orientation, molecular weight and size of morphological units. The effect of crystallinity on tensile properties has been assessed more on a qualitative basis than on a quantitative basis. Quantitative data on the effect of crystallinity are hard to obtain since it is difficult to isolate the effect of crystallinity from the effect of differing orientation, molecular and morphological variations in fibers (34,35)

If thermoplastic fibers such as nylon and polyester are exposed to temperatures in excess of their glass transition temperatures they shrink. Shrinkage occurs because stresses and strains introduced during the spinning and drawing processes are relaxed. If sufficient energy is made available to the polymer system, segments recrystallize into a structure with higher crystallinity, resulting in a partial or complete removal of the initial stresses and strains (63). As a result of heat treatment, the physical properties and dimensional stability of the fibers are altered.

The effect on the tensile properties of nylon and polyester fibers which are subjected to a high temperature heat treatment varies according to the experimental conditions. Several researchers (10,59,63,66,67) have shown the effect of heat treatment on the tensile properties of nylon and/or polyester.

Dismore and Statton (9) found that nylon 6.6 , in a slack condition, showed a drastic loss in strength occurring at about 230°C. This change in strength was accompanied by severe shrinkage. The elongation at break for the fiber was lowered by increasing the heat treatment temperature. Dumbleton (10) studied the tenacity of polyester fibers, also heat treated under slack conditions. Tenacity

decreased sharply after high temperature treatments, as in the case of nylon 6.6.

Venkatesh et al. (63) studied the tensile properties of nylon and polyester filament yarns after heat setting under slack tension and at constant length. They found that the breaking strength of nylon 6.6 and polyester remained constant over a wide range of heat treatment temperatures up to 240°C when treated under slack tension, but, under constant length condition, the breaking strength decreased. The elongation at break of both nylon 6.6 and polyester, when treated under slack tension increased by about 1-2.5 times the control value, but heat setting at a constant length produced a decrease in the case of nylon 6.6 and a marginal increase in the case of polyester. The initial modulus, however, decreased irrespective of the heat setting conditions.

Warwicker (66,67), in two studies on the structural causes of dyeing variations of nylon 6.6 and polyester yarns under constant tension of 7g, found the following: (a) the tenacity of nylon 6.6 yarn was slightly improved by the heat treatment but the breaking extension was reduced, (b) the initial modulus of nylon was improved but the toughness at the breaking point was reduced as the temperature was increased, (c) the tenacity and the toughness of the

polyester yarns were reduced as the temperature increased, (d) the elongation of polyester was increased by heating, and (e) the initial modulus was reduced for all the treated samples.

Dyeability in Relation to Heat Setting

The dyeing of polyester and polyamide fibers with disperse dyes has attracted considerable attention (54,55). Disperse dyes are a class of water-insoluble dyes originally introduced for cellulose acetates, usually applied from fine aqueous suspensions (48).

In dyed fibers, the disperse dyes are present chiefly in the monomolecular state (29). The disperse dyeing process can be described as follows (48):

- (a) some of the dye dissolves in the water of the dyebath,
- (b) molecules of dye are transferred from solution to the surface of the fiber,
- (c) the solution in the dyebath is replenished by the dissolution of more solid material from the dispersion,
- (d) the adsorbed dye diffuses monomolecularly into the fiber.

Synthetic fibers are generally considered to consist of three states of order in the constituent macromolecules: crystalline, semicrystalline and amorphous regions. During dyeing, it is assumed that dyes penetrate only the amorphous and semicrystalline portions of the fiber. The relative ratios and nature of the three states within the fiber are subject to manipulation through fiber orientation during manufacture and subsequent heat treatment (56).

Heat treatment of fibers can greatly influence the rate of dye absorption and the location of dye in the fiber. When nylon 6.6 yarns are heat set, the rate of dye uptake with direct, disperse, acid and metallized acid dyes varies. Heat setting of polyester also affects the dyeability of polyester with disperse dyes (56).

Changes in dyeing rate are attributed to differences in the internal morphology of the fiber such as the ratio of crystalline to amorphous areas and in the glass transition temperature (49,56,42).

Peters and White (50) stated that when nylon 6.6 yarns are subjected to dry heat, the physical fine structure of the yarns is altered and the effect of the heat treatment on dyeing with a particular dye depends on the sensitivity of the dye to the structural variations in the yarns. In addition, steam-induced heating of nylon has a markedly

different effect than dry heat due to the carrier-like action of moisture within nylon (56).

More detailed information is available on the effect of both dry heat and steam heat treatment on the dyeing behavior of nylon 6.6 (64,66) and polyester (11,39,65,67,68). The results of published works show that heat treatments of nylon and polyester at temperatures up to a certain point cause a decrease in the equilibrium uptake and rate of dyeing for all the classes of dyes investigated.

Again, Peters and White (50) showed that dry heat setting resulted in a decrease in the equilibrium uptake of acid, disperse and metal complex dyes in nylon 6.6 at a temperature of 200°C. The rate of dyeing rose rapidly at higher temperatures because of an increasing tendency for structural changes to occur before actual fusion of the polyamide. Results obtained by Warwicker (64) showed that the rate of dyeing of nylon 6.6 with a direct dye fell at first and then increased with higher heating temperature.

According to Warwicker (65), the uptake of disperse dyes by heat-set polyester initially decreased as the temperature of preheating was raised. But, at higher temperatures, the dye uptake increased with a rise in temperature and could be greater than that of the untreated control. Similar effects were noted for other polyesters and dyes by a couple of other researchers (20,40).

Warwicker (65), in the study of the dyeing properties of polyester yarn subjected to heat treatment, stated that the dye uptake of polyester yarns could be characterized by a constant defined as the uptake divided by the square root of time (A/\sqrt{t}), as in equations for diffusion. Also reported was that the constant was found to decrease to a minimum with an increase in the temperature of dry heat and then to increase to a value greater than that for the untreated yarn at high temperatures.

As mentioned previously, under normal setting conditions, the aqueous dyeability of heat set fibers is less than unset ones. But, when set within the range of 200-249°C, even though it is different according to the heat set condition and fiber type, a sharp increase in dyeability occurs. However, because of the critical control required in operating in this elevated temperature range, it is not recommended for a practical heat setting operation (61).

In a study of the effect of heat setting and draw ratios on the diffusion of a disperse dye in a polyester, Dumbleton, Bell and Murayama (11) suggested that the diffusion was controlled by the mobility of polymer-chain segments. Mobility could be indicated by a measurement of the glass transition temperature which depends on the crystallinity, orientation and other structural features.

Merian et al. (39) demonstrated other indications of the rate of dyeing besides the uptake of dye in a given time of dyeing under standard conditions. One of the indications was the diffusion coefficient of the dye within the fiber.

The temperature of the dyebath is important in the study of dyeability using heat treated samples. According to Weigmann et al. (68), the dyeing temperature should be based on the assumption that the temperature would be appropriate to reveal the effects of structural modifications on dyeing behavior and therefore would be suitable for comparative evaluations. It takes more than 20 hours (68) to obtain an equilibrium dye uptake; such prolonged dyeing times can result in a change in the structure of the fiber and this change might obscure the structural effects of the original heat treatment (65). Therefore, such a comparison should be based on a dye uptake after a predetermined and constant dyeing time.

Weigmann et al. (68), in the study of the dyeability of polyester yarns after heat treatment, compared the relative dye uptake of specimens treated under constant length conditions with those treated under slack tension. A decrease in relative dye uptake at lower temperature was observed for both yarns treated under slack conditions and constant length conditions. In contrast to the considerable

increase in relative dye uptake shown by unrestrained samples at temperatures above 180°C, a very moderate increase in relative dye uptake at very high temperatures was noted for samples treated under constant-length conditions.

The chemical nature of the fibers has little or no direct effect on the dyeing of nylon and polyester using a disperse dye, thus the variation of uptake along with heat treatment is due to structural differences (65). Therefore, the decrease in amine end-group content in nylon by dry heat setting mentioned earlier does not make much difference in the dyeing behavior when a disperse dye is used. This may affect the dyeability of the fiber when a dye which reacts with the end-group is used.

Amount of dye uptake of fibers can be estimated spectrophotometrically. According to Bouguer, Lambert and Beer's Law, the absorption of light in passage through any medium is proportional to the number of absorbing molecules in its path. The mathematical formula is, therefore, as follows (13):

$$\log (I_o/I_t) = e \cdot c$$

where I_o = intensity of the light entering the medium.

I_t = intensity of the light leaving the medium.

e = a constant (the molar extinction coefficient).

l = the thickness of the absorbing medium.

c = the molar concentration of absorbing substance.

The term $\log (I_0/I_t)$ is called absorbance, extinction or optical density, and has a linear relationship with the molar concentration of the absorbing substance. General concepts and procedures for the spectrophotometric analysis are available in the literature (13,32,60).

In summary, it can be seen that heat treatment provides better-defined crystalline regions to both nylon and polyester fibers. Structural change of fibers due to heat treatment can produce changes in physical properties and dyeability.

Chapter III

STATEMENT OF PROBLEM

This chapter is divided into the following sections: theoretical framework, experimental design, objectives, hypotheses, assumptions and limitations and definitions of terms.

Theoretical Framework

Nylon 6.6 and polyester do not show any significant difference in the structure of drawn fibers (23). However, subsequent heat treatment of the drawn fibers may result in somewhat different structural changes, which will result in different tensile properties and dyeability.

Normally, heat setting of a thermoplastic polymer system is thought to occur through a rearrangement of the polymer systems resulting in an increase in tenacity (17). However, the effect of heat treatment on the tensile properties of nylon 6.6 and polyester fibers varies according to the experimental conditions.

Under slack tension, according to some studies, nylon 6.6 shows a drastic loss in strength occurring at about 230°C and a continuous decrease in elongation at break.

Polyester also shows a sharp decrease in strength at a high temperature (9,10). Another study, however, shows that tenacity of nylon 6.6 and polyester remains constant over a wide range of temperatures up to 240°C and elongation of nylon and polyester increases by about 1-2.5 times (63).

On the other hand, under constant length conditions, tenacity of nylon and polyester decreases slightly over a wide range of heat treatment temperatures up to 240°C, and elongation at break of nylon 6.6 decreases and that of polyester increases marginally (63).

Under constant tension conditions (66,67), the tenacity and the initial modulus of nylon 6.6 yarn are slightly improved by the heat treatment. The other properties such as elongation and toughness at break show decreasing tendencies. But the tenacity, toughness and initial modulus of polyester fibers decrease and the elongation of the fibers increases.

Therefore, it can be said that the toughness at break and the initial modulus tend to decrease irrespective of the heat setting conditions. But, the tenacity and the elongation differ according to the heat setting conditions.

Heat treatments of nylon and polyester at increasing temperatures up to a certain point cause a decrease in the equilibrium dye uptake irrespective of the conditions under which the filaments are heat set. The dye uptake then rises

rapidly when the fiber is heat set within the range of 200-248°C because of an increasing tendency for structural changes to occur before actual fusion of the fibers (11,39,50,61,64,65,66,67,68). The temperature where the dye uptake rapidly rises is 200°C for both nylon 6.6 and polyester fibers in the case of constant tension conditions (66,67).

Heat treatments increase the crystallinity of the fibers whenever the fibers are heat set at temperatures above that of their previous treatment. The changes in the degree of crystallinity of nylon and polyester can be investigated by density measurement. As crystallinity is an increasing function of density, the amount of crystallinity increases as does the density (18,65). If a material is heat set, it experiences such effects as variation in crystallinity, orientation and molecular size.

The increase in crystallinity may explain the decrease in dye uptake at lower heating temperatures, but it does not explain the subsequent increases of dye uptake with increase in the temperature of heat setting (64,65). Also, it does not explain the decrease of tenacity and the increase of elongation. Even though the increase in crystallinity does not explain this completely, the significant increase in the crystallinity of the sample can still be a factor affecting fiber properties.

Experimental Design

One of the independent variables for this study was heat setting temperature. The other important factors (time, tension, and cooling rate) in heat setting were held constant. A second independent variable was fiber type. In order to concentrate on the effect of heat treatment on the type of fiber, factors such as denier, the number of filaments and cross sectional shape of fibers were held constant.

Therefore, this research utilized a repeated factorial design or a split-plot design with subsampling (14,26). It contained two factors; one was fiber type and the other, heat treatment temperature. Fiber type had two levels and the heat treatment temperature had eight levels including an untreated one. The design is shown in Table 1.

Each cell represents the interaction between each level of the factors. For the combination of each level of the factors, two replications were obtained; from each replication a fixed number of observations were obtained for the dependent variables, i.e. tensile properties, dyeability and density. The number of subsamples for each dependent variable was as follows: tenacity, elongation and toughness, 11; dye uptake, 2; density, 3.

TABLE 1
Diagram of Design

Objectives

The objectives of this study were:

1. To determine how type of fiber (nylon vs polyester) affects the tensile properties, dyeability and the degree of crystallinity of heat treated filament yarns.
2. To determine how heat treatment temperature affects the tensile properties, the dyeability and the degree of crystallinity of the filament yarns.
3. To determine if there is any interaction between fiber type and heat treatment temperature on the tensile properties, the dyeability and the degree of crystallinity.
4. To study relationships between the tensile properties and the degree of crystallinity, and between the amount of dye uptake and the degree of crystallinity.

Hypotheses

On the basis of the objectives, the following null hypotheses were developed:

$H_0(1)$: Type of fiber has no effect on the tenacity, elongation, toughness at break, the amount of dye uptake and the degree of crystallinity.

$H_0(2)$: Heat treatment temperature has no effect on the tenacity, elongation, toughness at break, the amount of dye uptake and the degree of crystallinity.

$H_0(3)$: There is no interaction effect between fiber type and heat treatment temperature on the tenacity, elongation, toughness at break, the amount of dye uptake and the degree of crystallinity.

Assumptions and Limitations

For this study the following assumptions were made:

1. That the prior drawing and thermal histories of the nylon and the polyester yarns are essentially the same.
2. That the transition temperatures of the nylon and the polyester are essentially the same.
3. That the tension used to wind specimens on the frame is essentially the same.
4. That the measurement techniques used to obtain data are sensitive enough to show differences.

This study was limited to the effect of heat treatment on the degree of crystallinity, tensile properties and dyeability for selected specimens of nylon 6.6 and polyester, which had a constant denier and number of filaments. Also, the specimens were held at constant length during the heat treatment which may be different from specimens heat treated in a slack position or under constant tension. The heat treatments were applied for three minutes using dry heat, the results of which may be different from

those done for shorter or longer periods of time and by using steam heat.

Definitions of Terms

Crystallinity - The local regular and ordered alignment of molecules or parts of molecules so that the crystalline assembly of molecules can behave as a unit. It is quantified by a density-crystallinity function (16,51)

Density - The weight per unit volume of material at 21° ± 1°C, expressed as g/cm³ and measured by the density-gradient technique (47).

Dye uptake - The amount of dye taken up by a fiber in 90 minutes at 90°C in units of mg of dye/g of dyed fiber (64).

Elongation at the breaking load - The increase in length of a specimen at breaking point during a tensile test, expressed as a percentage of the nominal gauge length (1).

Infinite dyebath - The dyebath in which no appreciable change in concentration of dye occurs during dyeing (13).

Standard Atmosphere - The atmospheric conditions of 65 ± 2% relative humidity and 21 ± 1°C (1).

Tenacity, breaking - The tensile stress (expressed as force per unit linear density of the unstrained specimen) applied to a specimen in a tensile test carried to rupture (1).

Toughness, breaking - The actual work per unit volume of material that is required to rupture the material. It is proportional to the area under the load-elongation curve from the origin to the breaking point (1).

Chapter IV

PROCEDURE

The procedure is divided into the following sections: test specimens, heat treatment method, measurement of tensile properties at break, dyeing experiments, estimation of dye uptake of samples, density measurements, calculation of degree of crystallinity and statistical analysis of data.

The test specimens were first heat treated at different temperatures. Then the tensile properties of the treated and untreated specimens were measured. For the dye uptake measurement, the heat treated and the untreated control samples were dyed and then the amount of dye taken up was obtained spectrophotometrically. Also, density measurements were done for both treated and untreated specimens and the degree of crystallinity was obtained from the density data.

Test Specimens

Nylon 6.6 and polyester multifilament yarns were used which were commercially available drawn yarns furnished by E. I. du Pont de Nemours & Company. Both yarns were 100/34, that is, 100 denier and 34 filaments. The filaments had round cross sections and were semidull. The nylon had a slight Z twist and the polyester was Rotoset[®].

Heat Treatment Method

Lengths of multifilament yarns were wound with minimum tension on a wooden frame (Appendix A) at constant length so that each turn was separate from its neighbor. Each frame contained approximately 47.0 ± 0.01 m (0.52 ± 0.005 g) of yarn. The frame was placed in the previously heated oven at the desired temperature for 3 minutes. Upon removal from the oven, the yarns were cooled at the standard atmosphere for textile testing before they were removed from the frame.

The oven used was checked by a potentiometer (Speedomax[®] Recorder, Leeds & Northrup Co.) for accuracy. Each setting of the oven always showed the same temperature value and the adjacent setting showed 15°C differences. Approximately 35 minutes were needed for the oven to reach the desired temperature and the temperature remained stable after that. When the door slit of the oven was opened and the wooden frame wound with the yarn was put through the slit, the temperature dropped by about $2-7^{\circ}\text{C}$. The higher the initial temperature, the greater the decrease. Therefore, the oven was preheated for about 40 minutes before the specimen was entered. After 3 minutes the final temperature was recorded.

The different oven temperature settings for nylon and polyester were:

150, 165, 180, 195, 210, 225, 235°C.

And the final temperatures recorded were:

148, 163, 176, 190, 205, 219, 228°C.

A specimen on the frame with heat treatment represented a sample; several subsamples were obtained from the sample. The order of oven temperature in which the frame was placed and the order of fiber type which was wound to the frame were determined randomly.

Measurement of Tensile Properties at Break

Single-filament specimens of a predetermined test length were broken on a constant-rate-of-extension testing machine (Instron Model 1130) using an appropriate load cell. The procedure for this test followed that of ASTM D 2101-79: Standard Test Method for Tensile Properties of Single Man-Made Textile Fibers taken from Yarns and Tows (1).

The rate of extension was adjusted to have an average breaking time of about 30 seconds. Samples were conditioned at the atmosphere for textile testing for at least 24 hours prior to testing.

From the load-elongation curve the average breaking tenacity and percent elongation at break were determined. The area under the load-elongation curve to be used for calculating breaking toughness was determined by cutting out the area of the chart, weighing it, and calculating area from the weight of a unit area.

The equations for breaking tenacity, elongation at break, and breaking toughness were as follows (1);

1. Breaking tenacity, $g/den = M/T$

where:

M = breaking load, in grams, and

T = linear density, in denier (100/34 den).

2. Elongation at break, percent = $100 \times (B/C)$

where:

B = filament elongation, in centimeters, and

C = calculated effective specimen length (10 cm).

3. Breaking toughness, $g.cm/den.cm = V/T$

where:

T = linear density, in den, and

V = work done in extending the fiber, in gram-centimeters per centimeter length, that is

$$= (AxSxR)/(GxWxL)$$

where:

A = area under the load-elongation curve, in square centimeters

S = full-scale load, in grams-force (20 g-f)

R = crosshead speed, centimeters per minute

(5.08 cm/min)

G = effective specimen length, in centimeters

W = chart width, in centimeters (15.24 cm), and

L = chart speed, in centimeters per minute

(5.08 cm/min).

The number of specimens to be used for tensile properties was determined by measuring the tenacity and coefficient of variation (v) of untreated fibers and calculating with the following equation (1):

$$n = 0.169 v^2$$

The number of specimens derived by this method was 11.

Dyeing Experiments

Prior to dyeing, 0.25 g samples were scoured in a solution composed of 2 g sodium carbonate, 1 g nonionic detergent (Triton[®] X-100, alkyl phenoxy polyethoxy ethanol type) and 1 liter distilled water. The scouring was done using the laboratory dyeing machine (Ahiba Texomat TC 101) at 50°C for 30 minutes to control agitation. Samples were then washed in distilled water, treated in 100 ml of a solution containing 1 ml 30% acetic acid per liter, and rewashed with distilled water. They were then dried at standard atmosphere.

The disperse dye used was Intrasperse Orange 2RN Ex. (C.I. Disperse Orange 3, 11005), a commercial dyestuff manufactured by the Crompton and Knowles Corporation. The dyebath contained 0.5 g dye and 10 ml 30% acetic acid made up to 1 liter.

Each specimen (0.25 g) was dyed using the laboratory dyeing machine. The specimens were introduced into the dyebath at a starting temperature of 50°C. The temperature was increased to 90°C at a rate of 2°C per minute, then dyeing was continued for 90 minutes. Before being introduced into the dyebath, the specimens were wet with distilled water which was heated to 50°C. The excess water was removed from the specimens by shaking the perforated basket which contained the specimen.

The dyeing conditions were such that dyeing took place in an infinite dyebath. Since only a total of 0.25 g of yarn was held loosely in place in each dyebath, and the uptake was small, the dyebath would be virtually an infinite one.

At the end of the dyeing, each specimen was rinsed thoroughly under running distilled water. Then it was rinsed 5 times in 20 ml portions of acetone for 5 seconds at room temperature to remove the remainder of the free surface-held dye. Following the final acetone rinse, the

dyed yarns were rewashed with distilled water. The specimens were dried in the oven at 80°C for 4-5 hours and then put into a desiccator to cool for at least 3 hours.

Estimation of Dye Uptake of Samples

A weighed amount (0.01 g) of dyed nylon fiber was dissolved in 10 ml of 20% calcium chloride in methanol (anhydrous calcium chloride dissolved in methanol), and the amount of dye uptake was estimated spectrophotometrically at 444.3 nm wave length. For the dyed polyester fiber, the same weighed amount of the fiber was dissolved in 5 ml of m-cresol. The solvent m-cresol used for dissolving the dyed polyester was vacuum-distilled several times (BP = 90°C/0.1 Torr) until the distillate was nearly colorless. The dye concentration was estimated by the same method as for the nylon at 428.7 nm wave length.

The Lambert and Beer relationship between concentration and absorbance of well-mixed suspensions of the dye in the solvent were obtained at 444.3 nm and 428.7 nm, respectively, in a 10 mm path-length cuvette. The spectrophotometer used was Spectronic 2000 (Bausch & Lomb) connected to a personal computer (Apple IIe).

The concentration-absorbance curve of Disperse Orange 3 in 20% calcium chloride in methanol used for nylon fiber is

given in Figure 2. The regression equation of the curve was:

$$Y = -0.0028 + 35.46X$$

where: X = concentration, and

Y = absorbance.

The standard deviation of the regression was 0.0014 and the correlation coefficient was 0.9999.

The concentration-absorbance curve of Disperse Orange 3 in m-cresol used for polyester is shown in Figure 3. The regression equation of the curve was:

$$Y = -0.0006 + 26.84X$$

The standard deviation of the regression was 0.0011 and the correlation coefficient was 0.9999.

Sample dye content was expressed as mg of dye/g of dyed fiber. For each dyed sample, two different solutions were prepared. From each solution, two readings were made and an average value was calculated.

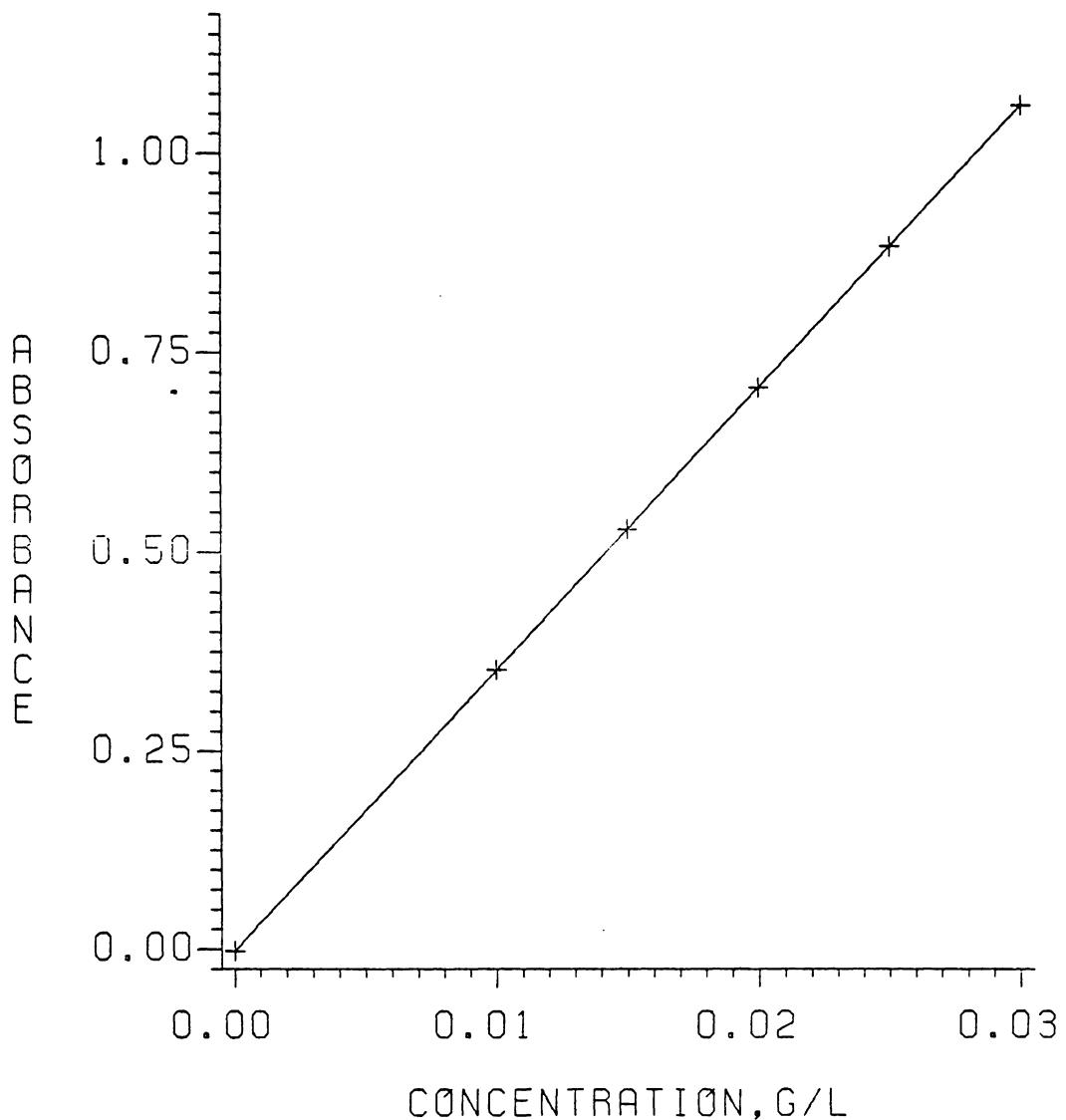


Figure 2: Concentration-Absorbance Curve of Disperse Orange 3 in 20% Calcium Chloride in Methanol

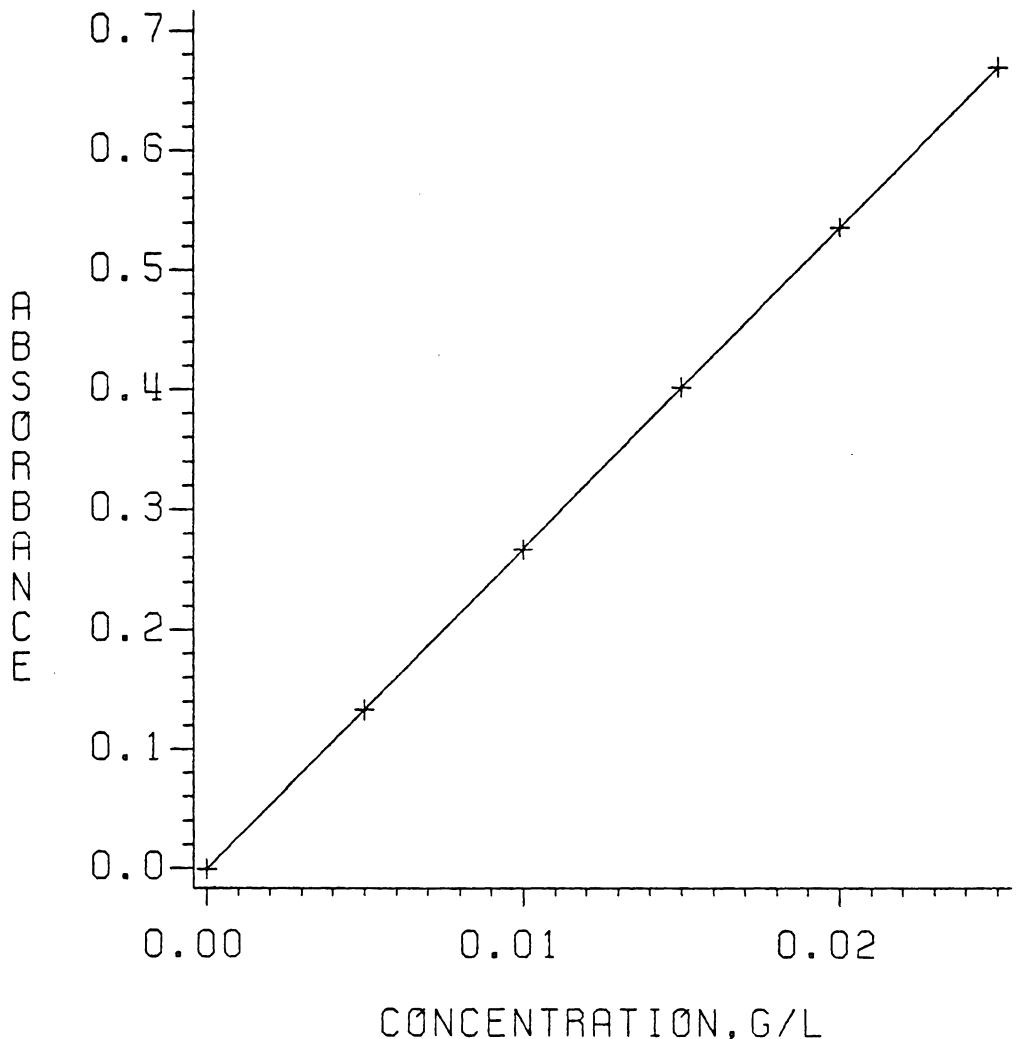


Figure 3: Concentration-Absorbance Curve of Disperse Orange 3 in M-Cresol

Density Measurements

To calculate the sample crystallinity, the fiber density of each specimen was measured according to the recommended ASTM procedure (D 1505-68: Standard Test Method for Density of Plastics by the Density Gradient Technique) (2). The mixtures for nylon 6.6 and polyester were ethanol ($\rho = 0.789 \text{ g/cm}^3$) and carbon tetrachloride ($\rho = 1.544 \text{ g/cm}^3$) (38). The solvent mixtures were considered to be inert toward both nylon and polyester (64, 67).

A density gradient was set up by a continuous filling method with liquid entering the gradient column becoming progressively more dense (2). The column was set up at $21^\circ \pm 1^\circ\text{C}$ by mixing various proportions of the heavy and the light solvent so that the density increased linearly from the top to the bottom. The diagram of the apparatus for gradient column preparation is shown in Appendix B.

The mixture of the heavy and the light solvent was proportioned for nylon so as to have a maximum density of 1.2728 and a minimum of 1.0155, and for polyester so as to have the maximum density at 1.5135 and the minimum at 1.2720. The gradient was determined with calibrated beads which had density values of 1.1304 , 1.1471 and 1.1605 g/cm^3 for nylon and 1.335 , 1.355 , 1.375 , 1.395 , and 1.415 g/cm^3 for polyester. Calibration curves for the density gradient

used for nylon and polyester fibers were obtained. Parts of them are shown in Figures 4 and 5.

After the gradient was established, small portions of fibers knotted into various shapes for identification were dropped into the column and the flotation level measured after an extended period of time (72 hours). This time period was considered sufficient for the samples to reach an equilibrium point. Four different density columns were set up to accommodate the replications and fiber types. Three determinations were made on each sample.

Calculation of Degree of Crystallinity

From the fiber density, sample crystallinity was calculated using the weight fraction percent crystallinity equation mentioned in the previous chapter. The equation is:

$$\beta_c = \frac{\rho_c (\rho_t - \rho_a)}{\rho_t (\rho_c - \rho_a)} \times 100$$

where β_c = weight fraction percent crystallinity

ρ_t = density of sample

ρ_c = density of 100% crystalline material

ρ_a = density of 100% amorphous material.

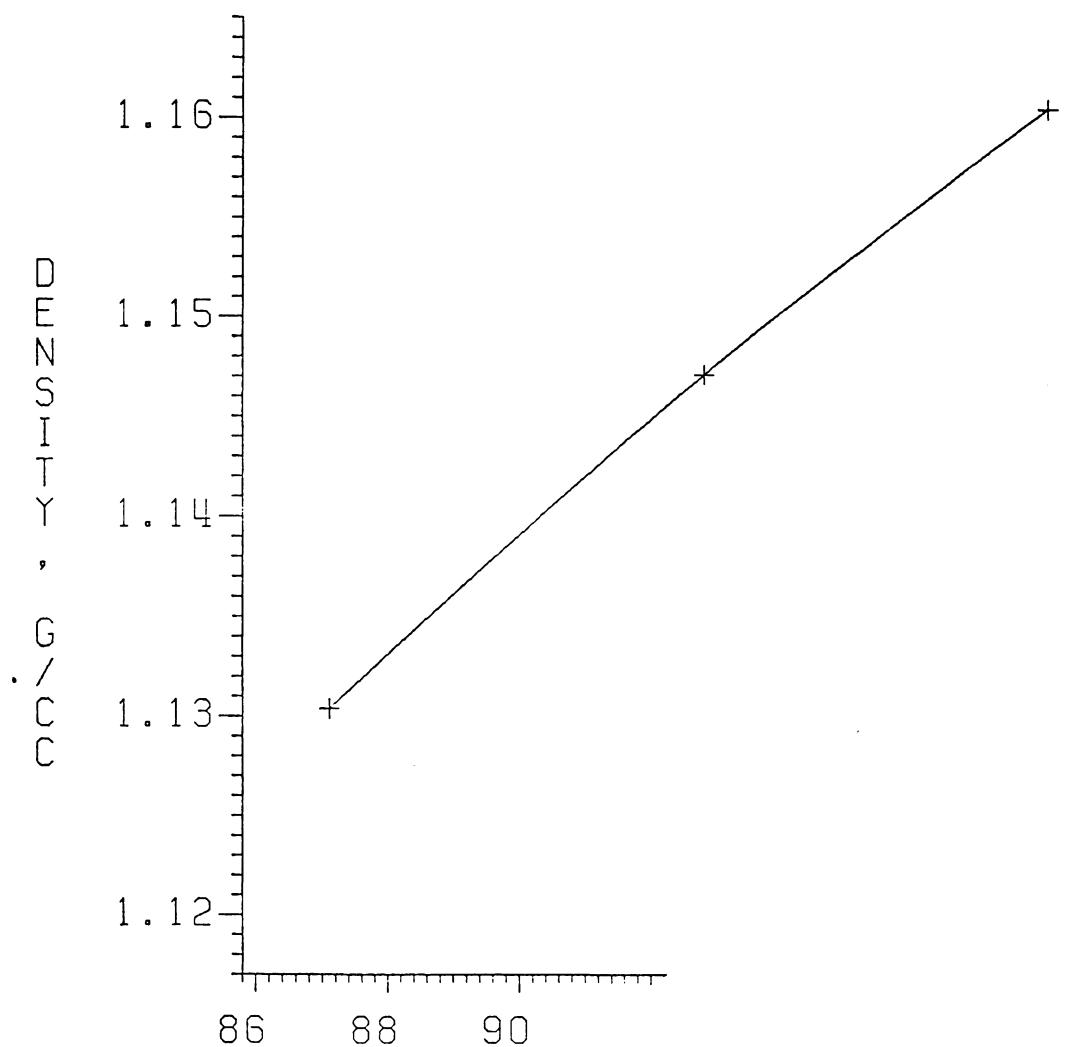


Figure 4: Calibratio.
Nylon 6.6

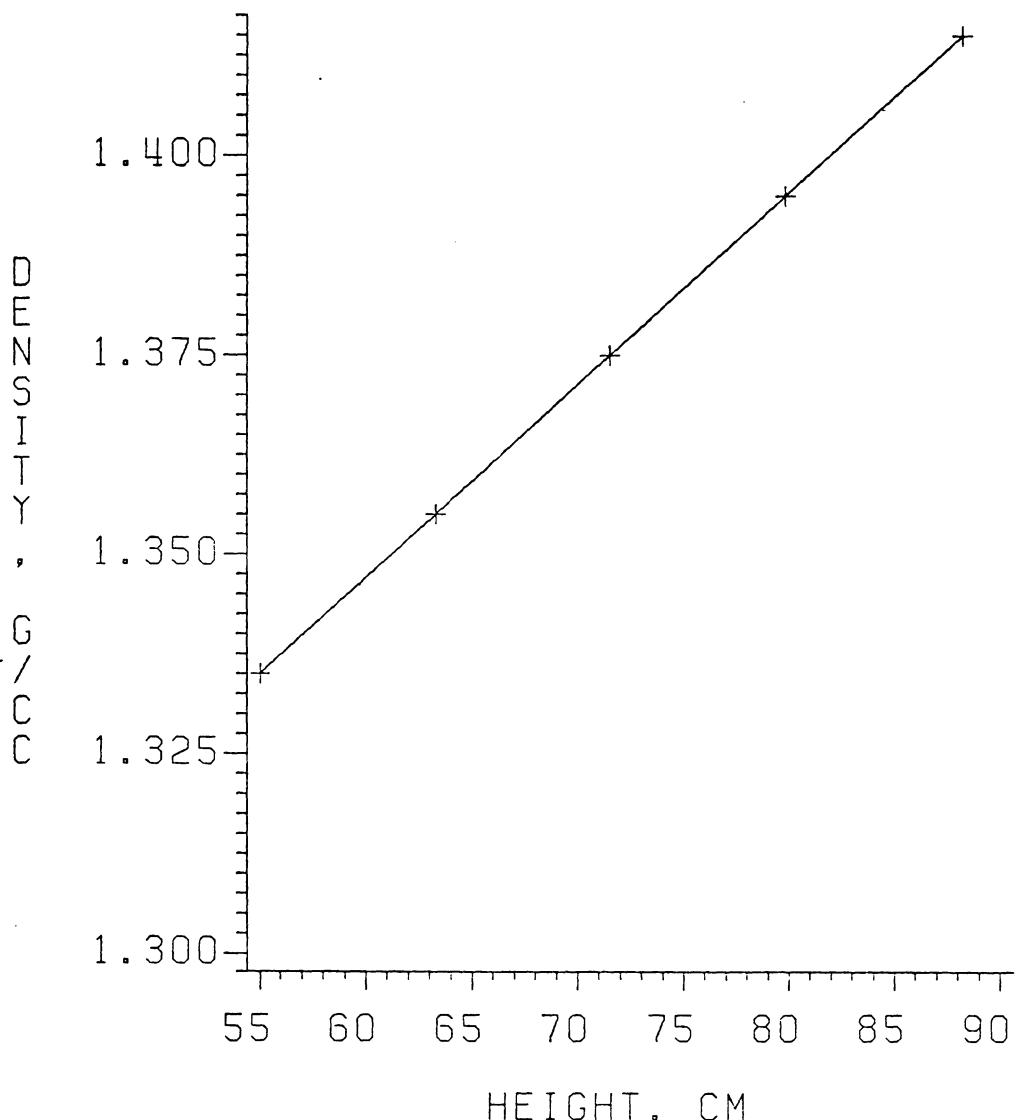


Figure 5: Calibration Curve of Density Gradient Used for Polyester

For nylon 6.6, the density values for crystalline and amorphous fiber were taken to be 1.240 g/cm^3 and 1.090 g/cm^3 , respectively (6,36,64,69). For polyester, they were taken to be 1.455 g/cm^3 and 1.335 g/cm^3 , respectively (7,36,62,69).

Statistical Analysis of Data

The heat treatment for all combinations of the temperatures and the fiber types represents one replication of the experiment. For this experiment, two replications were obtained, and from each sample, a fixed number of subsamples was chosen randomly.

The statistical model for this experiment is the repeated factorial design with subsampling (14) which can be expressed as follows:

$$Y_{ijkl} = \mu + R_i + A_j + B_k + (AB)_{jk} + (RA)_{ij} + (RB)_{ik} + (RAB)_{ijk} + e_{ijkl}$$

where: Y_{ijkl} = the observed value of the dependent variable at i th rep, j th fiber type, k th temperature and l th sample.

μ = overall mean

R_i = the effect of i th replication ($i=1,2$).

A_j = the effect of j th fiber type ($j=1,2$).

B_k = the effect of k th temperature ($k=1,\dots,8$).

$(AB)_{jk}$ = interaction of j th fiber type and k th

temperature.

$(RA)_{ij}$ = interaction of ith replication and jth fiber type.

$(RB)_{ik}$ = interaction of ith replication and kth temperature

$(RAB)_{ijk}$ = interaction of ith replication, jth fiber type and kth temperature.

e_{ijkl} = random error of lth sample of ith replication, jth fiber type and kth temperature.

The factors A (fiber type) and B (temperature) are both fixed effects and the factor R (replication) is a random effect. The analysis of variance model can be written as shown in the Table 2.

For the analysis, SAS (Statistical Analysis System) procedures were used. In the output of SAS programs, probability values (p values) in addition to F values are available. After the ANOVA table was obtained, the three hypotheses, which are listed in the previous chapter, were tested by observing the F values or p values. The significance level α was set to 0.05. Thus, for each hypothesis tested, if the p value was less than 0.05, the null hypothesis was rejected and it was concluded that there was a significant difference among the levels of the

TABLE 2
Analysis of Variance Model

Sources	df	ss	ms	F value
Rep	1	ss_R	ms_R	ms_R/ms_e
A	1	ss_A	ms_A	$ms_A/ms_{Rx A}$
B	7	ss_B	ms_B	$ms_B/ms_{Rx B}$
AxB	7	ss_{AB}	ms_{AB}	$ms_{AB}/ms_{Rx AxB}$
RepxA	1	$ss_{Rx A}$	$ms_{Rx A}$	$ms_{Rx A}/ms_e$
RepxB	7	$ss_{Rx B}$	$ms_{Rx B}$	$ms_{Rx B}/ms_e$
RepxAxB	7	$ss_{Rx AxB}$	$ms_{Rx AxB}$	$ms_{Rx AxB}/ms_e$
Residual		ss_e	ms_e	

Total

(Residual and total degrees of freedom
vary by dependent variable.)

corresponding factor (fiber type, temperature, or fiber type by temperature) for the dependent variable.

Besides these tests, the trends, especially linear and quadratic trends, of the dependent variables according to the temperature were detected. Trend tests can be performed by the contrast analysis (15) for each dependent variable. The linear contrast tests whether there exists an increasing or decreasing trend of the dependent variable as the level of temperature increases. The quadratic contrast tests whether there exists a quadratic trend of the dependent variable as the level of temperature increases, i.e. the dependent variable increases first and decreases or it decreases then increases. Also, using the contrast, differences between the control and the treated (no heat treatment vs average of heat treatment) for each dependent variable can be detected.

Regression analysis was used to study the relation between the crystallinity and the tensile properties, and between the crystallinity and dyeability. These variables (crystallinity, tensile properties and dyeability) were obtained as response variables in the experiment. One way of documenting the relationship was to plot the data in a two dimensional plane. Then, regression analysis was used with the tensile properties or the dyeability as the

dependent variable and the crystallinity as the independent variable. Three different models, cubic, quadratic and linear, were tried for the analysis. If the cubic form was significant in the whole model, the cubic regression was used. If quadratic form was significant in the model the quadratic regression was adopted. If neither the cubic nor the quadratic forms were significant, simple linear regression was utilized as the best fitting model.

Chapter V

RESULTS AND DISCUSSION

The results and discussion for this study are divided into five major parts: effect of heat setting on tensile properties, effect of heat setting on dye uptake, effect of heat setting on crystallinity, relationship of tensile properties and crystallinity and relationship of dyeability and crystallinity.

Effect of Heat Setting on Tensile Properties

Nylon 6.6 and polyester filament yarns were heat treated at temperature settings ranging from 150°C to 235°C in dry heat. Tenacity and elongation were measured using a constant-rate-of-extension machine and fiber toughness was obtained from the breaking load-extension graph.

The results for the mechanical properties of nylon 6.6 and polyester filament yarns after heat setting and those of untreated ones are given in Table 3. It can be seen that nylon 6.6 and polyester yarns behaved differently when heat treated with dry heat under constant length conditions.

The stress-strain curves, a diagrammatic representation of tensile properties, are shown in Figure 6 for nylon 6.6

TABLE 3

Tensile Properties of Heat Set Nylon 6.6 and Polyester Filament Yarns

Temperature °C	Tenacity g/d	Elongation %	Toughness g.cm/d.cm
Nylon 6.6			
untreated	5.63	46.5	1.95
150	5.42	41.9	1.66
165	5.38	39.7	1.59
180	5.30	39.0	1.55
195	5.16	35.8	1.37
210	4.44	22.4	0.66
225	3.09	12.5	0.21
235	2.47	10.3	0.14
Polyester			
untreated	4.94	37.2	1.39
150	4.93	33.2	1.27
165	4.92	29.9	1.13
180	5.10	32.5	1.30
195	5.18	32.6	1.30
210	5.09	25.7	0.94
225	5.25	29.1	1.12
235	5.17	30.4	1.15
SE	0.09	1.0	0.09

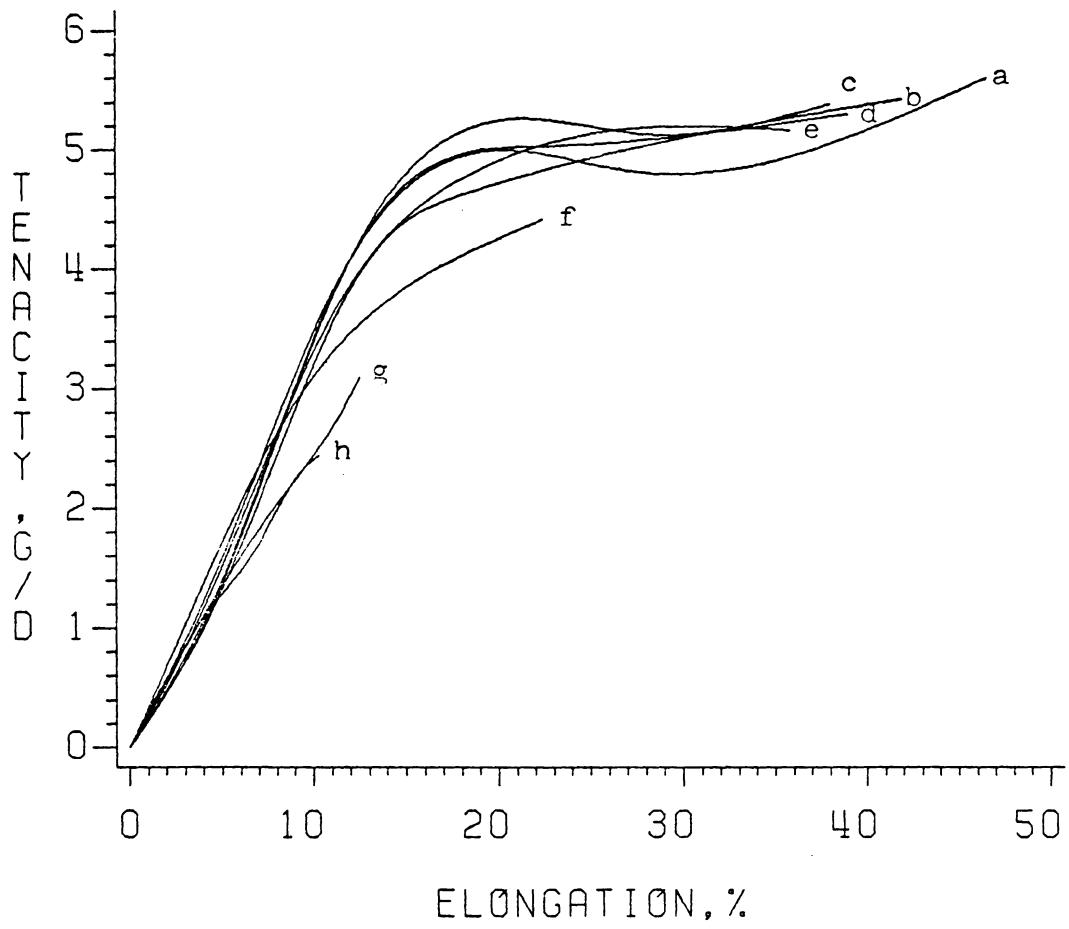
SE= Standard Error

and in Figure 7 for polyester. The shapes of the stress-strain curves for nylon 6.6 were different according to the treatment temperature. The curve for untreated nylon filament was noticeably longer than the curves for treated filaments indicating loss of breaking tenacity as temperature increased.

The shapes of the stress-strain curves for polyester were very similar, especially for the treated filaments. The untreated filament curve was noticeably flatter than the curves for treated filaments.

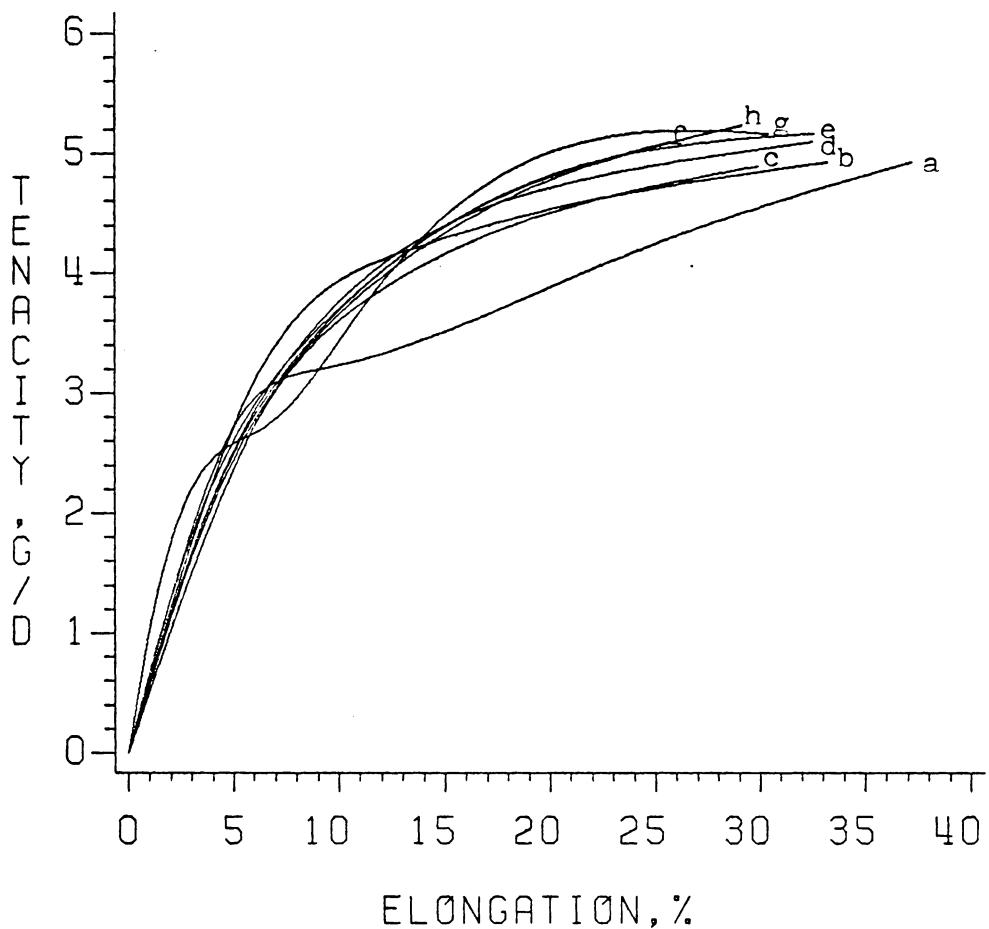
In general, the initial modulus, which is equal to the slope of the curve at the origin, of polyester was greater than that of nylon 6.6. Since an easily extensible fiber has a low modulus, it is noted that nylon 6.6 is more extensible than polyester.

More detailed information on tensile properties is given in Appendix C: Tensile Properties Data. Each variable, tenacity, elongation and toughness, is discussed in the following subsections.



a	UNTREATED	b	150
c	165	d	180
e	195	f	210
g	225	h	235

Figure 6: Stress-Strain Curves for Heat Treated Nylon 6.6 Filament Yarns



a	UNTREATED	b	150
c	165	d	180
e	195	f	210
g	225	h	235

Figure 7: Stress-Strain Curves for Heat Treated Polyester Filament Yarns

Tenacity

The tenacity of nylon 6.6 yarns heat set at a constant length decreased slightly up to 195°C, then a drastic loss in strength occurred. On the other hand, the tenacity of polyester treated under the same conditions marginally increased over a wide range of temperatures. The comparison of the tenacity change for nylon 6.6 and polyester at different heat setting temperatures is shown in Figure 8.

To test the null hypotheses developed for this study, analysis of variance (ANOVA) was used. The ANOVA table for tenacity is given in Table 4. According to the table, the parts of the three null hypotheses dealing with tenacity were all rejected. Therefore, there was a significant difference between fiber types (nylon vs polyester) on tenacity ($p<0.0043$). Secondly, there were highly significant differences among temperature settings for tenacity ($p<0.0001$), where the untreated control was included in the model. Also, a significant interaction existed between fiber type and temperature on tenacity ($p<0.0001$); that is, the tenacity trend according to temperature in nylon 6.6 showed a different shape when compared with that for polyester (see Figure 8).

Nylon 6.6 showed both a linear ($p<0.0001$) and a quadratic trend ($p<0.0001$) in tenacity across temperatures

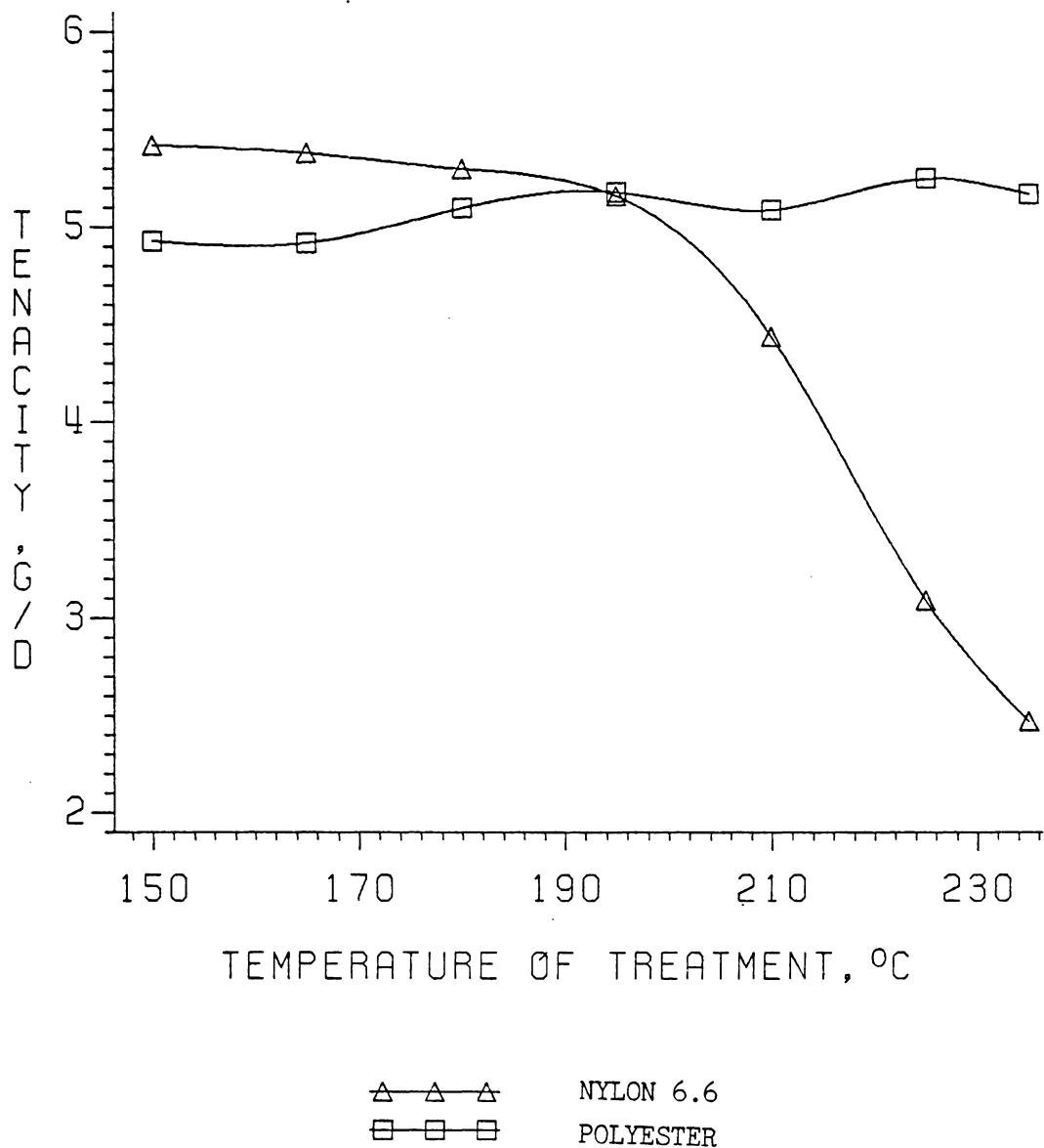


Figure 8: Effect of Heat Setting on the Tenacity of Nylon 6.6 and Polyester Filament Yarns

TABLE 4
ANOVA Table for Tenacity

Sources	df	ss	ms	F value	p
Rep	1	0.0014	0.0014	0.08	0.7817
Fiber	1	18.9337	18.9337	22241.74	0.0043
Temperature	7	93.8114	13.4016	428.69	0.0001
FibxTemp	7	127.9708	18.2815	339.20	0.0001
RepxFib	1	0.0008	0.0008	0.05	0.8261
RepxTemp	7	0.2188	0.0312	1.78	0.0906
RepxFibxTemp	7	0.3773	0.0539	3.06	0.0040
Residual	320	5.6319	0.0176		
Total	351	246.9461			

(Table 5). The tenacity curve represented a decline as well as a bend downward at about 200 °C. Polyester, however, showed only a linear trend ($p<0.0012$) between temperature and tenacity and did not show any quadratic relationship. The tenacity of polyester increased slightly at higher heat setting temperatures. A significant difference existed in the tenacity between untreated yarns and treated yarns for both nylon 6.6 ($p<0.0001$) and polyester (0.0227).

Therefore, it can be seen that the tenacity of nylon 6.6 yarns is reduced as the treatment temperature increases. On the other hand, the tenacity of polyester yarns marginally increases as temperature increases.

Elongation

The elongation at break for nylon 6.6, as for tenacity, decreased moderately up to 195°C and then dropped drastically. Elongation of polyester fluctuated slightly over the temperature range; changes of both nylon 6.6 and polyester yarns are shown in Figure 9.

The ANOVA table for the elongation variable is shown in Table 6. On the basis of the ANOVA table, a significant fiber by temperature interaction was observed for elongation ($p<0.0001$), which means that the trends for elongation change with temperature in nylon 6.6 and in polyester were

TABLE 5
Contrast Analyses for Tenacity

Contrast	df	ms	F value	p
Nylon 6.6				
control vs treated	1	25.95	481.49	0.0001
linear trend	1	160.12	2970.95	0.0001
quadratic trend	1	28.38	526.62	0.0001
Polyester				
control vs treated	1	0.45	8.46	0.0227
linear trend	1	1.49	27.70	0.0012
quadratic trend	1	0.16	3.01	0.1266

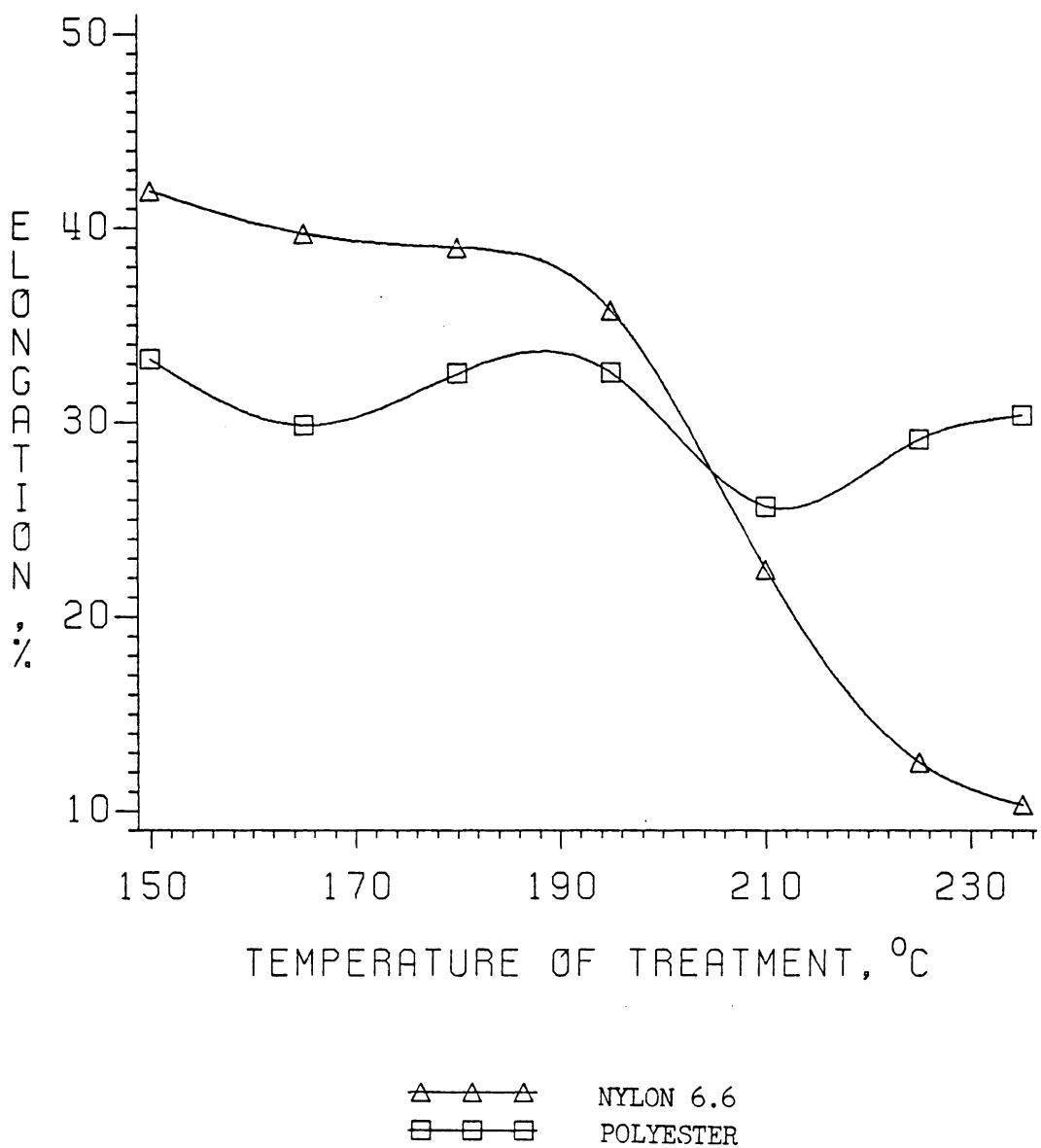


Figure 9: Effect of Heat Setting on the Elongation of Nylon 6.6 and Polyester Filament Yarns

TABLE 6
ANOVA Table for Elongation

Sources	df	ss	ms	F value	p
Rep	1	17.5510	17.5510	2.10	0.1479
Fiber	1	6.9891	6.9891	0.20	0.7308
Temperature	7	20835.1614	2976.4516	145.99	0.0001
FibxTemp	7	11009.2727	1572.7532	108.97	0.0001
RepxFib	1	34.5001	34.5001	4.14	0.0428
RepxTemp	7	142.7153	20.3879	2.44	0.0188
RepxFibxTemp	7	101.0335	14.4333	1.73	0.1004
Residual	320	2668.8455	8.3401		
Total	351	34816.0686			

different (Figure 9). Temperature had a significant effect ($p<0.0001$) on elongation. However, there was no significant difference between fiber types ($p<0.7308$). This is because the fiber effect was masked by the interaction of fiber by temperature.

According to the contrasts (Table 7), nylon 6.6 had both a linear trend ($p<0.0001$) and a quadratic trend ($p<0.0001$) for temperature and elongation change. Polyester, however, showed only a linear trend ($p<0.0056$) in elongation at the break over the range of temperatures. Even while fluctuating slightly, the elongation of polyester showed a decreasing trend over the temperature range, unlike tenacity. Therefore, it can be concluded that nylon 6.6 yarns became less extensible as the temperature of heat setting increased, and polyester yarns, though to a slighter degree, also became less extensible.

Toughness

The toughness of nylon 6.6 also showed trends of change with temperature similar to those for tenacity and elongation. Toughness dropped moderately up to 195°C and decreased sharply at higher temperatures. Toughness of polyester, however, fluctuated slightly over the temperature range as for elongation. The toughness changes of both nylon and polyester fibers are shown in Figure 10.

TABLE 7
Contrast Analyses for Elongation

contrast	df	ms	F value	p
Nylon 6.6				
control vs treated	1	6039.68	418.45	0.0001
linear trend	1	21603.74	1496.79	0.0001
quadratic trend	1	1154.72	80.00	0.0001
Polyester				
control vs treated	1	870.84	60.34	0.0001
linear trend	1	223.56	15.49	0.0056
quadratic trend	1	45.60	3.16	0.1187

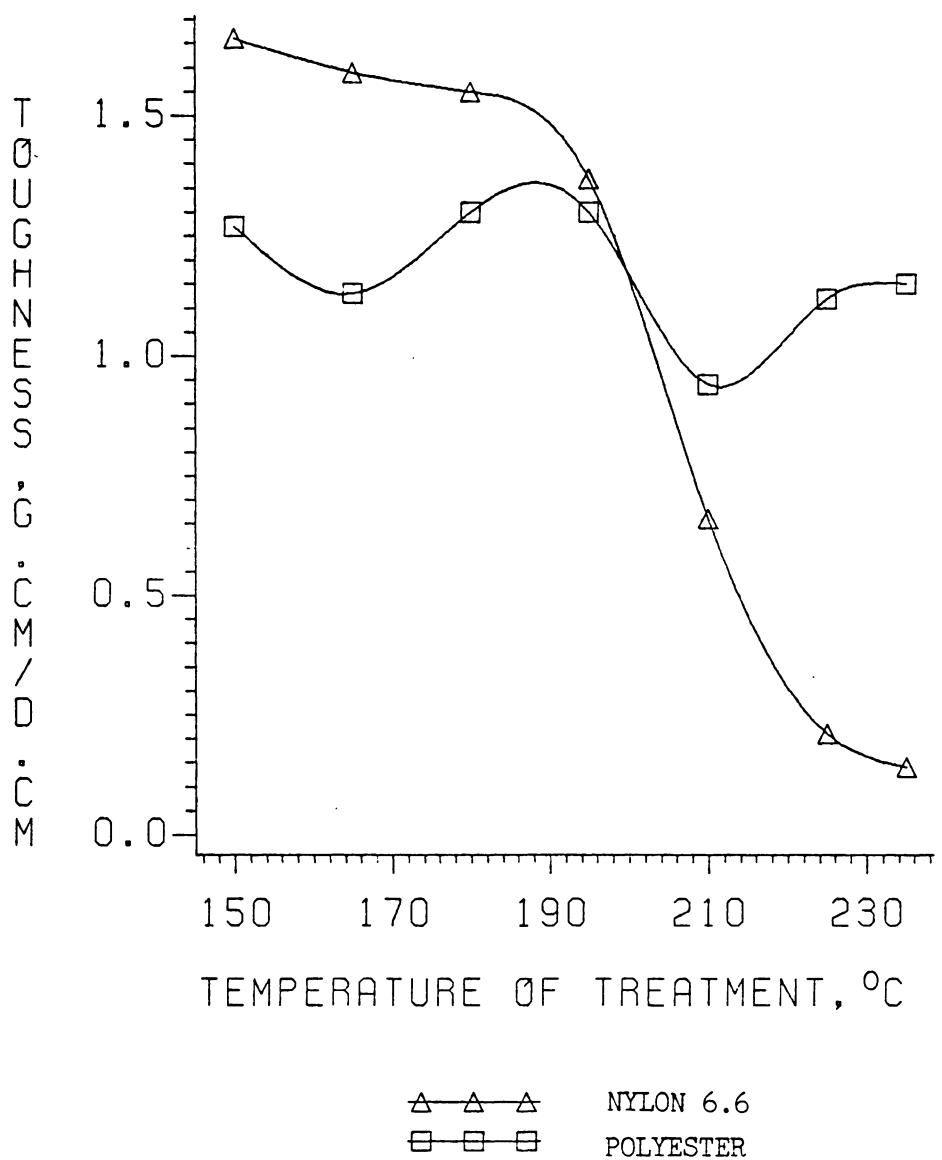


Figure 10: Effect of Heat Setting on the Toughness of Nylon 6.6 and Polyester Filament Yarns

The ANOVA for toughness is given in Table 8. Fiber by temperature interaction was observed for toughness ($p<0.0001$). In other words, the trends for toughness change with temperature in nylon 6.6 and in polyester were different from each other (Figure 10). There were significant differences among temperatures ($p<0.0001$). However, there was no significant difference between fiber types ($p<0.1604$). Again, this is because the fiber effect was masked by the fiber by temperature interaction.

Based upon the contrasts (Table 9), both linear and quadratic trends were observed between heat setting temperature and toughness for nylon 6.6. Polyester, on the other hand, demonstrated a significant linear trend ($p<0.0342$) but no significant quadratic trend ($p<0.6447$). Less work was required to break the fiber as temperature increased, but the change in work required among temperature settings for nylon 6.6 was greater than that for polyester.

As a reference, the least squares means by fiber type and by temperature for tenacity, elongation and toughness are shown in Table 10.

In summary, a significant interaction existed between fiber type and temperature for tenacity, elongation and toughness. Graphs of tensile properties of each fiber type with temperature depicted different shapes.

TABLE 8
ANOVA Table for Toughness

Sources	df	ss	ms	F value	p
Rep	1	0.0229	0.0229	1.01	0.3165
Fiber	1	0.2885	0.2885	15.09	0.1604
Temperature	7	49.9077	7.1297	111.99	0.0001
FibxTemp	7	29.0406	4.1486	63.70	0.0001
RepxFib	1	0.0191	0.0191	0.84	0.3595
RepxTemp	7	0.4456	0.0637	2.80	0.0077
RepxFibxTemp	7	0.4559	0.0651	2.87	0.0066
Residual	320	7.2670	0.0227		
Total	351	87.4473			

TABLE 9
Contrast Analyses for Toughness

Contrast	df	ms	F value	p
Nylon 6.6				
control vs treated	1	16.46	252.76	0.0001
linear trend	1	52.93	812.77	0.0001
quadratic trend	1	2.52	38.78	0.0004
Polyester				
control vs treated	1	0.90	13.92	0.0074
linear trend	1	0.44	6.89	0.0342
quadratic trend	1	0.01	0.23	0.6447

TABLE 10
Least Squares Means for Tensile Properties

	Tenacity g/d	Elongation %	Toughness g.cm/d.cm
Fiber Type			
nylon 6.6	4.61	31.0	1.14
polyester	5.07	31.3	1.19
SE	0.00	0.9	0.01
Temperature			
untreated	5.28	41.9	1.66
150	5.18	37.6	1.46
165	5.15	34.8	1.36
180	5.20	35.8	1.42
195	5.17	34.2	1.33
210	4.77	24.1	0.79
225	4.17	20.8	0.66
235	3.82	20.3	0.64
SE	0.04	1.1	0.06

SE= Standard Error

The breaking strength, extensibility and work of rupture of nylon 6.6 filament yarns heat set without allowing any shrinkage decreased as treatment temperature increased. These results for nylon 6.6 are in agreement with those of Venkatesh et al. (63). The breaking strength of polyester was found to increase marginally on heat setting under constant length condition and the extensibility of polyester has found to decrease as treatment temperature increased. But, Venkatesh et al. have observed a fall in the breaking strength and a marginal increase in the extensibility of polyester filament yarns. The work of rupture for polyester yarns could not be compared with other studies due to the absence of data in the other studies.

Effect of Heat Setting on Dye Uptake

After the specimens were dyed at 90°C for 90 minutes, the dye uptake of the fibers was measured spectrophotometrically by dissolving the dyed fibers in suitable solvents.

The experimental results for nylon 6.6 and polyester filament yarns are shown in Table 11. More specific breakdowns are listed in Appendix D: Dye Uptake Data.

The amount of dye taken up by the untreated nylon 6.6 fiber was 33.60 mg of dye/g of dyed fiber and as the

TABLE 11

Uptake of Dyes by Heat Set Nylon 6.6 and Polyester Filament Yarns

Temperature °C	Dye Uptake mg of dye/ g of dyed fiber	
	Nylon 6.6	Polyester
untreated	33.60	14.92
150	31.14	9.12
165	30.30	8.20
180	27.78	7.66
195	24.48	7.62
210	22.46	7.55
225	21.93	6.82
235	21.15	6.36
SE	0.28	0.28

SE= Standard Error

treatment temperature increased, the amount of dye taken up decreased. Polyester fibers, on the other hand, showed less dyeability than nylon 6.6 for the predetermined period of time. The amount of dye absorbed by the untreated polyester fiber was 14.92 mg of dye/g of dyed fiber. When the fiber was heat set at 150°C, the amount of dye uptake was reduced severely and within the treated fibers the uptake decreased moderately as the heat setting temperature increased. The comparison of dye uptake by nylon 6.6 and polyester filament yarns at various temperature settings is shown in Figure 11.

The ANOVA table for dye uptake is summarized in Table 12. Examining the ANOVA table, all parts of the three null hypotheses related to dyeability were rejected. Fiber by temperature interaction was observed in dye uptake ($p<0.0001$), which means that the trends for dye uptake change with temperature in nylon 6.6 and in polyester were different. There were significant differences among temperatures ($p<0.0001$) in dye uptake. Type of fiber affected the amount of dye uptake ($p<0.0145$) as well.

Unlike tensile properties, dye uptake showed differences between the two replications. This could be explained by the heat treated yarns being dyed in separate dye baths in which the dye concentration might have differed.

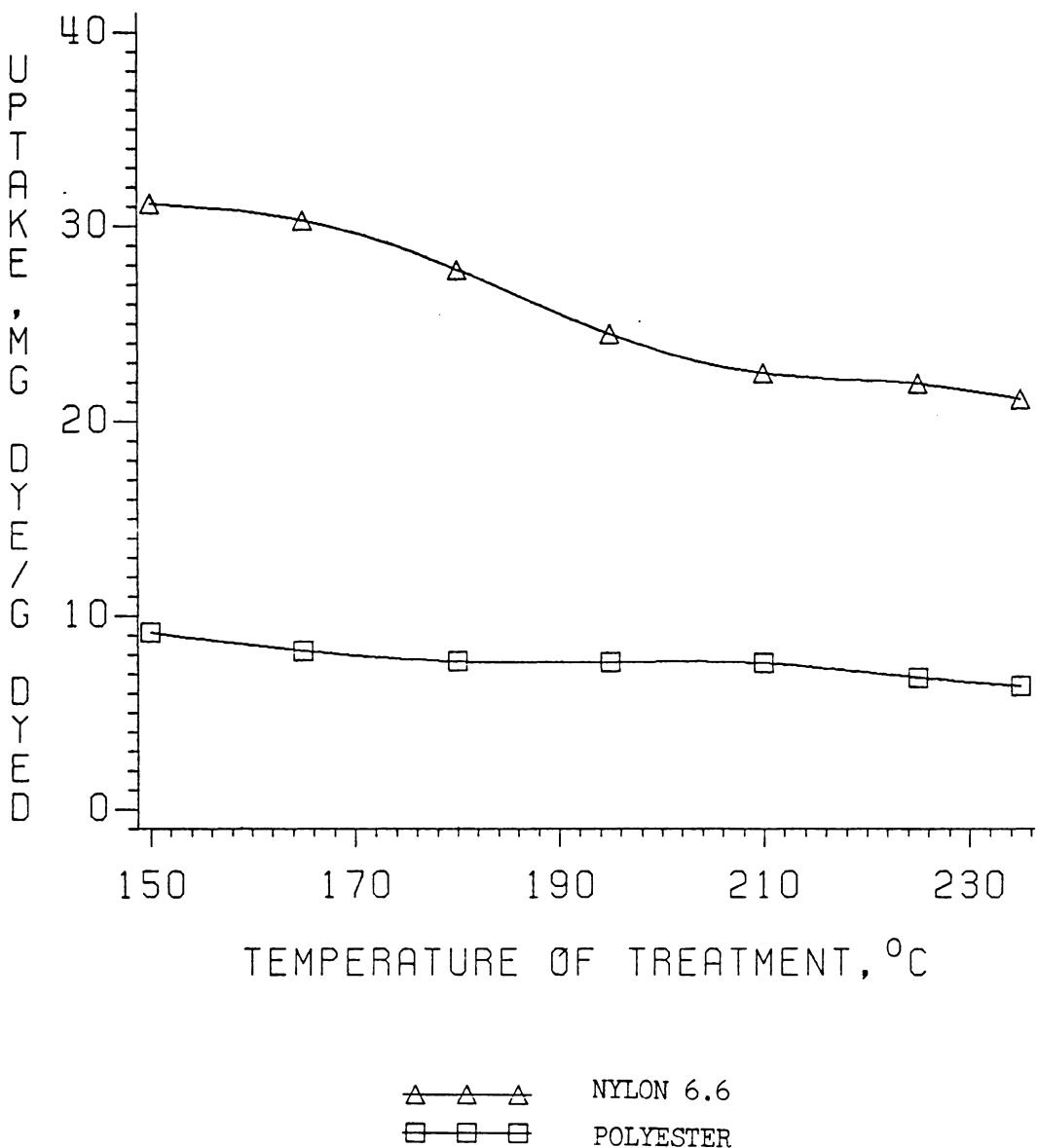


Figure 11: Effect of Heat Setting on the Uptake of Dye by Nylon 6.6 and Polyester Filament Yarns

TABLE 12
ANOVA Table for Dye Uptake

Sources	df	ss	ms	F value	p
Rep	1	2.4050	2.4050	9.05	0.0051
Fiber	1	5227.5929	5227.5929	1923.41	0.0145
Temperature	7	702.7326	100.3904	464.84	0.0001
FibxTemp	7	134.6125	19.2303	65.07	0.0001
RepxFib	1	2.7179	2.7179	10.23	0.0031
RepxTemp	7	1.5117	0.2159	0.81	0.5835
RepxFibxTemp	7	2.0686	0.2955	1.11	0.3797
Residual	32	8.5034	0.2657		
Total	63	6082.1446			

According to the contrasts (Table 13), nylon 6.6 demonstrated both a linear and a quadratic trend between temperature and dye uptake. The untreated fiber was excluded from the analysis to see the temperature and the dye uptake relationship. Polyester showed only a linear decrease, not a quadratic decrease, between temperature and dye uptake.

As a reference, the least squares means for dye uptake by fiber type and temperature are shown in Table 14.

In summary, there was a significant interaction between fiber type and temperature for dyeability. As treatment temperature increased, the dyeability of both nylon 6.6 and polyester filament yarns decreased. But, the trends for dyeability in nylon 6.6 were different from those in polyester filament yarns.

Dumbleton (11) and others (50,64,65) have shown that the dye uptake initially decreased as the temperature of heat setting was raised. However, at higher temperatures the rate of dye uptake increased with increasing temperature and could be greater than that for the untreated control. Generally, under normal setting conditions, the aqueous dyeability of heat set fibers increased as temperature increased, but when set within the range of 200-249°C, even though it is different according to the heat set condition and fiber type, a sharp increase in dyeability occurred.

TABLE 13
Contrast Analyses for Dye Uptake

Contrast	df	ms	F value	p
Nylon 6.6				
control vs treated	1	223.55	756.50	0.0001
linear trend	1	386.72	1308.65	0.0001
quadratic trend	1	7.80	26.40	0.0013
Polyester				
control vs treated	1	186.74	631.94	0.0001
linear trend	1	17.85	60.42	0.0001
quadratic trend	1	0.07	0.26	0.6274

TABLE 14
Least Squares Means for Dye Uptake

	Dye Uptake mg of dye/ g of dyed fiber
Type	
nylon 6.6	26.61
polyester	8.53
SE	0.93
Temperature	
untreated	24.26
150	20.13
165	19.25
180	17.72
195	16.05
210	15.01
225	14.37
235	13.75
SE	0.14

SE= Standard Error

The present results for both nylon 6.6 and polyester did not show any sharp increase in dye uptake at higher temperatures. This might be due to the different heat set condition.

Effect of Heat Setting on Crystallinity

Degree of crystallinity of the yarns was obtained from a density gradient column for the filament yarns treated at various temperature settings. The results, including those for untreated yarns, are listed in Table 15. More details are shown in Appendix E: Density and Crystallinity Data.

It can be seen that even if nylon showed no differences at lower temperature settings, density steadily increased as the treatment temperatures increased. Since the degree of crystallinity is a function of density, there is no doubt that crystallinity also increased as density increased.

Density of untreated nylon yarns was 1.140 g/cm^3 and the degree of crystallinity was 36.8%. When the nylon filaments were heat set at 150°C and 165°C , the density values were more or less the same. This would indicate that the particular samples did not undergo structural changes at low temperatures. Polyester has a density value of 1.380 g/cm^3 and a crystallinity value of 39.6% for the untreated yarns. When the yarns were heat set at 150°C , the density and degree of crystallinity increased slightly.

TABLE 15

Density and Degree of Crystallinity of Heat Set Nylon 6.6
and Polyester Filament Yarns

Temperature °C	Density g/cm ³	Crystallinity %
Nylon 6.6		
Untreated	1.140	36.8
150	1.141	37.4
165	1.141	37.1
180	1.143	38.4
195	1.147	41.4
210	1.149	42.5
225	1.155	47.1
235	1.157	47.9
Polyester		
untreated	1.380	39.6
150	1.384	43.6
165	1.385	44.4
180	1.391	48.8
195	1.393	50.7
210	1.395	52.9
225	1.397	54.5
235	1.399	56.0
SE	0.003	0.0

SE= Standard Error

The degree of crystallinity of the samples treated at 235°C was about 48% in the case of nylon 6.6 and 56% for polyester. Polyester obtained 48% crystallinity when the yarns were heat set at 180°C. In spite of similar values of crystallinity for the untreated sample of both nylon and polyester, polyester increased in degree of crystallinity faster than nylon 6.6 when heat treated at various temperatures.

The comparison of the density change for nylon 6.6 and polyester at different temperatures is shown in Figure 12. The relation between crystallinity and temperature is shown in Figure 13. Due to the inherent density differences between the fibers, the density graphs are widely separated. Crystallinity graphs showed an increasing tendency, but were somewhat different shapes.

The analysis of variance for degree of crystallinity is summarized in Table 16. On the basis of the table, all parts of the three null hypotheses related to crystallinity were rejected. Type of fiber had a significant effect ($p<0.0221$) on the degree of crystallinity. Also, temperature had a significant effect ($p<0.0001$) on the degree of crystallinity. There was a significant interaction between fiber type and temperature for degree of crystallinity ($p<0.0058$). That is, the slope of the line

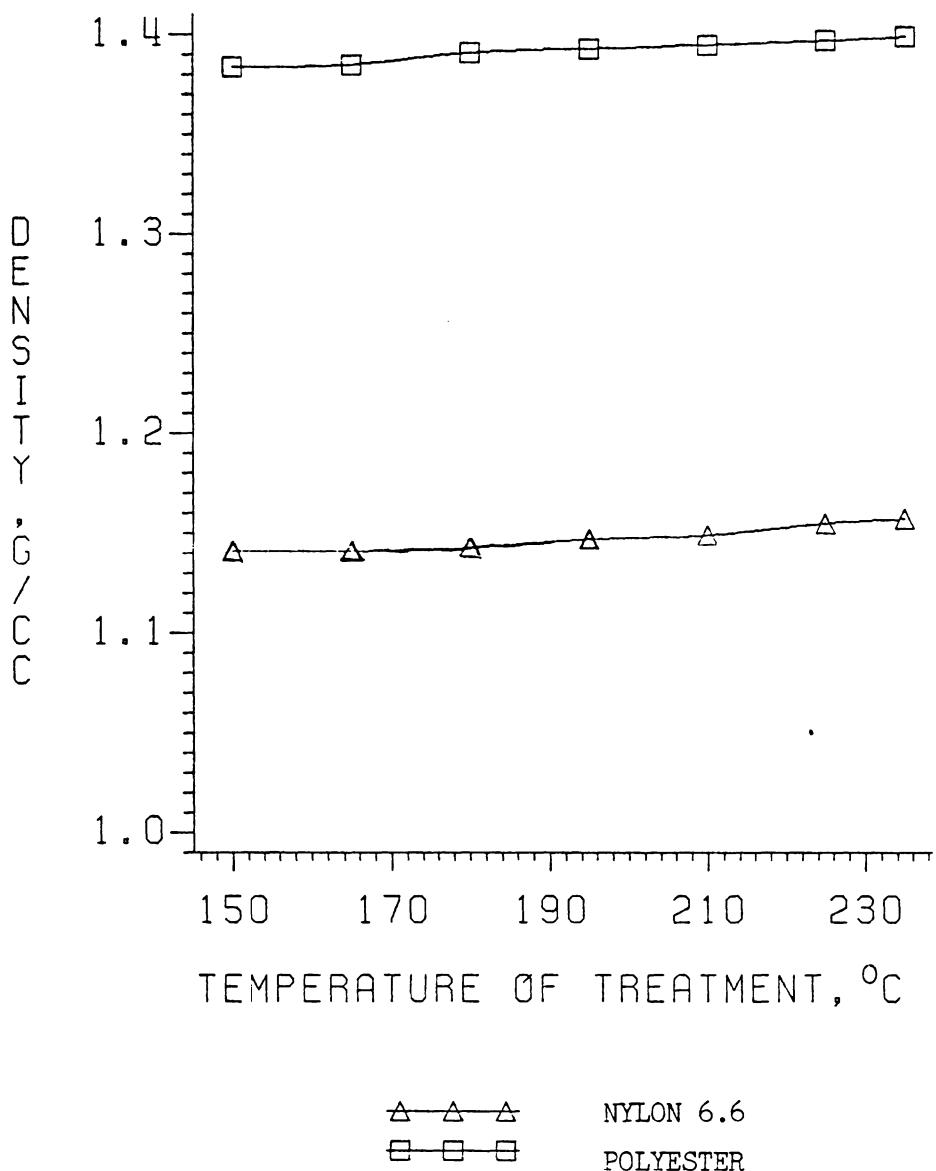


Figure 12: Effect of Heat Setting on the Density of Nylon 6.6 and Polyester Filament Yarns

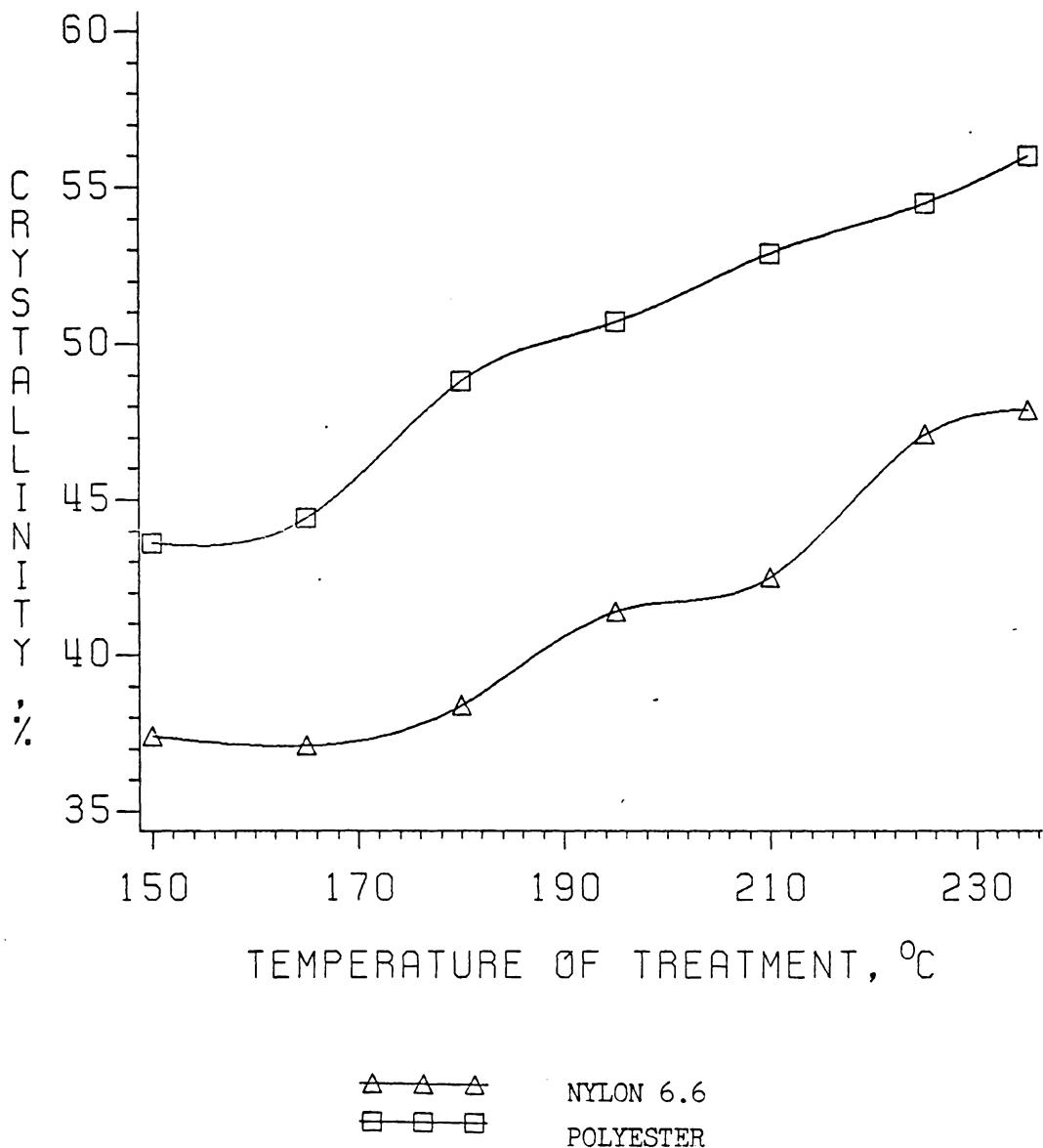


Figure 13: Effect of Heat Setting on the Degree of Crystallinity of Nylon 6.6 and Polyester Filament Yarns

TABLE 16
ANOVA Table for Crystallinity

Sources	df	ss	ms	F value	p
Rep	1	0.0000	0.0000	0.33	0.5684
Fiber	1	0.1437	0.1437	832.05	0.0221
Temperature	7	0.2125	0.0303	32.74	0.0001
FibxTemp	7	0.0132	0.0018	8.46	0.0058
RepxFib	1	0.0001	0.0001	0.68	0.4121
RepxTemp	7	0.0064	0.0009	3.66	0.0023
RepxFibxTemp	7	0.0015	0.0002	0.88	0.5284
Residual	64	0.0162	0.0002		
Total	95	0.3936			

for nylon 6.6 was different from that for polyester. This phenomenon can be seen in Figure 13.

Based upon contrast analyses for density and crystallinity, which are listed in Table 17, nylon 6.6 showed a significant linear trend ($p<0.0001$) between temperature and density. Also, there was a significant quadratic trend ($p<0.0076$) between density and temperature. On the other hand, polyester showed a significant linear trend ($p<0.0001$), but no significant quadratic trend in the density-temperature relationship.

Trends for crystallinity were exactly the same as for density. There were both linear and quadratic trends between crystallinity and temperature for treated nylon filaments. There was only a linear trend but no quadratic trend in the crystallinity-temperature relationship for treated polyester. Both analyses, linear and quadratic, excluded the data for untreated specimens to concentrate on the relationships of the temperature treatments.

There were significant differences in density and degree of crystallinity between untreated and treated yarns. Therefore, it can be seen that the portion of amorphous regions in the fiber structure apparently decreased at higher temperatures.

TABLE 17

Contrast Analyses for Density and Crystallinity

Contrast	df	ms	F value	p
<u>Density</u>				
Nylon 6.6				
control vs treated	1	0.0002	72.33	0.0001
linear trend	1	0.0014	391.09	0.0001
quadratic trend	1	0.0000	14.53	0.0066
Polyester				
control vs treated	1	0.0008	224.51	0.0001
linear trend	1	0.0011	317.46	0.0001
quadratic trend	1	0.0000	2.56	0.1534
<u>Crystallinity</u>				
Nylon 6.6				
control vs treated	1	0.0124	55.65	0.0001
linear trend	1	0.0667	299.18	0.0001
quadratic trend	1	0.0024	10.81	0.0133
Polyester				
control vs treated	1	0.0581	260.74	0.0001
linear trend	1	0.0811	363.84	0.0001
quadratic trend	1	0.0006	3.13	0.1200

As a reference, the least squares means for crystallinity by fiber and temperature are shown in Table 18.

In summary, there was a significant interaction between fiber type and temperature for degree of crystallinity. Crystallinity for both nylon 6.6 and polyester filament yarns steadily increased as the heat setting temperature increased. But, the graphs of crystallinity of each fiber type with temperature depicted different shapes.

Heat setting in general above a particular temperature increases the degree of crystallinity. The results for nylon 6.6 and polyester are in agreement with those of Venkatesh et al. (63) and others (64,65).

Relationship of Tensile Properties and Crystallinity

To study the relationships among the tensile properties (tenacity, elongation and toughness) and the degree of crystallinity, correlation coefficients among the tenacity, elongation, toughness, temperature and crystallinity were obtained. Furthermore, to document the relationship visually, each tensile property variable was plotted against crystallinity. Also, regression analysis was used with the tensile property as the dependent variable and the crystallinity as the independent variable. According to the

TABLE 18
Least Squares Means for Crystallinity

	Crystallinity %
Fiber Type	
Nylon 6.6	41.1
Polyester	48.9
SE	0.1
Temperature	
untreated	38.3
150	40.5
165	40.8
180	43.7
195	46.1
210	47.7
225	50.9
235	52.0
SE	2.0

SE= Standard Error

significance levels of the sources of variation used for the model and the goodness of fit (R^2 square), regression models were determined.

Since there were significant fiber by temperature interactions on the tensile properties, the relationship between the variables and the degree of crystallinity was considered separately for each fiber type.

Nylon 6.6

The relationship between tensile properties (tenacity, elongation and toughness) and degree of crystallinity in nylon 6.6 filament yarns was studied. Statistical analyses used include correlation coefficients and regression.

The correlation coefficients of tenacity, elongation and toughness with crystallinity are shown in Table 19. It was found that crystallinity was negatively correlated with tenacity ($r=-0.84$), with elongation ($r=-0.81$), and with toughness ($r=-0.81$). Crystallinity was also highly correlated with temperature ($r=0.85$), suggesting that both crystallinity and temperature would be inefficient as independent variables in the same regression model.

To document the relationship between the degree of crystallinity and the tensile properties, two-dimensional plots of the data were made. Those plots including the possible regression line are shown in Figures 14, 15 and 16.

TABLE 19

Correlation Coefficients among Variables for Nylon 6.6
Filament Yarns

	1	2	3	4	5
1.Tenacity	-				
2.Elongation	0.95 *	-			
3.Toughness	0.94 *	0.99 *	-		
4.Dye Uptake	0.80 *	0.81 *	0.82 *	-	
5.Temperature	-0.89 *	-0.91 *	-0.91 *	-0.96 *	-
6.Crystallinity	-0.84 *	-0.81 *	-0.81 *	-0.81 *	0.85 *

* Significant at 0.05 level

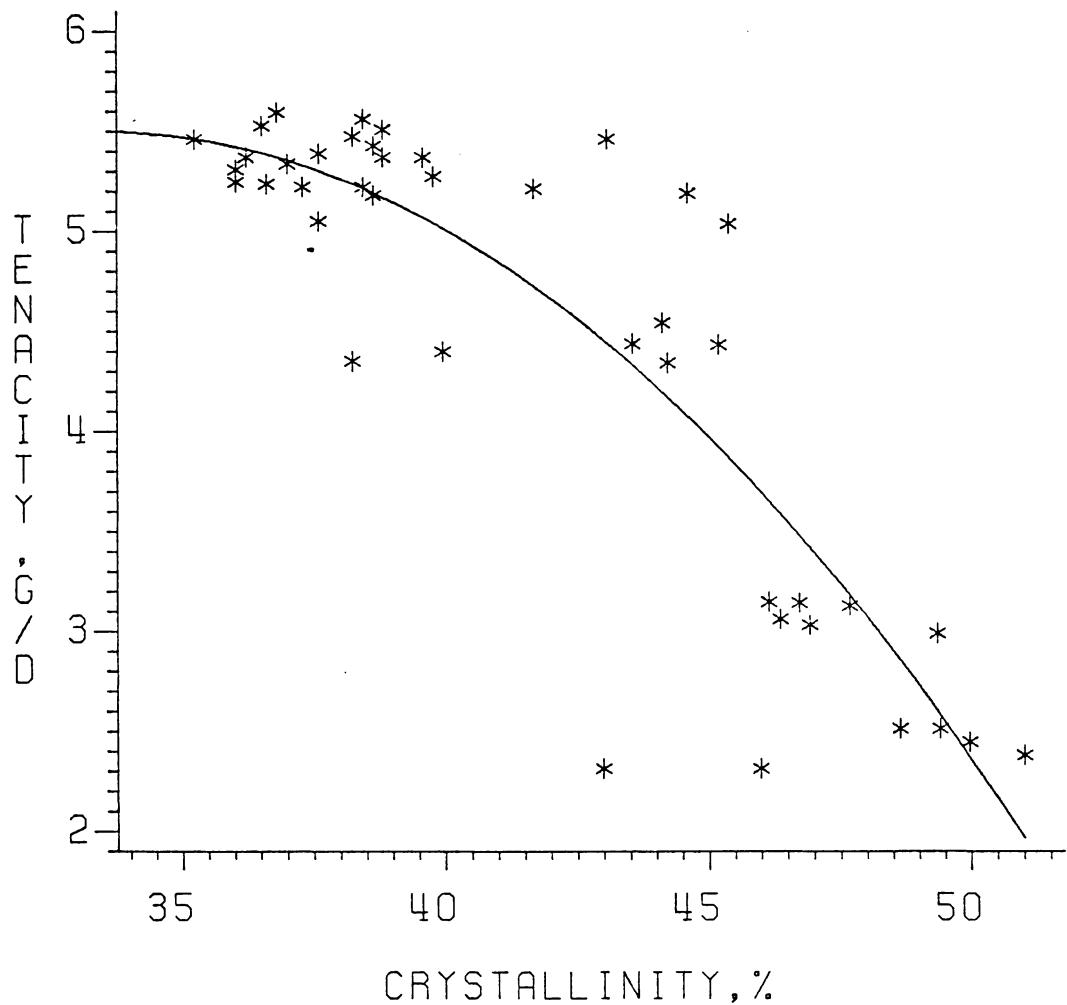


Figure 14: Plot of Tenacity vs Crystallinity for Nylon 6.6 Filament Yarns

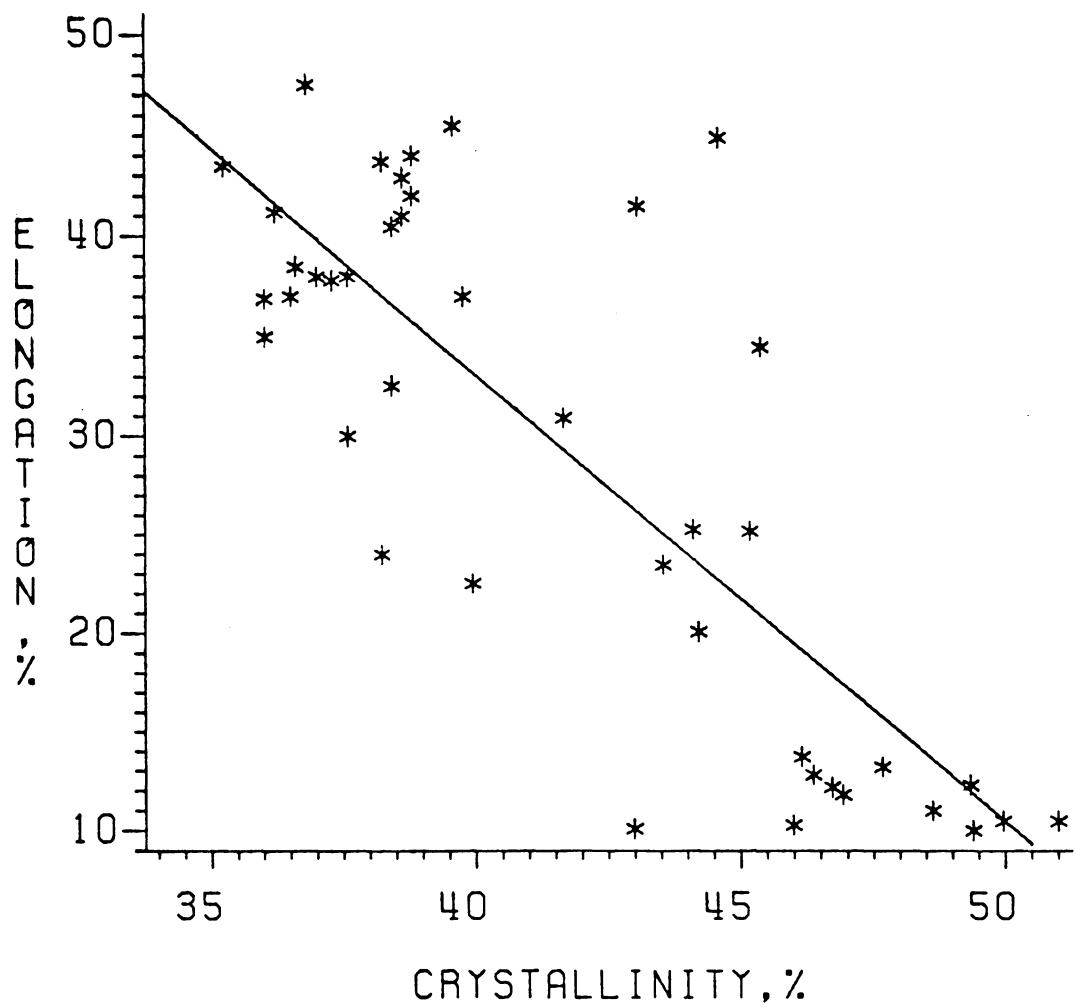


Figure 15: Plot of Elongation vs Crystallinity for Nylon 6.6 Filament Yarns

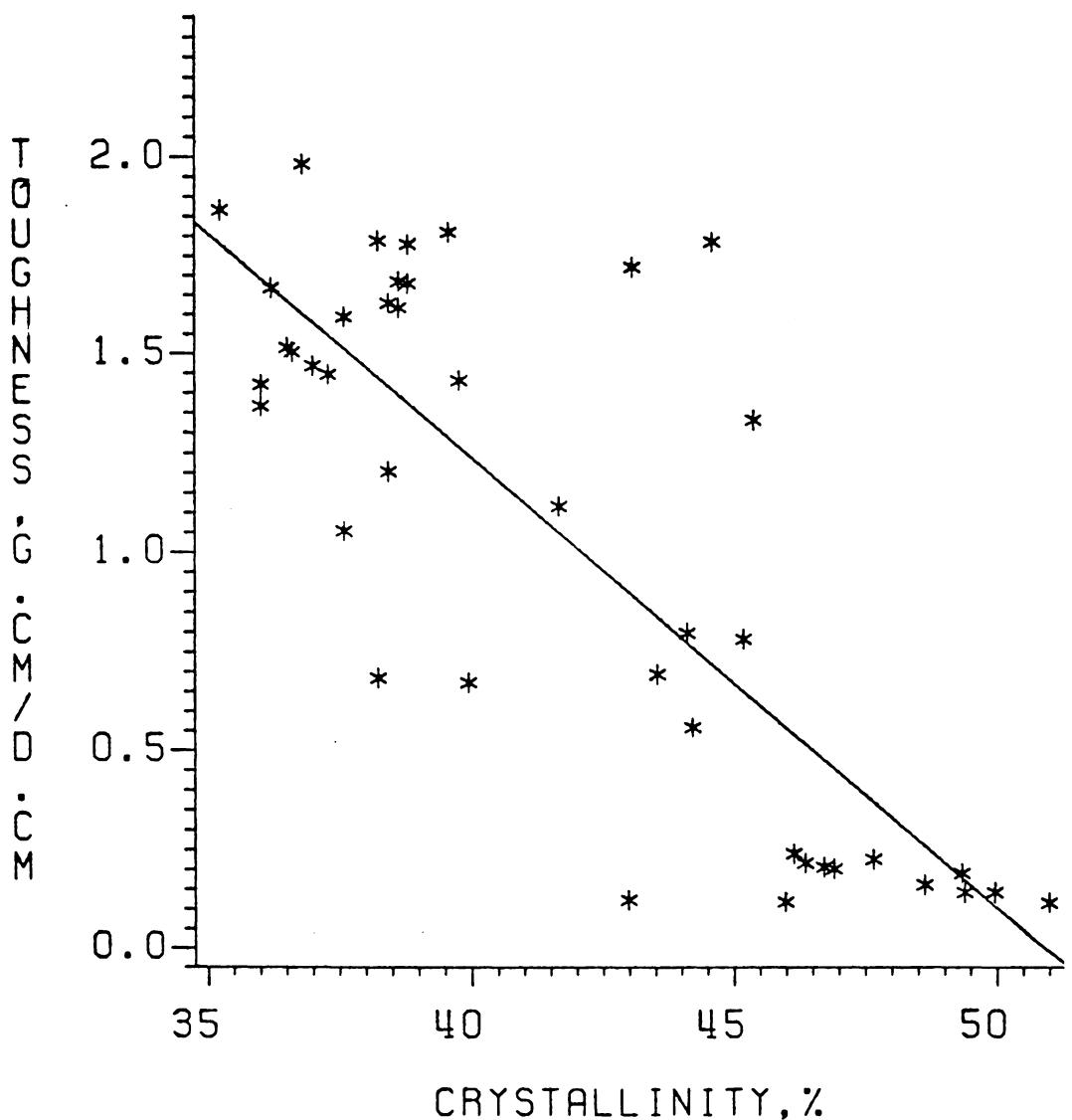


Figure 16: Plot of Toughness vs Crystallinity for Nylon 6.6 Filament Yarns

For regression analyses, three different models were tried: cubic, quadratic and simple linear regressions. If the cubic form was significant in the whole model, the cubic regression was used and graphed. If the quadratic form was significant in the model, the quadratic regression was adopted and graphed. If neither the cubic nor the quadratic forms were significant, simple linear regression was utilized and graphed as the best fitting model. As a result, quadratic regression was adopted as the best model for tenacity and simple linear regressions were best for elongation and toughness.

The estimates of the parameters for tensile properties are given in Table 20. Tenacity, elongation and toughness, therefore, can be predicted from crystallinity as follows:

$$\text{tenacity} = -7.38 + 0.77X - 0.01X^2$$

$$\text{elongation} = 123.38 - 2.26X$$

$$\text{toughness} = 5.78 - 0.11X$$

where: X = percent crystallinity.

Crystallinity in nylon fiber increased as temperature increased; however, tenacity decreased with increasing crystallinity. As Densmore (8) pointed out, tenacity of nylon fibers might be less dependent on crystallinity than on molecular chain length. However, increased crystallinity

TABLE 20

Regression Parameters for Tensile Properties and Dyeability
as Predicted by Crystallinity for Nylon 6.6 and Polyester

Variable	Intercept	Regression Coefficients			R^2
		Linear	Quadratic	Cubic	
Nylon 6.6					
Tenacity	-7.38	0.77	-0.01	-	0.75
Elongation	123.38	-2.26	-	-	0.66
Toughness	5.78	-0.11	-	-	0.66
Dyeability	53.10	-0.65	-	-	0.67
Polyester					
Tenacity	3.83	0.02	-	-	0.51
Elongation	-2606.09	161.32	-3.27	0.02	0.34
Toughness	-113.47	7.01	-0.14	0.01	0.27
Dyeability	15.75	-0.16	-	-	0.78

in a degraded fiber might counteract some of the loss in strength due to molecular chain breaking. It was observed that when nylon 6.6 filament yarns were heat set at temperatures above 195°C , discoloration of the treated yarns took place and the yarns became slack, suggesting degradation of fibers. The discoloration and the slackness both were greater as the temperature increased to 235°C . To investigate the degradation of nylon 6.6 fibers, viscosity measurements can be utilized.

Polyester

The relationship between fiber strength and degree of crystallinity in polyester filament yarns heat set at various temperatures was investigated by means of regression analyses. Other properties such as fiber extensibility and work required to break the fiber were related to degree of crystallinity.

It was found that tenacity was highly correlated to crystallinity ($r=0.71$). But the correlation coefficients with elongation and toughness were very low and negatively related with crystallinity. In particular, crystallinity was highly correlated with temperature ($r=0.96$), suggesting that in a regression model crystallinity and temperature would be inefficient as independent variables in the same

model. The correlation coefficients among variables for treated polyester yarns are in Table 21.

As mentioned in the statistical analyses section, one way of documenting the relationship was to plot the obtained data in a two-dimensional plane. Plots of tenacity versus crystallinity, elongation versus crystallinity, and toughness versus crystallinity are shown in Figures 17, 18, and 19, respectively.

For regression analysis, three different models, cubic, quadratic and linear, were tried as in the case of nylon. The method of choosing the best model among them was the same as for nylon 6.6 fibers. The estimates of the parameters for the tensile variables are given in Table 20. It can be seen that the simple linear model was adopted as the best model for tenacity, while the cubic model was better for elongation and toughness. Therefore, the tensile properties can be predicted from crystallinity as follows:

$$\text{tenacity} = 3.83 + 0.02X$$

$$\text{elongation} = -2606.09 + 161.32X - 3.27X^2 + 0.02X^3$$

$$\text{toughness} = -113.47 + 7.01X - 0.14X^2 + 0.01X^3$$

where: X = percent crystallinity.

Elongation and toughness statistically fitted to a cubic formd better than a linear or quadratic one, but from

TABLE 21

Correlation Coefficients among Variables for Polyester
Filament Yarns

	1	2	3	4	5
1.Tenacity	-				
2.Elongation	0.18*	-			
3.Toughness	0.32*	0.96*	-		
4.Dye uptake	-0.76*	0.20	0.13	-	
5.Temperature	0.60*	-0.34*	-0.29*	-0.93*	-
6.Crystallinity	0.71*	-0.35*	-0.29	-0.88*	0.96*

* Significant at 0.05 level

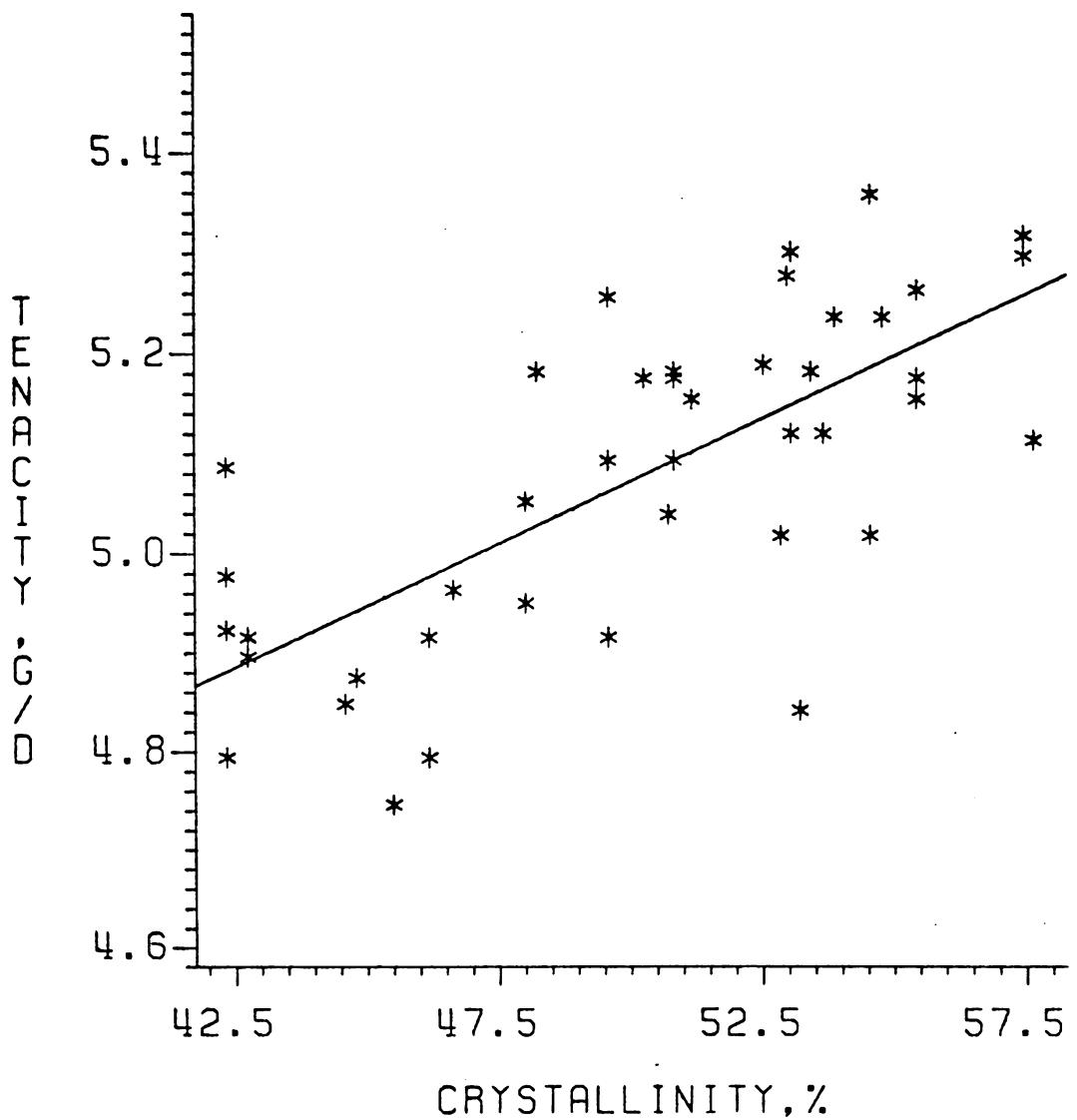


Figure 17: Plot of Tenacity vs Crystallinity for Polyester Filament Yarns

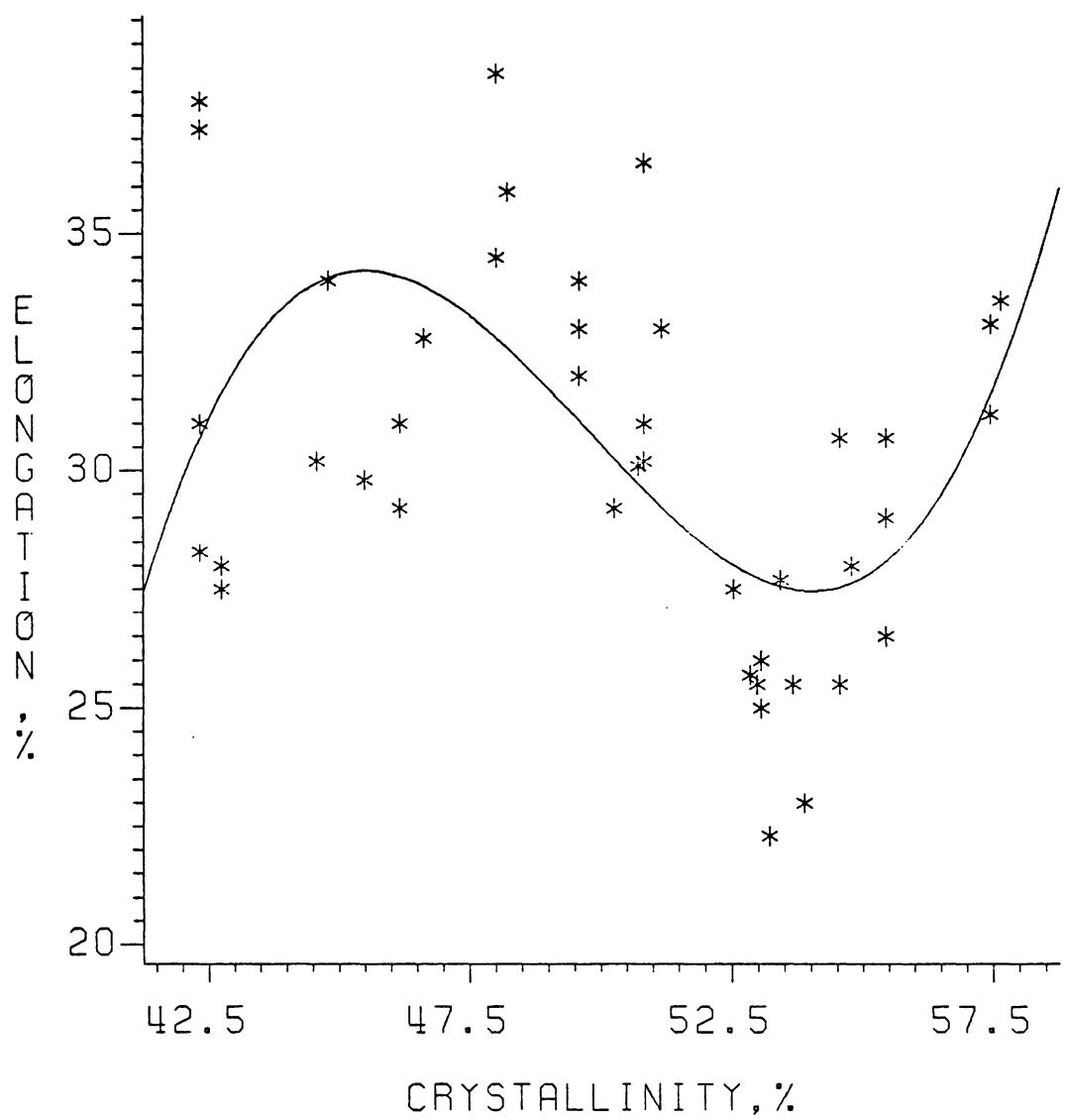


Figure 18: Plot of Elongation vs Crystallinity for Polyester Filament Yarns

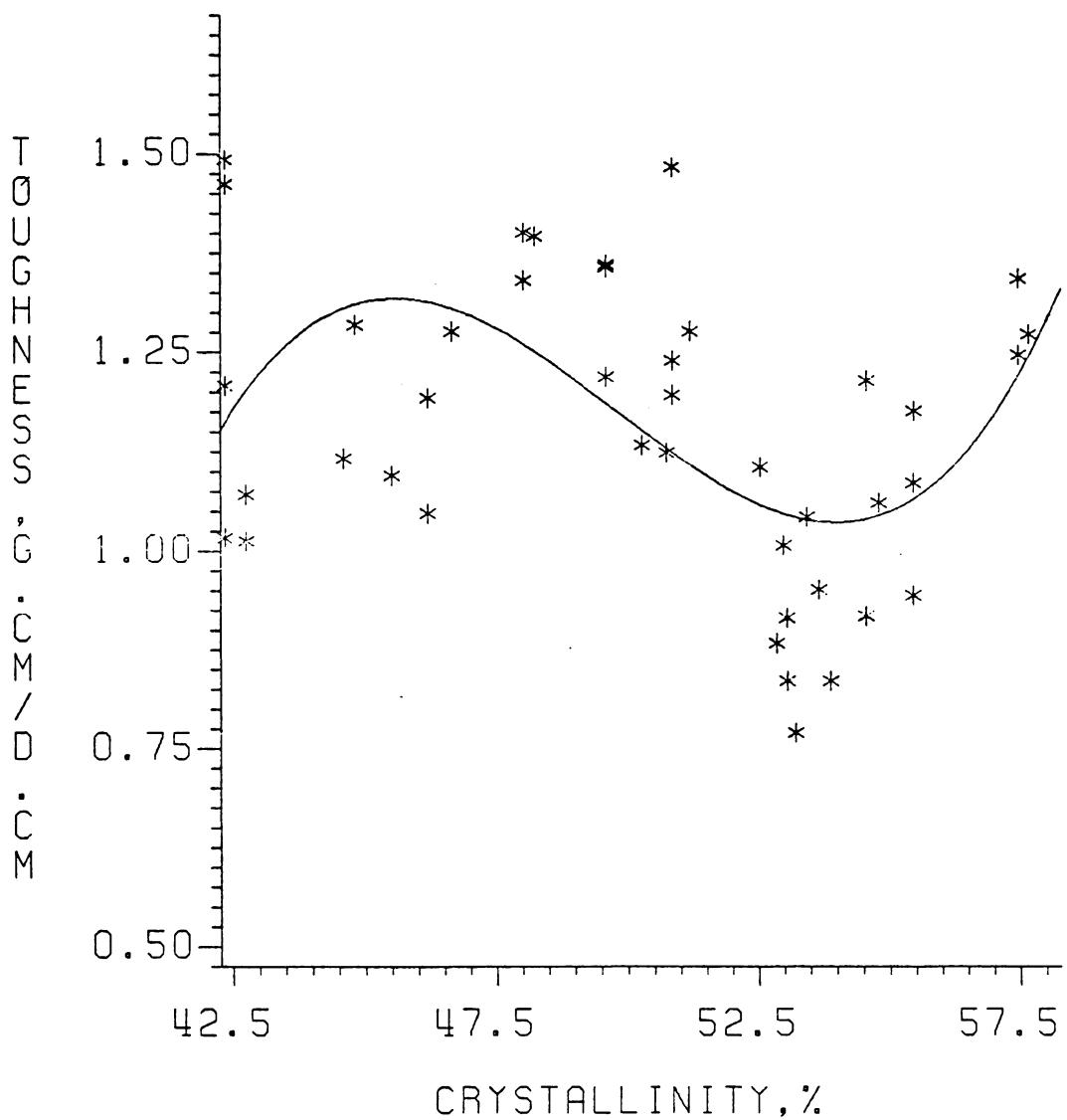


Figure 19: Plot of Toughness vs Crystallinity for Polyester Filament Yarns

a theoretical point of view there is not much meaning to the relationship. There was low correlation between crystallinity and the variables, and high variability in both elongation and toughness. Crystallinity in polyester fiber was more highly correlated with tenacity. To predict the elongation and the toughness by the structural parameters, measurement of the degree of orientation by the birefringence method or other equivalent methods might be utilized in addition to the crystallinity measurement.

Relationship of Dyeability and Crystallinity

For studying the relationship between the amount of dye absorbed and the degree of crystallinity, correlation coefficients were obtained among dye uptake, temperature, and crystallinity. Similarly, to document the relationship, plots were drawn between variables. Depending upon the significance levels of the sources used for the model and the goodness of fit (R^2), the regression model was determined.

Nylon 6.6

The relationship between dyeability and crystallinity for nylon 6.6 fibers was evaluated from the correlation coefficients and the plot of dye uptake versus

crystallinity. Regression analyses were used to get the best fitting model.

According to the correlation coefficients (Table 19) for treated nylon yarns, dye uptake was negatively correlated with degree of crystallinity ($r=-0.81$), and the plot of dye uptake versus crystallinity clearly delineated the negative relationship (Figure 20).

The estimates of the parameters for dyeability are given in Table 20. The best regression model for predicting dye uptake from crystallinity was a simple linear regression. The equation of the model, therefore, can be written as follows:

$$\text{dyeability} = 53.10 - 0.65X$$

where: X = percent crystallinity.

Since dye molecules chiefly locate in the amorphous regions, the increased crystallinity in nylon 6.6 fibers decreases the amount of dye absorbed by the fibers.

Polyester

The amount of dye uptake by heat set polyester fibers was interrelated with the amount of crystallinity developed by the treatment. Regression analyses were used to secure a possible equation to predict the degree of crystallinity

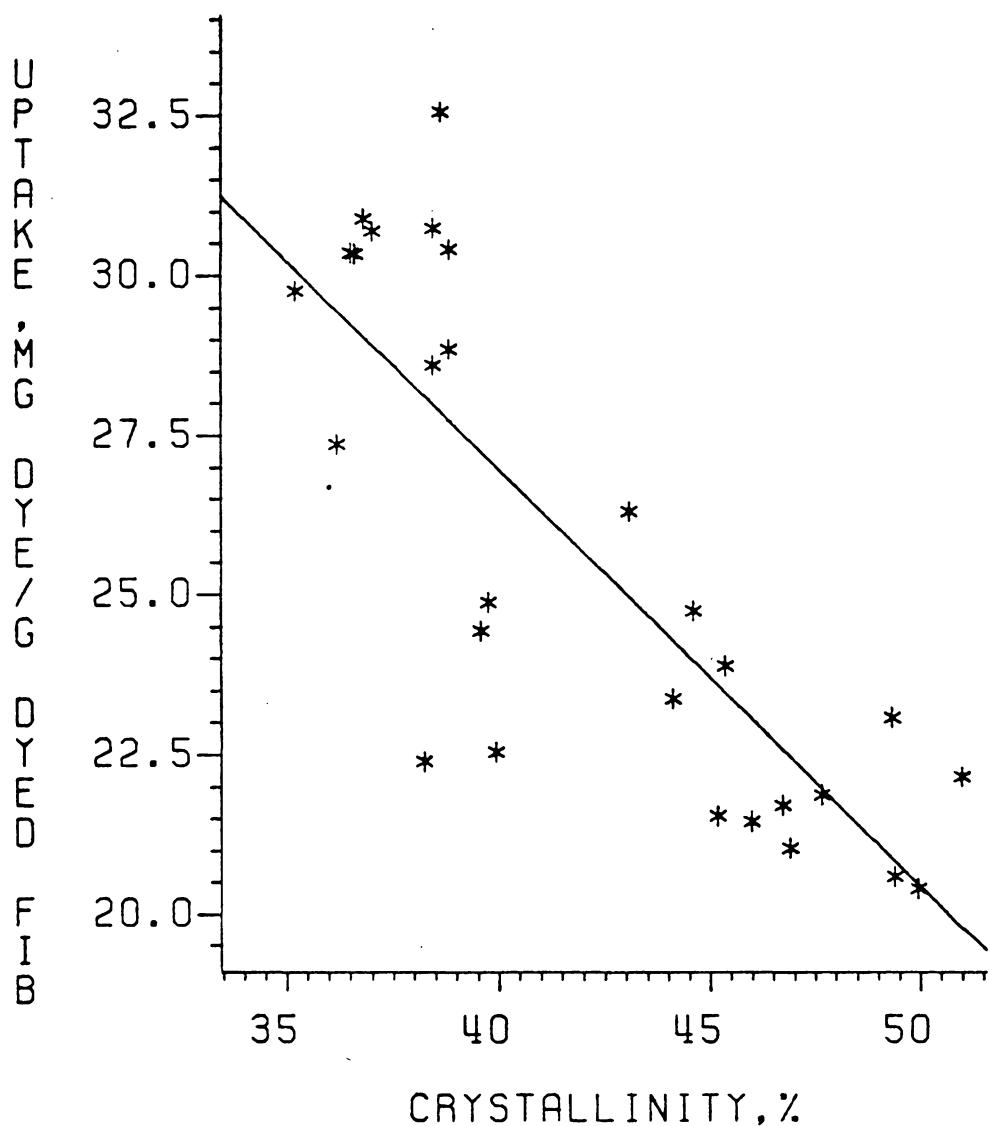


Figure 20: Plot of Dye Uptake vs Crystallinity for Nylon 6.6 Filament yarns

when the amount of dye uptake of the fiber would be given or vice versa.

According to the correlation coefficients (Table 21) for treated polyester yarns, dye uptake was negatively correlated with crystallinity ($r=-0.88$), and the plot of dye uptake versus crystallinity delineated a negative relationship clearly (Figure 21).

The estimates of the parameters for dye uptake are in Table 20. The best fitting regression model for predicting dyeability from crystallinity was also a simple linear regression as in the case of nylon. The equation can be written as follows:

$$\text{dyeability} = 15.75 - 0.16X$$

where: X = percent crystallinity.

Again, the increased crystallinity of the treated polyester fibers resulted in a decrease of dye uptake due to the decrease in amorphous regions.

In terms of the two-phase theory of structure involving a crystalline and an amorphous region, two opposing factors play a part in the dye uptake of the heat set fibers. The dyeing properties were quite consistent with the two-phase theory of structure. An increase in the degree of crystallinity resulted in a reduction of the dye uptake.

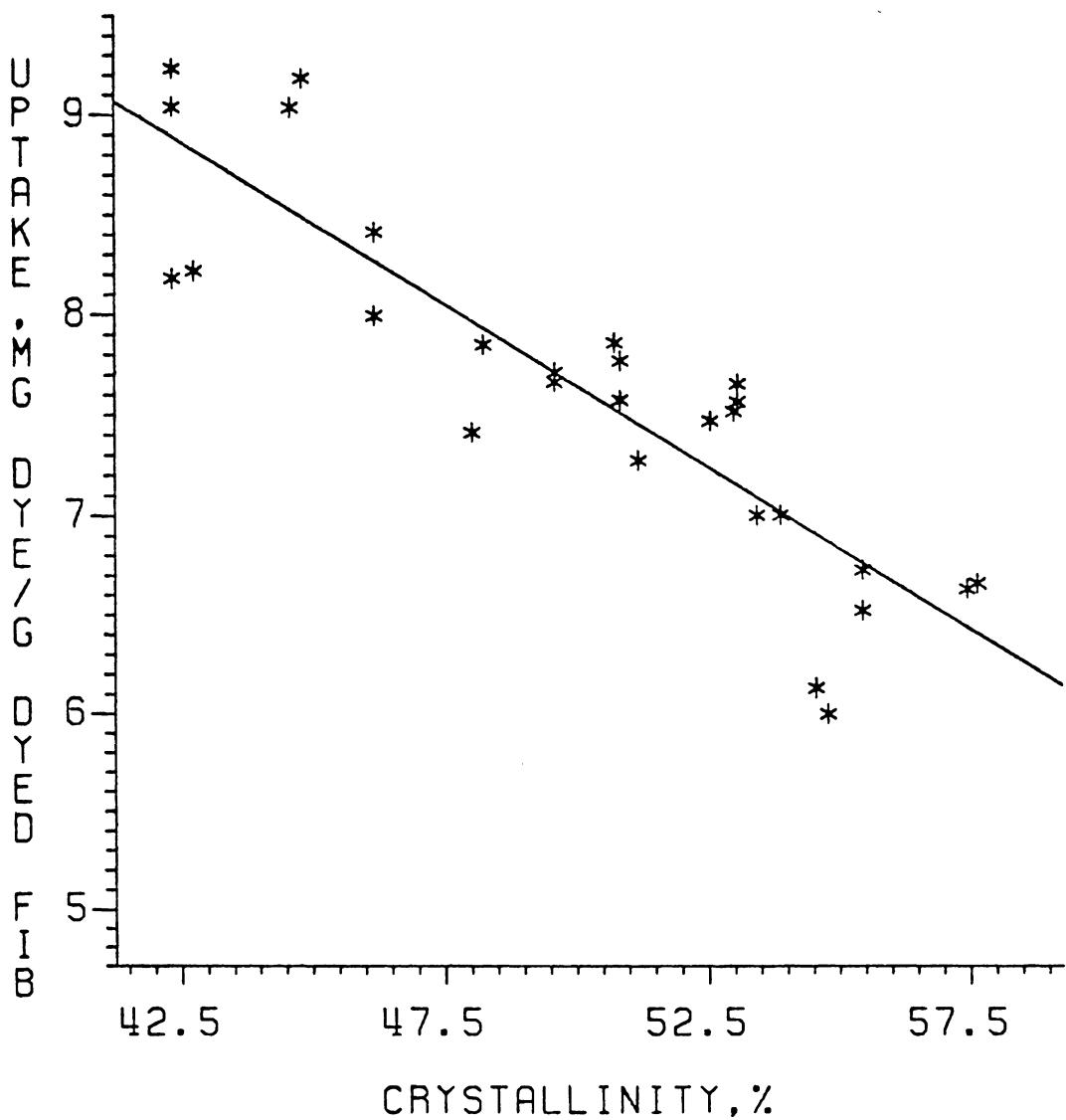


Figure 21: Plot of Dye Uptake vs Crystallinity for Polyester Filament Yarns

Venkatesh et al. (63) have found that the disorientation of the amorphous regions which increased with increasing heat setting temperature led to increased dye uptake. But, they have observed that because the changes in the overall crystallinity were considerable, the net effect was a decrease in the dye uptake. In practice, the dyeability of heat set fibers could be explained in terms of structure, especially, in terms of degree of crystallinity.

Chapter VI

SUMMARY AND CONCLUSIONS

This study was undertaken to investigate how heat treatment affected the degree of crystallinity, tensile properties and the amount of dye uptake of nylon 6.6 and polyester filament yarns and to investigate how the degree of crystallinity was related with the tensile properties and the dyeability.

Materials and Methods

The specimens used for this research were nylon 6.6 and polyester filament yarns which were identical in denier and number of filaments (100/34), had round cross sectional shape and semidull brightness. Heat treatment of the specimens was done at constant length for 3 minutes in dry heat. The different temperature settings were 150, 165, 180, 195, 210, 225, and 235 °C for both nylon and polyester.

Tensile properties at the break were measured on a constant-rate-of-extension testing machine. For this test, single-filament specimens of a predetermined test length were broken according to the recommended procedure. From the load-elongation chart, tenacity, elongation and toughness of the specimens were calculated.

Dyeing of loosely held specimens was done in the laboratory dyeing machine. The disperse dye used was Intrasperse Orange 2RN Ex. (C.I. Disperse Orange 3). The starting temperature of the dyebath was 50°C and the bath was heated to 90°C at a rate of 2°C per minute. Then dyeing was continued for 90 minutes. To estimate the dye uptake of samples, a weighed amount of dyed fiber was dissolved in 20% calcium chloride in methanol for nylon 6.6 and in m-cresol for polyester. The concentration of dye in the solutions was measured spectrophotometrically.

A density gradient column technique was used to measure the density of untreated and treated specimens. From the fiber density, crystallinity was calculated using the weight fraction percent crystallinity equation. The density values for crystalline and amorphous fiber were taken to be 1.240 g/cm³ and 1.090 g/cm³ for nylon 6.6, 1.455 g/cm³ and 1.335 g/cm³ for polyester.

The design of the experiments was a repeated factorial design with subsampling. The design included two factors: fiber type and temperature. Statistical analyses utilized for this study included analysis of variance, contrast tests, least squares means, correlation coefficients and regression.

Conclusions Based on Findings

The following general conclusions may be drawn regarding the hypotheses:

Hypothesis 1: Type of fiber (nylon vs polyester) will affect the tensile properties, dye uptake and degree of crystallinity of heat treated filament yarns.

Tenacity at the breaking point varied significantly but elongation and toughness did not, thus supporting the hypothesis partially. Type of fiber affected the amount of dye uptake significantly. Nylon 6.6 absorbed approximately four times more dye than polyester. These findings support the hypothesis. Type of fiber also affected the degree of crystallinity; that is, there was a significant difference in crystallinity between nylon 6.6 and polyester. These findings also support the hypothesis.

Hypothesis 2: Temperature of heat treatment will affect the tensile properties, dye uptake and degree of crystallinity.

Temperature of heat treatment had a significant effect on all of the above variables. Tensile properties at the break decreased as temperature increased. The amount of dye uptake decreased as temperature increased. The degree of crystallinity of the treated yarns increased as temperature increased. These results support the hypothesis.

Hypothesis 3: There will be significant interaction effect between fiber type and temperature on the tensile properties, dye uptake and degree of crystallinity.

There was a significant interaction effect for all of the above variables. The tensile properties, the amount of dye uptake and the degree of crystallinity showed different trends with temperature for the two fibers. Tenacity of nylon 6.6 decreased moderately up to 195°C and then decreased steeply. Polyester, however, showed a marginal increase in tenacity. Elongation and toughness of nylon 6.6 also dropped moderately up to 195°C and dropped suddenly thereafter. Polyester showed a decreasing elongation and toughness with temperature even though some fluctuation occurred. Dye uptake of nylon 6.6 showed a decreasing tendency as temperature increased. Polyester also showed a decreasing tendency as temperature increased, but the slopes of the graphs were different. Degree of crystallinity for both nylon 6.6 and polyester gradually increased with temperature, but the slopes of the graphs were different. Therefore, these findings support the hypothesis.

The relationships between tensile properties and degree of crystallinity were examined. Crystallinity was negatively correlated with tenacity, elongation and toughness for nylon 6.6. Tenacity of polyester, however, was

positively correlated with degree of crystallinity. Elongation and toughness of polyester showed negative relationships with crystallinity; however, the relationship between toughness and crystallinity was not significant. In spite of increased crystallinity, tenacity of nylon 6.6 decreased, suggesting a degradation of the fibers. Therefore, degree of crystallinity was not an important contributor to change in tensile strength for degraded nylon 6.6.

Dye uptake and crystallinity were highly correlated for both nylon 6.6 and polyester. The increased crystallinity of the treated fibers was accompanied by decreased dye uptake. In other words, crystallinity was an important contributor to change in dyeability for both nylon 6.6 and polyester filament yarns. Therefore, dye uptake would be a fair way to measure changes in crystallinity.

Chapter VII

RECOMMENDATIONS

The information obtained in this study may serve as a basis for the further investigation of heat treatment of thermoplastic fibers and in the interpretation of the structural changes which take place during heat treatment. This study would have been strengthened by using more than a single method for measuring the degree of crystallinity of the fiber.

The findings of the study indicate a need for further investigation in the areas of the degree of orientation and molecular size of the polymers which may affect the tensile properties and the dyeability. Further investigation might well be limited to a more thorough study of a single polymer while varying the treatment conditions. Work needs to be done on yarns texturized by various processes which involve heat. Texturizing could bring about possible structural changes from tension, torque or other physical stresses.

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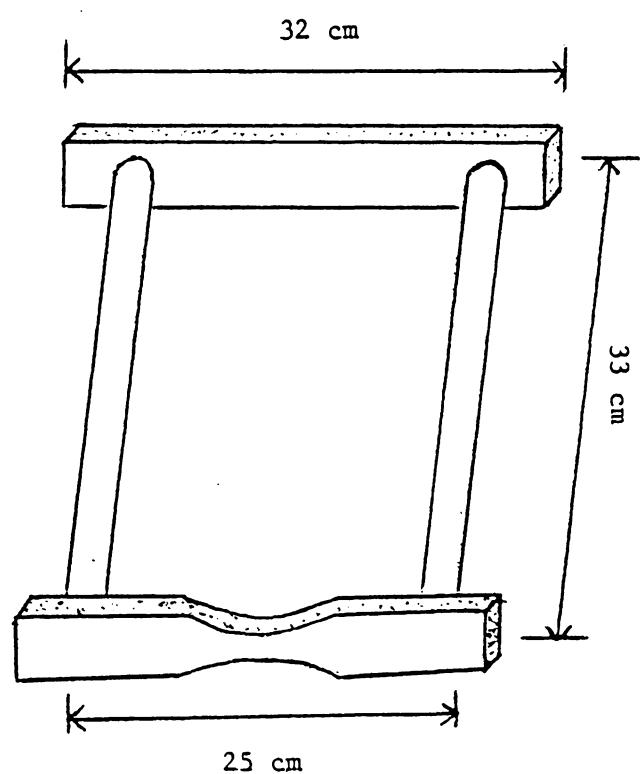
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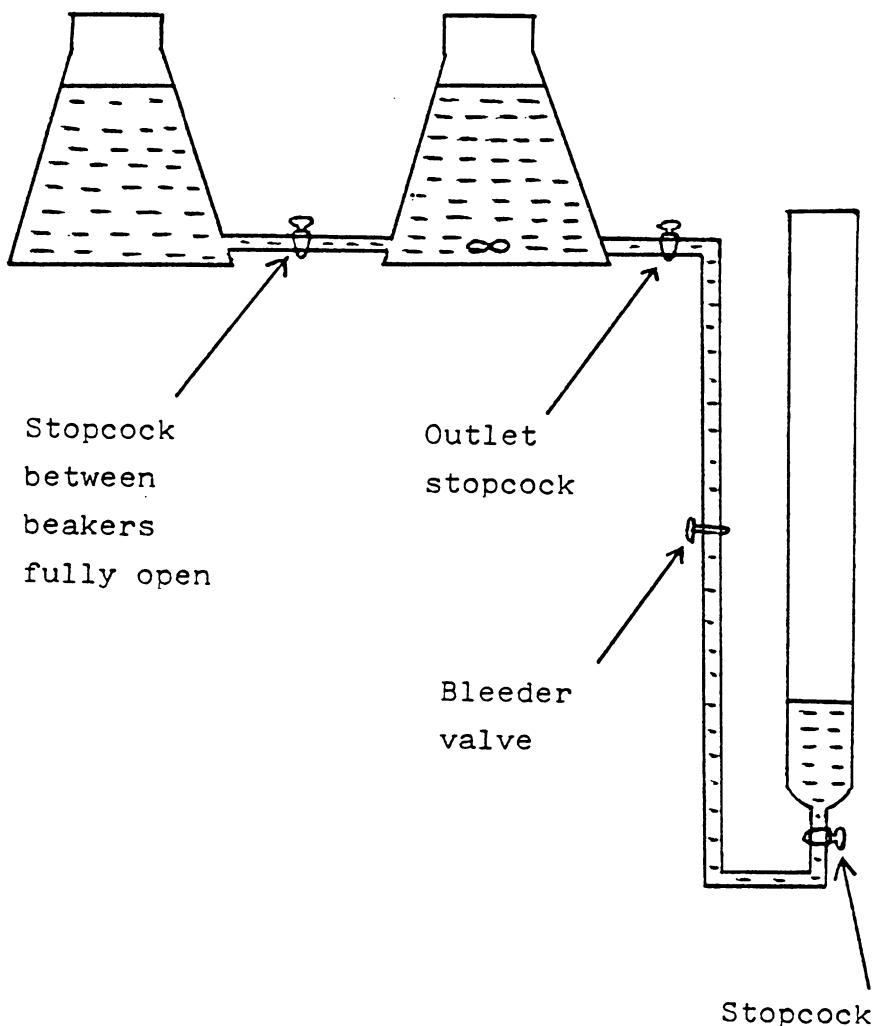
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Appendix A
DRAWING OF THE WOODEN FRAME



Appendix B

APPARATUS FOR DENSITY GRADIENT COLUMN



Appendix C
TENSILE PROPERTIES DATA

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEM=20 REP=A -----						
BL	11	16.76363636	0.62768261	15.62000000	17.62000000	0.18925343
EL	11	4.74000000	0.36619667	4.00000000	5.38000000	0.11041245
TH	11	0.22287273	0.02514013	0.17710000	0.26360000	0.00758003
TENA	11	5.69963636	0.21341209	5.31080000	5.99080000	0.06434617
ELONG	11	47.40000000	3.66196668	40.00000000	53.80000000	1.10412450
TOUGH	11	2.02948008	0.22892615	1.61267342	2.40034281	0.06902383
----- FIB=N TEM=20 REP=B -----						
BL	11	16.32909091	0.63739242	15.22000000	17.16000000	0.19218104
EL	11	4.56545455	0.21407305	4.19000000	4.89000000	0.06454545
TH	11	0.20555455	0.01462562	0.18460000	0.22410000	0.00440979
TENA	11	5.55189091	0.21671342	5.17480000	5.83440000	0.06534156
ELONG	11	45.65454545	2.14073055	41.90000000	48.90000000	0.64545455
TOUGH	11	1.87178064	0.13318095	1.68096845	2.04065563	0.04015557
----- FIB=N TEM=150 REP=A -----						
BL	11	15.94909091	0.30441598	15.36000000	16.40000000	0.09178487
EL	11	4.25454545	0.36426264	3.78000000	4.80000000	0.10982932
TH	11	0.18717273	0.01885487	0.15910000	0.22190000	0.00568496
TENA	11	5.42269091	0.10350143	5.22240000	5.57600000	0.03120686
ELONG	11	42.54545455	3.64262643	37.80000000	48.00000000	1.09829319
TOUGH	11	1.70439572	0.17169255	1.44876533	2.02062242	0.05176725
----- FIB=N TEM=150 REP=B -----						
BL	11	15.92000000	0.46112905	15.26000000	16.46000000	0.13903564
EL	11	4.12818182	0.39579839	3.65000000	4.75000000	0.11933770
TH	11	0.17707273	0.02558715	0.13550000	0.21790000	0.00771482
TENA	11	5.41280000	0.15678388	5.18840000	5.59640000	0.04727212
ELONG	11	41.28181818	3.95798388	36.50000000	47.50000000	1.19337704
TOUGH	11	1.61242507	0.23299669	1.23386362	1.98419840	0.07025115
----- FIB=N TEM=165 REP=A -----						
BL	11	15.84000000	0.46784613	15.00000000	16.36000000	0.14106092
EL	11	3.91363636	0.35660266	3.30000000	4.35000000	0.10751975
TH	11	0.16896364	0.01705287	0.13920000	0.19070000	0.00514164
TENA	11	5.38560000	0.15906768	5.10000000	5.56240000	0.04796071
ELONG	11	39.13636364	3.56602656	33.00000000	43.50000000	1.07519746
TOUGH	11	1.53858365	0.15528356	1.26755584	1.73651508	0.04681975
----- FIB=N TEM=165 REP=B -----						
BL	11	15.78363636	0.51573778	15.00000000	16.56000000	0.15550079
EL	11	4.03090909	0.37657548	3.40000000	4.45000000	0.11354178
TH	11	0.18129091	0.02246226	0.14250000	0.20840000	0.00677262
TENA	11	5.36643636	0.17535084	5.10000000	5.63040000	0.05287027
ELONG	11	40.30909091	3.76575478	34.00000000	44.50000000	1.13541779
TOUGH	11	1.65083585	0.20454140	1.29760566	1.89769136	0.06167155

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEM=180 REP=A -----						
BL	11	15.56363636	0.29309632	15.18000000	16.10000000	0.08837187
EL	11	3.97181818	0.48379372	3.10000000	4.48000000	0.14586930
TH	11	0.16926364	0.02448752	0.12770000	0.19670000	0.00738326
TENA	11	5.29163636	0.09965275	5.16120000	5.47400000	0.03004643
ELONG	11	39.71818182	4.83793720	31.00000000	44.80000000	1.45869295
TOUGH	11	1.54131545	0.22298345	1.16283679	1.79115111	0.06723204
----- FIB=N TEM=180 REP=B -----						
BL	11	15.62545455	0.46708380	14.72000000	16.28000000	0.14083106
EL	11	3.83272727	0.34788190	3.25000000	4.20000000	0.10489034
TH	11	0.17015455	0.02016519	0.13770000	0.20400000	0.00608003
TENA	11	5.31265455	0.15880849	5.00480000	5.53520000	0.04788256
ELONG	11	38.32727273	3.47881903	32.50000000	42.00000000	1.04890340
TOUGH	11	1.54942807	0.18362428	1.25389683	1.85762494	0.05536480
----- FIB=N TEM=195 REP=A -----						
BL	11	15.28727273	0.44499642	14.36000000	15.80000000	0.13417147
EL	11	3.52636364	0.44032426	3.09000000	4.55000000	0.13276276
TH	11	0.14686364	0.02330636	0.12040000	0.19890000	0.00702713
TENA	11	5.19767273	0.15129878	4.88240000	5.37200000	0.04561830
ELONG	11	35.26363636	4.40324261	30.90000000	45.50000000	1.32762760
TOUGH	11	1.33734095	0.21222785	1.09636295	1.81118432	0.06398910
----- FIB=N TEM=195 REP=B -----						
BL	11	15.04363636	0.40760944	14.54000000	15.80000000	0.12289887
EL	11	3.62909091	0.45759053	3.00000000	4.49000000	0.13796874
TH	11	0.15486364	0.02613210	0.11590000	0.19640000	0.00787912
TENA	11	5.11483636	0.13858721	4.94360000	5.37200000	0.04178562
ELONG	11	36.29090909	4.57590528	30.00000000	44.90000000	1.37968735
TOUGH	11	1.41018899	0.23795900	1.05538593	1.78841930	0.07174734
----- FIB=N TEM=210 REP=A -----						
BL	11	13.08181818	0.26958554	12.80000000	13.48000000	0.08128310
EL	11	2.24454545	0.16330117	2.00000000	2.53000000	0.04923716
TH	11	0.07070909	0.00781786	0.06000000	0.08770000	0.00235717
TENA	11	4.44781818	0.09165908	4.35200000	4.58320000	0.02763625
ELONG	11	22.44545455	1.63301172	20.00000000	25.30000000	0.49237156
TOUGH	11	0.64387731	0.07118945	0.54636028	0.79859660	0.02146443
----- FIB=N TEM=210 REP=B -----						
BL	11	13.03636364	0.16463734	12.78000000	13.34000000	0.04964003
EL	11	2.24454545	0.18774257	2.00000000	2.52000000	0.05660651
TH	11	0.07340909	0.01001214	0.06030000	0.08810000	0.00301877
TENA	11	4.43236364	0.05597670	4.34520000	4.53560000	0.01687761
ELONG	11	22.44545455	1.87742570	20.00000000	25.20000000	0.56606515
TOUGH	11	0.66846352	0.09117058	0.54909208	0.80223901	0.02748896

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEM=225 -----						
BL	11	8.85636364	0.27008416	8.42000000	9.20000000	0.08143344
EL	11	1.23000000	0.09110434	1.10000000	1.38000000	0.02746899
TH	11	0.02230000	0.00232938	0.01820000	0.02610000	0.00070233
TENA	11	3.01116364	0.09182862	2.86280000	3.12800000	0.02768737
ELONG	11	12.30000000	0.91104336	11.00000000	13.80000000	0.27468991
TOUGH	11	0.20306390	0.02121132	0.16572928	0.23766672	0.00639545
----- FIB=N TEM=225 -----						
BL	11	9.32000000	0.32483842	8.58000000	9.62000000	0.09794247
EL	11	1.27181818	0.07573879	1.12000000	1.37000000	0.02283610
TH	11	0.02430909	0.00264063	0.01820000	0.02690000	0.00079618
TENA	11	3.16880000	0.11044506	2.91720000	3.27080000	0.03330044
ELONG	11	12.71818182	0.75738786	11.20000000	13.70000000	0.22836103
TOUGH	11	0.22135869	0.02404556	0.16572928	0.24495152	0.00725001
----- FIB=N TEM=235 -----						
BL	11	7.04181818	0.32328991	6.60000000	7.70000000	0.09747557
EL	11	1.01363636	0.04588523	0.95000000	1.09000000	0.01383492
TH	11	0.01407273	0.00128226	0.01270000	0.01680000	0.00038661
TENA	11	2.39421818	0.10991857	2.24400000	2.61800000	0.03314170
ELONG	11	10.13636364	0.45885232	9.50000000	10.90000000	0.13834918
TOUGH	11	0.12814632	0.01167623	0.11564626	0.15298088	0.00352052
----- FIB=N TEM=235 -----						
BL	11	7.49090909	0.21454391	7.20000000	7.80000000	0.06468742
EL	11	1.04818182	0.05192652	1.00000000	1.15000000	0.01565644
TH	11	0.01677273	0.00146362	0.01510000	0.01990000	0.00044130
TENA	11	2.54690909	0.07294493	2.44800000	2.65200000	0.02199372
ELONG	11	10.48181818	0.51926522	10.00000000	11.50000000	0.15656435
TOUGH	11	0.15273253	0.01332773	0.13750067	0.18120949	0.00401846
----- FIB=P TEM=20 -----						
BL	11	14.41454545	0.45317466	13.84000000	15.20000000	0.13663730
EL	11	3.69272727	0.25807328	3.32000000	4.11000000	0.07781202
TH	11	0.15150909	0.01525945	0.13460000	0.17420000	0.00460090
TENA	11	4.90094545	0.15407938	4.70560000	5.16800000	0.04645668
ELONG	11	36.92727273	2.58073281	33.20000000	41.10000000	0.77812022
TOUGH	11	1.37964248	0.13895265	1.22566822	1.58626600	0.04189580
----- FIB=P TEM=20 -----						
BL	11	14.63818182	0.48969007	13.84000000	15.58000000	0.14764711
EL	11	3.74636364	0.28706350	3.30000000	4.25000000	0.08655290
TH	11	0.15347273	0.01531758	0.13060000	0.18240000	0.00461842
TENA	11	4.97698182	0.16649462	4.70560000	5.29720000	0.05020002
ELONG	11	37.46363636	2.87063503	33.00000000	42.50000000	0.86552903
TOUGH	11	1.39752336	0.13948193	1.18924420	1.66093524	0.04205538

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEM=150 REP=A -----						
BL	11	14.41454545	0.40040888	13.88000000	15.08000000	0.12072782
EL	11	3.28272727	0.24637739	2.98000000	3.75000000	0.07428558
TH	11	0.13794545	0.01789851	0.10580000	0.16390000	0.00539660
TENA	11	4.90094545	0.13613902	4.71920000	5.12720000	0.04104746
ELONG	11	32.82727273	2.46377390	29.80000000	37.50000000	0.74285578
TOUGH	11	1.25613194	0.16298393	0.96341529	1.49247416	0.04914150
----- FIB=P TEM=150 REP=B -----						
BL	11	14.60181818	0.42964679	13.96000000	15.50000000	0.12954338
EL	11	3.36181818	0.32043153	2.83000000	3.78000000	0.09661374
TH	11	0.14200000	0.01846218	0.11160000	0.16400000	0.00556656
TENA	11	4.96461818	0.14607991	4.74640000	5.27000000	0.04404475
ELONG	11	33.61818182	3.20431527	28.30000000	37.80000000	0.96613741
TOUGH	11	1.29305265	0.16811667	1.01623011	1.49338476	0.05068908
----- FIB=P TEM=165 REP=A -----						
BL	11	14.57636364	0.34290736	14.10000000	15.14000000	0.10339046
EL	11	3.06454545	0.31097793	2.71000000	3.83000000	0.09376337
TH	11	0.12919091	0.01897675	0.10060000	0.17230000	0.00572170
TENA	11	4.95596364	0.11658850	4.79400000	5.14760000	0.03515276
ELONG	11	30.64545455	3.10977930	27.10000000	38.30000000	0.93763374
TOUGH	11	1.17641301	0.17280234	0.91606406	1.56896459	0.05210187
----- FIB=P TEM=165 REP=B -----						
BL	11	14.35818182	0.14925268	14.14000000	14.62000000	0.04500138
EL	11	2.90636364	0.14451801	2.75000000	3.17000000	0.04357382
TH	11	0.11883636	0.00896619	0.10880000	0.13420000	0.00270341
TENA	11	4.88178182	0.05074591	4.80760000	4.97080000	0.01530047
ELONG	11	29.06363636	1.44518008	27.50000000	31.70000000	0.43573819
TOUGH	11	1.08212447	0.08164616	0.99073330	1.22202582	0.02461724
----- FIB=P TEM=180 REP=A -----						
BL	11	15.08545455	0.33670057	14.46000000	15.66000000	0.10151904
EL	11	3.24090909	0.33874635	2.76000000	3.69000000	0.10213587
TH	11	0.14516364	0.01845645	0.11680000	0.17490000	0.00556483
TENA	11	5.12905455	0.11447819	4.91640000	5.32440000	0.03451647
ELONG	11	32.40909091	3.38746352	27.60000000	36.90000000	1.02135868
TOUGH	11	1.32186074	0.16806452	1.06358134	1.59264021	0.05067336
----- FIB=P TEM=180 REP=B -----						
BL	11	14.90545455	0.33058626	14.40000000	15.46000000	0.09967551
EL	11	3.25818182	0.30049353	2.86000000	3.84000000	0.09060221
TH	11	0.13961818	0.01494355	0.11810000	0.17010000	0.00450565
TENA	11	5.06785455	0.11239933	4.89600000	5.25640000	0.03388967
ELONG	11	32.58181818	3.00493533	28.60000000	38.40000000	0.90602209
TOUGH	11	1.27136381	0.13607602	1.07541914	1.54893138	0.04102846

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEM=195 -----						
BL	11	15.13818182	0.30442793	14.76000000	15.82000000	0.09178847
EL	11	3.07727273	0.15139953	2.85000000	3.30000000	0.04564868
TH	11	0.13196364	0.00847753	0.12010000	0.14200000	0.00255607
TENA	11	5.14698182	0.10350550	5.01840000	5.37880000	0.03120808
ELONG	11	30.77272727	1.51399532	28.50000000	33.00000000	0.45648676
TOUGH	11	1.20166148	0.07719644	1.09363115	1.29305265	0.02327560
----- FIB=P TEM=195 -----						
BL	11	15.34545455	0.51295933	14.14000000	15.98000000	0.15466306
EL	11	3.43363636	0.30965377	3.02000000	3.89000000	0.09336412
TH	11	0.15261818	0.01885374	0.12990000	0.18100000	0.00568462
TENA	11	5.21745455	0.17440617	4.80760000	5.43320000	0.05258544
ELONG	11	34.33636364	3.09653766	30.20000000	38.90000000	0.93364123
TOUGH	11	1.38974187	0.17168227	1.18287000	1.64818683	0.05176415
----- FIB=P TEM=210 -----						
BL	11	15.10363636	0.47132309	14.24000000	15.62000000	0.14210926
EL	11	2.66090909	0.31677925	2.23000000	3.18000000	0.09551254
TH	11	0.11124545	0.01936483	0.08460000	0.14200000	0.00583872
TENA	11	5.13523636	0.16024985	4.84160000	5.31080000	0.04831715
ELONG	11	26.60909091	3.16779246	22.30000000	31.80000000	0.95512536
TOUGH	11	1.01300162	0.17633625	0.77036799	1.29305265	0.05316738
----- FIB=P TEM=210 -----						
BL	11	14.86636364	0.29422008	14.46000000	15.59000000	0.08871069
EL	11	2.47454545	0.12644079	2.21000000	2.65000000	0.03812333
TH	11	0.09458182	0.00653021	0.07890000	0.10370000	0.00196893
TENA	11	5.05456364	0.10003483	4.91640000	5.30060000	0.03016164
ELONG	11	24.74545455	1.26440787	22.10000000	26.50000000	0.38123332
TOUGH	11	0.86126247	0.05946412	0.71846376	0.94429268	0.01792911
----- FIB=P TEM=225 -----						
BL	11	15.42363636	0.35997980	15.00000000	16.00000000	0.10853799
EL	11	2.76545455	0.21125168	2.30000000	3.01000000	0.06369478
TH	11	0.11623636	0.01172231	0.09180000	0.13050000	0.00353441
TENA	11	5.24403636	0.12239313	5.10000000	5.44000000	0.03690292
ELONG	11	27.65454545	2.11251681	23.00000000	30.10000000	0.63694778
TOUGH	11	1.05844886	0.10674341	0.83593122	1.18833360	0.03218435
----- FIB=P TEM=225 -----						
BL	11	15.46727273	0.28667371	15.16000000	16.20000000	0.08643538
EL	11	3.05818182	0.24862897	2.65000000	3.45000000	0.07496445
TH	11	0.12923636	0.01511524	0.10370000	0.15330000	0.00455742
TENA	11	5.25887273	0.09746906	5.15440000	5.50800000	0.02938803
ELONG	11	30.58181818	2.48628968	26.50000000	34.50000000	0.74964454
TOUGH	11	1.17682692	0.13763946	0.94429268	1.39595051	0.04149986

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEM=235 REP=A -----						
BL	11	15.21454545	0.28327950	14.76000000	15.76000000	0.08541198
EL	11	2.83454545	0.21233764	2.55000000	3.19000000	0.06402221
TH	11	0.11631818	0.01181083	0.10030000	0.13340000	0.00356110
TENA	11	5.17294545	0.09631503	5.01840000	5.35840000	0.02904007
ELONG	11	28.34545455	2.12337639	25.50000000	31.90000000	0.64022207
TOUGH	11	1.05919390	0.10754945	0.91333226	1.21474101	0.03242738
----- FIB=P TEM=235 REP=B -----						
BL	11	15.20727273	0.27441177	14.74000000	15.64000000	0.08273826
EL	11	3.23818182	0.26419001	2.84000000	3.70000000	0.07965629
TH	11	0.13631818	0.01480107	0.10770000	0.15930000	0.00446269
TENA	11	5.17047273	0.09330000	5.01160000	5.31760000	0.02813101
ELONG	11	32.38181818	2.64190014	28.40000000	37.00000000	0.79656286
TOUGH	11	1.24131399	0.13477860	0.98071670	1.45058653	0.04063728

Appendix D
DYE UPTAKE DATA

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEMP=20 REP=A -----						
CONC1	2	0.03345865	0.00061243	0.03302560	0.03389170	0.00043305
CONC2	2	0.03345345	0.00057990	0.03304340	0.03386350	0.00041005
CONC	2	0.03345605	0.00059616	0.03303450	0.03387760	0.00042155
DYEPICK	2	33.45605000	0.59616173	33.03450000	33.87760000	0.42155000
----- FIB=N TEMP=20 REP=B -----						
CONC1	2	0.03371065	0.00125943	0.03282010	0.03460120	0.00089055
CONC2	2	0.03378115	0.00143889	0.03276370	0.03479860	0.00101745
CONC	2	0.03374590	0.00134916	0.03279190	0.03469990	0.00095400
DYEPICK	2	33.74590000	1.34915974	32.79190000	34.69990000	0.95400000
----- FIB=N TEMP=150 REP=A -----						
CONC1	2	0.03140130	0.00136835	0.03043373	0.03236887	0.00096757
CONC2	2	0.03158460	0.00166746	0.03040553	0.03276368	0.00117908
CONC	2	0.03149295	0.00151791	0.03041963	0.03256627	0.00107332
DYEPICK	2	31.49294975	1.51790660	30.41962770	32.56627180	1.07332205
----- FIB=N TEMP=150 REP=B -----						
CONC1	2	0.03104569	0.00047539	0.03070953	0.03138184	0.00033615
CONC2	2	0.03053807	0.00020260	0.03039481	0.03068133	0.00014326
CONC	2	0.03079188	0.00013640	0.03069543	0.03088832	0.00009645
DYEPICK	2	30.79187810	0.13639623	30.69543140	30.88832480	0.09644670
----- FIB=N TEMP=165 REP=A -----						
CONC1	2	0.03028737	0.00008734	0.03022561	0.03034913	0.00006176
CONC2	2	0.03082318	0.00063053	0.03037733	0.03126904	0.00044585
CONC	2	0.03055527	0.00027160	0.03036323	0.03074732	0.00019205
DYEPICK	2	30.55527350	0.27159604	30.36322610	30.74732090	0.19204740
----- FIB=N TEMP=165 REP=B -----						
CONC1	2	0.03046757	0.00101380	0.02975070	0.03118443	0.00071686
CONC2	2	0.02963565	0.00020260	0.02949239	0.02977891	0.00014326
CONC	2	0.03005161	0.00040560	0.02976481	0.03033841	0.00028680
DYEPICK	2	30.05160742	0.40559931	29.76480540	30.33840945	0.28680202
----- FIB=N TEMP=180 REP=A -----						
CONC1	2	0.02882092	0.00032663	0.02858996	0.02905189	0.00023096
CONC2	2	0.02863762	0.00002752	0.02861816	0.02865708	0.00001946
CONC	2	0.02872927	0.00017708	0.02860406	0.02885448	0.00012521
DYEPICK	2	28.72927240	0.17707580	28.60406090	28.85448390	0.12521150

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEMP=180 REP=B -----						
CONC1	2	0.02702707	0.00050171	0.02667231	0.02738184	0.00035477
CONC2	2	0.02664636	0.00100024	0.02593909	0.02735364	0.00070728
CONC	2	0.02683672	0.00075098	0.02630570	0.02736774	0.00053102
DYEPICK	2	26.83671740	0.75097689	26.30569655	27.36773825	0.53102085
----- FIB=N TEMP=195 REP=A -----						
CONC1	2	0.02454140	0.00033652	0.02430344	0.02477936	0.00023796
CONC2	2	0.02476763	0.00029752	0.02455725	0.02497800	0.00021038
CONC	2	0.02465451	0.00031702	0.02443034	0.02487868	0.00022417
DYEPICK	2	24.65451210	0.31702150	24.43034405	24.87868016	0.22416805
----- FIB=N TEMP=195 REP=B -----						
CONC1	2	0.02464411	0.00119327	0.02380034	0.02548787	0.00084377
CONC2	2	0.02398139	0.00001675	0.02396954	0.02399323	0.00001184
CONC	2	0.02431275	0.00060501	0.02388494	0.02474055	0.00042781
DYEPICK	2	24.31274672	0.60500901	23.88494075	24.74055270	0.42780598
----- FIB=N TEMP=210 REP=A -----						
CONC1	2	0.02277371	0.00046884	0.02244219	0.02310523	0.00033152
CONC2	2	0.02299746	0.00090492	0.02235759	0.02363734	0.00063988
CONC	2	0.02288559	0.00068688	0.02239989	0.02337128	0.00048570
DYEPICK	2	22.88558505	0.68688056	22.39988715	23.37128295	0.48569790
----- FIB=N TEMP=210 REP=B -----						
CONC1	2	0.02231754	0.00037569	0.02205189	0.02258319	0.00026565
CONC2	2	0.02177012	0.00179436	0.02050131	0.02303892	0.00126880
CONC	2	0.02204383	0.00070933	0.02154225	0.02254540	0.00050158
DYEPICK	2	22.04382820	0.70933417	21.54225320	22.54540320	0.50157500
----- FIB=N TEMP=225 REP=A -----						
CONC1	2	0.02233474	0.00096474	0.02165257	0.02301692	0.00068218
CONC2	2	0.02263085	0.00074539	0.02210378	0.02315792	0.00052707
CONC	2	0.02248280	0.00085507	0.02187817	0.02308742	0.00060462
DYEPICK	2	22.48279747	0.85506877	21.87817255	23.08742240	0.60462492
----- FIB=N TEMP=225 REP=B -----						
CONC1	2	0.02148562	0.00059504	0.02106486	0.02190637	0.00042076
CONC2	2	0.02127660	0.00153512	0.02019111	0.02236210	0.00108550
CONC	2	0.02138111	0.00047004	0.02104874	0.02171348	0.00033237
DYEPICK	2	21.38110965	0.47004259	21.04873935	21.71347995	0.33237030
----- FIB=N TEMP=235 REP=A -----						
CONC1	2	0.02193993	0.00028675	0.02173717	0.02214270	0.00020276
CONC2	2	0.02167202	0.00070551	0.02117315	0.02217090	0.00049887
CONC	2	0.02180598	0.00049613	0.02145516	0.02215680	0.00035082
DYEPICK	2	21.80597852	0.49613133	21.45516070	22.15679635	0.35081782
----- FIB=N TEMP=235 REP=B -----						
CONC1	2	0.02079470	0.00065486	0.02033164	0.02125776	0.00046306
CONC2	2	0.02020497	0.00093689	0.01954249	0.02086746	0.00066248
CONC	2	0.02049983	0.00014102	0.02040012	0.02059955	0.00009971
DYEPICK	2	20.49983500	0.14101654	20.40012125	20.59954875	0.09971375

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEMP=20 REP=A -----						
CONC1	2	0.02992220	0.00002630	0.02990360	0.02994080	0.00001860
CONC2	2	0.03014575	0.00002638	0.03012710	0.03016440	0.00001865
CONC	2	0.01501699	0.00001317	0.01500767	0.01502630	0.00000931
DYEPICK	2	15.01698750	0.01316986	15.00767500	15.02630000	0.00931250
----- FIB=P TEMP=20 REP=B -----						
CONC1	2	0.02968000	0.00052694	0.02930740	0.03005260	0.00037260
CONC2	2	0.02964275	0.00052687	0.02927020	0.03001530	0.00037255
CONC	2	0.01483069	0.00026345	0.01464440	0.01501697	0.00018629
DYEPICK	2	14.83068750	0.26345031	14.64440000	15.01697500	0.18628750
----- FIB=P TEMP=150 REP=A -----						
CONC1	2	0.01811143	0.00023711	0.01794377	0.01827909	0.00016766
CONC2	2	0.01833497	0.00018442	0.01820457	0.01846538	0.00013040
CONC	2	0.00911160	0.00010538	0.00903708	0.00918612	0.00007452
DYEPICK	2	9.11160029	0.10538141	9.03708437	9.18611620	0.07451591
----- FIB=P TEMP=150 REP=B -----						
CONC1	2	0.01829772	0.00028980	0.01809280	0.01850264	0.00020492
CONC2	2	0.01824183	0.00026345	0.01805554	0.01842812	0.00018629
CONC	2	0.00913489	0.00013831	0.00903708	0.00923269	0.00009780
DYEPICK	2	9.13488650	0.13831309	9.03708437	9.23268862	0.09780213
----- FIB=P TEMP=165 REP=A -----						
CONC1	2	0.01634167	0.00047422	0.01600635	0.01667700	0.00033532
CONC2	2	0.01647208	0.00071132	0.01596909	0.01697506	0.00050298
CONC	2	0.00820344	0.00029639	0.00799386	0.00841301	0.00020958
DYEPICK	2	8.20343757	0.29638522	7.99386157	8.41301357	0.20957600
----- FIB=P TEMP=165 REP=B -----						
CONC1	2	0.01637893	0.00005269	0.01634167	0.01641619	0.00003726
CONC2	2	0.01641619	0.00005269	0.01637893	0.01645345	0.00003726
CONC	2	0.00819878	0.00002635	0.00818015	0.00821741	0.00001863
DYEPICK	2	8.19878032	0.02634535	8.18015135	8.21740930	0.01862898
----- FIB=P TEMP=180 REP=A -----						
CONC1	2	0.01535434	0.00013173	0.01526119	0.01544748	0.00009314
CONC2	2	0.01541022	0.00000000	0.01541022	0.01541022	0.00000000
CONC	2	0.00769114	0.00003293	0.00766785	0.00771443	0.00002329
DYEPICK	2	7.69114067	0.03293170	7.66785445	7.71442690	0.02328622
----- FIB=P TEMP=180 REP=B -----						
CONC1	2	0.01524256	0.00060594	0.01481410	0.01567103	0.00042847
CONC2	2	0.01529845	0.00063229	0.01485136	0.01574555	0.00044710
CONC	2	0.00763525	0.00030956	0.00741636	0.00785414	0.00021889
DYEPICK	2	7.63525372	0.30955791	7.41636322	7.85414422	0.21889050

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEMP=195 REP=A -----						
CONC1	2	0.01503765	0.00063229	0.01459055	0.01548474	0.00044710
CONC2	2	0.01524256	0.00102747	0.01451603	0.01596909	0.00072653
CONC	2	0.00757005	0.00041494	0.00727665	0.00786346	0.00029341
DYE PICK	2	7.57005230	0.41493935	7.27664587	7.86345872	0.29340642
----- FIB=P TEMP=195 REP=B -----						
CONC1	2	0.01529845	0.00047422	0.01496313	0.01563377	0.00033532
CONC2	2	0.01539160	0.00007904	0.01533571	0.01544748	0.00005589
CONC	2	0.00767251	0.00013831	0.00757471	0.00777031	0.00009780
DYE PICK	2	7.67251169	0.13831311	7.57470955	7.77031382	0.09780214
----- FIB=P TEMP=210 REP=A -----						
CONC1	2	0.01483273	0.00002635	0.01481410	0.01485136	0.00001863
CONC2	2	0.01514942	0.00010538	0.01507490	0.01522393	0.00007452
CONC	2	0.00749554	0.00003293	0.00747225	0.00751882	0.00002329
DYE PICK	2	7.49553639	0.03293168	7.47225017	7.51882260	0.02328621
----- FIB=P TEMP=210 REP=B -----						
CONC1	2	0.01526119	0.00036883	0.01500039	0.01552200	0.00026081
CONC2	2	0.01518668	0.00010538	0.01511216	0.01526119	0.00007452
CONC	2	0.00761197	0.00006586	0.00756540	0.00765854	0.00004657
DYE PICK	2	7.61196751	0.06586337	7.56539507	7.65853995	0.04657244
----- FIB=P TEMP=225 REP=A -----						
CONC1	2	0.01395716	0	0.01395716	0.01395716	0
CONC2	2	0.01406894	0	0.01406894	0.01406894	0
CONC	2	0.00700653	0	0.00700653	0.00700653	0
DYE PICK	2	7.00652570	0	7.00652570	7.00652570	0
----- FIB=P TEMP=225 REP=B -----						
CONC1	2	0.01324926	0.00031614	0.01302572	0.01347281	0.00022355
CONC2	2	0.01324926	0.00026345	0.01306297	0.01343555	0.00018629
CONC	2	0.006662463	0.00014490	0.00652217	0.00672709	0.00010246
DYE PICK	2	6.62463164	0.14489946	6.52217225	6.72709102	0.10245939
----- FIB=P TEMP=235 REP=A -----						
CONC1	2	0.01215015	0.00018442	0.01201975	0.01228056	0.00013040
CONC2	2	0.01211290	0.00018442	0.01198249	0.01224330	0.00013040
CONC	2	0.006060576	0.00009221	0.00600056	0.00613096	0.00006520
DYE PICK	2	6.06576227	0.09220874	6.00056085	6.13096370	0.06520143
----- FIB=P TEMP=235 REP=B -----						
CONC1	2	0.01330515	0.00007904	0.01324926	0.01336104	0.00005589
CONC2	2	0.01328652	0.00000000	0.01328652	0.01328652	0.00000000
CONC	2	0.00664792	0.00001976	0.00663395	0.00666189	0.00001397
DYE PICK	2	6.64791786	0.01975902	6.63394612	6.66188960	0.01397174

Appendix E
DENSITY AND CRYSTALLINITY DATA

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEM=20 REP=A -----						
HEIGHT	3	91.06666667	0.50332230	90.60000000	91.60000000	0.29059326
DENSITY	3	1.14166964	0.00139126	1.14037970	1.14314386	0.00080325
CRYSTAL	3	0.37412465	0.00961574	0.36520481	0.38431081	0.00555165
----- FIB=N TEM=20 REP=B -----						
HEIGHT	3	74.36666667	0.65064071	73.70000000	75.00000000	0.37564759
DENSITY	3	1.14012784	0.00184863	1.13823368	1.14192729	0.00106730
CRYSTAL	3	0.36344550	0.01281605	0.35030745	0.37591325	0.00739935
----- FIB=N TEM=150 REP=A -----						
HEIGHT	3	91.50000000	0.43588989	91.00000000	91.80000000	0.25166115
DENSITY	3	1.14286744	0.00120487	1.14148536	1.14369669	0.00069563
CRYSTAL	3	0.38239853	0.00831676	0.37285832	0.38812093	0.00480169
----- FIB=N TEM=150 REP=B -----						
HEIGHT	3	74.50000000	0.26457513	74.20000000	74.70000000	0.15275252
DENSITY	3	1.14050667	0.00075172	1.13965430	1.14107492	0.00043401
CRYSTAL	3	0.36608220	0.00520904	0.36017548	0.37001893	0.00300744
----- FIB=N TEM=165 REP=A -----						
HEIGHT	3	91.30000000	0.60827625	90.60000000	91.70000000	0.35118846
DENSITY	3	1.14231461	0.00168137	1.14037970	1.14342027	0.00097074
CRYSTAL	3	0.37857732	0.01162005	0.36520481	0.38621633	0.00670884
----- FIB=N TEM=165 REP=B -----						
HEIGHT	3	74.43333333	0.60277138	73.80000000	75.00000000	0.34801022
DENSITY	3	1.14031725	0.00171262	1.13851780	1.14192729	0.00098878
CRYSTAL	3	0.36476026	0.01187064	0.35228303	0.37591325	0.00685352
----- FIB=N TEM=180 REP=A -----						
HEIGHT	3	91.63333333	0.15275252	91.50000000	91.80000000	0.08819171
DENSITY	3	1.14323599	0.00042223	1.14286744	1.14369669	0.00024378
CRYSTAL	3	0.38494537	0.00291063	0.38240437	0.38812093	0.00168045
----- FIB=N TEM=180 REP=B -----						
HEIGHT	3	75.43333333	2.05020324	74.20000000	77.80000000	1.18368539
DENSITY	3	1.14315849	0.00582512	1.13965430	1.14988276	0.00336313
CRYSTAL	3	0.38427570	0.04004829	0.36017548	0.43050548	0.02312189
----- FIB=N TEM=195 REP=A -----						
HEIGHT	3	92.60000000	0.60827625	92.20000000	93.30000000	0.35118846
DENSITY	3	1.14590802	0.00168137	1.14480235	1.14784293	0.00097074
CRYSTAL	3	0.40331336	0.01152831	0.39573012	0.41657982	0.00665587

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=N TEM=195 REP=B -----						
HEIGHT	3	77.53333333	2.20302822	75.00000000	79.00000000	1.27191894
DENSITY	3	1.14912510	0.00625933	1.14192729	1.15329225	0.00361383
CRYSTAL	3	0.42518321	0.04284268	0.37591325	0.45367159	0.02473524
----- FIB=N TEM=210 REP=A -----						
HEIGHT	3	93.46666667	1.70977581	91.50000000	94.60000000	0.98713953
DENSITY	3	1.14830362	0.00472609	1.14286744	1.15143634	0.00272861
CRYSTAL	3	0.41964042	0.03237043	0.38240437	0.44107841	0.01868908
----- FIB=N TEM=210 REP=B -----						
HEIGHT	3	77.83333333	1.43643076	76.20000000	78.90000000	0.82932369
DENSITY	3	1.14997747	0.00408124	1.14533678	1.15300813	0.00235631
CRYSTAL	3	0.43108493	0.02785775	0.39940278	0.45174632	0.01608368
----- FIB=N TEM=225 REP=A -----						
HEIGHT	3	96.56666667	0.80208063	95.80000000	97.40000000	0.46308147
DENSITY	3	1.15687252	0.00221708	1.15475333	1.15917598	0.00128003
CRYSTAL	3	0.47783204	0.01492334	0.46355716	0.49332872	0.00861599
----- FIB=N TEM=225 REP=B -----						
HEIGHT	3	79.63333333	0.20816660	79.40000000	79.80000000	0.12018504
DENSITY	3	1.15509170	0.00059145	1.15442875	1.15556524	0.00034147
CRYSTAL	3	0.46584165	0.00399520	0.46136322	0.46903972	0.00230663
----- FIB=N TEM=235 REP=A -----						
HEIGHT	3	95.96666667	2.17332311	94.00000000	98.30000000	1.25476868
DENSITY	3	1.15521402	0.00600741	1.14977784	1.16166373	0.00346838
CRYSTAL	3	0.46652856	0.04051140	0.42979040	0.50997560	0.02338927
----- FIB=N TEM=235 REP=B -----						
HEIGHT	3	81.06666667	0.35118846	80.70000000	81.40000000	0.20275875
DENSITY	3	1.15916415	0.00099781	1.15812236	1.16011123	0.00057609
CRYSTAL	3	0.49324549	0.00669219	0.48625676	0.49959532	0.00386374
----- FIB=P TEM=20 REP=A -----						
HEIGHT	3	80.50000000	0.10000000	80.40000000	80.60000000	0.05773503
DENSITY	3	1.38053471	0.00027131	1.38026341	1.38080602	0.00015664
CRYSTAL	3	0.39992330	0.00230427	0.39761889	0.40222742	0.00133037
----- FIB=P TEM=20 REP=B -----						
HEIGHT	3	73.53333333	0.40414519	73.30000000	74.00000000	0.23333333
DENSITY	3	1.37976093	0.00097500	1.37919801	1.38088677	0.00056292
CRYSTAL	3	0.39334417	0.00828676	0.38855980	0.40291290	0.00478436
----- FIB=P TEM=150 REP=A -----						
HEIGHT	3	82.66666667	0.20816660	82.50000000	82.90000000	0.12018504
DENSITY	3	1.38641308	0.00056477	1.38596089	1.38704613	0.00032607
CRYSTAL	3	0.44963639	0.00475529	0.44582849	0.45496637	0.00274547
----- FIB=P TEM=150 REP=B -----						
HEIGHT	3	75.00000000	0	75.00000000	75.00000000	0
DENSITY	3	1.38329928	0	1.38329928	1.38329928	0
CRYSTAL	3	0.42335652	0	0.42335652	0.42335652	0
----- FIB=P TEM=165 REP=A -----						
HEIGHT	3	83.26666667	0.11547005	83.20000000	83.40000000	0.06666667
DENSITY	3	1.38804093	0.00031328	1.38786006	1.38840268	0.00018087
CRYSTAL	3	0.46332981	0.00263169	0.46181040	0.46636862	0.00151941

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- FIB=P TEM=165 REP=B -----						
HEIGHT	3	75.13333333	0.11547005	75.00000000	75.20000000	0.06666667
DENSITY	3	1.38362095	0.00027857	1.38329928	1.38378178	0.00016083
CRYSTAL	3	0.42607663	0.00235569	0.42335652	0.42743669	0.00136006
----- FIB=P TEM=180 REP=A -----						
HEIGHT	3	84.70000000	0	84.70000000	84.70000000	0
DENSITY	3	1.39192969	0	1.39192969	1.39192969	0
CRYSTAL	3	0.49591048	0	0.49591048	0.49591048	0
----- FIB=P TEM=180 REP=B -----						
HEIGHT	3	77.83333333	0.05773503	77.80000000	77.90000000	0.03333333
DENSITY	3	1.39013472	0.00013929	1.39005431	1.39029556	0.00008042
CRYSTAL	3	0.48089471	0.00116663	0.48022115	0.48224181	0.00067355
----- FIB=P TEM=195 REP=A -----						
HEIGHT	3	85.20000000	0.20000000	85.00000000	85.40000000	0.11547005
DENSITY	3	1.39328624	0.00054262	1.39274362	1.39382886	0.00031328
CRYSTAL	3	0.50723174	0.00452456	0.50270659	0.51175571	0.00261226
----- FIB=P TEM=195 REP=B -----						
HEIGHT	3	79.20000000	0	79.20000000	79.20000000	0
DENSITY	3	1.39343182	0	1.39343182	1.39343182	0
CRYSTAL	3	0.50844672	0	0.50844672	0.50844672	0
----- FIB=P TEM=210 REP=A -----						
HEIGHT	3	86.16666667	0.15275252	86.00000000	86.30000000	0.08819171
DENSITY	3	1.39590889	0.00041443	1.39545671	1.39627064	0.00023927
CRYSTAL	3	0.52905986	0.00344304	0.52530301	0.53206481	0.00198784
----- FIB=P TEM=210 REP=B -----						
HEIGHT	3	80.26666667	0.05773503	80.20000000	80.30000000	0.03333333
DENSITY	3	1.39600517	0.00013929	1.39584433	1.39608558	0.00008042
CRYSTAL	3	0.52986017	0.00115697	0.52852421	0.53052814	0.00066798
----- FIB=P TEM=225 REP=A -----						
HEIGHT	3	86.50000000	0.10000000	86.40000000	86.60000000	0.05773503
DENSITY	3	1.39681325	0.00027131	1.39654195	1.39708456	0.00015664
CRYSTAL	3	0.53656801	0.00225087	0.53431699	0.53881874	0.00129954
----- FIB=P TEM=225 REP=B -----						
HEIGHT	3	81.50000000	0	81.50000000	81.50000000	0
DENSITY	3	1.39898059	0	1.39898059	1.39898059	0
CRYSTAL	3	0.55452143	0	0.55452143	0.55452143	0
----- FIB=P TEM=235 REP=A -----						
HEIGHT	3	86.93333333	0.05773503	86.90000000	87.00000000	0.03333333
DENSITY	3	1.39798893	0.00015664	1.39789849	1.39816980	0.00009044
CRYSTAL	3	0.54631378	0.00129727	0.54556479	0.54781174	0.00074898
----- FIB=P TEM=235 REP=B -----						
HEIGHT	3	82.53333333	0.05773503	82.50000000	82.60000000	0.03333333
DENSITY	3	1.40147352	0.00013929	1.40139310	1.40163436	0.00008042
CRYSTAL	3	0.57510280	0.00114783	0.57444010	0.57642820	0.00066270

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