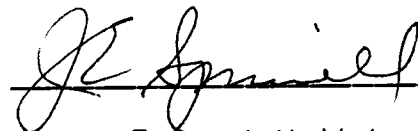


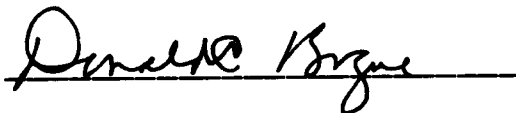
To the Graduate Council:

I am submitting herewith a thesis written by Changhong Yin entitled "Effect of Pigments on the Development of Structure and Properties of Polypropylene Drawn Filaments." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.



Joseph E. Spruiell, Major Professor

We have read this thesis
and recommend its acceptance



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

**EFFECT OF PIGMENTS ON THE DEVELOPMENT OF
STRUCTURE AND PROPERTIES OF POLYPROPYLENE
DRAWN FILAMENTS**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Changhong Yin

May, 1996

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DEDICATION

This thesis is dedicated to my father, Mr. Zuowei Yin, my mother, Mrs. Qiwen Zhang, and my wife, Mrs. Wen Chen. It was their love, encouragement, support and sacrifice that ensured that I was totally dedicated to this work.

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ABSTRACT

A study of the effects of pigment additions on the development of structure and properties of drawn yarn prepared from isotactic polypropylene (PP) is presented. Two pigments, one inorganic and one organic, were selected to produce colored spun and drawn polypropylene filaments with black and blue colors, respectively. Wide angle x-ray diffraction (WAXS), differential scanning calorimetry (DSC), density, and birefringence were used in the analysis of structural characteristics for both pigmented and unpigmented PP drawn filaments. Uniaxial tensile tests were also carried out.

The influence of pigment additions on the way that drawing process conditions influence the development of fine structure, as well as the mechanical properties of pigmented PP filaments, were investigated. An extensive statistical analysis is also provided to enhance a quantitative understanding of the effect of pigment types, pigment concentration, draw ratio, draw temperature and draw speed on the final structure and properties of pigmented drawn PP filaments.

The results show that pigment additions have marked effects on the PP drawn yarn mechanical properties. Under similar processing conditions the presence of pigments increases

elongation, but lowers tenacity, yield strength and modulus. Compared with the inorganic pigment, Cabot 660 furnace black, the organic pigment, Phthalyl blue, has more impact on PP drawn yarn mechanical properties.

The drawability and drawn yarn mechanical properties are also greatly affected by the pigment concentration. Finally, changes of draw ratio and draw temperature may improve or damage fine structure of PP drawn filaments and therefore affect pigmented PP drawn properties. The structure and properties differences between the natural, unpigmented PP and pigmented PP are also discussed.

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CHAPTER 1

INTRODUCTION AND PURPOSE

The effects of pigment additions on the development of structure and properties of as-spun filaments of isotactic polypropylene (PP) were recently studied in our laboratory. It was reported that pigments that produce a marked effect on crystallization kinetics also affect mechanical properties of the PP spun filaments.

In this work, we continued the study of the influence of pigments on the melt spun-dyed PP filament and expanded it to include the drawing process. This continuation involves the melt spinning of a series of natural PP and pigmented PP filaments over a range of conditions, followed by drawing them at temperatures from 25 °C to 100 °C at different draw ratios and various draw speeds. The influence of pigment types and concentrations on the structure and properties of PP filaments in the drawing process, and the way that the drawing process parameters influence the development of fine structure, as well as the mechanical properties of pigmented PP filaments, were investigated. The structure of the melt spun and drawn fibers was characterized in terms of wide-angle x-ray scattering (WAXS), density, differential scanning calorimetry (DSC),

birefringence, etc. Uniaxial tensile tests were also carried out using an Instron testing machine.

Two pigments, Cabot 660 furnace black and Phthalyl blue, were selected for this study. The melt-dyed PP samples with different dye colors and varied pigment concentrations were spun from a single position spinning machine and drawn on a small drawing apparatus in our lab.

The main **purposes** of this study include the following:

- To provide a fundamental understanding of how pigment additions affect the fine structure, and properties of drawn PP filaments.
- To investigate the relative degree of influence among different pigments and compare the effects of inorganic pigments (Cabot 660 furnace black) with those of organic pigments (Phthalyl blue pigments) on the drawn PP filaments.
- To examine how drawing process conditions, such as draw ratio, draw temperature and draw speed, influence the development of fine structure, as well as the mechanical properties of pigmented PP filaments.

- To determine if the presence of the pigments has unfavorable impact on the drawn PP mechanical properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Polypropylene (PP) and Pigmented PP Fibers

Polypropylene (PP) is a comparatively new fiber and one of the most commercially important fibers in the world today. Technology and continued product improvement drive PP's market growth. Global PP demand is expected to grow as a result of the product's competitive pricing structure, process improvements, and the impact of more efficient production catalysts. In 1994 PP sales rose by 9% in the US and 13% in Europe [1]. In Japan, demand of PP is reaching all-time highs and will likely outpace supply in 1996 [1]. PP producers are profiting through expanding capacity and raising prices. PP prices are partly being driven by the increasing cost of propylene, which is in short supply. However, PP fiber is still less expensive in comparison with other major synthetic fibers such as nylon and polyester.

New technology and continued product improvement also drive the process of continually finding new areas of end uses for PP. The future of PP as a manufactured material, however, is closely tied to its technical properties. Due to its excellent soil and stain

resistance, PP fiber has found a diverse number of uses in the home furnishings market. In the past few years, PP filaments have been increasingly used in BCF (bulked continuous filaments) extrusion for carpet manufacture. PP is especially well suited for application in commercial carpeting and heavier denier ranges where it competes with nylon yarns. In addition, PP filament yarns are now being used more and more in the fine denier range in the textile sector as oriented and textured yarns as well as flat yarns [2-3]. PP has also entered the market for fine fabrics and knitwear which has, up to now, been nearly exclusively dominated by polyester filament yarns.

These many commercial applications in apparel, carpets and home furnishings make dye behavior and tensile properties of PP fiber extremely important. It is a well known fact, however, that PP fiber, in contrast to other synthetic fibers, has no dyeable sites and contains high crystallinity so that it cannot be dyed by the bath dyeing method, commonly used for other synthetic fibers [4-6]. The difficulties in the dyeing process are also due to its hydrophobic nature and absence of positions in which hydrogen bonds or electrostatic interactions with dye molecules may occur [7].

In recent years there has been considerable research and development to overcome this difficulty. Dyeing methods applied to PP fibers have been investigated by many laboratories throughout the world. The dyeability of PP has been improved by blending or

grafting with other polymers [8-15] or adding low molecular weight additive [16] , or melt complexes [17-18]. Gardner et al. [19] have studied the changes in morphology of PP in relation to dyeing behavior. It has also been recognized [20] that the crystallinity of PP can be reduced by incorporating small amounts of polyester and polystyrene. These different approaches have been discussed in an excellent review [21]. However, these attempts have not given satisfactory results except for the recent introduction of some dyeable PP fibers by the method known as "mass coloration" or "pigmentation." This method is also considered as the most effective method for coloring PP fibers [22]. In contrast to the vast majority of other synthetic fibers which are spun in a clear state and colored via a post dyeing process, the melt pigmentation and coloring involve the intermixing of colorants with the PP melt prior to fiber extrusion [22-23]. The presence of pigments in a molten polymer results in some modifications of the crystallization conditions. Recent investigations [5, 22, 23] have revealed that the introduced pigments serve as nuclei that accelerate the crystallization.

In addition to concentrated pellets, another type of coloring technique used is liquid color introduced and uniformly mixed into PP melt during the extrusion process. A comparison of liquid PP colorant to PP concentrate colorants has been recently given by Krajewski [24].

Pigmented spun-dyed PP fiber has excellent fastness properties vs. conventional post-spinning dyed textile fibers. PP fiber has the lightest weight per unit volume of all commercial fibers, which enhances its economics and its use in such applications as automotive interiors. Pigmented PP fiber also offers many economical, environmental, and product advantages [25-26]; i.e. no effluents from dye systems and no subsequent heat energy is required to fix the dye. In essence, the melt spin dyeing process for PP fiber "locks" the color into the fiber. On the other hand, consumers desire for enhanced stain and fade resistance also create many new opportunities for pigmented PP fibers as well. Technology development and many improvements, just now commercially available, also enhance the performance of color concentrates used in fine denier fiber as well as in heavier carpet yarn deniers, permitting the continued growth of PP pigmented fiber. These facts make basic studies of the development of structure and properties of pigmented PP fibers as a function of process conditions, particularly in drawn pigmented PP filaments, of considerable interest.

By far, however, most of the research on structure and properties of pigmented PP fiber reported in the literature was only involved in as-spun pigmented PP filaments. There seem to be no detailed reports dealing with the structure development and properties of drawn pigmented PP filaments. In particular, no

detailed descriptions exist in the open literature investigating the effect of drawing conditions on the resulting structure and mechanical properties of drawn pigmented PP filaments. To help fill this gap, the present study was therefore undertaken to determine how draw processing conditions and various pigment additions influence the development of fine structure and affect the mechanical properties of pigmented PP fiber.

2.2 Selection of Pigments

Due to the many end use possibilities the selection of pigments for PP fiber is quite complex. The proper selection of pigments demands a thorough understanding of the requirements of the product, cost and the process to be used.

First, pigments added into PP melt during extrusion must be well dispersed, insoluble in PP at and below the polymer melting point, and have equivalent particle size distribution to flake PP spinning grade resin so that contamination and undispersed pigment particles can be eliminated by the screen pack without affecting pack life and spinability [3].

Second, pigments used should melt well above the PP melting point and preferably without decomposition.

Third, particle size of the pigments must be small enough to prevent disrupting fiber production since discrete pigment particles change the rheological characteristics and morphological structure of PP and have direct influence on the processing behavior of PP and the properties of the products [3, 27, 28]. This requirement becomes even more critical for fine denier filaments, high speed production, and the desire for higher efficiencies.

Fourth, the molten PP polymer is extruded at temperatures as high as 300 °C and consequently the used colorants or pigments must have high thermal stability.

Fifth, pigments used in melt spinning should be nonvolatile towards its environment, and should exhibit no interactions between pigments and all the components that go into the production of fiber. These components are, the fiber producer's personnel, equipment, PP melt or resin, additives, and spin finish [25].

Last, but not least, understanding the roles of pigments is extremely important because many organic and inorganic pigments act as nucleating agents for the crystallization of PP and may have selective influence on the morphological structure and properties of PP spun filaments [5, 22, 23, 29]. The flow behavior of various pigmented PP melts are also different. According to the study of Li [27], flow resistance of PP increases with the addition of

phthalocyanine blue, carbon black, and titanium dioxide, but decreases with the presence of BR red and GGL orange. It seems quite reasonable to consider that these differences depend on the nature of the pigment, the amount added, and the interactions that occur between the pigment and the polypropylene. Also, if possible, it should possess a crystalline structure similar to that of polypropylene.

The major characteristic difference between the organic and inorganic pigments has been reported elsewhere [30-32] and summarized in reference [23]. In general, inorganic pigments have harder and coarser particles than those of organic pigments. The presence of inorganic pigments increases the viscosity of the polymer and hence the deformation of macromolecular chains is more difficult so that the flow resistance of PP increases. On the other hand, organic pigments vary widely in their chemical structures and therefore have wide range of color and properties. However, organic pigments are usually inferior to inorganic pigments in heat stability. They may tend to be decomposed or to induce catalytic decomposition of the polymer under high temperature. The results, to some extent, may act for internal lubrication. Concentrate carriers can be a source of physical "contamination" or immiscible inclusions if the carrier and base resin are thermodynamically immiscible [33]. Also, impact strengths are more sensitive than low strain rate tensile

mechanical properties to the presence of organic or inorganic pigments. Generally, one chooses organic pigments mainly due to their wide color selection, and selects inorganic pigments when mechanical property retention is a key property to consider for pigmented PP fiber.

2.3 PP Fiber Formation

In the course of PP fiber formation, there are two important deformation processes which govern the thickness and the physical properties of the resultant filament: one is melt-spinning and the other is drawing. Molten polymer is extruded through small holes of the spinneret to form filaments which are drawn down and solidified on rotating rolls. In a second stage the solidified as-spun filaments are continuously passed from a slow roller to a fast roller drawing them down several times in diameter. The filament formation process is known as melt spinning; the solid state stretching process is named drawing. The former merely attenuates the cross-sectional area of the filament and is not very effective in the orientation of polymer molecules, whereas the latter results in a reorganization of the substructure and markedly improves the physical properties of the resultant filament. Except for the recent development in the high speed spinning where fiber forming and the drawing steps occur on the threadline, most fibers produced involve separate spinning and drawing steps. PP fibers for textile use are

generally produced by the process of melt spinning and subsequent drawing. During the PP fiber spinning (in the spinning speed range of 500-3000 m/min), a relatively low crystallinity material is produced which has low strength and high elongation at break. Thus, it is necessary to stretch PP filaments which are melt spun in normal production to several times their original length. This produces a significantly increased orientation of the macromolecules in the direction of the fiber axis and therefore generates high tenacity and normal extensibility values. The character of the structure reorganization is expected to depend not only on the environmental drawing conditions but on the original structure present in the spun fiber as well [34]. Each time the environmental conditions of spinning and drawing are changed, the details of the path and the structure of the final yarn are different.

2.4 Structure and Mechanical Properties Characteristics of Drawn PP Filaments

It is well known that PP fiber is a polycrystalline polymer and has structural order on the molecular, interlamellar, and spherulitic levels [35]. The character of its structure will vary with conditions of fabrication. The mechanical properties of a PP fiber greatly depend upon its morphological structure, which is controlled by the methods and conditions of fiber formation.

Because of its importance as a commercial synthetic fiber, numerous studies have been devoted to the melt spinning of PP fiber. The pioneer studies of melt spinning of PP were those of Capuccio et al. [36], Compostella et al. [37], and Sheehan and Cole [38]. These and later researches [39-52] have emphasized the importance of spinning conditions on fiber structure development and the resulting mechanical properties of the filaments. They used birefringence as a measure of molecular orientation and followed its variation with spinning speed. They concluded that molecular orientation increased with spinline tension or draw ratio. They reported that the structure and properties of as-spun filaments can be varied over a wide range by changing the processing conditions. More recently, several investigations [4, 5, 22, 23, 29], describing the effect of pigments on the development of structure and development of properties of as-spun PP filaments, have been published. Prior research [22, 23] from our laboratory noted that the pigments additions acting as nucleating agents not only produce a marked effect on crystallization kinetics and morphology of spherulites, but also affect the mechanical properties of as-spun filaments. Wu [5] and Lin et al. [22, 23] both found that at any spinning speed pure as-spun filaments without pigmentation always possess higher tenacity, higher yield strength and lower elongation than pigmented PP as-spun filaments. Wu concluded that tensile properties of PP and pigmented PP as-spun filaments substantially depend on configuration of the amorphous phase and not on crystallinity. The

higher the orientation of the amorphous phase and the more the tie molecules between crystal lamellae, the higher the tenacity of fibers and the lower the elongation of fibers. Accordingly, the initial modulus and yield strength of the fiber will follow the same trend as that of tenacity. As pigmented as-spun filaments, however, the influence on the structure and mechanical properties of as-spun PP filaments also greatly depend on the pigment type and its content [5, 22, 23]. It has been found [29] that the pigments and their concentrations, as used in industrial production, increase the crystal content. The work of Lin et al. [22, 23] revealed that both structural characteristics and mechanical properties of as-spun filaments can be correlated with the stress in the spinline at the point of crystallization. These results are in good agreement with the recent study by Jovanovic. He used x-ray diffraction (WAXS) to examine the influence of pigments on the structure of as-spun PP fiber. His results confirmed [29] that pigment additions increase crystallization rate of the filament during spinning. Thus crystallinity of pigmented PP filaments is always higher than with non-pigmented, natural PP filaments.

In the drawing operation, the stress, orientation and crystallinity of PP fibers increase along with the draw ratio; the fiber becomes much stronger. The crystalline morphology changes from spherulitic to elliptical and finally to band-shape structures along the drawing direction. During drawing the crystallites change

from an unstable quasicrystalline form to a stable α form [53]. Bodaghi et al. observed [54] that the drawn PP filaments possess a much higher level of crystalline orientation than the melt spun filaments and crystalline orientation increases with draw ratios. These authors also found that crystalline orientation function, f_c , is significantly higher for filaments drawn from melt spun filaments with higher initial orientation. The orientation difference in as-spun filaments and drawn filaments at different draw ratio can also be clearly described by the wide angle x-ray scattering patterns. According to Samuels [55] and Tadmor et al. [56], WAXS patterns of drawn filaments are functions of draw ratio for a given draw temperature and draw velocity. The melt spun PP filaments exhibit a continuous ring of nearly uniform intensity at a low take-up speed. The first four diffraction rings of the x-ray patterns represent the 110, 040, 130 and 111 planes in the monoclinic crystal lattice of polypropylene. As fibers are drawn, the crystallites are oriented with the c-axis parallel to the fiber axis. Hence, the smaller the angles of the first four diffraction rings, the shorter the rings (or arcs), the higher the degree of crystalline orientation. In other words, the WAXS reflections of the filaments drawn at lower draw ratio should be broader in the azimuthal direction than at higher draw ratio.

2.5 Effect of Draw Conditions on the Development of Structure and Mechanical Properties

Perhaps the most important aspect of the drawing process is the relationship between the draw conditions and the structure and properties of the drawn fiber. It is a well-known fact that the function of the drawing operation is to orient the molecules and crystallites of the polymer in the direction of the fiber axis. In view of practical purpose, a follow-up drawing process after PP melt spinning is often required in order to produce a certain level of tensile properties.

Maximum Draw Ratio or Drawability

The mechanical properties of the drawn filaments are determined by orientation, crystallinity and morphological structure produced in drawing. The production of PP filaments with high tenacity requires that the filaments be drawn to a maximum. The maximum amount that a fiber could be drawn depends upon its molecular weight, molecular weight distribution, the amount of stretch introduced during spinning, and the drawing temperature and time. The maximum draw ratio of as-spun filament varies with the preceding melt-draw ratio; as the melt-draw ratio is increased, or for increased spinning speed, the maximum draw ratio, or the residual elongation of the filament is decreased [57]. It is reported [38] that PP filaments having the paracrystalline structure could be drawn more easily, and to higher draw ratio, than filaments having the α crystalline structure. In theory, the maximum draw ratio,

which depends upon the as-spun crystallinity, can be measured by the stress-strain curves of as-spun filaments. An increase of as-spun crystallinity is extremely damaging because the rupture point occurs not only at lower extensions but also at lower stresses. Thus, the maximum draw-ratio is lowered by increasing the degree of crystallinity in fibers prior to the drawing operation.

Draw Point

In the drawing process, filaments first exhibit local necking but they eventually become uniform at a point known as the natural draw ratio, which is defined by Marshal and Thompson [58] as the ratio of the undrawn to drawn filament cross-sectional area. The necked regions and drawn out filaments exhibit significantly increased levels of polymer chain orientation [59-64]. In order to obtain drawn filaments with uniform denier and physical-mechanical properties, it is extremely important to maintain or fix the draw point at a certain location. Otherwise, the shifting of the draw point during drawing may cause drawn yarn denier variability and variations of dye uniformity. It has been reported [65] that uniformity of denier is determined by the ratio of natural draw ratio and given drawn ratio.

For one-stage drawing, an optimum draw speed can be derived using the following equation [65].

$$V_x = [V_2(NDR-DR)]/[DR(NDR-1)]$$

where, V_2 -- the surface velocity of draw roller
 V_x -- the surface velocity at draw point
 NDR --natural draw ratio, $NDR = A_1/A_2$
 DR --true draw ratio, $DR = V_2/V_1$
 V_1 --the surface velocity of feed roller
 A_1 --the cross section area of undrawn fiber
 A_2 --the cross section area of drawn fiber

From the above equation, it can be easily found that

- (i) when $NDR-DR = 0$, or $NDR = DR$ and $V_x = 0$, the draw point is stably controlled.
- (ii) when $NDR-DR > 0$, or $DR < NDR$ and $V_x > 0$, the necked regions will develop along the drawing down direction so that some undrawn regions will occur on final drawn fibers.
- (iii) when $NDR-DR < 0$, or $DR > NDR$ and $V_x < 0$, the necked region will move to upper draw direction (feed roller direction).

Apparently, for two-stage drawing setting DR_1 (first stage draw ratio) = NDR (natural draw ratio) appears to be a better choice for fixing the draw point and drawing safely without too frequent

breaks. In the case of drawing with heating elements, Ziabicki [66] pointed out that the draw ratio for stable drawing is dependent on the NDR (T) (natural draw ratio) and DR_{max} (T) (maximum draw ratio). He thought the range of admissible draw ratios for stable drawing (see Figure 1) is wider and determined by the following inequality:

$$\text{NDR } (T_h) < \text{DR} < \text{DR}_{\text{max}} (T_o)$$

where, T_o = the temperature of the supplied fiber
 T_h = the maximum temperature of heated apparatus
 NDR = natural draw ratio
 DR = total draw ratio
 DR_{max} = maximum draw ratio

For example, the range of stable drawing lies above the natural draw ratio corresponding to the maximum temperature (T_h) and below the deformation corresponding to breakage at the lower temperature (T_o).

Draw Ratio

Draw ratio, draw temperature and draw speed are believed to be the three major factors of the drawing process that can largely influence the morphology development and the mechanical properties of PP filaments. The changes in morphology development are

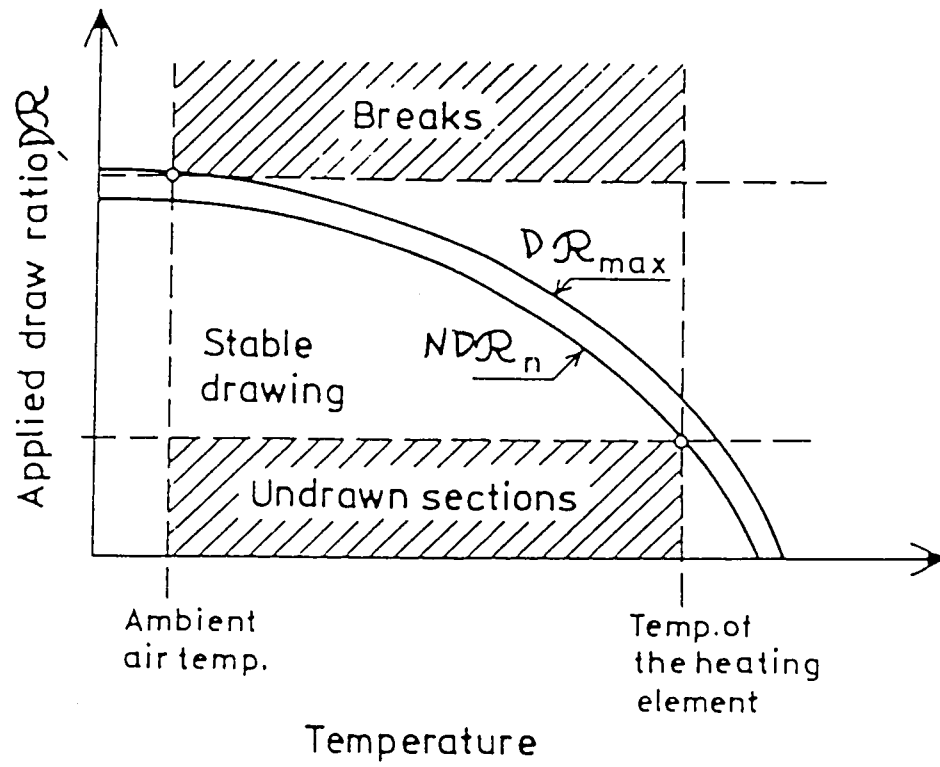


Figure 1 Schematic of Regions of Stability in Hot Drawing

accompanied by significant mechanical property changes [43]. Higher tenacity, with consequent lower elongation to break, can be achieved by increased draw ratio. Ziabicki et al. [65] found that tensile strength, tensile modulus and yield strength increase monotonically with draw ratio; elongation to break and total deformation work decrease monotonically with increasing draw ratio. This remarkable behavior is likely due to the fact that the average molecular orientation in the samples is a major factor which controls such properties [67, 68]. Samuels indicated [34] that the tenacity of drawn PP filaments is associated with the development of higher orientation in the filaments, and is controlled primarily by the orientation of the amorphous fraction of the samples and has little relationship to the crystallinity or crystalline orientation. Birefringence, which represents total fiber orientation and is widely used to define amorphous orientation, tends to increase with draw ratio and the orientation of the initial melt spun filaments [22, 23, 55, 66].

Draw Temperature

Draw temperature is one of the most important factors which influence the behavior of natural PP and pigmented drawn PP filaments. Usually, drawing of a fiber may be performed at temperatures from the glass transition point up to a point close to the crystalline melting temperature. This is because the drawing

process rearranges large molecular chains. When stretching the fiber at a temperature near the T_g , the relatively low mobility of the molecules evidently causes the opening up of the folded molecular segments in the amorphous regions to be the dominant process. When drawn above the T_g , the molecular chains are more mobile and the relaxation processes are accelerated. The upper limit depends on the degree and type of crystallinity present prior to drawing. It has been observed [67] that a substantial increase in tenacity can be achieved if pre-oriented fiber is stretched at a temperature between the temperature of maximum crystallization rate and melting point.

Abhiraman and co-workers [69] have shown that PET fibers of high order can be obtained through drawing at a temperature close to T_m after crystallization of oriented precursor fibers between T_g and T_m .

For PP, T_g and T_m are $-10\text{ }^{\circ}\text{C}$ and $165\text{ }^{\circ}\text{C}$ respectively [70]. It seems that natural PP and pigmented PP can be drawn at room temperature. However, all of these melt spun samples already possess a certain crystallinity, especially for pigmented PP filaments [5, 22, 23, 29]. For an improved drawability, therefore, draw temperature above room temperature ($\sim 25\text{ }^{\circ}\text{C}$) appears to be necessary for pigmented PP filaments. The higher draw temperature provides greater mobility for thermal crystallization and, hence, higher crystallinity of drawn PP filaments. On the other hand, the

lower the draw temperature, the higher the draw force, and the more extended will be the conformation of the molecules obtained. Moreover, Lu and Spruiell reported [71] that the relationship between measured crystallinity and drawing temperature of the PP filaments is almost linear. Variations in the temperature and rate of drawing also have a marked effect on maximum draw ratio. It has been demonstrated [38] that attainable maximum draw ratios increase with increasing stretch-bath immersion time and with increasing bath temperature, which in turn increases the temperature of the filaments. Sheehan et al. [38] revealed that the increase in the maximum draw ratio with increasing filament temperature is due to the following two factors: (i) the increase in filament temperature increases the amount the filament could be stretched during drawing; and (ii) it decreases the amount of shrinkage after drawing, apparently by increasing the rate of crystallization, which stabilizes the filaments in the stretched state.

Draw Speed

To efficiently increase draw capacity, or effectively balance high throughput and high take-up speed in melt spinning, a high draw speed in drawing production is often required. In addition to draw ratio and draw temperature, draw speed also plays an important role in governing the overall properties of fiber. Hence, it is important to understand the effect of stretching rates on the structure and

properties of pigmented PP filaments. The effect of draw speed on the different polymers has been investigated by several authors [72-80]. The systematic study carried out by Abhiraman and Song [81] showed that drawing at temperature not far from the glass transition offers a stable situation as far as rate induced fluctuation in morphology is concerned. Due to viscous dissipation and any additional crystallization accompanying drawing, the internal temperature of the polymer increases and this increase is greater at higher rates of drawing [81]. The increase in temperature can cause a change in the rate of crystallization in either direction, depending on the temperature of the material entering the drawing zone. The birefringence of Nylon-6 has been reported to increase [72], decrease [73], or be essentially unaffected [74] by rate of drawing. This implies that the effect of draw speed is less simple. Increasing draw speed may have more complex influence on the structure and properties of drawn filaments. Generally speaking, the rate of drawing determines the time of deformation-induced transformation. Higher draw speeds mean less time during the draw process for relaxation processes. From this viewpoint, one can expect viscoelastic effects leading to higher orientations at higher deformation rates due to minimizing the relaxation process, thus preserving higher molecular orientation. On the other hand, an increase of draw speed as accompanied by increased filament temperature can lead to the reduction of relaxation times (disorientation), lower effective orientations, and/or temperature-

induced crystallization. The net effect of these two factors determines the morphological parameters in the drawn filaments [66].

CHAPTER 3

MATERIALS, EQUIPMENT, AND MEASUREMENTS

3.1 Materials and Preparation

The source of the investigated polymer in this study was Exxon Chemical Company. The resin was a commercial grade of isotactic polypropylene resins with the basic characteristics [82] tabulated in Table 1. Two selected color concentrates, carbon black and phthalyl blue, supplied by Standridge Color Corporation were studied. Carbon black, an inorganic pigment, has a high pigmentation power and it improves many of the physical properties of polymer, such as light stability, processibility, and mechanical properties. Phthalyl blue, an organic pigment, has good light stability, good resistance to chemicals and high tinctorial strength as well as relatively low cost. The master batch information [83] of these pigments are summarized in Table 2. It is worth noting that the isotactic PP resin and the black and blue pigments used here are the same as those previously used by Lin [23], who studied the effect of pigment additions on the development of structure and properties of as-spun PP filaments.

The isotactic PP chips were mixed with the pellets of black

Table 1 As-Received Isotactic PP Resin Properties

PP Resin Properties	Value
Melt Flow Rate (g/10 min)	45.6
Intrinsic Viscosity (dl/g)	1.036
Weight Average Molecular Weight, M_w	138993
Number Average Molecular Weight, M_n	65241
Polydispersity, M_w/M_n	2.16

Table 2 As-Received Pigment Master Batch Information

Color	Loading (%)	Comments
Black	25	Cabot 660 furnace black
Phthalyl blue	25	Red Shade

and blue pigments before the melt spinning. For each of the two color concentrates studied, three samples were prepared with the pigment concentrations of 0.05%, 0.5%, and 1.0% by weight. It should be noted that the concentrations of the pigments used here are in the range of an industrial production. These mixed materials were each fed into the extruder through the machine hopper of the spinning machine to obtain melt spun-dyed PP filaments. Natural PP samples were directly melt spun from a screw extruder and spinning head.

3.2 Melt Spinning

The melt spinning equipment used in the experiment is shown in Figure 2. Briefly, the PP melt and the color concentrates blended prior to the extruder were melt spun from a Fourné Associates screw extruder and spinning head.

The extruder had a 13 mm diameter screw and was equipped with a nitrogen purged hopper with a seven liter capacity. The throat of the extruder was cooled by running cooling water to prevent molten polymer from backwashing into the hopper feed section. The melt was fed through a Zenith gear pump, a 325 mesh filter screen and a one-hole capillary spinneret with a 0.762 mm diameter and 3.81 mm length (L/D ratio = 5.0). The extrusion temperature was kept constant at 210 °C. The melt temperature in

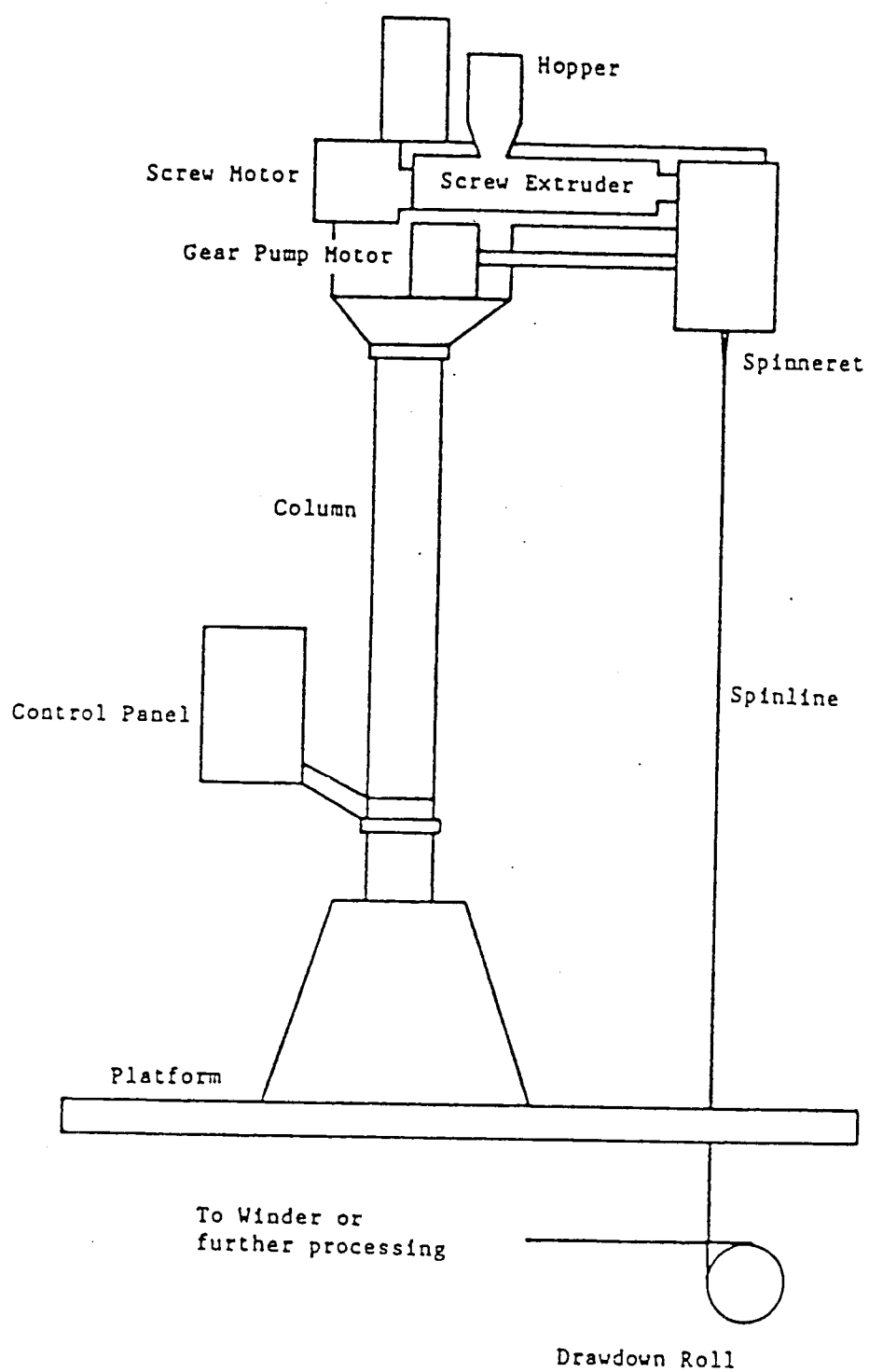


Figure 2 Schematic of the University of Tennessee's Melt Spinning Equipment Stage

the discharged stream was measured by two platinum-resistance thermometers which are placed in the polymer stream. The pressure between the extruder and the gear pump was in the range of 1,000-2,000 psi. Mass throughput determined by the gear pump speed was manually adjusted by means of a variable speed gear box. Natural PP and pigmented PP polymer were extruded at a fixed mass flow rate of 3.2 g/min. The filaments were melt spun through ambient air at a temperature of 25 °C and were passed around a 3-inch diameter, constant-speed feed roll placed 10 feet from the spinneret. After leaving the feed roll, the filaments were taken up on a LEESONA 955 constant-tension winder. Filaments were taken up at a constant speed of 700 m/min. The take-up speed was controlled by adjusting the speed of the take-up device. Several groups of bobbin samples of pigmented and natural PP spun filaments were collected by the portable winder.

In order to maintain continuity of the study on the drawn pigmented PP filaments, the same PP resins and pigments, and similar melt spinning conditions (except for a higher throughput and a lower spinning speed) as in reference [23] were used to generate the pigmented and natural PP as-spun filaments for subsequent drawing process study. The general melt spinning conditions listed in Table 3 are quite similar to commercial spinning conditions in order to obtain the resulting final drawn yarn deniers at or near 12 denier per filament.

Table 3 Process Conditions for Melt Spinning of PP Natural and Pigmented PP Filaments

Process Conditions	Value
Mass throughput	3.2 g
spinneret hole count	1
Capillary diameter	0.762 mm
Extruder pressure	1000-2000 psi
Extrusion temperature	210 °C
Take-up speed	700 m/min
Sinline cooling	static ambient air
Spinning length	4.3 m
Calculated spun denier	41.24

The final fiber denier per filament (dpf) was mainly determined by the mass throughput, spinneret hole count, take-up speed, and total draw ratio. Mass throughput for a certain fiber denier can be easily calculated according to the following fiber formation equations.

$$Q = \frac{N \times V \times D \times K \times DR}{9000} \quad (1)$$

$$\text{or} \quad D = \frac{9000 \times Q}{N \times V \times K \times DR} \quad (2)$$

where, Q = mass throughput, (g/min)
 D = denier of drawn fiber, (g/9000m)
 V = take-up speed, (m/min)
 N = spinneret hole count
 DR = total draw ratio
 K = shrinkage coefficient, $\sim 0.85-0.95$ [65]

$$K = \frac{\text{Theoretical denier of drawn filament}}{\text{True denier of drawn filament}}$$

The natural and pigmented (black and blue) PP as-spun samples with varied pigment concentration, 0.05%, 0.5% and 1.0% by weight, were collected on bobbins for continuous drawing operation.

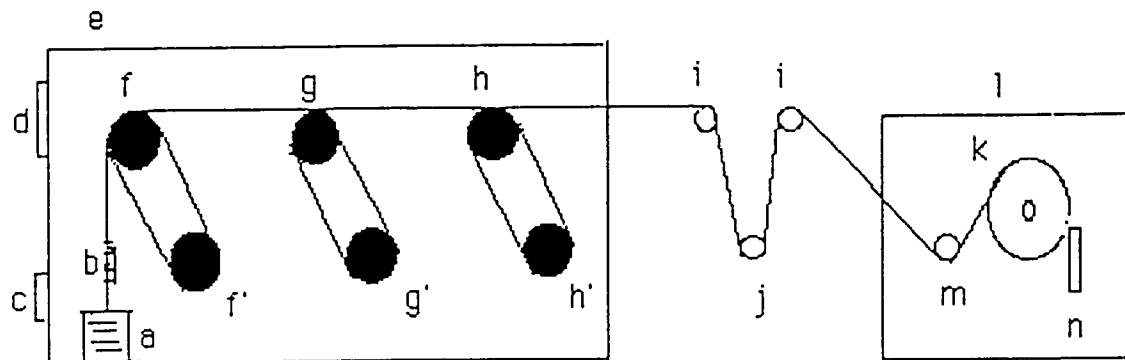
3.3 Filament Drawing

Physical, in particular mechanical, characteristics of as-spun fibers are usually rather far from those required by textile industry. Undrawn fibers exhibits low tenacity, high irreversible (plastic) deformability, and low modulus, etc. From a structural point of view as-spun fibers have very low molecular orientation. The molecules approximate to a random arrangement with respect to the fiber axis. Therefore, all the spun fibers have to undergo drawing in

order to improve their mechanical properties and make the fibers usable for textile applications. To give a certain time for relaxation of spun orientation, all the spun samples were drawn within 24-48 hours after spinning.

Drawing Apparatus

The as-spun filaments previously collected on bobbins were drawn continuously using a typical two stage drawing apparatus, even though only one stage drawing was used in this study. The drawing apparatus is illustrated in Figure 3. Filaments were unwound from a bobbin and passed over a pre-tension guide to heated rollers f and f' , which were operating at a constant speed. The undrawn filaments passed from rollers f and f' to unheated rollers g and g' , which rotated at a higher speed, then continued from rollers 2 and $2'$ to unheated rollers h and h' , which rotated at the same speed as rollers g and g' . From rollers h and h' , the drawn filament passed over a guide, through a tensioner, and onto a bobbin on a constant tension winder. The temperature of the rollers was monitored through a thermocouple which controlled the draw temperature. The temperature readings for each set of the rollers are indicated on a meter on the control panel. The drawing operation is generally determined by passing the fiber from one to another set of rotating rollers, each set of the rollers rotating at a surface speed which is greater than that of the preceding set. The ratio of the higher to the



where,

a = spun yarn sample;

b = yarn guide;

c = draw speed control;

d = draw temperature control;

e = drawing machine;

f = feed roller or first roller (upper);

f' = first roller (down);

g = second roller (upper);

g' = second roller (down);

h = third roller (upper);

h' = third roller (down);

i = guide roll;

j = take-up arm;

k = drawn fiber;

n = break block;

First stage drawing: occurring between roller one (f and f') to roller two (g and g');

Second stage drawing: occurring between roller two (g and g') to roller three (h and h')

Figure 3 Schematic of the University of Tennessee's Drawing Equipment

lower surface speeds determines the extent of fiber drawing. The draw ratios were varied by changing the speed of the second set of rollers. Since the diameters of each set of rollers are the same, draw ratio can be controlled by adjusting the rotation frequency (rpm).

In this study, the effect of draw conditions, such as draw ratio, draw temperature and draw speed, on the structure and properties of pigmented PP filaments were investigated. As-spun filaments were drawn over the first stage only. A first set of samples were drawn at a series of draw ratios, 3, 4, 5 or 6 and above with a constant draw temperature (feed-roll temperature) of 50°C and feed-roll speed (not draw-roll speed) of 45 rpm. A second set of drawn samples were produced at the fixed draw ratio of 4 and draw speed of 180 rpm but varied draw temperature at 25, 50, 75, and 100 °C. A third set of samples drawn with varied draw speeds (or draw-roll speeds) of 90, 135 and 180 rpm with a fixed draw ratio of 3 and draw temperature of 50 °C were also collected. In each case, the temperature of the second and the third set rollers were maintained at 25 °C (room temperature).

Definition of Draw Ratio

Draw ratio is the length of the drawn filament divided by the length of undrawn filament which is equivalent to the ratio of the

denier of the undrawn filament to the denier of the drawn filament. The ratio of the draw-roll speed to the feed-roll speed in the drawing process is called the apparent draw ratio.

For a single stage drawing used here,

$$\text{Apparent Draw Ratio} = \frac{\text{surface speed of roller two}}{\text{surface speed of roller one}} \quad (3)$$

If the diameter of roller one is equal to that of roller two, and $V = \pi DN$, then, the following equation can be easily derived from equation 3.

$$\text{Draw Ratio} = \frac{V_2}{V_1} = \frac{\pi D_2 \times N_2}{\pi D_1 \times N_1} = \frac{N_2}{N_1} \quad (4)$$

where, N = rotation frequency of roller (rpm)

V = surface speed of roller (cm/min)

D = diameter of the roller (cm)

In this case, draw ratio here can also be determined by adjusting the rotation frequency of the rollers 2 and 1 on the drawing machine.

3.4 Filament Characterization

Structural and property characterization of natural and pigmented PP filaments were carried out by density, DSC, WAXS, and birefringence as well as Instron measurement.

Birefringence

A major structural feature of fibers is the level of orientation of the polymer molecules and of the crystalline material relative to the fiber axis [84]. The birefringence, which is defined as the difference between the refractive index in the axial direction and the refractive index in the transverse direction, reflects the total orientation of molecules in both crystalline and amorphous phases. The measurement was made with crossed polars on the microscope. At the zero reading on the compensator a black band was observed across the field of view. When a birefringent fiber was brought into view the black band was shifted and the fiber appeared bright on a black background. The optical crystal of the compensator was tilted until the black band was brought back to zero reference position. The optical retardation on the samples was determined using an Olympus polarizing microscope (model No. 206080) and Olympus 4 order Berek compensator (Model No, CIPI-200105). The retardation was calculated from the compensator reading and the diameter of the fiber was measured using a filar eyepiece. The birefringence is the ratio of the optical retardation to the fiber diameter, that is

$$\Delta n = \frac{R}{d} \quad (5)$$

where Δn is fiber birefringence, R is the retardation reading, d is measured fiber diameter. An average of fifteen readings was taken for each sample.

Density and Crystallinity

The densities of the spun and drawn filaments were determined using a distilled water-isopropyl alcohol density gradient column at 23 °C according to ASTM standard D1505-68. The column was calibrated using glass beads of known density. The densities of the glass floats were known within ± 0.002 g/c.c.. Approximately twenty four hours were allowed for the filaments to reach their equilibrium levels of displacement. In the absence of voids, the fraction of crystalline natural PP filaments may be calculated from the fiber densities by use of the following equation, reported by Sobue and Tobate [85]:

$$X = (1/\rho - 1/\rho_c) / (1/\rho_{am} - 1/\rho_c) \quad (6)$$

For pigmented PP samples, It was assumed [23] that there were three phases existing in a pigmented filament, namely crystalline, amorphous and pigment, and that each had a distinct

density. The following equation of crystallinity calculation was derived by assuming the existence of distinct phases.

$$X = [1/\rho - 1/\rho_a - c_p(1/\rho_p - 1/\rho_a)] / (1 - c_p)(1/\rho_c - 1/\rho_a) \quad (7)$$

where X is the crystallinity of the filament sample, ρ is measured sample density, ρ_a and ρ_c are amorphous and crystalline densities of polypropylenes, respectively. The values used for ρ_a (0.854 g/cm^3) and ρ_c (0.932 g/cm^3) were the same as those quoted by Samuels [86]. ρ_p is the density of the pigment and c_p is the pigment concentration. Since we do not have information of the exact chemical content for the pigments used, we estimated the density of the pigments referred to in reference [87]. According to Binsbergen [87], ρ_p is 1.8 g/cm^3 for both carbon black and blue phthalyl pigments.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-7 Thermal Analysis Differential Scanning Calorimeter was used to measure the heat of fusion for melt spun and drawn samples. The heat of fusion was determined from the area under peaks in the graphing of heat content versus temperature. Tin with a melting point of 231.9°C and a heat of fusion of 14.45 cal/g was used as a calibration standard. To minimize the effect of fiber shrinkage upon heating [88], small samples (from 2 to 10 mg)

were cut and weighed on a Mettler analytical balance to a tenth of a milligram; then they were sealed in aluminum sample pans. During DSC experiments the samples were heated from 25 °C to 210 °C at a rate of 20 °C/min. The calorimetrically derived crystallinity (X_c) was calculated assuming that the heat of fusion of 100% crystalline PP is 49.95 cal/g [89]. For natural PP filaments, the crystallinity could be determined from the following equation [90]:

$$X_c = \frac{E_{\text{sample}}}{E_{100\%}} \quad (8)$$

where E_{sample} is the energy to melt the sample and $E_{100\%}$ is the energy to melt a perfectly crystalline (both adjusted for masses of polymer). Due to the small weight fraction of pigment in the sample, its effect on the sample energy was neglected. An average of two readings was taken for each cell.

Wide Angle X-ray Scattering (WAXS)

For a qualitative analysis of the crystalline structure involved in the filaments, Astbury pictures were taken. These WAXS photographs of the spun and drawn samples were obtained using a Philips Norelco x-ray generator with nickel filtered $\text{CuK}\alpha$ radiation of wavelength 1.542 Å. The X-ray unit was operated at 40 kv and 20 mA. About 100 filaments were wound on a plastic plate so that all fibers were parallel. The plastic frame was then mounted on the X-

ray diffractometer unit in such a way the X-ray beam was perpendicular to the fiber axis.

These patterns were used as indicators of the crystalline form and qualitative features of the orientation of the spun and drawn fibers. The first three diffraction rings of the x-rays patterns represent the 110, 040 and 130 planes parallel to the c axis of the monoclinic crystal of PP. As fibers are drawn, the crystallites are oriented with the c axis parallel to the fiber axis. Hence, the smaller the angle of the first three diffraction rings, i.e., the shorter the arcs, the higher the degree of orientation.

Mechanical Properties

The tensile properties of the spun and drawn fibers were tested at room temperature and 65% R.H. on a table model Instron tensile frame by ASTM method D204-57T. All specimens were conditioned under the standard conditions of temperature and relative humidity for at least 24 hours prior to the determination of tensile properties. A gauge length of 25.4 mm and crosshead speed of 50 mm/min were used. From the stress-strain curves, the tenacity, initial modulus and elongation at break parameters were computed. The values given for these properties are the average of at least 15 measurements in each case.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Pigments on the Stress-Strain Curves of As-Spun PP Filaments

Drawing conditions and the structure and properties of the resulting fibers strongly depend on the characteristics of the original (as-spun) materials [66]. Therefore in order to determine the range of drawability and to optimize the drawing process for pigmented PP filaments, it is imperative to know the structure and mechanical properties of undrawn pigmented PP filaments. The mechanical properties can be characterized by the so-called stress-strain curves, which measure tensile properties, natural draw-ratio, and maximum draw ratio to which the fiber can be drawn. The structural characteristics evaluated include crystallinity from density gradient column and DSC and orientation from birefringence.

To illustrate the type of data obtained from the Instron test, the engineering stress vs. the engineering strain curves of the natural and (black and blue) pigmented PP as-spun filaments are plotted in Figure 4 for various pigment concentrations. The mechanical properties of the black and blue pigmented PP filaments

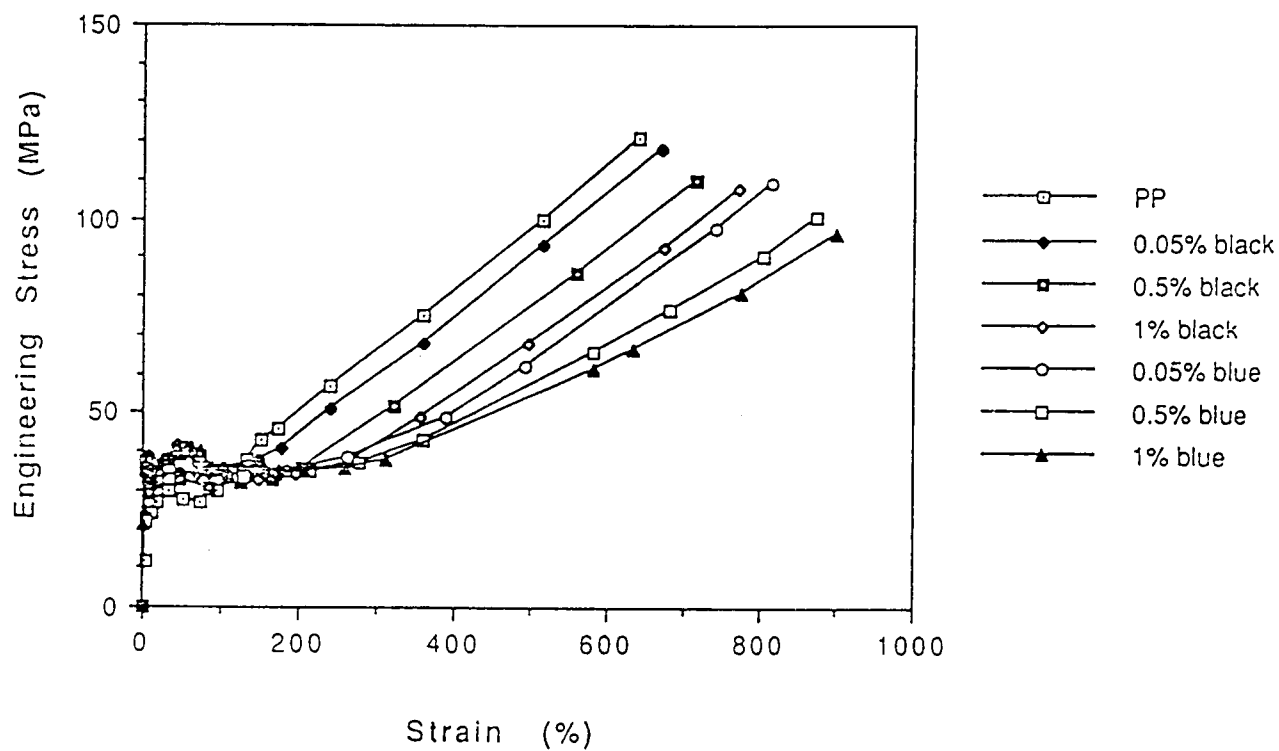


Figure 4 Typical Strain-Stress Curves of As-Spun Neat and Pigmented PP Filaments

with varied pigment concentrations spun at a fixed spinning speed are quite different from those of natural PP filaments. The shapes of the curves indicate that the natural PP filament has higher tenacity and lower elongation at break than all pigmented PP filaments spun at the same processing conditions. It is noteworthy that different pigment types (blue vs. black) and pigment concentrations (0.05%, 0.5% and 1.0%) have different amounts of influence on the mechanical properties of the pigmented as-spun PP filaments. The stress-strain characteristics of 0.05% black pigmented as-spun filaments spun at the same conditions are quite close to the natural PP filament. On the other hand, The blue pigment appears to have greater influence on tenacity and elongation at break than the black pigment. The change in tenacity and elongation at break increases as the concentration of pigment increases for each pigment. Accordingly, the modulus and yield strength of the pigmented as-spun filaments follows the same trend as that of tenacity. The measured DSC and density crystallinity results, shown in Table 4, indicate that the crystallinities of pigmented PP as-spun filaments tend to be higher than those of the natural PP as-spun filament, but their birefringence values are lower than those of the natural PP as-spun filament. These results demonstrate clearly that the presence of pigment in a molten polymer results in some modifications of the crystallization. According to Lin et al. [22, 23], the difference between natural and pigmented PP filament is possibly due to the different morphology.

Table 4 Structural Characteristics and Mechanical Properties of the Natural and Pigmented PP As-spun Filaments

As-Spun Sample	Xc (%) (By DSC)	Xc (%) (By Density)	Birefringence (x10 ³)	Elongation (%)	Tenacity (MPa)	Yield Strength (MPa)	Modulus (GPa)
Natural PP	37.35	48.05	12.20	639.0	120.3	29.9	0.903
0.05% black pigmented PP	38.29	50.43	11.69	670.9	118.1	31.8	0.901
0.5% black pigmented PP	38.86	48.67	11.08	714.6	110.2	32.2	0.853
1.0% black pigmented PP	39.42	46.80	10.47	772.0	107.9	35.0	0.824
0.05% blue pigmented PP	39.92	53.27	11.15	815.7	109.3	35.2	0.771
0.5% blue pigmented PP	40.38	51.24	10.85	874.6	100.7	36.3	0.752
1.0% blue pigmented PP	41.08	51.55	10.23	898.0	96.2	36.6	0.717

They stated that the differences among the pigmented samples appear to reflect the differences of nucleating power previously established among the different pigments. These results indicate that pigment additions cause quantitative variations of structural properties and that changes in the polymer structural characteristics influence the properties of as-spun PP filaments. The type and the range of these variations strongly depend on the pigment types and pigment concentrations.

Examination of the stress-strain curves shown on Figure 4 reveals one more fact: that is due to higher elongation at break, or lower spun orientation, pigmented PP as-spun filaments may be drawn to higher draw ratios than the natural PP filaments. The blue pigmented filaments, which possess lower spun orientation, should have higher maximum draw ratio than either the natural or black pigmented PP filaments. And increased pigment concentrations from 0.05% to 1.0% lead to increased maximum draw ratio. However, stress-strain curves as well as attainable maximum draw ratios are not only sensitive to the spun orientation, but also dependent upon the molecular and crystalline texture of the as-spun PP filaments. In most cases, the maximum draw-ratio is lowered by increasing the degree of crystallinity in fibers prior to the drawing operation. Some fibers once crystallized in the undrawn state cannot be even drawn at all. However, Ziabicki [66] explained that in some cases an increase in crystallinity of the undrawn fiber also modifies the

deformation curves which may result in increased natural draw ratio and, therefore, possibly higher maximum draw ratio. Although we did not quantitatively measure the natural draw ratio on the stress-strain curves for the samples, it still can be seen from the Figure 4 that blue and black pigmented PP filaments possessing higher crystallinity show considerably higher natural draw ratios as well as yield strength than those of natural PP filament. This increased drawability is presumably due to a loosening function of the pigments [5]. Wu [5] stated that the occurrence of pigment powders or small molecules weakens the entanglement of macromolecules and the force among the molecules. Thus, the molecular chains packed in pigmented fibers can be deformed easily, and pigmented PP filaments can be drawn out more and safely at higher draw ratios without too frequent breaks. By increasing the maximum draw ratio, the tensile strength and other tensional properties of the pigmented PP filaments are also increased or improved.

4.2 Effect of Draw Conditions and Pigments on the Structures of Drawn Pigmented PP Filaments

The experiments were carried out on the SHAM semi-industrial drawing apparatus with (i) varied draw ratios at a given draw temperature of 50 °C and fixed feed roll speed at 45 rpm; (ii) with varied draw temperature at a fixed draw ratio of 4.0 and fixed draw speed at 180 fpm; and (iii) with varied draw speed at fixed draw

ratio of 3.0 and draw temperature at 50 °C. Data for the structural and mechanical properties of natural and pigmented PP drawn samples are summarized in Tables 5, 6 and 7.

4.2.1 Variation of Birefringence

Draw Ratio

Birefringence, which can be interpreted as the sum of contributions from crystalline and amorphous regions [91], has been calculated from the experimental measurements of retardation and filament diameter. Figure 5 shows the variation of the birefringence of natural and pigmented PP drawn filaments as a function of draw ratios. Similar results of natural PP drawn fiber were reported by Bodaghi et al. [54]. The birefringence increases monotonically with draw ratio. In particular, the birefringence of pigmented samples tends to approach lower values at high draw ratios. At a fixed draw ratio of 5.0, the birefringence values of the blue and black pigmented filaments are substantially lower than the natural PP filament, and the blue pigmented PP filament with 1.0% pigment concentration has the lowest birefringence value. Note that the as-spun filaments have different starting birefringence, but the difference in birefringence between the different samples increases with draw ratio. This could mean that the orientation of the unpigmented PP fiber develops more rapidly and fully for filaments

Table 5 Effect of Draw Ratio on the Structural and Mechanical Properties of Natural and Pigmented PP Filaments

Samples	DR	Xc (%) (DSC)	Tm (°C) (DSC)	Deduced		Birefring-		Yield		
				Density (gm/cm ³)	Xc (%) (density)	-ence (x10 ⁻³)	Elongation (%)	Tenacity (MPa)	Strength (MPa)	Modulus (GPa)
Natural PP As-Spun	1.0	37.35	160.4	0.8898	48.05	12.20	639.0	120.6	29.9	0.903
Natural PP Drawn	3.0	42.43	162.2	0.8919	50.72	22.18	93.8	359.6	239.8	1.641
Natural PP Drawn	4.0	45.28	162.3	0.8930	52.23	25.10	57.5	439.0	368.2	3.271
Natural PP Drawn	5.0	46.69	162.4	0.8938	53.18	27.63	30.5	558.5	532.0	4.408
0.05% Black Pigmented PP As-Spun	1.0	38.29	160.9	0.8919	50.43	11.69	670.9	118.1	31.8	0.901
0.05% Black Pigmented PP Drawn	3.0	42.51	162.6	0.8924	51.18	21.33	103.4	335.8	233.9	1.632
0.05% Black Pigmented PP Drawn	4.0	45.78	164.7	0.8938	52.89	24.26	60.1	418.3	366.9	3.090
0.05% Black Pigmented PP Drawn	5.0	47.55	164.9	0.8942	53.46	26.89	34.0	522.8	478.5	4.161
0.5% Black Pigmented PP As-Spun	1.0	38.86	161.2	0.8925	48.67	11.08	714.6	110.2	32.2	0.853
0.5% Black Pigmented PP Drawn	3.0	43.05	162.9	0.8935	49.91	20.88	107.0	327.1	220.1	1.628
0.5% Black Pigmented PP Drawn	4.0	46.24	163.9	0.8936	50.10	23.24	76.8	402.4	352.8	3.014
0.5% Black Pigmented PP Drawn	5.0	48.44	164.1	0.8945	51.24	26.26	40.2	507.4	468.7	4.059
0.5% Black Pigmented PP Drawn	5.7	48.77	164.2	0.8950	51.80	27.20	32.8	533.8	517.5	4.356
1.0% Black Pigmented PP As-Spun	1.0	39.42	161.5	0.8933	46.80	10.47	772.0	107.9	35.0	0.824
1.0% Black Pigmented PP Drawn	3.0	43.21	163.3	0.8951	49.08	19.72	112.4	317.2	210.1	1.515
1.0% Black Pigmented PP Drawn	4.0	44.87	164.1	0.8957	49.84	22.52	81.5	378.5	315.6	2.040
1.0% Black Pigmented PP Drawn	5.0	45.99	165.1	0.8958	49.94	25.05	50.7	471.9	429.6	3.203
1.0% Black Pigmented PP Drawn	6.0	46.83	165.3	0.8958	50.03	26.87	48.7	507.4	466.2	3.515
1.0% Black Pigmented PP Drawn	6.5	46.93	165.6	0.8961	50.32	27.63	47.0	519.3	471.7	3.651
0.05% Blue Pigmented PP As-Spun	1.0	39.92	161.9	0.8941	53.27	11.15	815.7	109.3	35.2	0.771
0.05% Blue Pigmented PP Drawn	3.0	43.11	163.2	0.8954	54.96	19.05	114.6	295.1	194.6	1.428
0.05% Blue Pigmented PP Drawn	4.0	45.71	163.8	0.8964	56.19	23.57	88.0	386.1	289.0	2.163
0.05% Blue Pigmented PP Drawn	5.0	47.85	163.9	0.8970	56.94	26.55	48.7	425.1	398.6	2.964
0.05% Blue Pigmented PP Drawn	6.0	48.38	164.0	0.8975	57.59	27.57	39.7	469.3	434.2	3.406
0.05% Blue Pigmented PP Drawn	7.0	49.04	164.1	0.8982	58.53	28.15	27.0	534.8	522.1	3.713
0.5% Blue Pigmented PP As-Spun	1.0	40.38	162.3	0.8945	51.24	10.85	874.6	100.7	36.3	0.752
0.5% Blue Pigmented PP Drawn	3.0	43.35	163.1	0.8960	53.13	18.73	131.4	286.4	188.7	1.385
0.5% Blue Pigmented PP Drawn	4.0	46.64	163.6	0.8971	54.54	22.77	96.9	379.2	286.7	2.122
0.5% Blue Pigmented PP Drawn	5.0	48.23	164.3	0.8977	55.30	25.85	53.6	395.2	362.8	2.919
0.5% Blue Pigmented PP Drawn	6.0	48.74	164.5	0.8984	56.24	26.77	42.4	465.5	419.9	3.307
0.5% Blue Pigmented PP Drawn	6.3	48.97	165.1	0.8987	56.52	27.41	39.3	479.1	450.6	3.395
0.5% Blue Pigmented PP Drawn										
1.0% Blue Pigmented PP As-Spun	1.0	41.08	163.1	0.8970	51.55	10.23	898.0	96.2	36.6	0.717
1.0% Blue Pigmented PP Drawn	3.0	44.05	163.6	0.8986	53.54	18.31	162.6	266.4	176.0	1.173
1.0% Blue Pigmented PP Drawn	4.0	47.08	164.7	0.8998	55.05	21.65	103.8	346.5	288.7	1.990
1.0% Blue Pigmented PP Drawn	5.0	48.75	165.4	0.9006	56.08	23.28	67.4	376.8	360.2	2.828
1.0% Blue Pigmented PP Drawn	6.0	49.1	165.6	0.9009	56.55	24.82	56.9	456.7	409.8	3.537

Note: Draw Temperature = 50 °C; Tm = Melting Temperature measured by the DSC method

Table 6 Effect of Draw Temperature on the Structural and Mechanical Properties of Natural and Pigmented PP Filaments

Samples	Draw		Deduced			Yield				
	Temperature (C)	Xc (%) (DSC)	Tm °C (DSC)	Density (gm/cm^3)	Xc (%) (density)	Birefringence (x10^3)	Elongation (%)	Tenacity (MPa)	Strength (MPa)	Modulus (GPa)
Natural PP Drawn	25	45.13	162.87	0.8926	51.66	25.05	56.8	428.6	363.3	2.71
0.5% Black Pigmented PP Drawn	25	45.96	165.4	0.8938	50.29	23.06	75.1	405.5	347.7	2.559
0.5% Blue Pigmented PP Drawn	25	42.82	164.4	0.8952	52.09	22.1	89.8	368.8	281.1	2.145
Natural PP Drawn	50	45.28	166.44	0.8921	51.00	25.1	57.5	439	368.2	3.271
0.5% Black Pigmented PP Drawn	50	46.24	163.86	0.8938	50.29	23.24	76.8	418.3	352.8	3.014
0.5% Blue Pigmented PP Drawn	50	46.64	163.06	0.8971	54.54	22.17	96.9	372.9	288.7	2.559
Natural PP Drawn	75	46.25	163.72	0.8964	56.47	24.5	62.9	405.5	361.8	2.421
0.5% Black Pigmented PP Drawn	75	46.71	165.22	0.8967	54.07	22.79	78.5	389.2	326	2.263
0.5% Blue Pigmented PP Drawn	75	48.39	163.02	0.8973	54.83	21.96	98.6	328	270.7	1.947
Natural PP Drawn	100	47.47	164.34	0.8968	57.04	23.33	65.7	369.4	338.9	2.065
0.5% Black Pigmented PP Drawn	100	48.08	164.56	0.8975	55.01	22.1	82.1	357.8	322	1.97
0.5% Blue Pigmented PP Drawn	100	50.46	163.06	0.8993	57.36	21.33	101.3	314	265.2	1.622

Note: Draw Ratio = 4.0; Draw Speed = 180 rpm; Tm = Melting Temperature measured by the DSC method

Table 7 Effect of Draw Speed on the Structural and Mechanical Properties of Natural and Pigmented PP Filaments

Samples	Draw	Deduced					Yield			
	Speed (rpm)	Xc (%) (DSC)	Tm ° (DSC)	Density (gm/cm^3)	Xc (%) (density)	Birefringence (x10^3)	Elongation (%)	Tenacity (MPa)	Strength (MPa)	Modulus (GPa)
Natural PP Drawn	90	42.43	162.23	0.8917	50.53	22.18	93.8	359.5	239.8	1.641
0.5% Black Pigmented PP Drawn	90	43.05	162.91	0.8935	49.91	21.94	103.4	327.1	220.1	1.628
0.5% Blue Pigmented PP Drawn	90	44.03	163.57	0.8973	54.83	20.8	131.4	286.4	194.6	1.385
Natural PP Drawn	135	42.3	162.07	0.8919	50.72	21.93	109.3	346.5	209.3	1.527
0.5% Black Pigmented PP Drawn	135	43.05	162.81	0.8935	49.91	21.44	123.9	318.2	203.9	1.497
0.5% Blue Pigmented PP Drawn	135	43.55	162.27	0.8960	53.13	19.45	151.9	278.8	173.6	1.228
Natural PP Drawn	180	42.22	161.74	0.8919	50.81	21.61	133.2	327.4	195.3	1.248
0.5% Black Pigmented PP Drawn	180	42.97	162.77	0.8921	48.20	21.12	153.5	301.7	180.2	1.173
0.5% Blue Pigmented PP Drawn	180	43.87	162.08	0.8936	50.10	19.19	191.8	274.7	167.5	1.045

Note: Draw Ratio = 3.0; Draw Temperature = 50°C; Tm = Melting Temperature measured by the DSC method

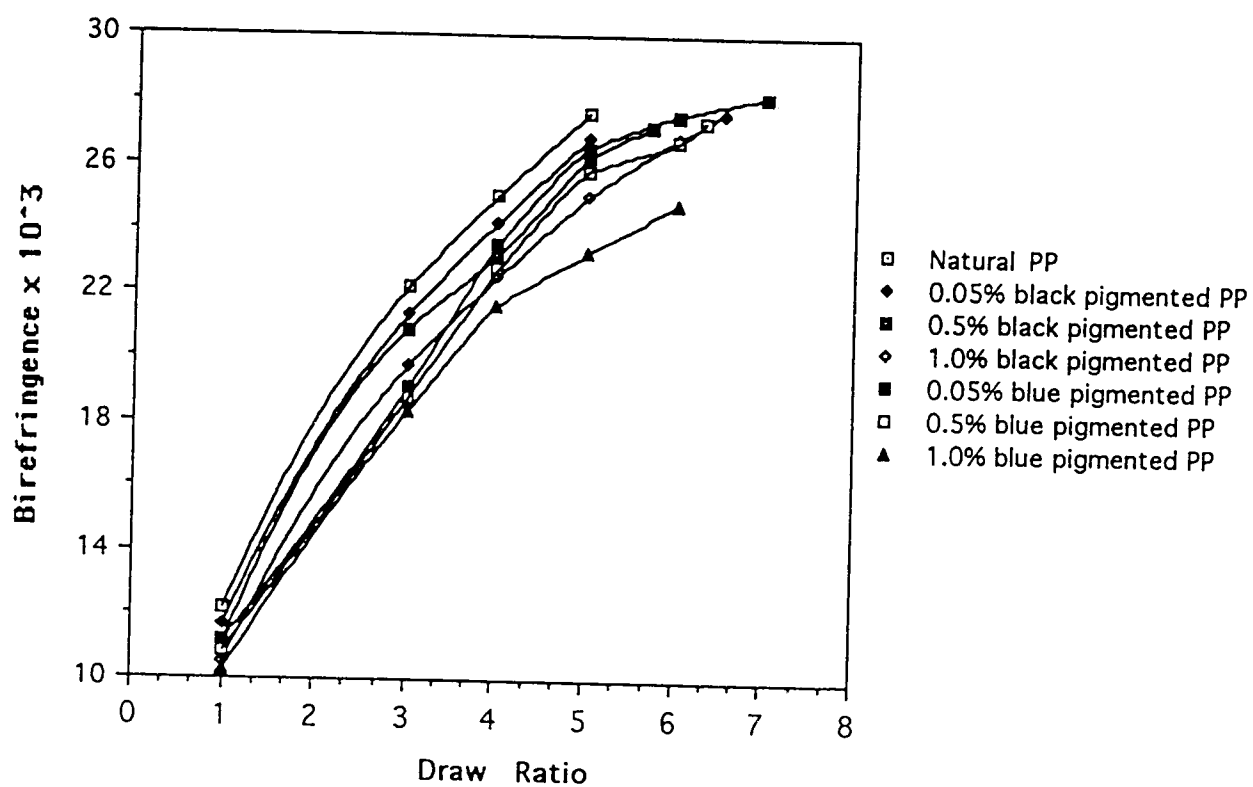


Figure 5 Effect of Draw Ratio on Birefringence of Natural and Pigmented PP

drawn at the same process conditions due to the higher initial orientation. Our statistical studies shown in Appendix further reveal that in addition to draw ratio, pigments and concentrations, the combination of pigments and concentrations, as used in the experiment, also greatly affect the values of birefringence.

Draw Temperature

As mentioned in Chapter 2, another important factor in the drawing of polymer material is the draw temperature. Figure 6 shows a comparison of the way the birefringence varies with draw temperature for three selected drawn yarn samples, natural PP, 0.5% black and 0.5% blue pigmented PP filaments. It appears that there is little change in birefringence (at fixed draw ratio) with increase in draw temperature up to 50 °C. Beyond this temperature, the birefringence of both the natural and pigmented filaments studied shows a decreasing trend. The above effect may be explained in the following manner. As-spun PP filaments, especially pigmented PP as-spun filaments, already possess a fairly high level of crystallinity. Therefore, the filaments drawn at lower temperature (below or near 25 °C), the motion available for the molecules to rearrange themselves in the orientation direction is much limited. At higher draw temperature (above 50 °C), the molecules have enough mobility for rearrangement of the internal structure to relieve the stress. At this stage, the spherulitic structure is slowly

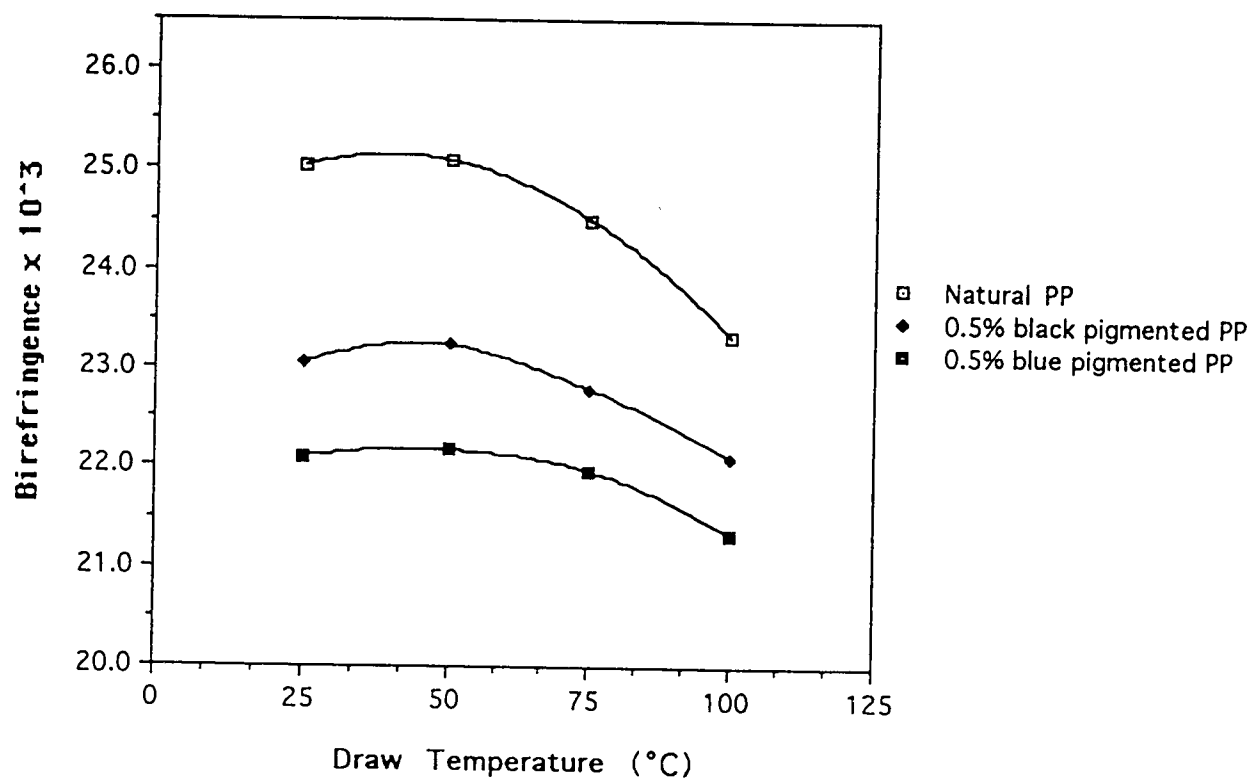


Figure 6 Effect of Draw Temperature on Birefringence of Natural and Pigmented PP

destroyed, and a microfibrillar structure develops [92]. At still higher draw temperature (above 100 °C), gross relaxation of the molecules in the amorphous region takes over the orientation process and results in reorganization of the structure. This fact coincides with the results of other research in other earlier publications [54, 82].

Draw Speed

As described in Chapter 3, draw speed is calculated from the r.p.m. and the diameter of the exit godet, or roller. Birefringence as a function of draw speed is plotted in Figure 7 for a fixed draw ratio of 3.0 and a draw temperature of 50 °C. Slight decreases of birefringence with increases of draw speed are observed for all the natural and pigmented samples. The behavior may be explained by the following theories. According to the viscoelastic mechanism discussed in Chapter 2, a higher draw speed minimizes the relaxation process and should bring about an increase in drawing tension and stress. However, higher deformation is often accompanied by more intensive heat production and reduction of the effective relaxation time and viscosity. The increase in temperature inside the fiber at higher speeds of drawing could be caused by viscous dissipation and any additional crystallization during drawing. Increased temperature developed inside the fiber might cause relaxation of the molecular chain at higher draw speed.

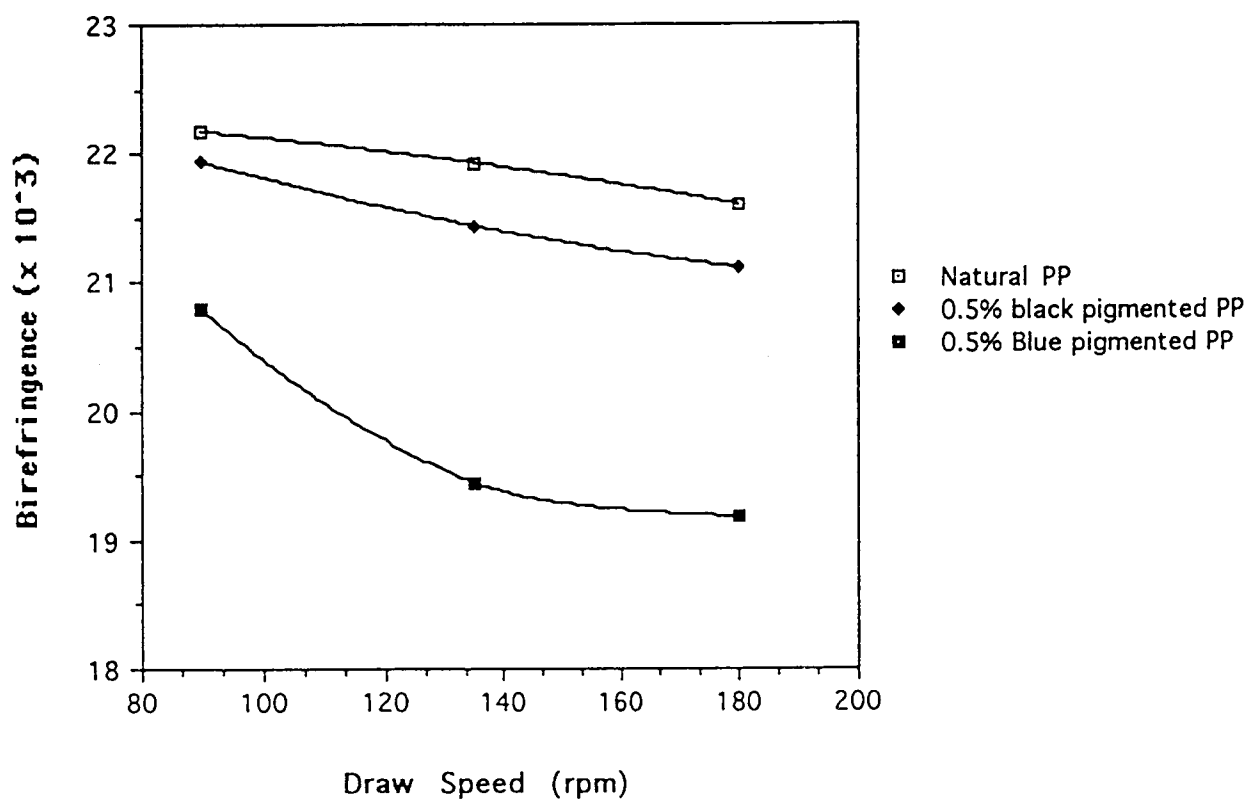


Figure 7 Effect of Draw Speed on Birefringence of Natural and Pigmented PP Filaments

Under essentially adiabatic conditions this can lead to compensation of the viscoelastic effects and even reduction of the fiber orientation [66].

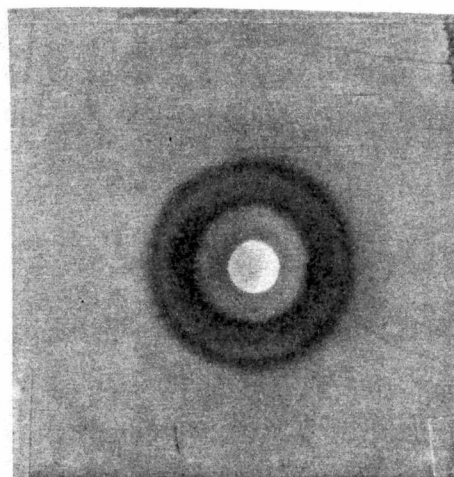
From Figure 7, it is also noted that the draw speed appears to have more impact on the birefringence values of the blue pigmented filaments than those of the natural and black pigmented filaments. It is not clear why this is the case.

4.2.2 Variation of WAXS Patterns

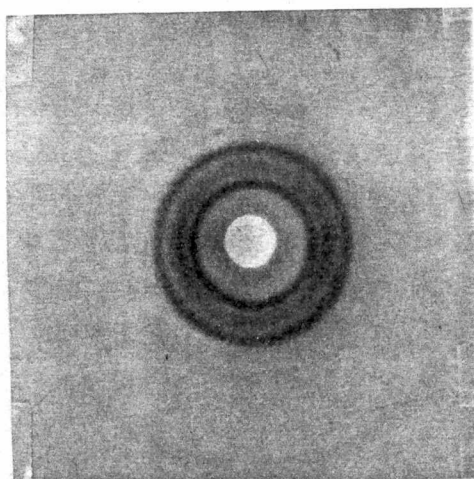
To obtain a better understanding of the structural evolution as a function of drawing, a series of WAXS patterns were recorded for the natural and pigmented PP filaments at varied draw conditions.

Draw Ratio

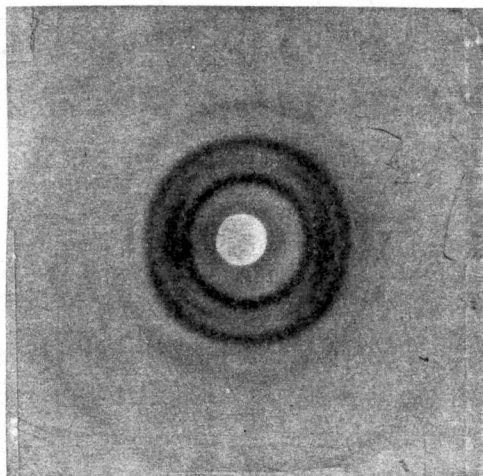
Figure 8 shows WAXS patterns for as-spun filaments of three polypropylenes, natural PP, pigmented PP with black color and pigmented PP with blue color. Based on these x-ray patterns it appears that the natural PP is essentially smectic, not monoclinic. At this low spinning speed this may be the case due to the low temperature at which the sample freezes. The pigmented samples freeze at higher temperature due to their ability to nucleate the crystallization of α -phase. The first four Debye rings correspond to



(a)



(b)



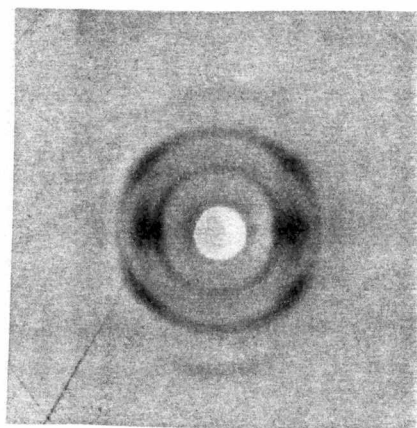
(c)

Figure 8 Typical WAXS patterns of as-spun natural and pigmented PP filaments spun at a take-up speed of 700 m/min and a throughput of 3.2 gm/min

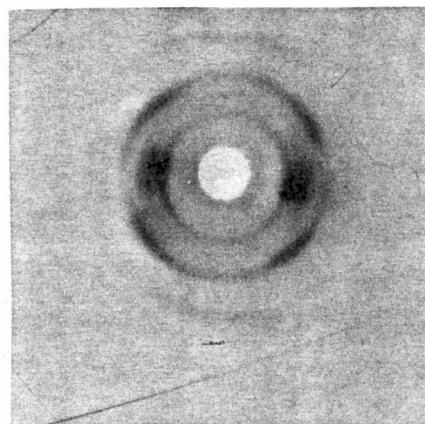
- (a) Natural as-spun PP filament, or draw ratio = 1.0
- (b) 1.0% black as-spun pigmented PP filaments, or draw ratio = 1.0
- (c) 1.0% blue as-spun pigmented PP filaments, or draw ratio = 1.0

the 110, 040, 130 and 111 reflections. The orientation difference among the natural and pigmented PP filaments is small. However, all of the as-spun samples, which exhibit continuous rings, have relatively low orientation.

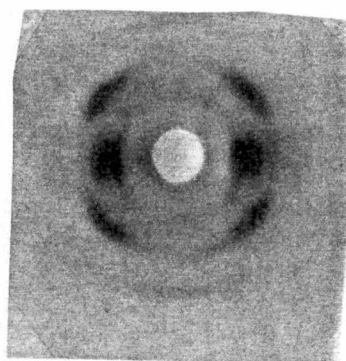
Typical WAXS patterns of the blue and black pigmented filaments drawn at different draw ratios are shown in Figures 9 and 10, respectively. It can be clearly seen that the levels of crystalline orientation of pigmented PP filaments are functions of draw ratios at a given draw temperature and draw velocity. With increasing draw ratio, a preferential orientation of the different lattice planes of the crystals occurred. The orientation of the 040 plane (second diffraction ring) was predominant in the initial stage of drawing, followed by orientation of the 130 plane (third diffraction ring). On further stretching, or at higher draw ratios, the 110 and 111 planes (first and fourth diffraction rings) began to orient and soon all planes were rather highly oriented. It is also noticed that the reflections broaden substantially as draw ratio increases and ultimately result in overlapping of the reflections. This presumably is caused by break-up of the crystalline lamellae into smaller microfibrillar domains during the drawing process as well as lattice strains. One could argue that the material no longer possesses the α -monoclinic crystal structure when drawn under these conditions.



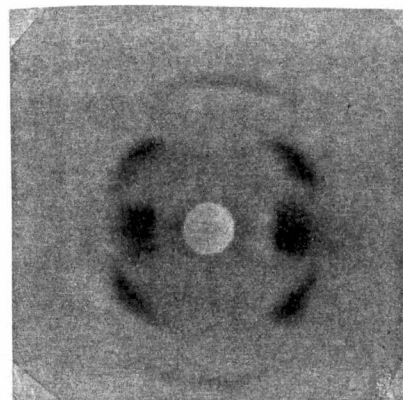
(a)



(b)



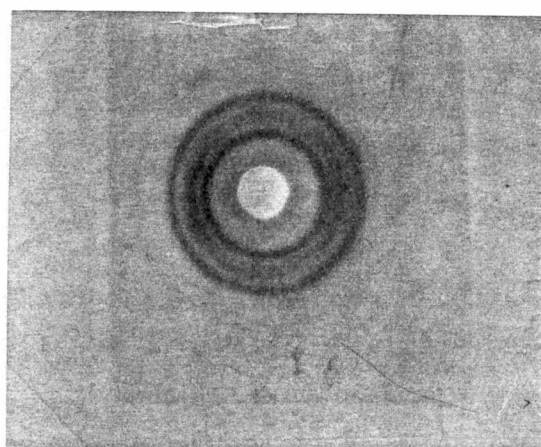
(c)



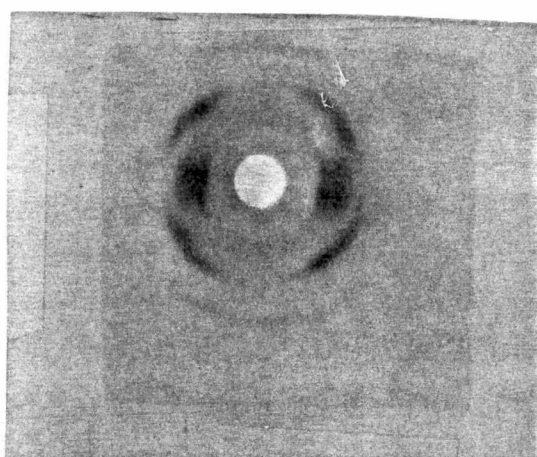
(d)

Figure 9 Typical WAXS patterns of 1.0% blue pigmented PP drawn filaments as a function of draw ratio

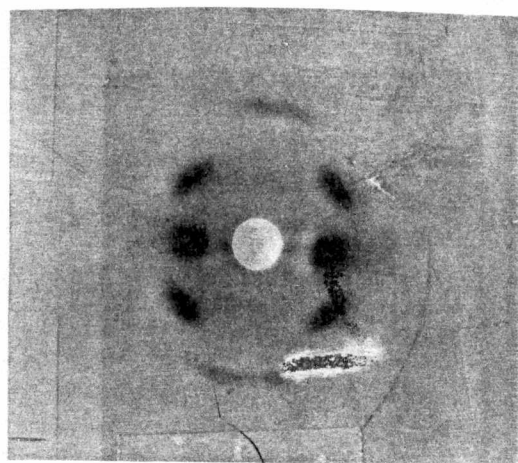
- (a) 1.0% blue pigmented PP filament drawn at draw ratio = 3.0
- (b) 1.0% blue pigmented PP filament drawn at draw ratio = 4.0
- (c) 1.0% blue pigmented PP filament drawn at draw ratio = 5.0
- (d) 1.0% blue pigmented PP filament drawn at draw ratio = 6.0



(a)



(b)



(c)

Figure 10 Typical WAXS patterns of 1.0% black pigmented PP drawn filaments as a function of draw ratio

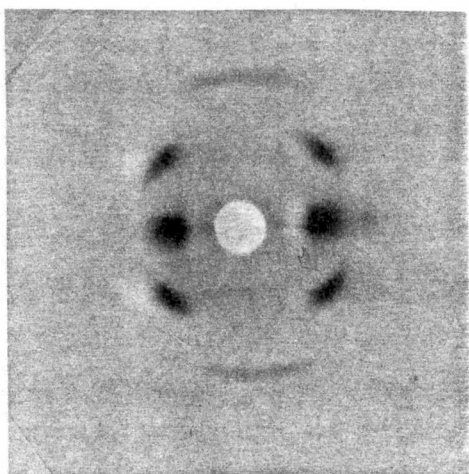
- (a) 1.0% black pigmented PP filament drawn at draw ratio = 1.0
- (b) 1.0% black pigmented PP filament drawn at draw ratio = 3.0
- (c) 1.0% black pigmented PP filament drawn at draw ratio = 5.0

It is also noted from these WAXS patterns that under the same draw conditions the blue pigmented PP filaments seem to have longer trace lengths, or lower crystalline orientation compared to the unpigmented and black pigmented PP filaments. This behavior is in general agreement with the birefringence measurements and confirms that different pigments added into melt PP will bring about rather different effects on the structure development.

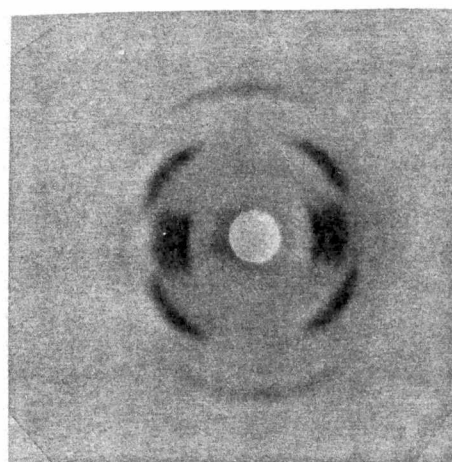
Comparing Figures 8, 9 and 10 also reveals that the drawn filaments possess a much higher level of crystalline orientation than the as-spun filaments.

Draw Temperature

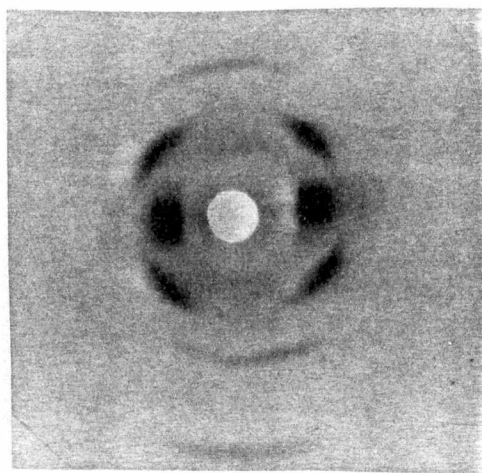
The WAXS patterns with various draw temperature are shown in Figure 11. It may be seen that the fibers, especially 1.0% blue pigmented PP, drawn at higher temperature exhibit narrower diffraction lines of the well defined monoclinic structure similar to that seen in the as-spun filaments. The WAXS reflections of the filaments drawn at 100 °C also have longer azimuthal arcs than those of the filaments drawn at 25 C° suggesting that the crystalline orientations of the samples tend to decrease with increase of the draw temperature. This result is consistent with the studies of Bodaghi et al. [54]. These authors reported that



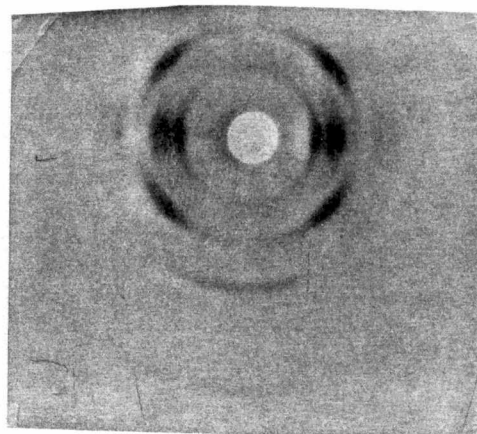
(a)



(b)



(c)



(d)

Figure 11 Typical WAXS patterns of natural and 0.5% blue pigmented PP drawn at various draw temperature and a fixed draw ratio of 4.0

- (a) Natural PP filament drawn at a draw temperature of 25 °C
- (b) Natural PP filament drawn at draw temperature of 100 °C
- (c) 0.5% blue pigmented PP drawn at a draw temperature of 25 °C
- (d) 0.5% blue pigmented PP drawn at draw temperature of 100 °C

crystalline orientation of PP filaments decreased slightly with increasing draw temperature and increased with draw ratio.

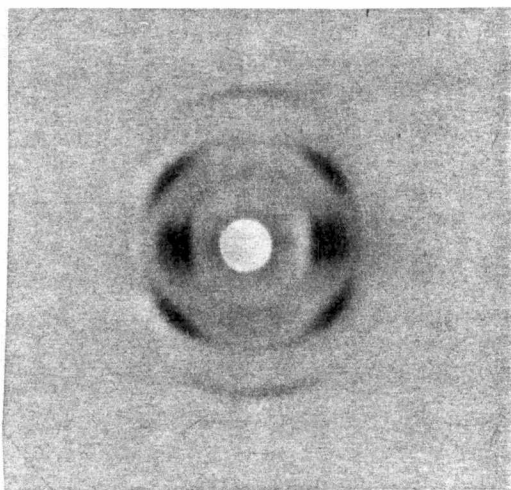
Draw Speed

The WAXS patterns of the PP filaments drawn at varied draw speed are shown in Figure 12. It may be seen that there is a relatively little effect of draw speed on the crystalline orientation.

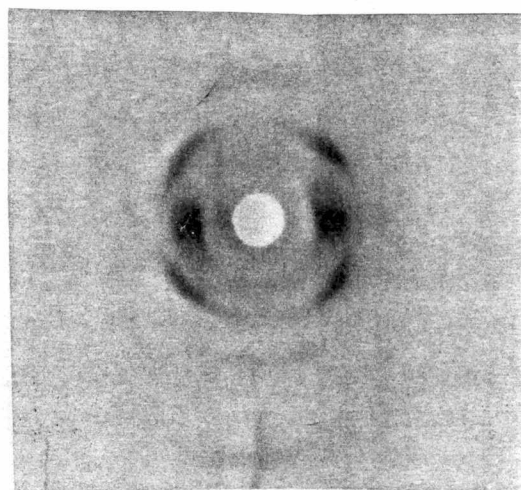
4.2.3 Variation of Crystallinity (by DSC and Density)

Draw Ratio

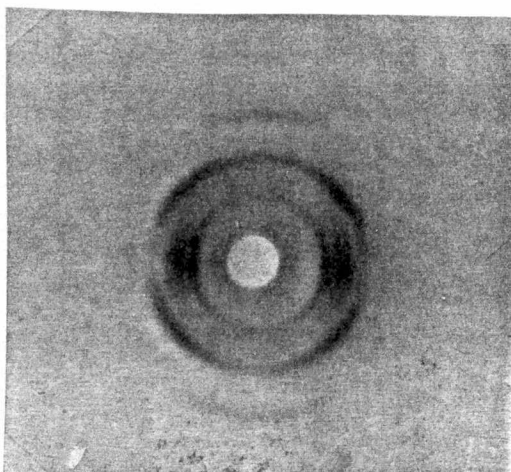
The DSC crystallinity and density crystallinity for selected natural and pigmented PP drawn filaments are plotted as a function of draw ratio in Figures 13 and 14, respectively. Data for the DSC and density crystallinities are presented in Table 5. It is found that both the crystallinity measured by DSC and density methods increases with draw ratio. In the range of draw ratio below 5.0, both the crystallinities rapidly increase with increasing draw ratio, and blue and black pigmented PP drawn filaments result in higher crystallinity. On the other hand, at draw ratio above 5.0, further increases in DSC crystallinity and density crystallinity becomes small.



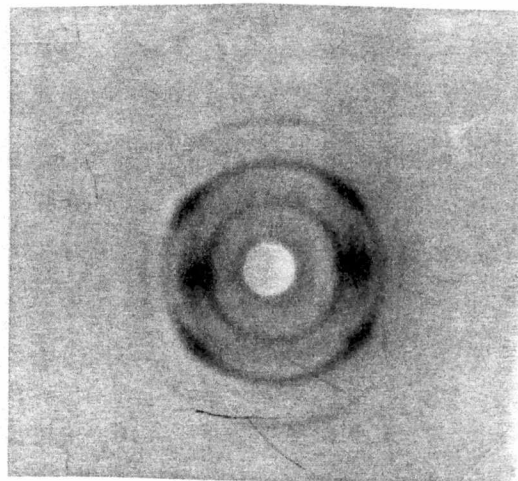
(a)



(b)



(c)



(d)

Figure 12 Typical WAXS patterns of natural and 0.5% blue pigmented PP drawn at various draw speeds and a fixed draw ratio of 3.0 and draw temperature of 50 °C

- (a) Natural PP filament drawn at a draw temperature of 25 °C
- (b) Natural PP filament drawn at draw temperature of 100 °C
- (c) 0.5% blue pigmented PP drawn at a draw temperature of 25 °C
- (d) 0.5% blue pigmented PP drawn at draw temperature of 100 °C

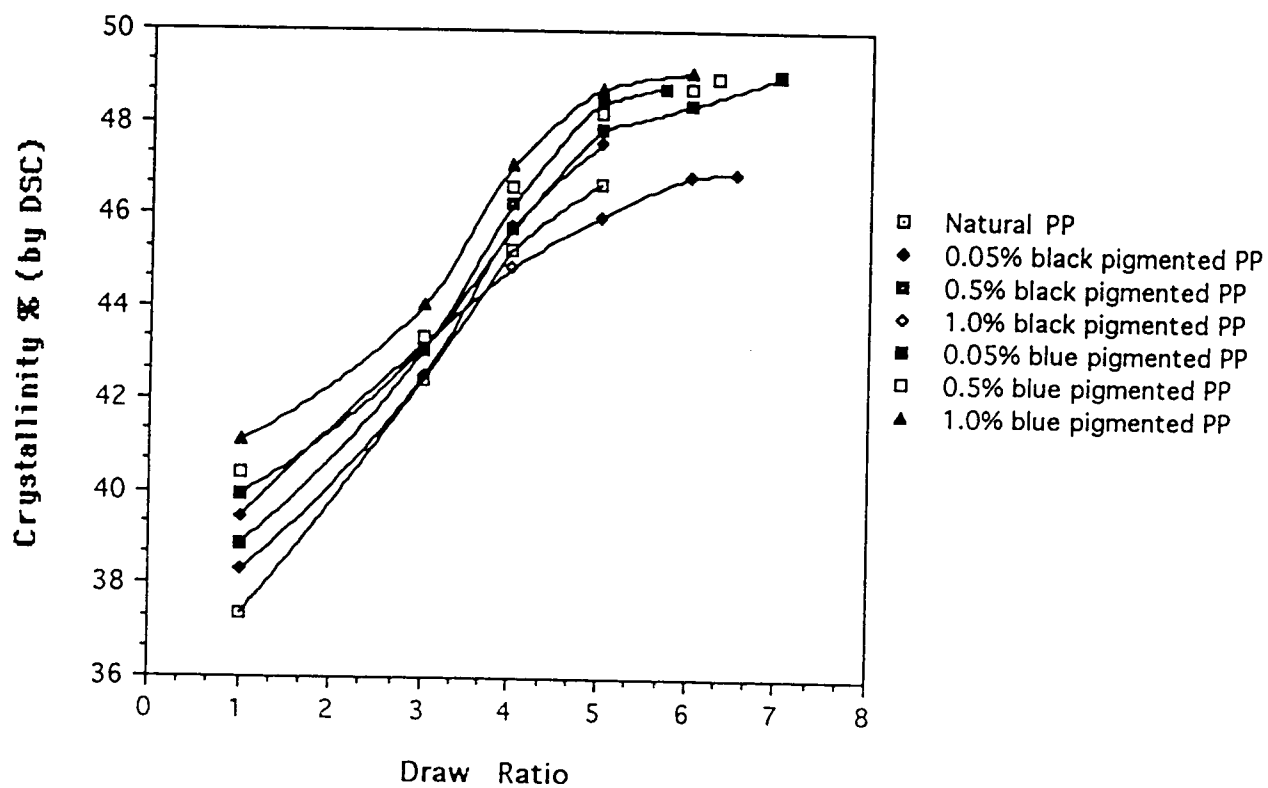


Figure 13 Effect of Draw Ratio on Crystallinity (by DSC) of Natural and Pigmented PP Filaments

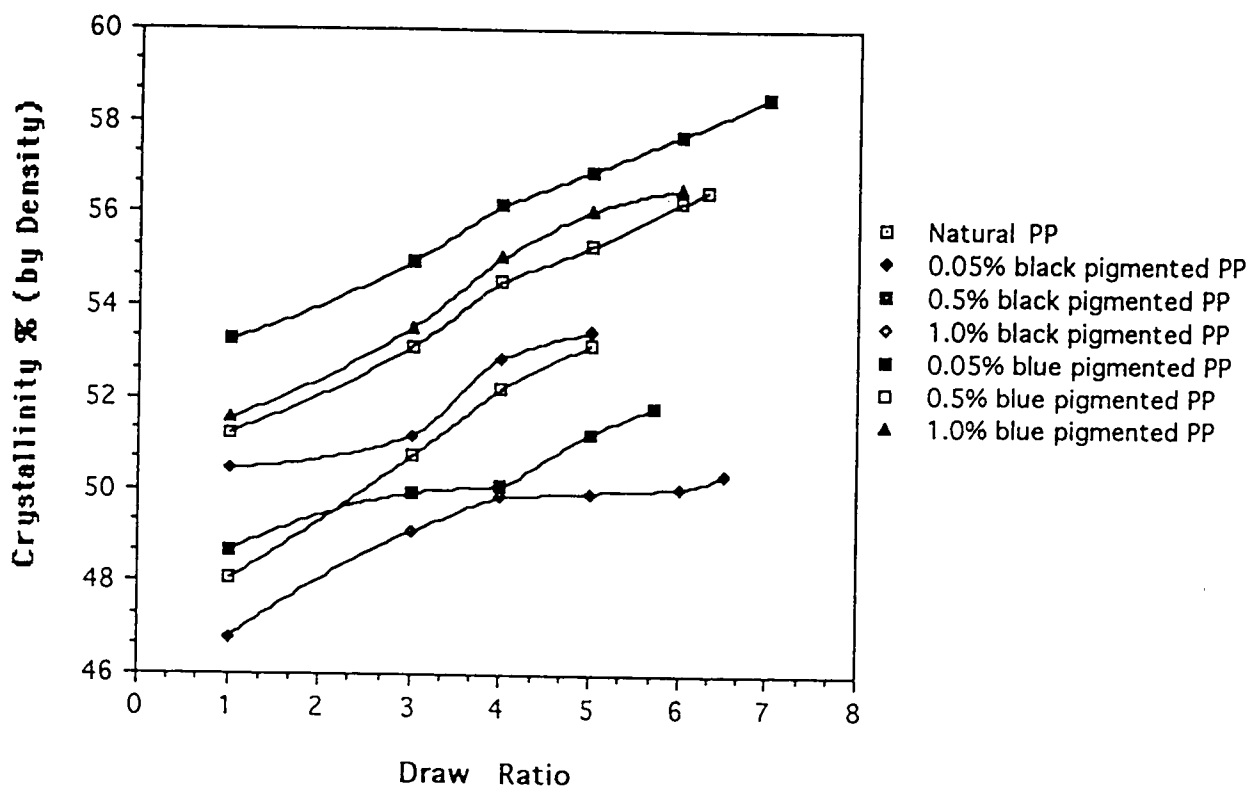


Figure 14 Effect of Draw Ratio on Crystallinity (by Density) of Natural and Pigmented PP Filaments

Draw Temperature

The DSC crystallinity and density crystallinity for selected natural and pigmented PP drawn filaments are also plotted as a function of draw temperature (see Figures 15 and 16). The degree of crystallinity measured by the DSC and density methods show an increase with draw temperature. The increase in DSC and density crystallinity with increasing draw temperature refers to a separation of crystalline and amorphous region as distinct phases. It is because higher draw temperature provides greater mobility for thermal crystallization and hence higher crystallization. This finding confirms the earlier studies of Bodaghi et al. [54] and Mukhopadhyay [81]. These authors reported that the increase in draw temperature would cause an increase in the chain mobility leading to higher crystallinity and crystal perfection. This is consistent with the x-ray data shown in Figure 11.

Draw Speed

Figures 17 and 18 illustrate the effects of draw speed on the DSC crystallinity and density crystallinity. Increasing draw speed may slightly decrease the crystallinities. However, our statistical analysis results, as shown in the Appendix imply that changing draw speed from 90 to 180 rpm has little or no effect on the crystallinities of the natural and pigmented PP filaments. The drop

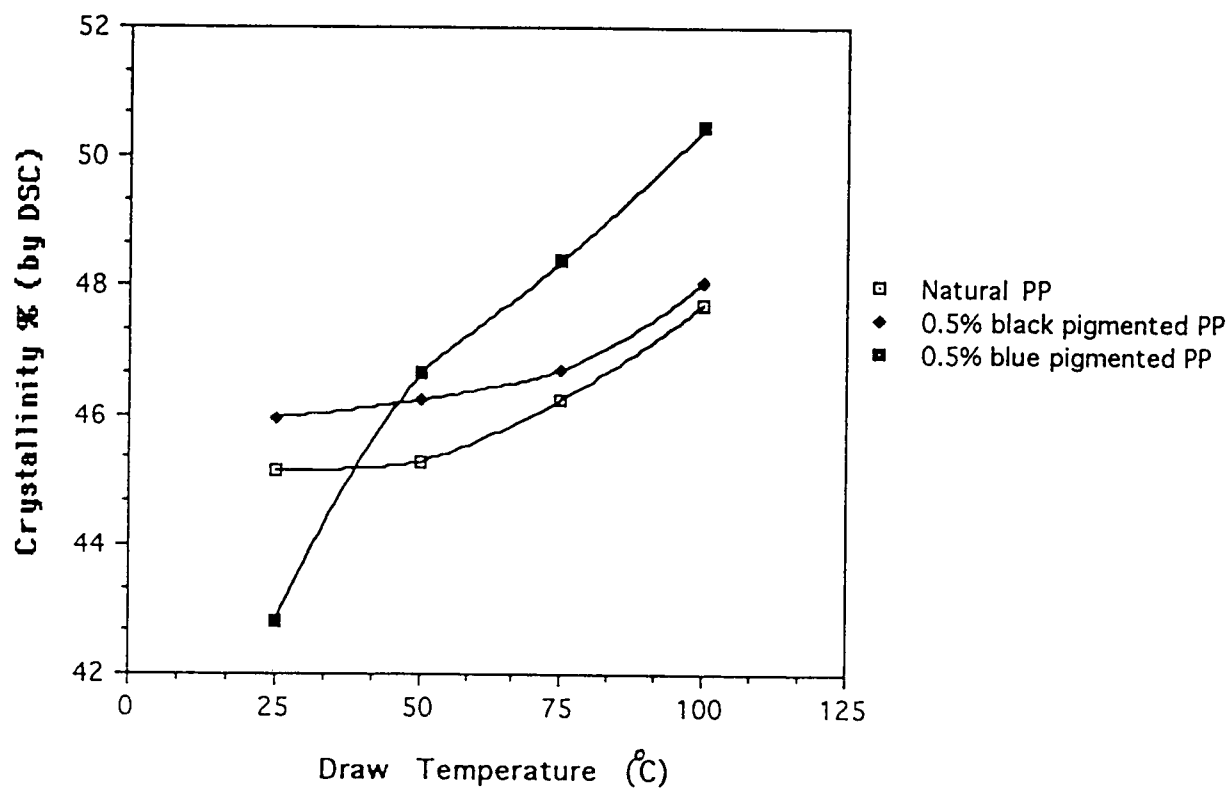


Figure 15 Effect of Draw Temperature on Crystallinity (by DSC) of Natural and Pigmented PP

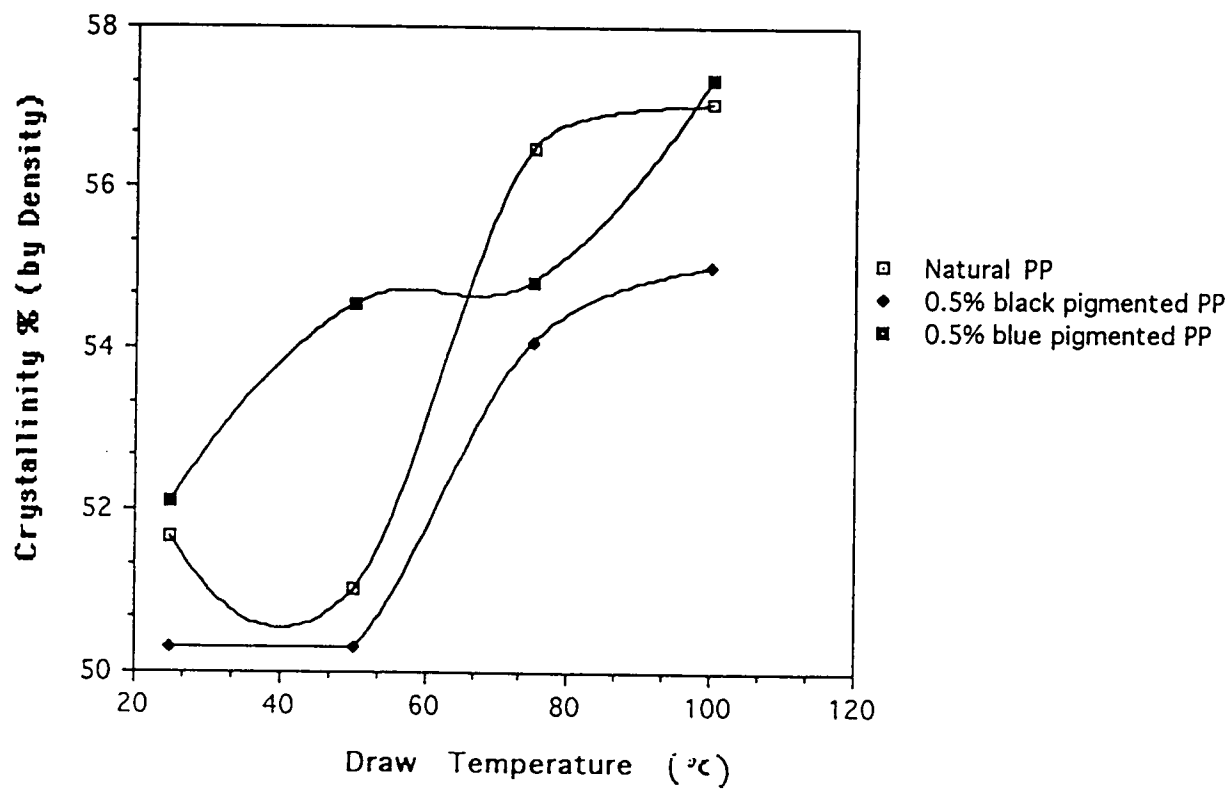


Figure 16 Effect of Draw Temperature on Crystallinity (by Density) of Natural and Pigmented PP

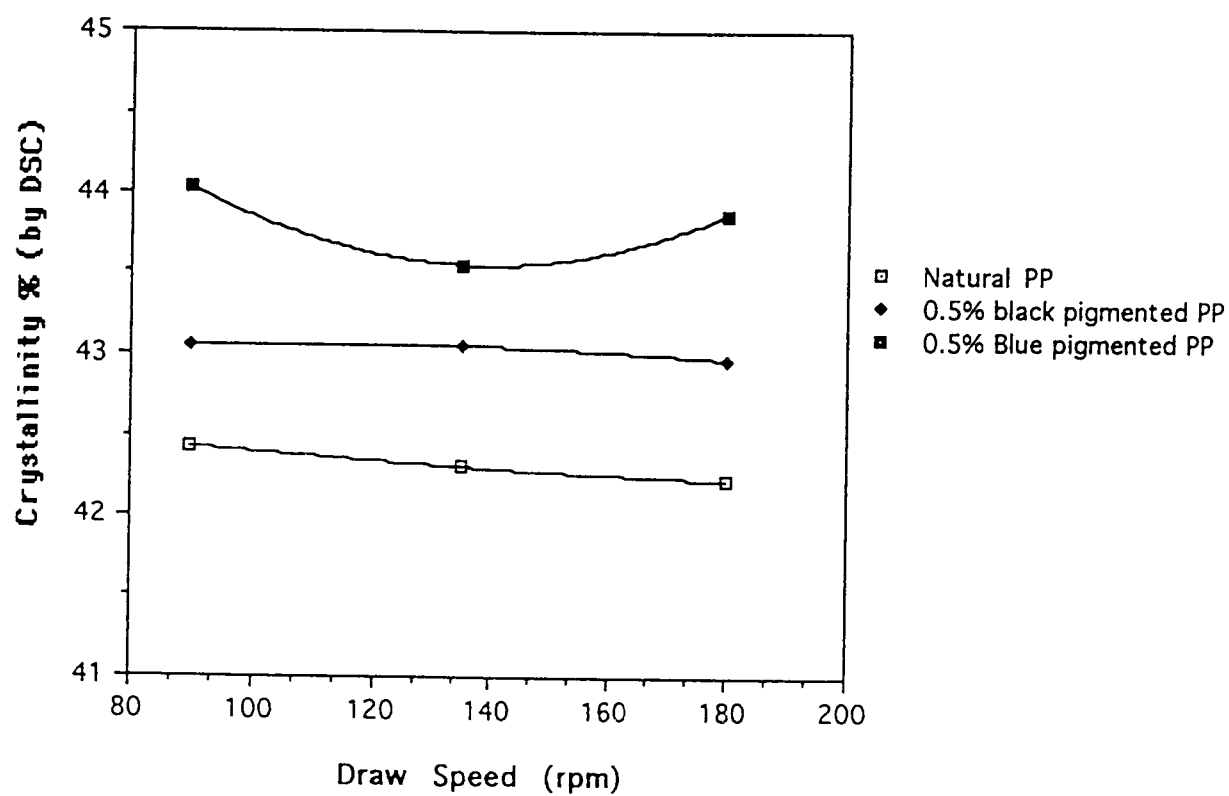


Figure 17 Effect of Draw Speed on Crystallinity (by DSC) of Natural and Pigmented PP

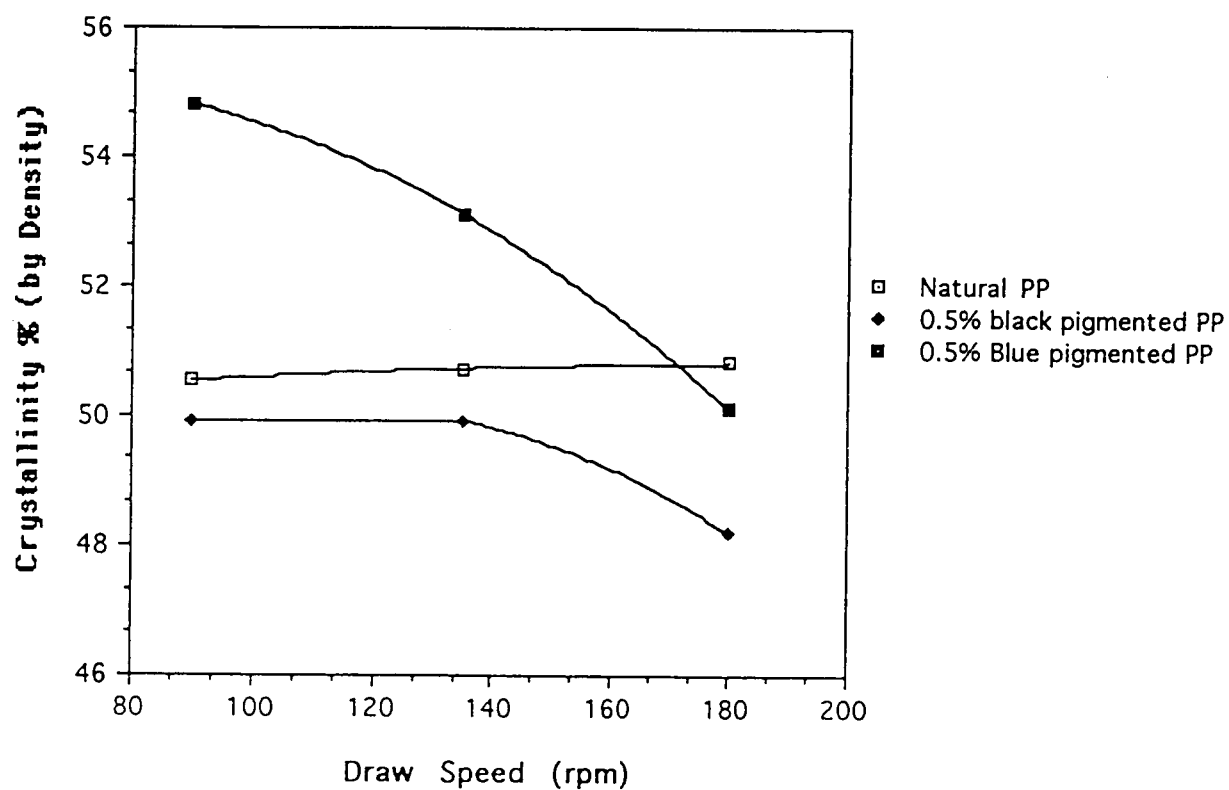


Figure 18 Effect of Draw Speed on Crystallinity (by Density) of Natural and Pigmented PP

off of density crystallinity observed in Figure 18 may be related to increased void formation in the filaments at higher draw speed.

4.2.4 Variation of Melting Temperature

The melting temperature measured by the DSC method is found to be a function of draw ratio. Figure 19 shows that the melting temperature increases with an increase of draw ratio. These trends are evidently due to a change of crystal size with draw ratio [95]. This interpretation is consistent with the line broadening observed in the x-ray patterns.

Another interesting finding is shown in Figure 20 that the melting temperature measured by DSC tends to decrease as the draw speed increases. This change is likely related to the change of crystal size as well.

4.3 Effect of Draw Conditions on the Mechanical Properties of Pigmented PP Filaments

Draw Ratio

The large differences in morphology which occur in the natural and pigmented PP filaments are also reflected by the mechanical

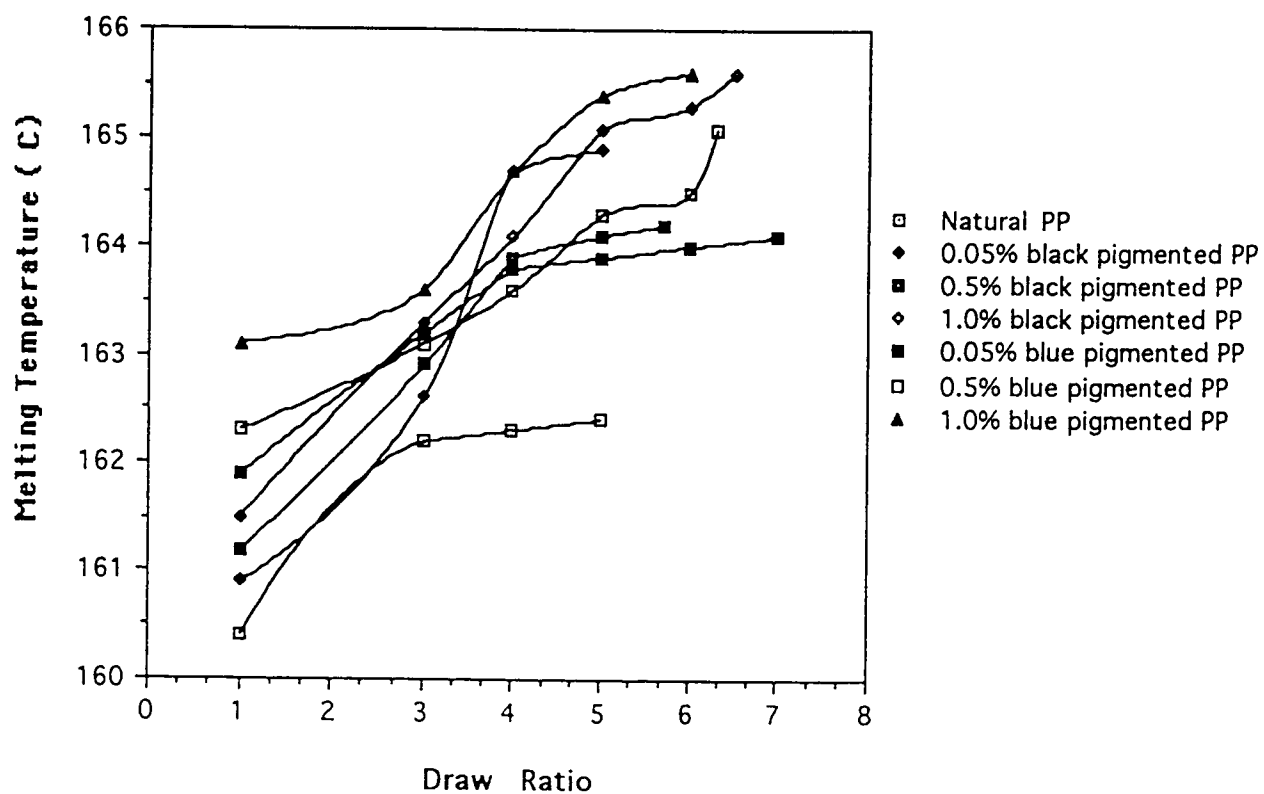


Figure 19 Effect of Draw Ratio on Melting Temperature (by DSC) of Natural and Pigmented PP

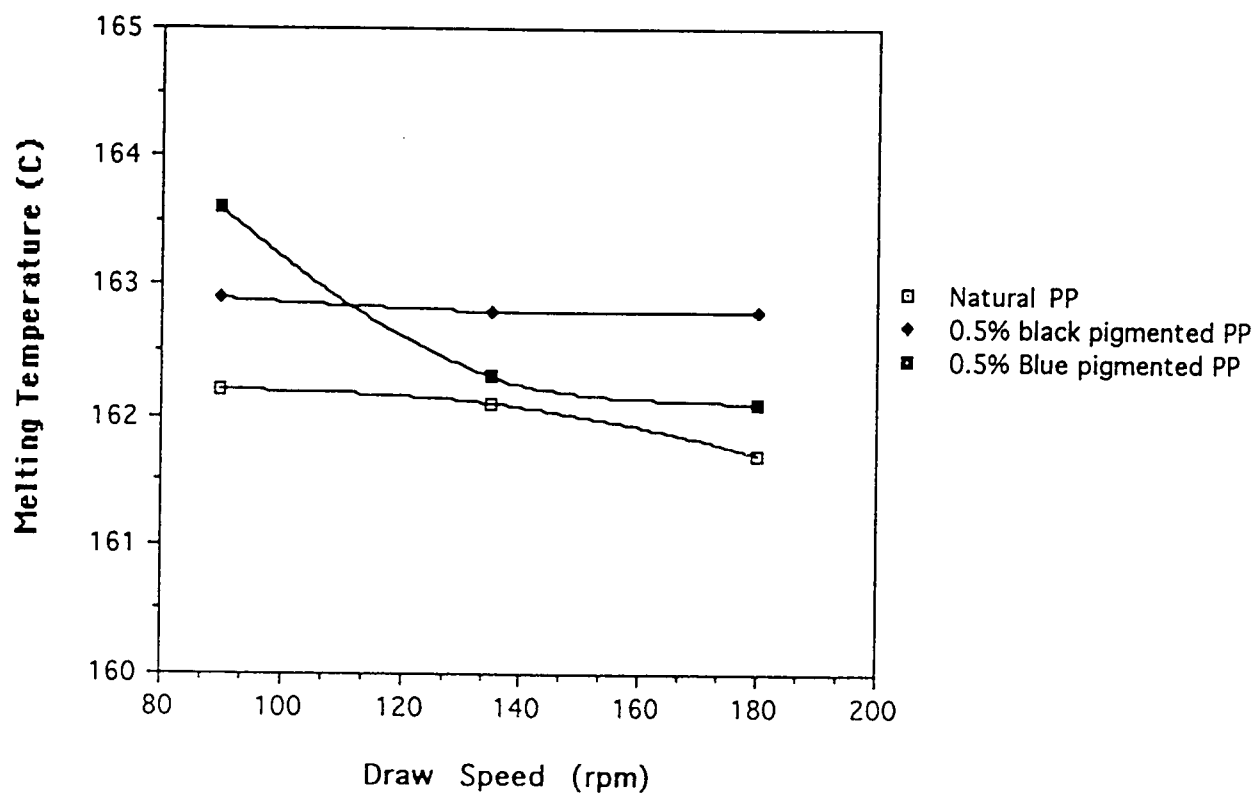


Figure 20 Effect of Draw Speed on Melting Temperature (by DSC) of Natural and Pigmented PP

properties. Typical engineering stress vs. the engineering strain curves of the black and blue pigmented PP filaments at different draw ratio are plotted in Figures 21 and 22, respectively. It is seen that increasing draw ratio results in an increase in yield strength and tenacity and a reduction in elongation at break. It also leads to a decrease or elimination of the natural draw ratio. The "yield point" seems to disappear at high draw ratio. Figures 23, 24, 25 and 26 show the tenacity, yield strength, modulus and elongation at break of both natural and pigmented PP drawn filaments plotted versus draw ratio. The samples include seven groups of natural and pigmented samples with varied pigment concentrations. It is apparent from these figures that tenacity, yield strength and modulus increase with increasing draw ratio, while the elongation to break decreases. Further observation shows that modulus for each filament increases slowly at first, then more rapidly, and finally somewhat slower with increasing draw ratio. This trend is similar to other reports [5, 94, 95] and is also consistent with the studies of Bodaghi et al. [54], Nedella et al [64] and Kitao et al [68] in our laboratories. Bodaghi et al [54] noted this remarkable behavior is likely due to the fact that the average molecular orientation in the sample is a major factor which controls such properties in the range of samples and variables studied.

From the above figures the influence of pigment type and pigment concentration are demonstrated to be quite systematic. At

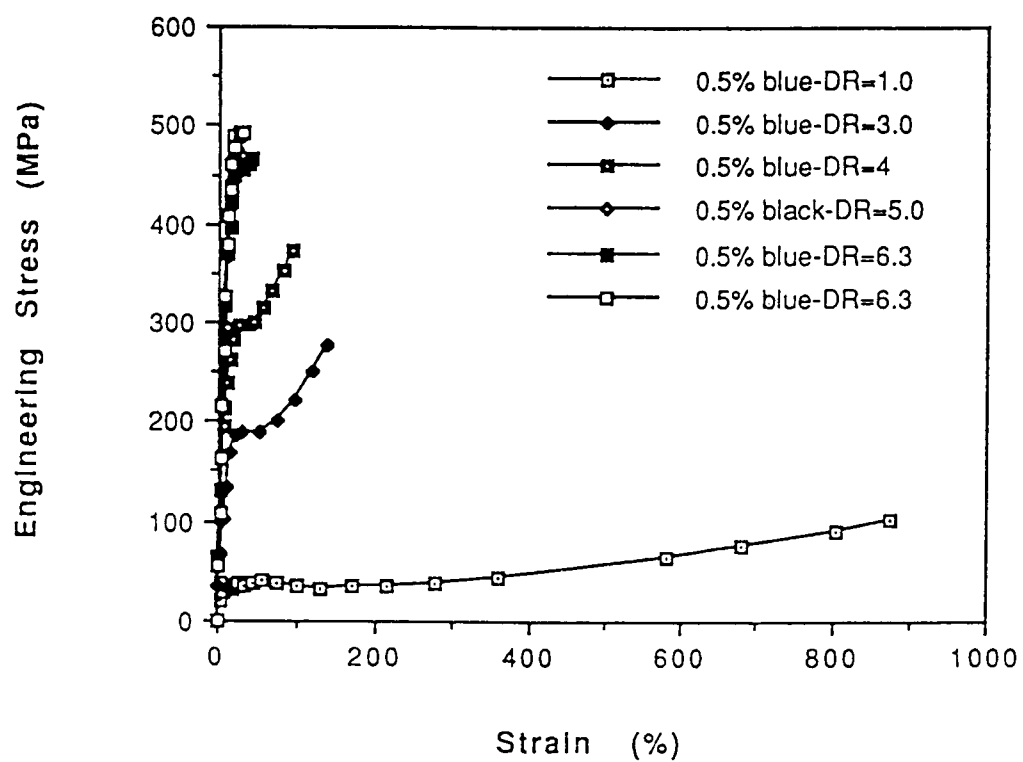


Figure 21 Typical Strain-Stress Curves of As-Spun and Drawn Blue Pigmented PP

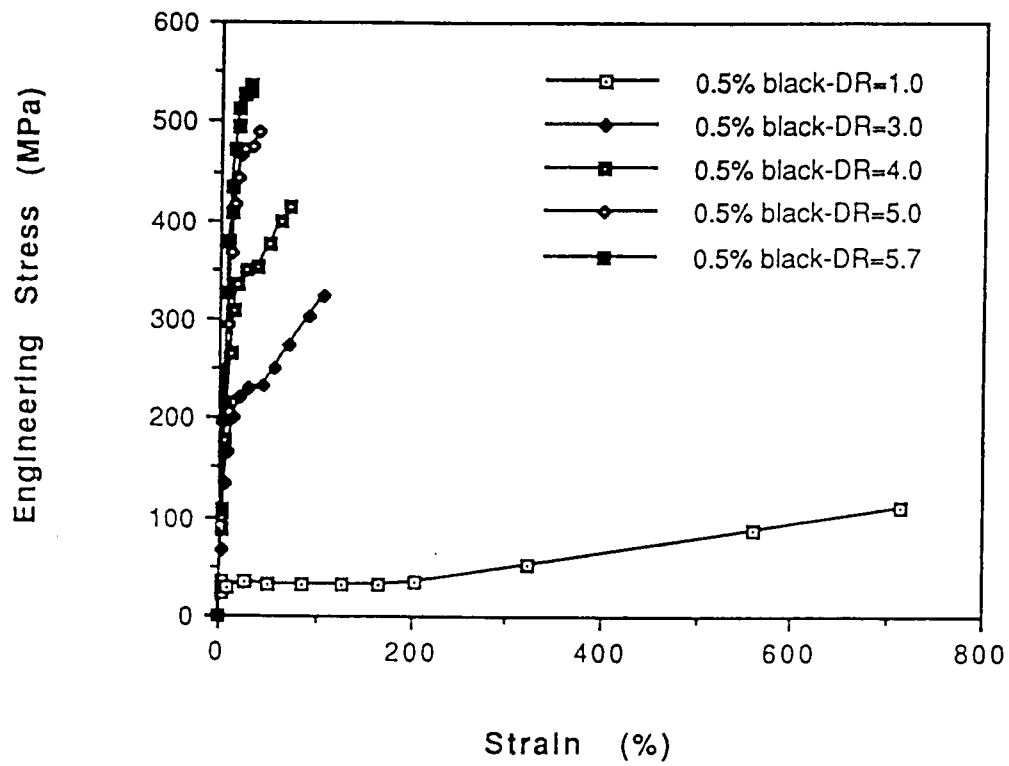


Figure 22 Typical Strain-Stress Curves of As-Spun and Drawn Black Pigmented PP

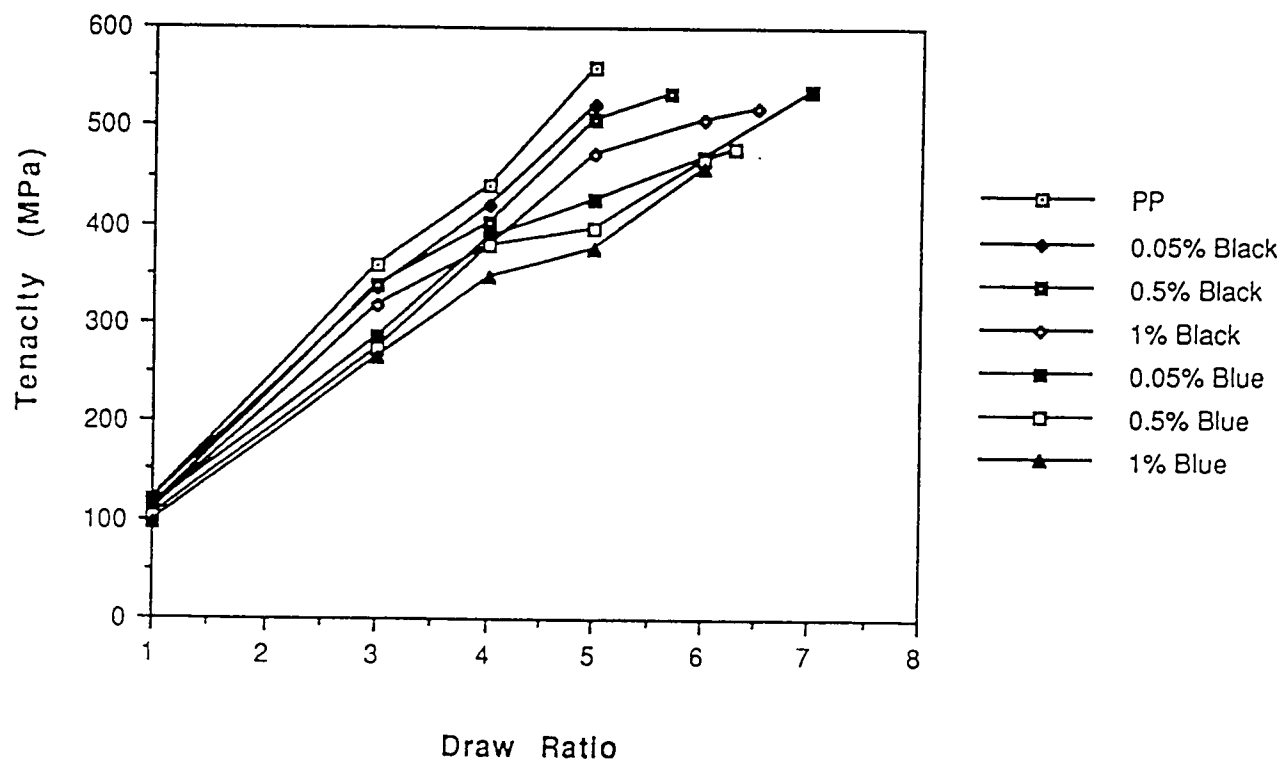


Figure 23 Effect of Draw Ratio on Tenacity of Natural and Pigmented PP

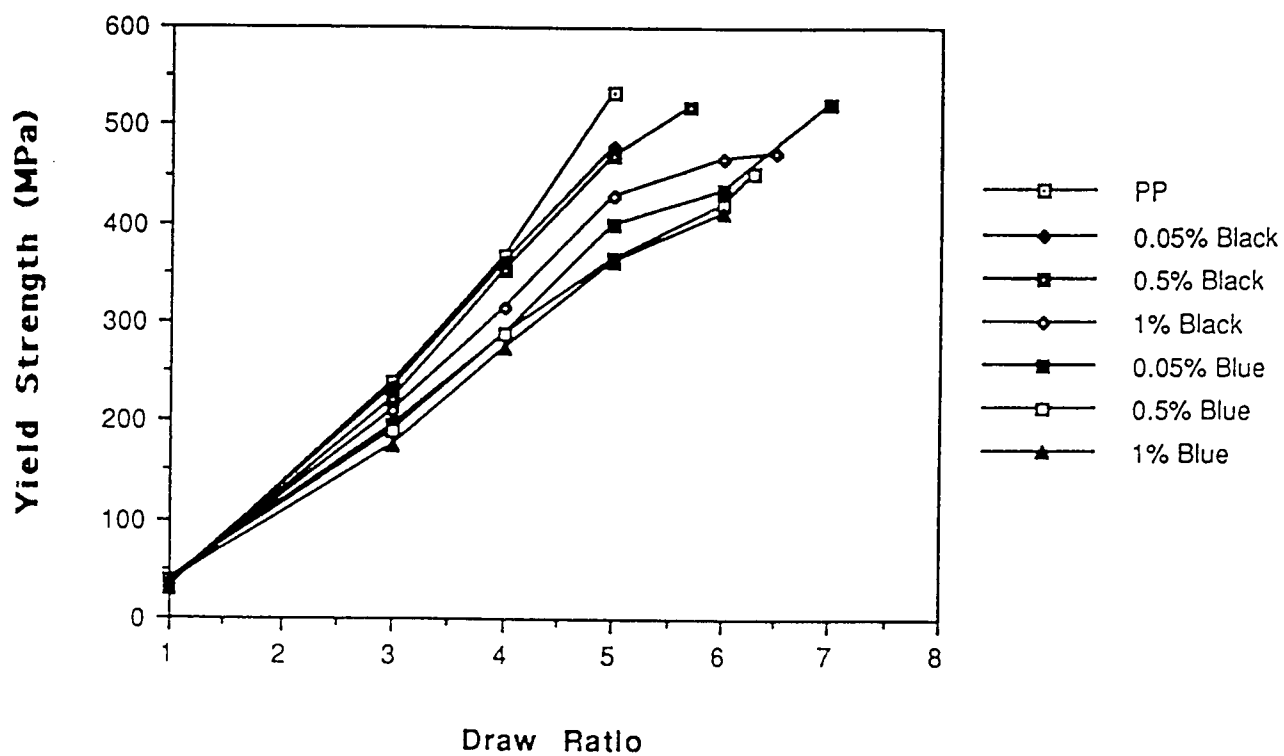


Figure 24 Effect of Draw Ratio on Yield Strength of Natural and Pigmented PP

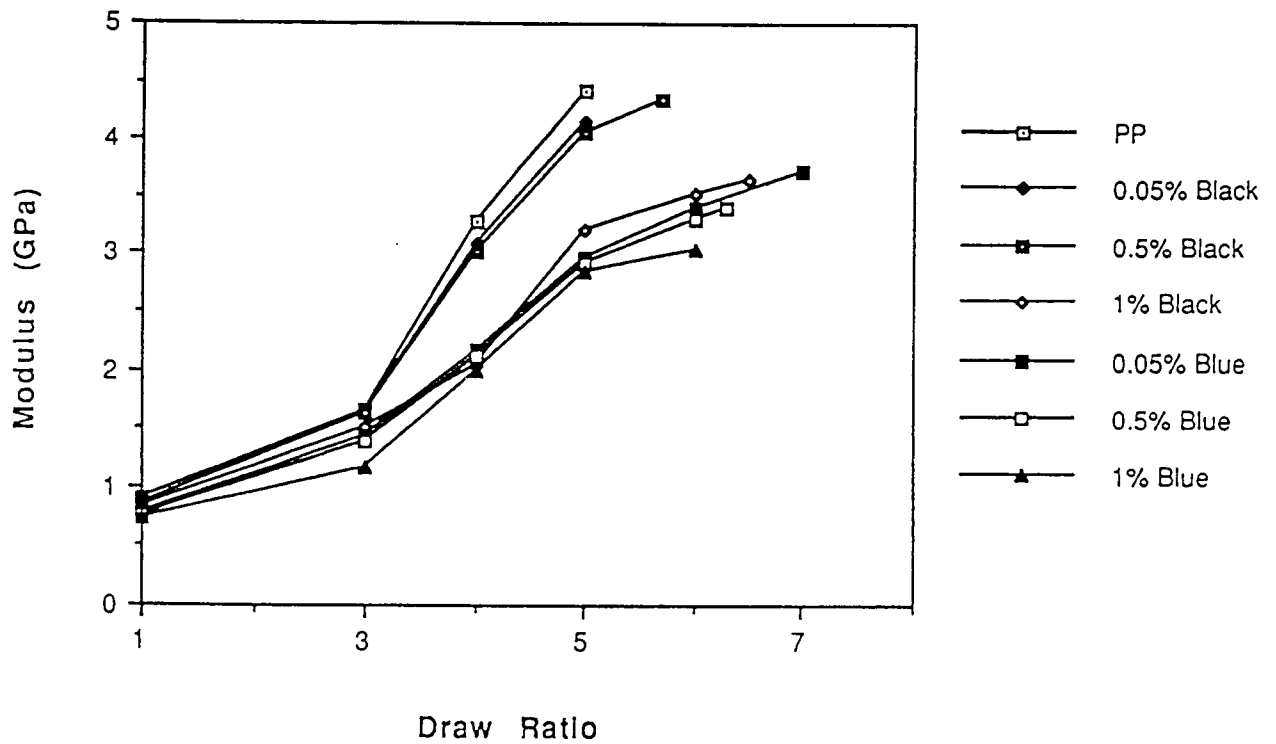


Figure 25 Effect of Draw Ratio on Modulus of Natural and Pigmented PP

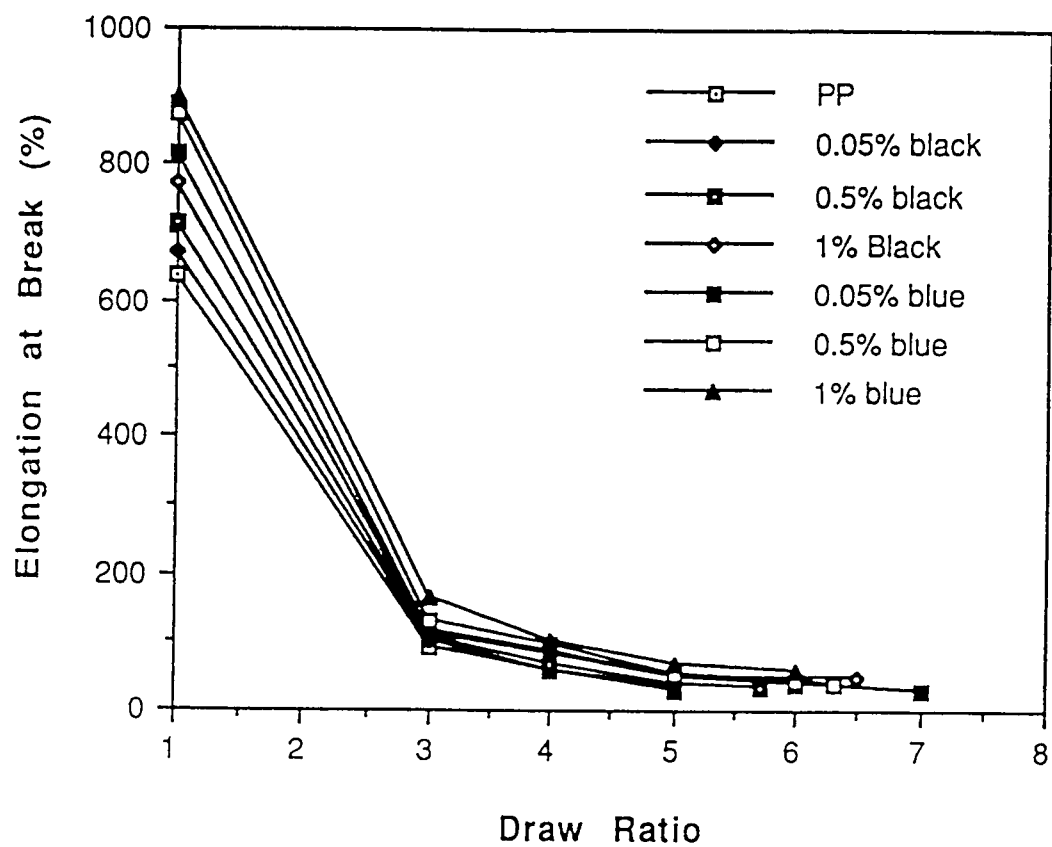


Figure 26 Effect of Draw Ratio on Elongation at Break of Natural and Pigmented PP

any draw ratio, the pure PP filaments without pigmentation always have the highest tenacity, yield strength, modulus and the lowest elongation at break. The blue pigmented filaments have the lowest tenacity and the largest elongation and the black pigmented filaments are in the median position.

Draw Temperature

The relationships between draw temperature and tensile properties of the natural and pigmented PP drawn filaments are shown in Figures 27-30. It can be seen that at an equivalent draw ratio of 4.0 and an equivalent draw speed of 180 rpm increasing the draw temperature from 25 °C to 100 °C results in slightly increased elongation at break for both the natural and pigmented PP filaments. The tenacity, yield strength and modulus for each type filaments increased slightly at first, than gradually decreased with continually increasing draw temperature. It is further seen that at any draw temperature the natural PP filaments without pigmentation always have the highest tenacity, yield strength, and modulus and the lowest elongation at break. Again the blue pigmented filaments have lowest tenacity and largest elongation and the black pigmented filaments are in the median position.

Draw Speed

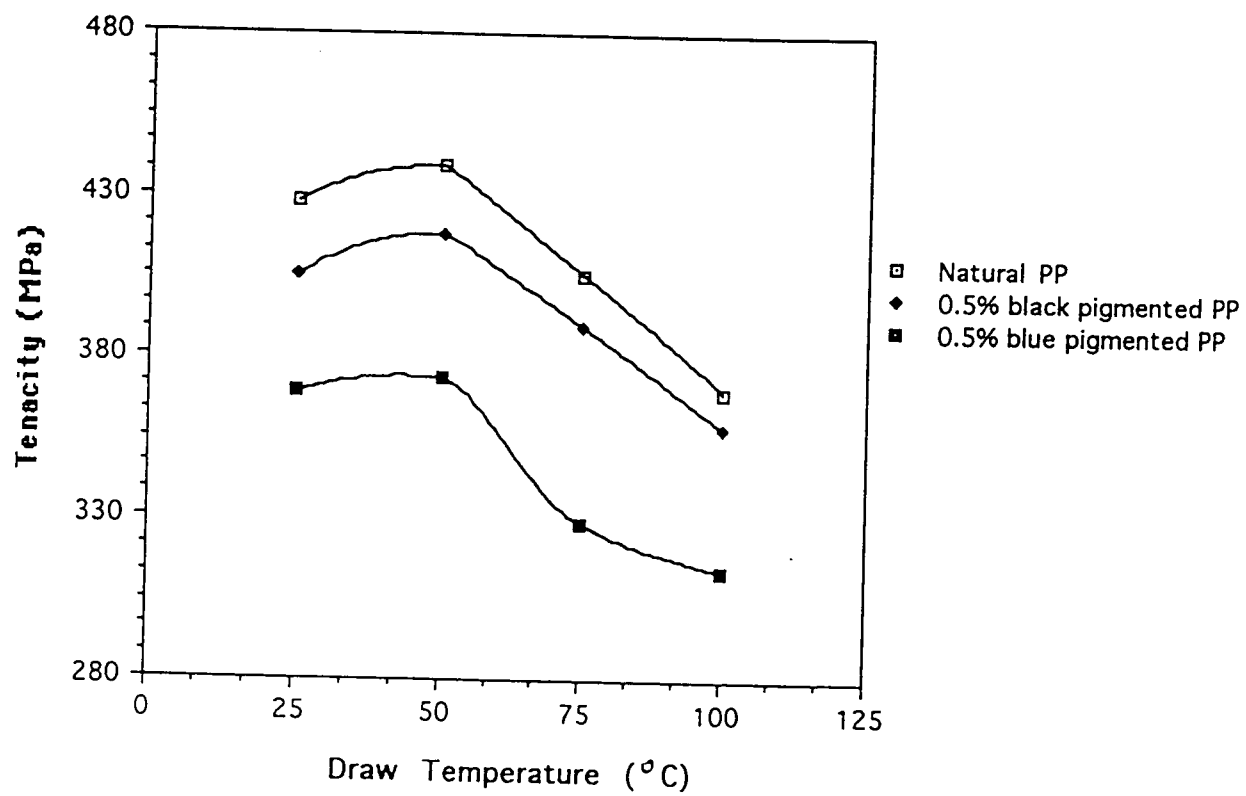


Figure 27 Effect of Draw Temperature on Tenacity of Natural and Pigmented PP

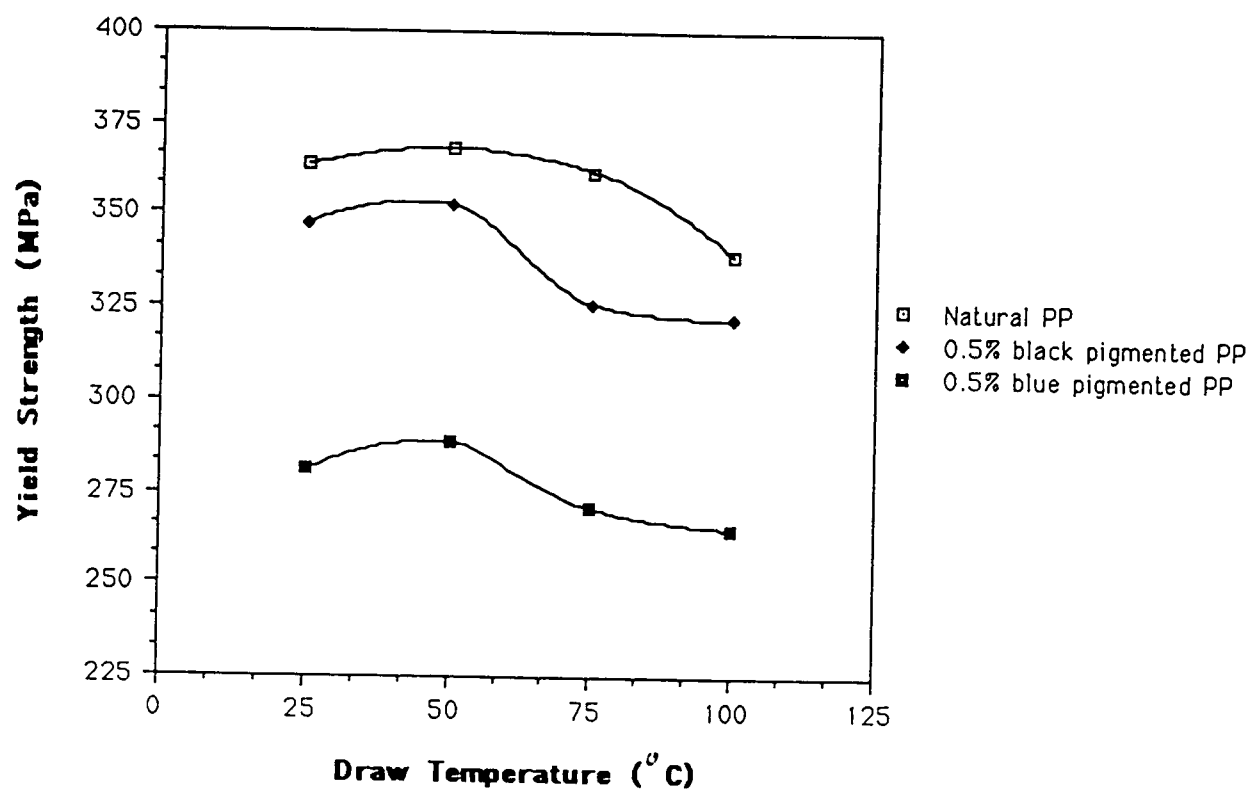


Figure 28 Effect of Draw Temperature on Yield Strength of Natural and Pigmented PP

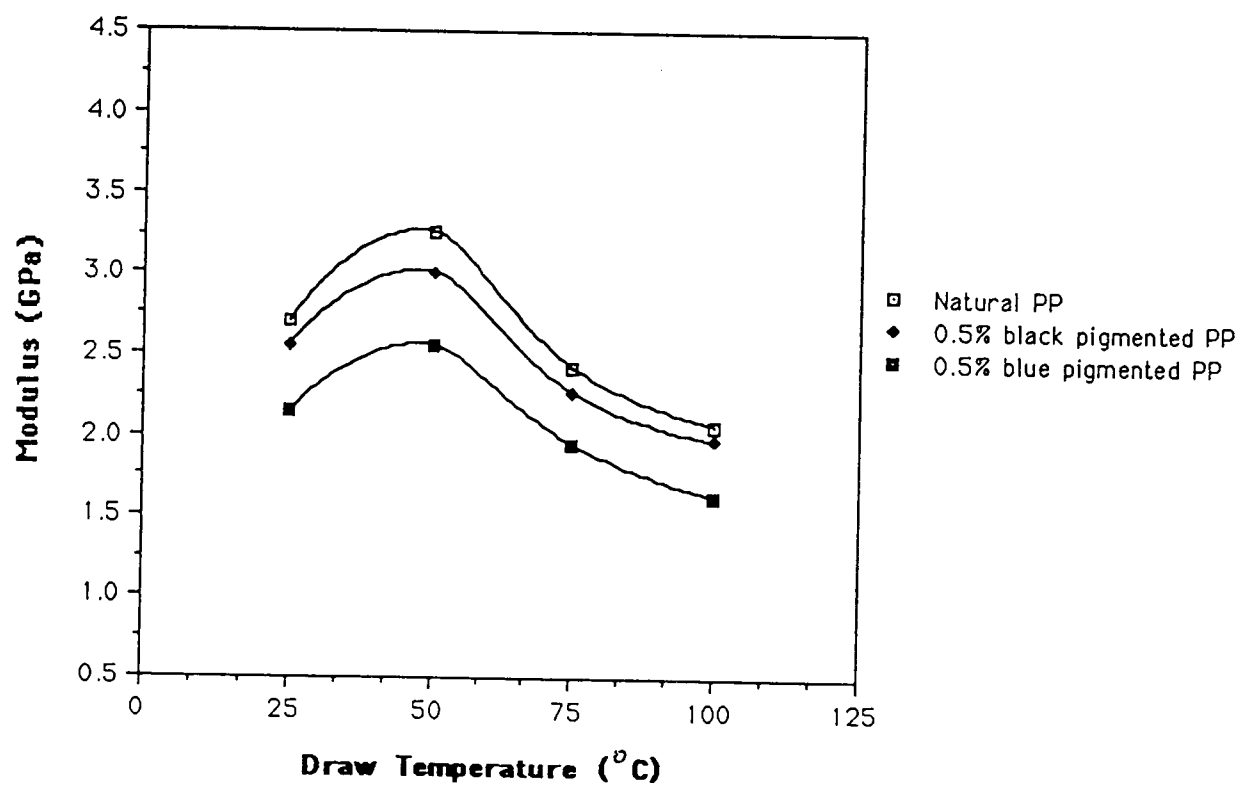


Figure 29 Effect of Draw Temperature on Modulus of Natural and Pigmented PP

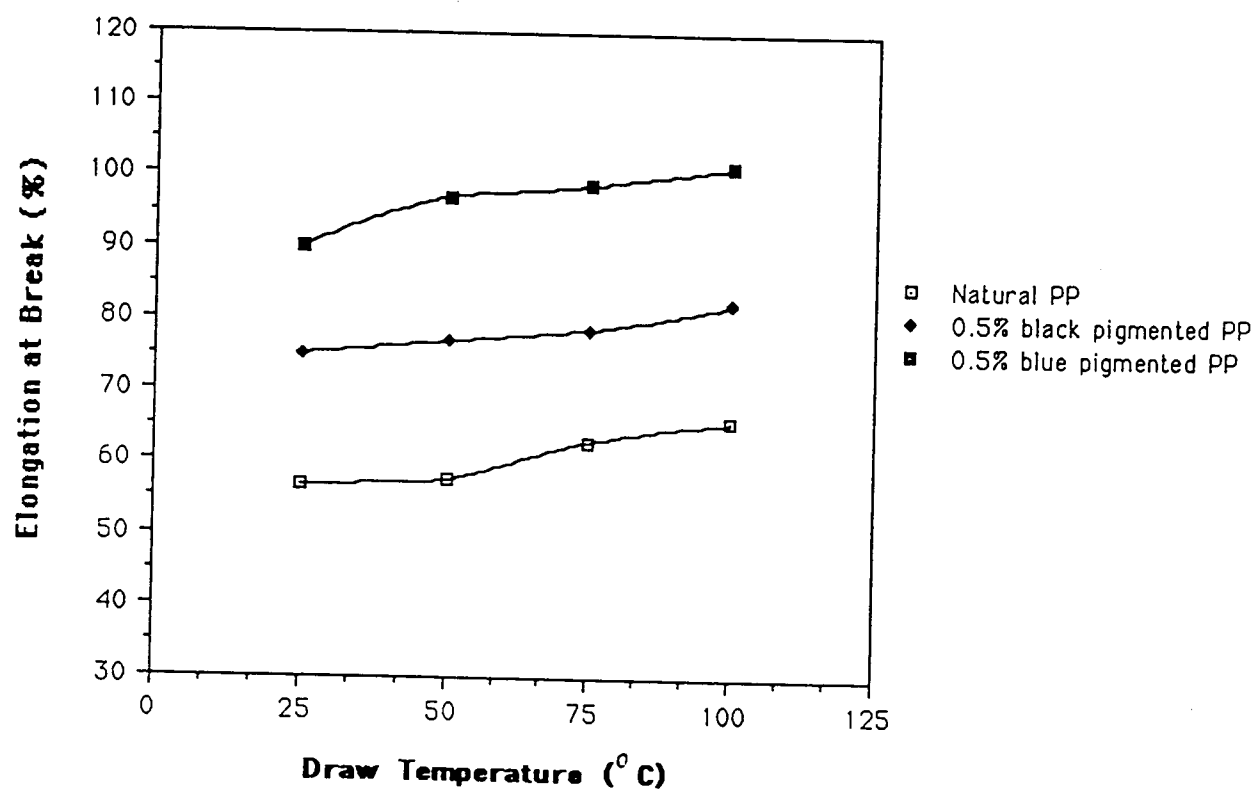


Figure 30 Effect of Draw Temperature on Elongation at Break of Natural and Pigmented PP

Figures 31-34 show plots of tensile properties of the filaments plotted versus draw speed for the natural and pigmented PP filaments. The experimental results show clearly that at an equivalent draw ratio of 3.0 and an equivalent draw temperature of 50 °C, the increase in draw speed from 90 rpm to 180 rpm produces a slight increase in elongation at break and small but significant decreases in tenacity, yield strength and modulus for both the natural and pigmented PP filaments. It is likely that the higher draw speed results in lower heat dissipation from the filament and higher internal temperature which results in more relaxation, especially in the amorphous regions with the result that the elongation increases and tenacity, modulus and yield strength decrease.

4.4 Further Discussion of the Effect of Pigments and Concentration on the Structural and Mechanical Properties of Pigmented PP Filaments

The results summarized in Table 8 clearly show that the pigment type and pigment concentration have strong influence on the structural and mechanical properties of PP drawn filaments. For example, the presence of the pigment additions and the variation of the concentrations greatly change the drawability of the pigmented PP filaments. As shown in Figure 35, it is seen that the estimated maximum draw ratio of the pigmented filaments are significantly

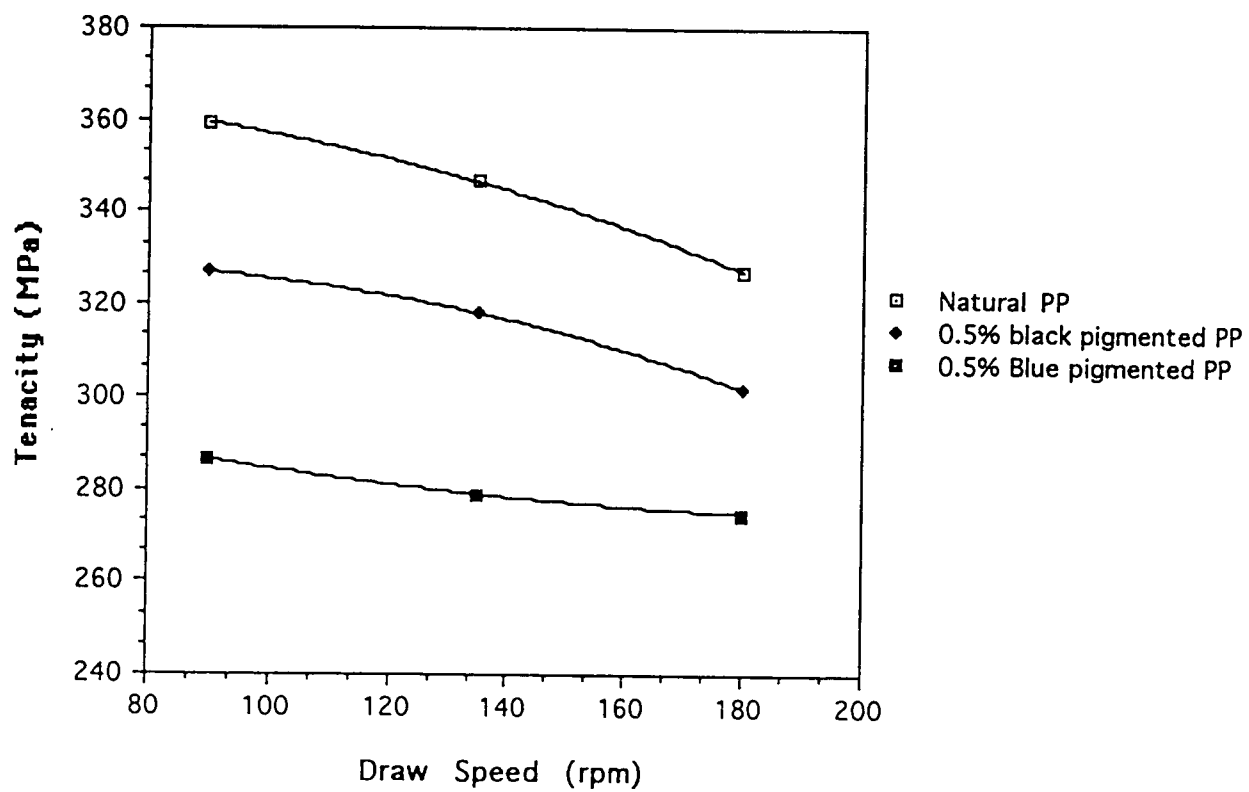


Figure 31 Effect of Draw Speed on Tenacity of Natural and Pigmented PP

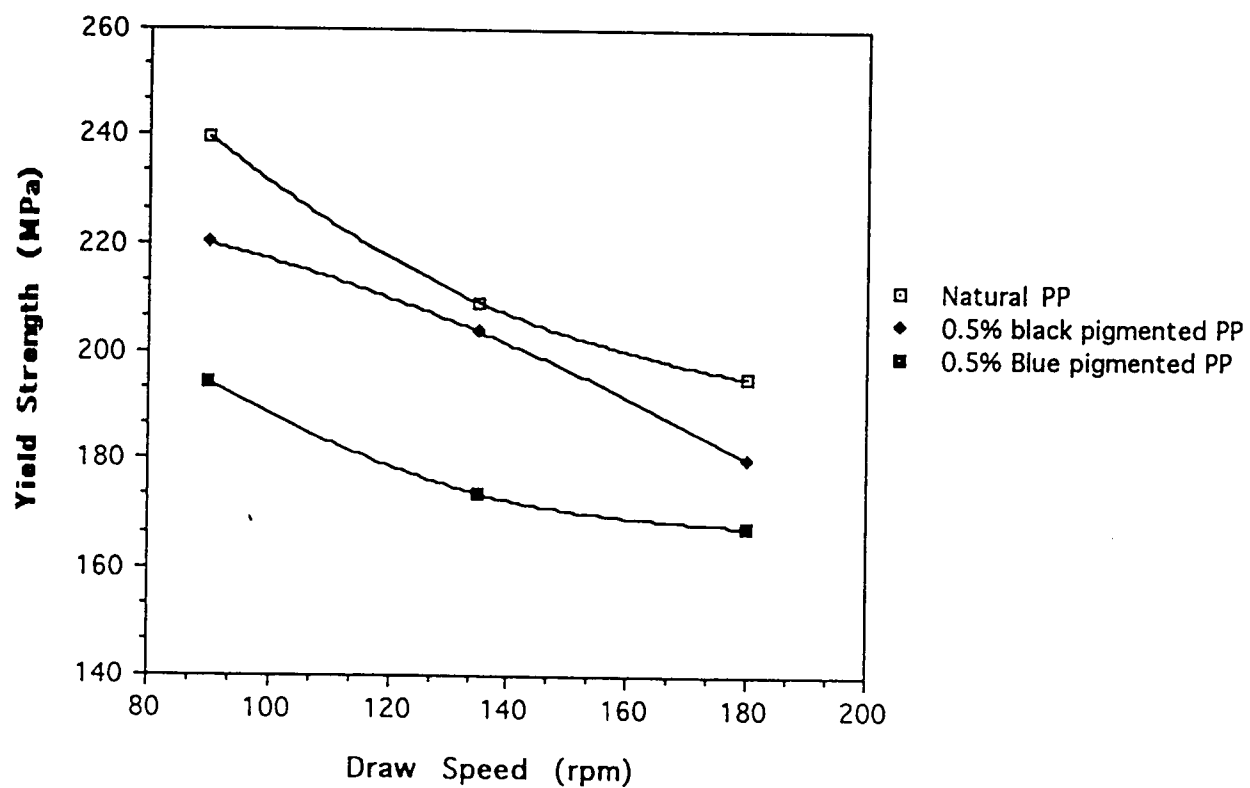


Figure 32 Effect of Draw Speed on Yield Strength of Natural and Pigmented PP

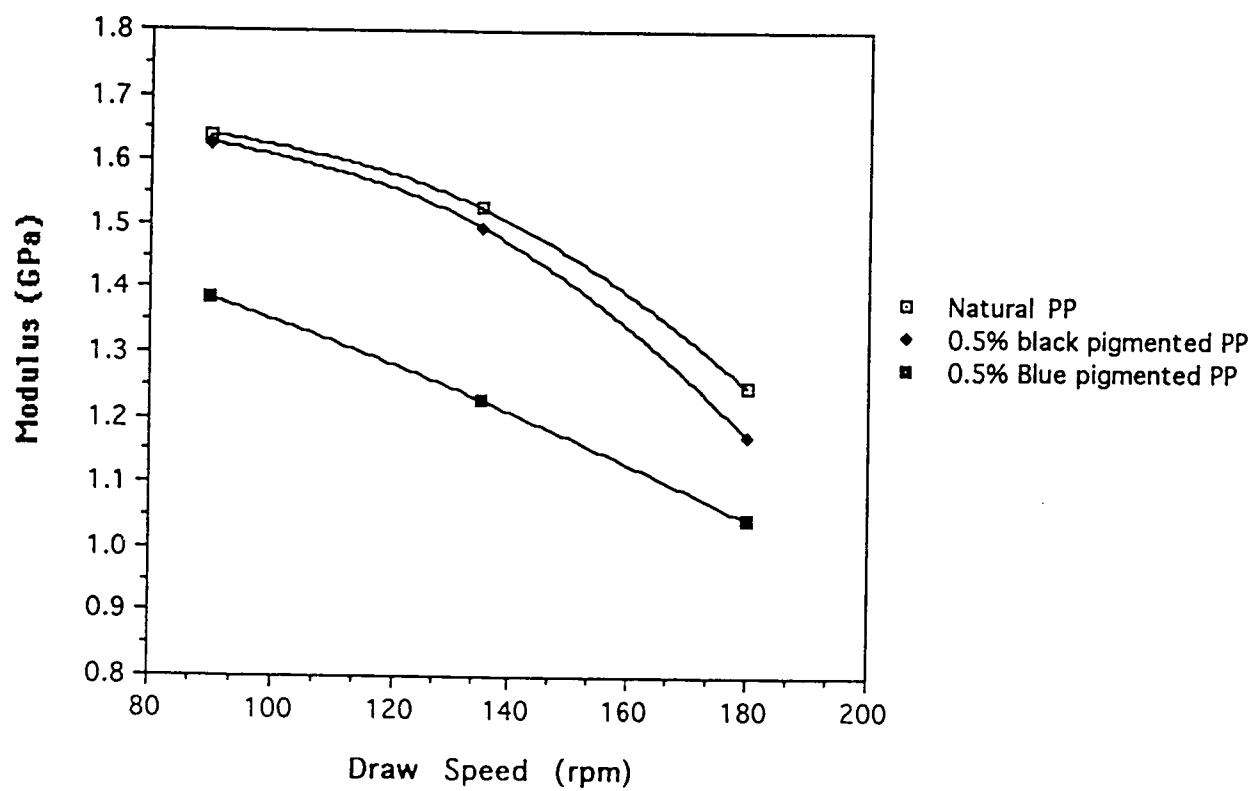


Figure 33 Effect of Draw Speed on Modulus of Natural and Pigmented PP

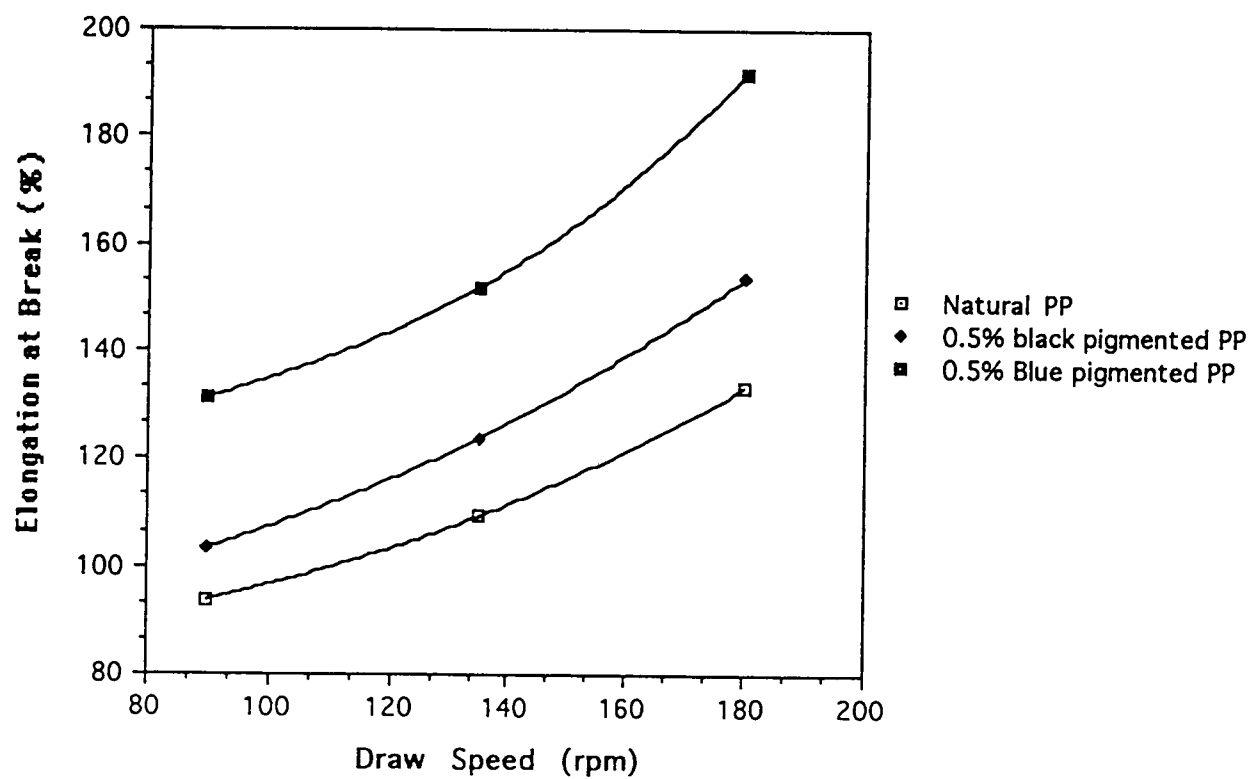


Figure 34 Effect of Draw Speed on Elongation at Break of Natural and Pigmented PP

Table 8 Effect of Pigments Concentration on the Structural and Mechanical Properties of Natural and Pigmented PP Filaments

Samples	Concen-		Deduced				Yield			
	-tration	Xc (%)	Tm (°C)	Density	Xc (%)	Birefringence	Elongation	Tenacity	Strength	Modulus
	(%)	(DSC)	(DSC)	(gm/cm^3)	(density)	(x10^3)	(%)	(MPa)	(MPa)	(GPa)
Black Pigmented PP Drawn Filament	0.05	45.78	164.7	0.8938	52.89	24.26	60.1	418.3	366.9	3.090
Black Pigmented PP Drawn Filament	0.50	46.24	163.9	0.8936	50.10	23.24	76.8	402.4	352.8	3.014
Black Pigmented PP Drawn Filament	1.00	44.87	164.1	0.8957	49.84	22.52	81.5	378.5	315.6	2.040
Blue Pigmented PP Drawn Filament	0.05	45.71	163.8	0.8964	56.19	23.57	88.0	386.1	289.0	2.163
Blue Pigmented PP Drawn Filament	0.50	46.64	163.6	0.8971	54.54	22.77	96.9	379.2	286.7	2.122
Blue Pigmented PP Drawn Filament	1.00	47.08	164.7	0.8998	55.05	21.65	103.8	346.5	288.7	1.990

Note: Draw Ratio = 4.0; Draw Temperature = 50°C; Draw Speed = 180 rpm; Tm = Melting Temperature measured by the DSC method

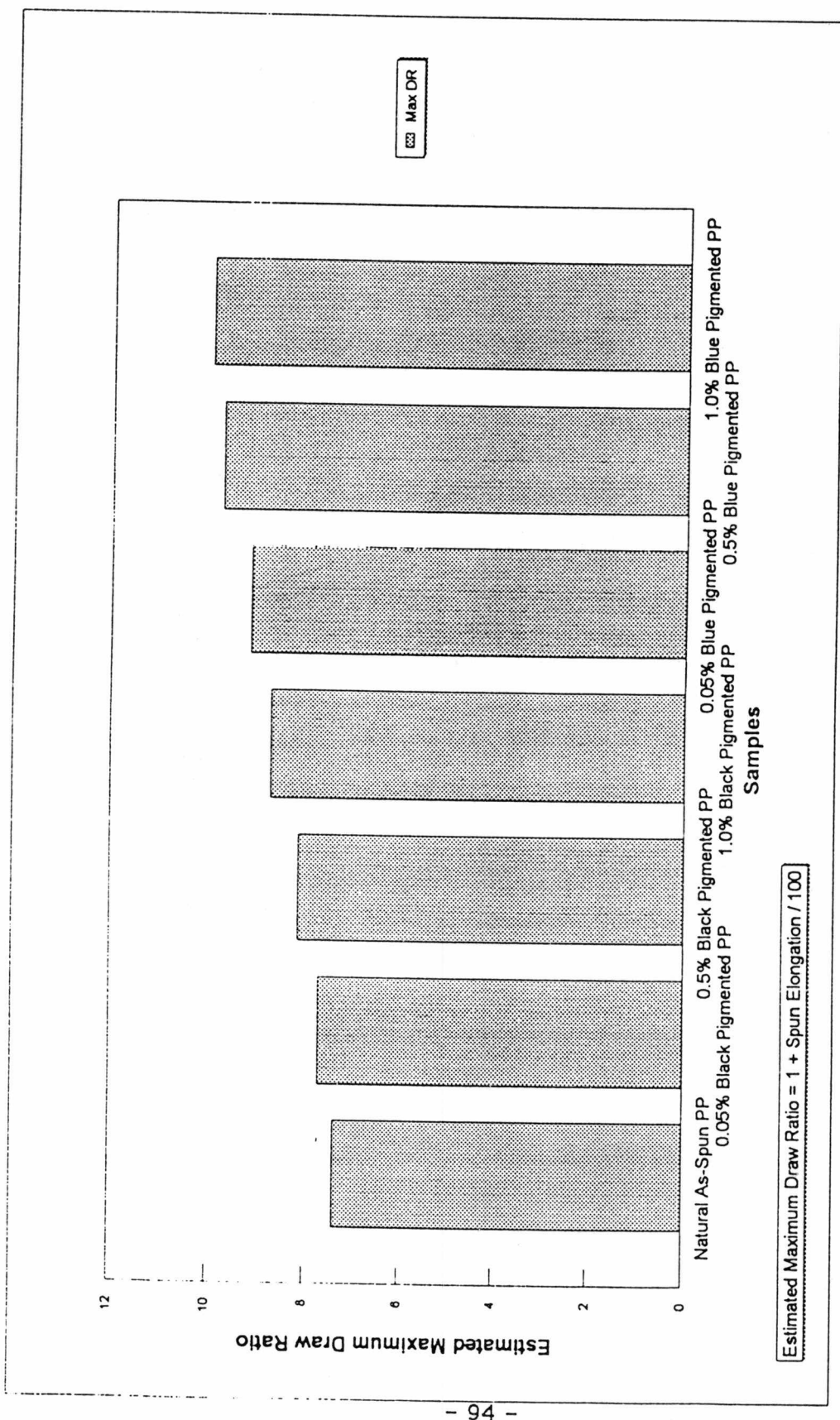


Figure 35 Effect of Pigments and Concentration on the
(Estimated) Maximum Draw Ratio of PP Filaments

higher than that of the natural PP filaments. It may be concluded that the higher the pigment concentration, the higher the as-spun elongation, or the higher the maximum draw ratio. In particular, the presence of 1% of blue pigment in the melt PP causes the highest (estimated) maximum draw ratio in comparison to the other pigments used for PP fiber dying.

4.5 Relationships between the Structural and Mechanical Properties of Pigmented PP Drawn Filament

As noted in the previous section, the mechanical properties of the natural and pigmented PP drawn filaments are controlled largely by orientation, crystallinity and morphological structure produced during drawing. The changes in morphology are frequently accompanied by significant mechanical property changes.

Figures 36, 37, 38 and 39 show the tenacity, yield strength, modulus and elongation at break of both natural and pigmented (black and blue) PP drawn filaments plotted versus birefringence. The results on the drawn fibers include samples which were subjected to different draw ratio, draw temperature and draw speed as well as varied pigment concentrations. It is apparent from these figures that tenacity, yield strength and modulus all increase with increasing birefringence. Elongation at break exhibits the reverse trend. In Figure 39, a large decrease in the elongation is observed as

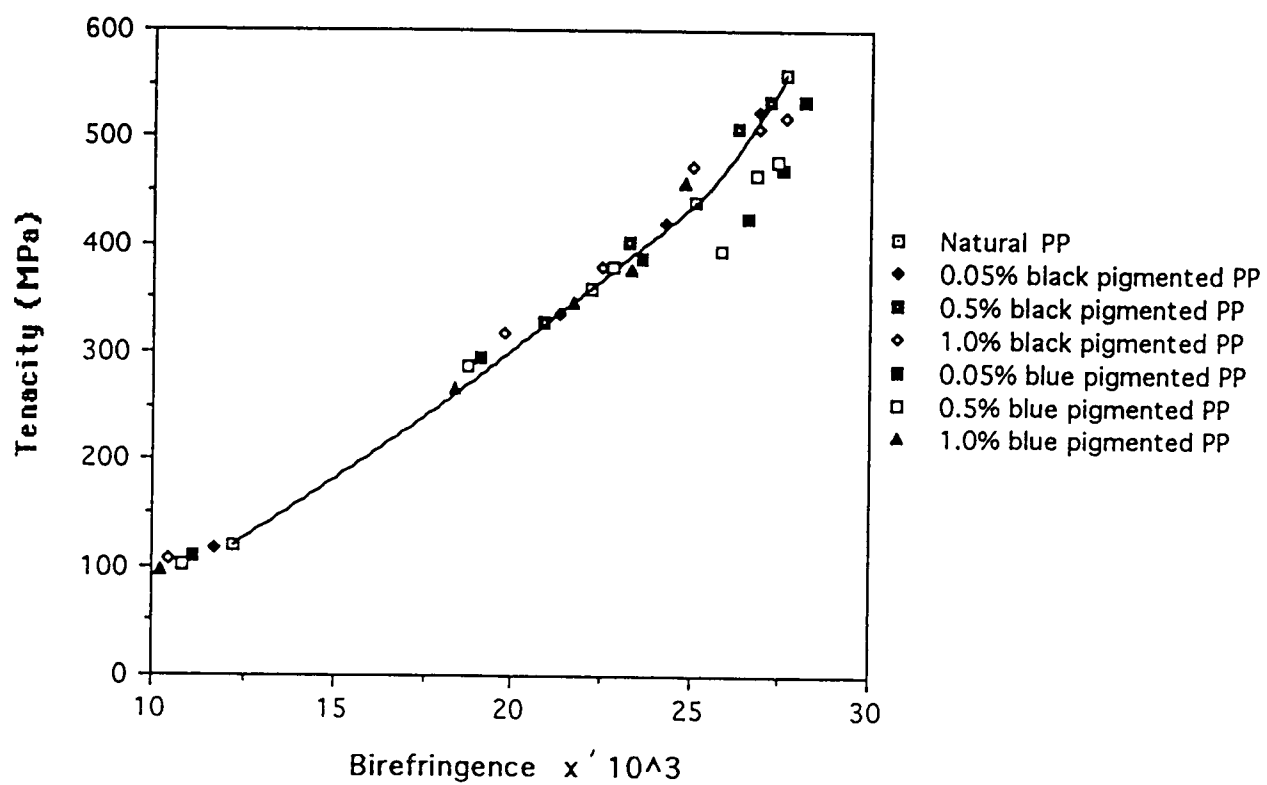


Figure 36 Tenacity as a Function of Birefringence for Natural and Pigmented PP

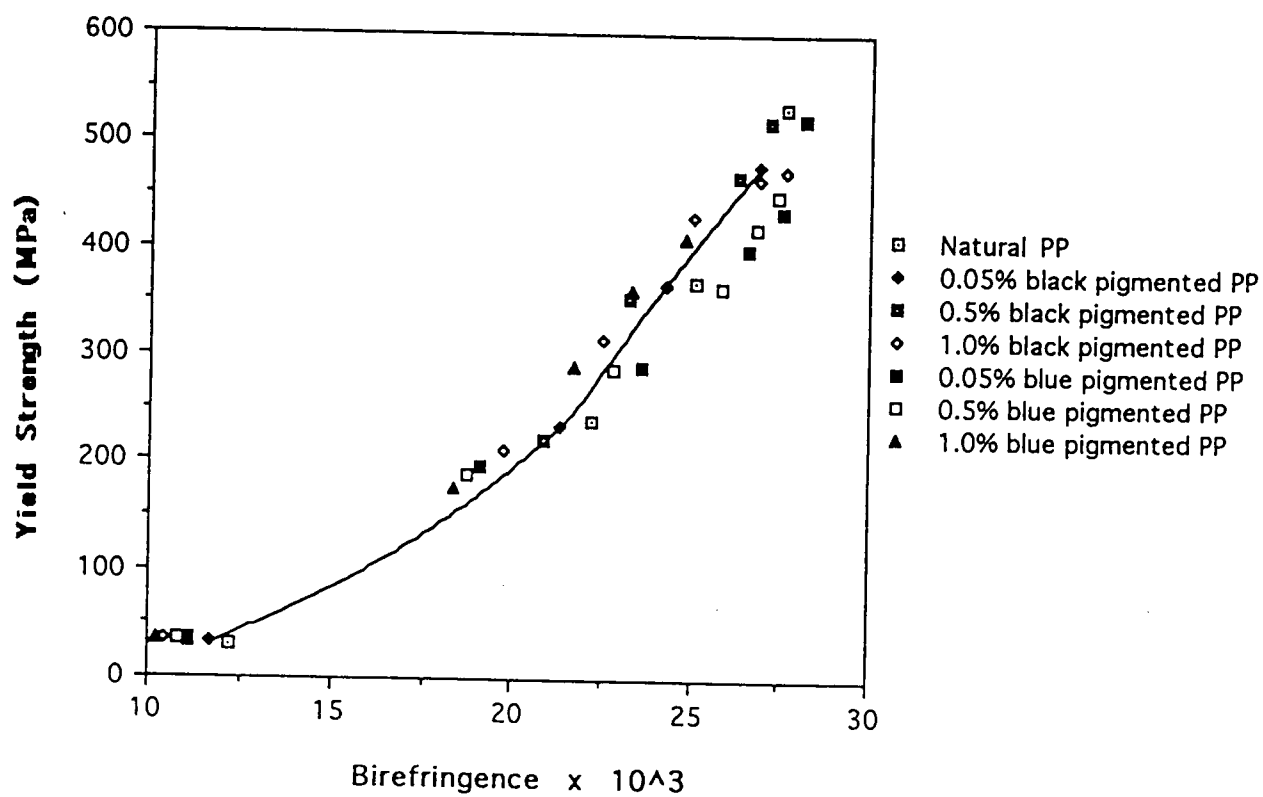


Figure 37 Yield Strength as a Function of Birefringence for Natural and Pigmented PP

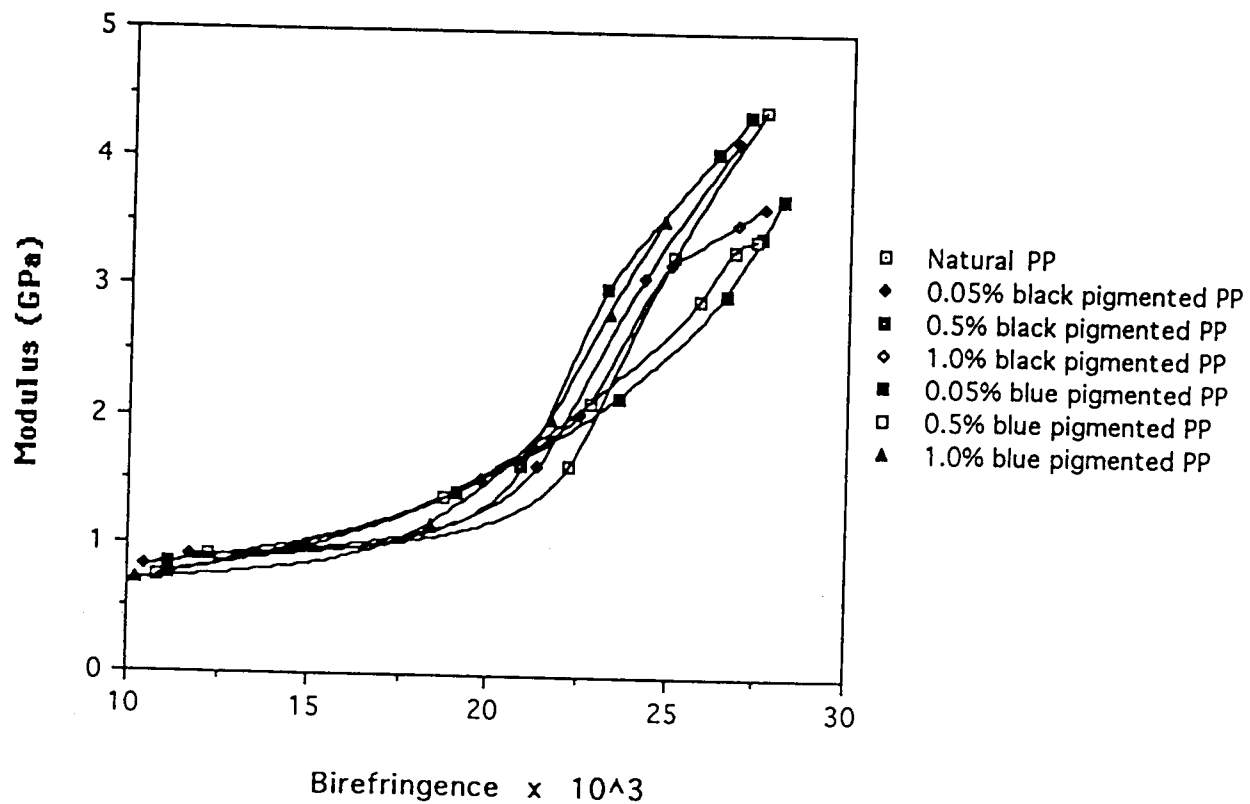


Figure 38 Modulus as a Function of Birefringence for Natural and Pigmented PP

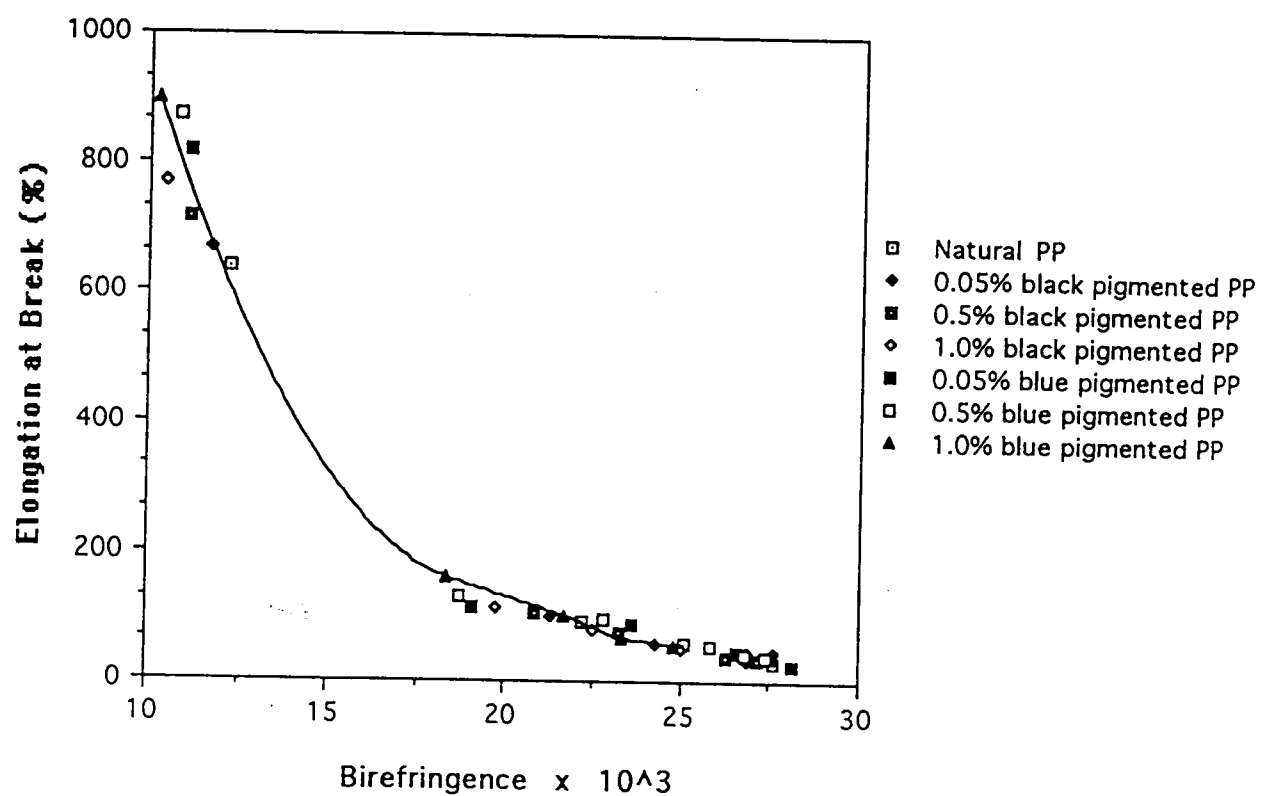


Figure 39 Elongation at Break as a Function of Birefringence for Natural and Pigmented PP

the birefringence begins to increase. Further increase of birefringence in the drawn filament produces smaller decrease of elongation at break. The most striking feature of these plots is that with the possible exception of the modulus, the other properties correlate well with the birefringence. That is the data for all the different pigment concentrations fall on a single curve within the experimental error. Note that there does not appear to be any systematic deviation from the curve with change in pigment concentration or type. This fact indicates that it is the final orientation in the filament which largely determines its properties and the pigment additions merely influence the way in which the orientation develops with processing conditions. The greater scatter in the modulus correlation with birefringence is probably due to its strong dependence on crystallinity as well as orientation.

The correlation of mechanical properties with crystallinity is not nearly so strong or as independent of pigment concentration as illustrated for tenacity and elongation at break in Figures 40 and 41.

Similar correlations have been used by Spruiell [44, 96] and White [97] and others [98-99] from our laboratories for polypropylene and polyethylene.

4.6 Statistical Analysis of Experimental data

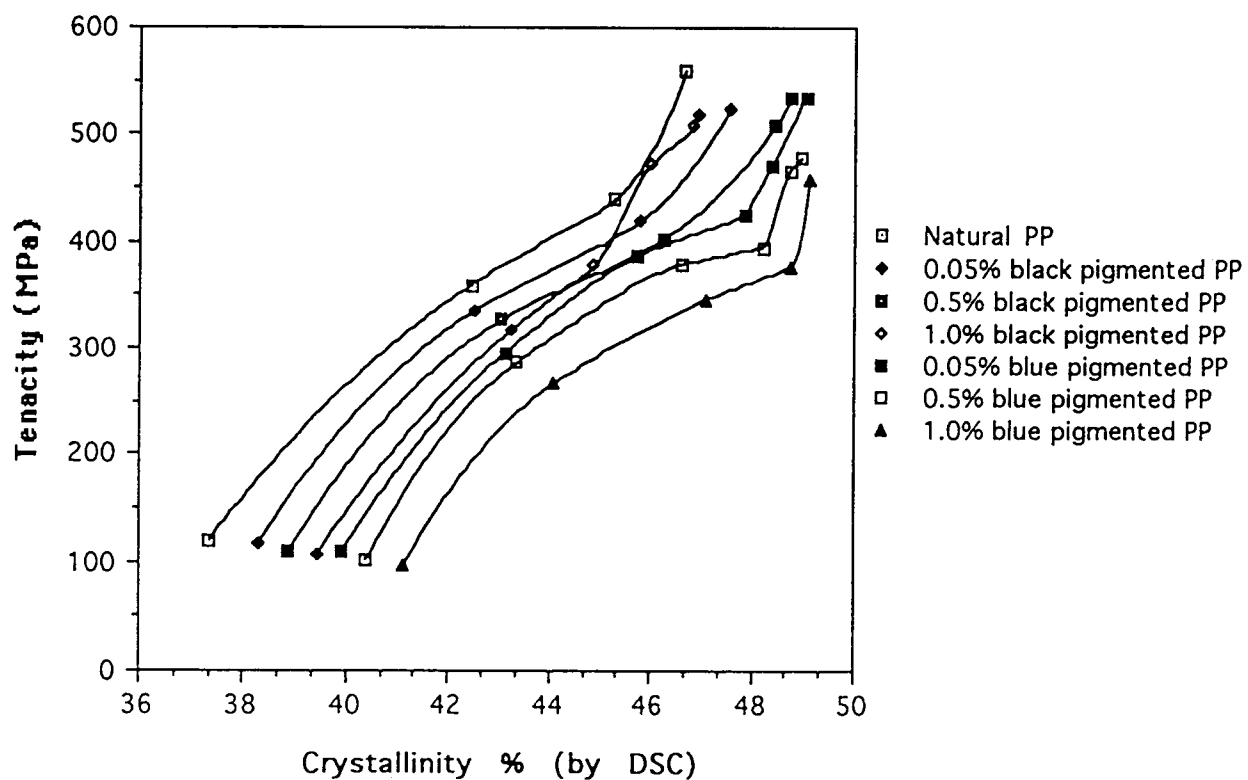


Figure 40 Tenacity as a Function of Crystallinity (by DSC) for Natural and Pigmented PP

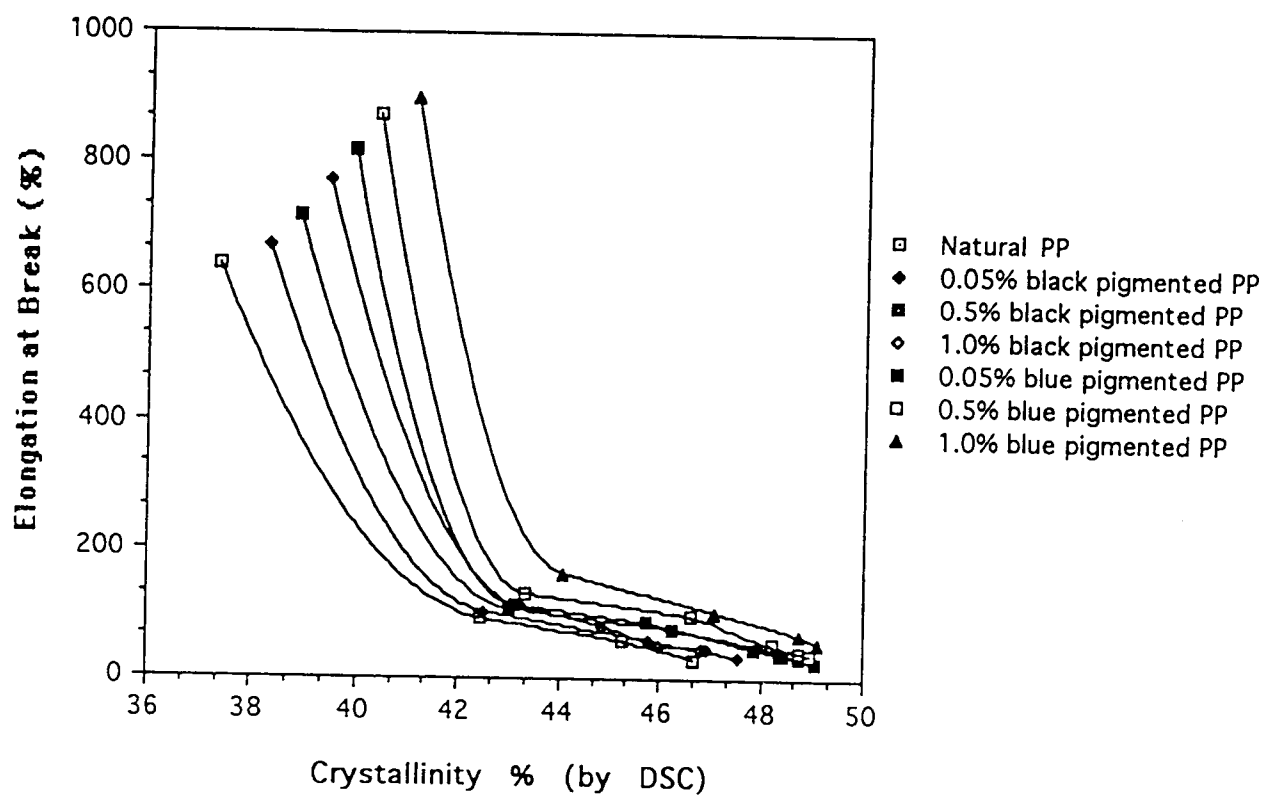


Figure 41 Elongation at Break as a Function of Crystallinity (by DSC) for Natural and Pigmented PP

Finally, an extensive statistical analysis is also provided in this study to enhance a quantitative understanding of the effect of pigment types, pigment concentration, draw ratio, draw temperature and draw speed on the final structure and properties of pigmented PP drawn filaments. All the sample conditions, draw processing parameters and measurement results are tabulated in Table 9. It should be noted that in order to employ the data in the MINITAB program for statistical analysis, the special codes, shown in Table 10, are defined and used throughout this section.

Three independent drawing variables, namely, draw ratio (DR), draw temperature (Draw Temp), and draw speed (D. Speed) and two materials variables, i.e., pigment type (pigment) and pigment concentration (%) (Conc.) along with three levels each are given in Table 11 and investigated by the statistical central composite second order rotatable design [102]. The general form of quadratic equation is:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}(X_1X_2) + b_{13}(X_1X_3) + \\ + b_{14}(X_1X_4) + b_{15}(X_1X_5) + b_{23}(X_2X_3) + b_{24}(X_2X_4) + b_{25}(X_2X_5) + \\ + b_{34}(X_3X_4) + b_{35}(X_3X_5) + b_{45}(X_4X_5)$$

where X subscripts correspond to the numbers given above for independent variables. Center points and unit value for the five predictor variables are determined and also given in Table 11. To

Table 9 Summary of Experimental Conditions and Measurement Results

Cell	Pigment Type	Pigment Conc. (%)	Draw Ratio	Draw Temp (C)	Draw Speed (rpm)	Xc (DSC) (%)	Tm (DSC) (C)	Deduced Density (gm/cm ³)	Xc (density) (%)	Birefring- -ence (x10 ⁻³)	Elongation (%)	Tenacity (MPa)	Yield Strength (MPa)	Modulus (GPa)
1	0	0.00	1.0	50	45.0	37.35	160.4	0.8898	48.05	12.20	639.0	120.6	29.9	0.903
2	0	0.00	3.0	50	135.0	42.43	162.2	0.8919	50.72	22.18	93.8	359.6	239.8	1.641
3	0	0.00	4.0	50	180.0	45.28	162.3	0.8930	52.23	25.10	57.5	439.0	368.2	3.271
4	0	0.00	5.0	50	225.0	46.69	162.4	0.8938	53.18	27.63	30.5	558.5	532.0	4.408
5	2	0.05	1.0	50	45.0	38.29	160.9	0.8919	50.43	11.69	670.9	118.1	31.8	0.901
6	2	0.05	3.0	50	135.0	42.51	162.6	0.8924	51.18	21.33	103.4	335.8	233.9	1.632
7	2	0.05	4.0	50	180.0	45.78	164.7	0.8938	52.89	24.26	60.1	418.3	366.9	3.090
8	2	0.05	5.0	50	225.0	47.55	164.9	0.8942	53.46	26.89	34.0	522.8	478.5	4.161
9	2	0.50	1.0	50	45.0	38.86	161.2	0.8925	48.67	11.08	714.6	110.2	32.2	0.853
10	2	0.50	3.0	50	135.0	43.05	162.9	0.8935	49.91	20.88	107.0	327.1	220.1	1.628
11	2	0.50	4.0	50	180.0	46.24	163.9	0.8936	50.10	23.24	76.8	402.4	352.8	3.014
12	2	0.50	5.0	50	225.0	48.44	164.1	0.8945	51.24	26.26	40.2	507.4	468.7	4.059
13	2	0.50	5.7	50	256.5	48.77	164.2	0.8950	51.80	27.20	32.8	533.8	517.5	4.356
14	2	1.00	1.0	50	45.0	39.42	161.5	0.8933	46.80	10.47	772.0	107.9	35.0	0.824
15	2	1.00	3.0	50	135.0	43.21	163.3	0.8951	49.08	19.72	112.4	317.2	210.1	1.515
16	2	1.00	4.0	50	180.0	44.87	164.1	0.8957	49.84	22.52	81.5	378.5	315.6	2.040
17	2	1.00	5.0	50	225.0	45.99	165.1	0.8958	49.94	25.05	50.7	471.9	429.6	3.203
18	2	1.00	6.0	50	270.0	46.83	165.3	0.8958	50.03	26.87	48.7	507.4	466.2	3.515
19	2	1.00	6.5	50	292.5	46.93	165.6	0.8961	50.32	27.63	47.0	519.3	471.7	3.651
20	3	0.05	1.0	50	45.0	39.92	161.9	0.8941	53.27	11.15	815.7	109.3	35.2	0.771
21	3	0.05	3.0	50	135.0	43.11	163.2	0.8954	54.96	19.05	114.6	295.1	194.6	1.428
22	3	0.05	4.0	50	180.0	45.71	163.8	0.8964	56.19	23.57	88.0	386.1	289.0	2.163
23	3	0.05	5.0	50	225.0	47.85	163.9	0.8970	56.94	26.55	48.7	425.1	398.6	2.964
24	3	0.05	6.0	50	270.0	48.38	164.0	0.8975	57.69	27.57	39.7	469.3	434.2	3.406
25	3	0.05	7.0	50	315.0	49.04	164.1	0.8982	58.53	28.15	27.0	534.8	522.1	3.713
26	3	0.50	1.0	50	45.0	40.38	162.3	0.8945	51.24	10.85	874.6	100.7	36.3	0.752
27	3	0.50	3.0	50	135.0	43.35	163.1	0.8960	53.13	18.73	131.4	286.4	188.7	1.385
28	3	0.50	4.0	50	180.0	46.64	163.6	0.8971	54.54	22.77	96.9	379.2	286.7	2.122
29	3	0.50	5.0	50	225.0	48.23	164.3	0.8977	55.30	25.85	53.6	395.2	362.8	2.919
30	3	0.50	6.0	50	270.0	48.74	164.5	0.8984	56.24	26.77	42.4	465.5	419.9	3.307
31	3	0.50	6.3	50	283.5	48.97	165.1	0.8987	56.52	27.41	39.3	479.1	450.6	3.395
32	3	1.00	1.0	50	45.0	41.08	163.1	0.8970	51.55	10.23	898.0	96.2	36.6	0.717
33	3	1.00	3.0	50	135.0	44.05	163.6	0.8986	53.54	18.31	162.6	266.4	176.0	1.173
34	3	1.00	4.0	50	180.0	47.08	164.7	0.8998	55.05	21.65	103.8	346.5	288.7	1.990
35	3	1.00	5.0	50	225.0	48.75	165.4	0.9006	56.08	23.28	67.4	376.8	360.2	2.828
36	3	1.00	6.0	50	270.0	49.1	165.6	0.9009	56.55	24.82	56.9	456.7	409.8	3.537
37	0	0.00	4.0	25	180.0	45.13	162.9	0.8926	51.66	25.05	56.8	428.6	363.3	2.710
38	2	0.50	4.0	25	180.0	45.96	165.4	0.8938	50.29	23.06	75.1	405.5	347.7	2.559
39	3	0.50	4.0	25	180.0	42.82	164.4	0.8952	52.09	22.10	89.8	368.8	281.1	2.145
40	0	0.00	4.0	50	180.0	45.28	166.4	0.8921	51.00	25.10	57.5	439.0	368.2	3.271
41	2	0.50	4.0	50	180.0	46.24	163.9	0.8938	50.29	23.24	76.8	418.3	352.8	3.014
42	3	0.50	4.0	50	180.0	46.64	163.1	0.8971	54.54	22.17	96.9	372.9	288.7	2.559
43	0	0.00	4.0	75	180.0	46.25	163.7	0.8964	56.47	24.50	62.9	405.5	361.8	2.421
44	2	0.50	4.0	75	180.0	46.71	165.2	0.8967	54.07	22.79	78.5	389.2	326.0	2.263
45	3	0.50	4.0	75	180.0	48.39	163.0	0.8973	54.83	21.96	96.6	328.0	270.7	1.947
46	0	0.00	4.0	100	180.0	47.47	164.3	0.8968	57.04	23.33	65.7	369.4	338.9	2.065
47	2	0.50	4.0	100	180.0	48.08	164.6	0.8975	55.01	22.10	82.1	357.8	322.0	1.970
48	3	0.50	4.0	100	180.0	50.46	163.1	0.8993	57.36	21.33	101.3	314.0	265.2	1.622
49	0	0.00	3.0	50	90.0	42.43	162.2	0.8917	50.53	22.18	93.8	359.5	239.8	1.641
50	2	0.50	3.0	50	90.0	43.05	162.9	0.8935	49.91	21.94	103.4	327.1	220.1	1.628
51	3	0.50	3.0	50	90.0	44.03	163.6	0.8973	54.83	20.80	131.4	286.4	194.6	1.385
52	0	0.00	3.0	50	135.0	42.3	162.1	0.8919	50.72	21.93	109.3	346.5	209.3	1.527
53	2	0.50	3.0	50	135.0	43.05	162.8	0.8935	49.91	21.44	123.9	318.2	203.9	1.497
54	3	0.50	3.0	50	135.0	43.55	162.3	0.8960	53.13	19.45	151.9	278.8	173.6	1.228
55	0	0.00	3.0	50	180.0	42.22	161.7	0.8919	50.81	21.61	133.2	327.4	195.3	1.248
56	2	0.50	3.0	50	180.0	42.97	162.8	0.8921	48.20	21.12	153.5	301.7	180.2	1.173
57	3	0.50	3.0	50	180.0	43.87	162.1	0.8936	50.10	19.19	191.8	274.7	167.5	1.045

Table 10 Special Codes Used For Statistical Analysis

CODE	SAMPLE
0	Natural PP Filament
2	Black Pigmented PP Filament
3	Blue Pigmented PP Filament
0.05	0.05% Pigment Concentration
0.5	0.5% Pigment Concentration
1.0	1.0% Pigment Concentration

Table 11 Independent Variables and Their Mean

Independent Variable	Mean	Unit
Pigment Type (Pigment)	2.0351	n/a
Pigment Concentration (Conc)	0.421	%
Draw Ratio (DR)	3.781	n/a
Draw Temperature (DT or D Temp)	52.632	°C
Draw Speed (D. Speed)	45	rpm

(note: the mean given here is the average of total 57 cells).

test the estimated regression equation for goodness of fit, the F-test was employed and the coefficient of determination and standard error of estimates were also determined. All the analyses were done with the help of MINITAB statistical analysis program.

The results of stepwise regression analysis summarized in Table 12 and Appendix reveal that the dependent variables are functions of several independent variables. The structure and mechanical properties of the natural and pigmented PP filaments are also greatly influenced by effects of their interactions. In particular, the combinations of pigment and concentration, pigment and draw ratio as well as draw ratio and draw temperature have statistically significant effects on the structural characteristics and mechanical properties of pigmented PP drawn filaments. The influence of the individual variable and/or the combined variables on the structural and mechanical properties of pigmented PP drawn filaments are summarized in Table 13.

Table 12 Results of Stepwise Regression Analysis

REGRESSION RESULTS IN TERMS OF CODED VARIABLES

X% (DSC) =		44.8	+1.92*DR	+0.0681*(Draw Temp)	+0.659*Pigment	+1.41*(Pigment*Conc.)	-0.235*(Pigment*DR)	+0.0184*(Pigment*Draw Temp)	-0.470*(Conc.*DR)
t-ratio		312.85	22.87	7.9	4.22	3.2	-2.58	2.75	-2.32
p		0.000	0.000	0.000	0.000	0.002	0.073	0.008	0.024
s		1.42	1.42	1.13	1.05	0.996	0.947	0.899	0.862
R-square		79.2	87.08	89.05	90.29	91.4	92.4	93.15	
X% (density) =		51.4	0.986*DR	0.077*(Draw Temp)	2.86*Pigment	-5.04*Conc.	+4.66*(Pigment*Conc.)	+0.0334*(Draw Temp*Draw Speed)	-0.0525*(Pigment*Draw Speed)
t-ratio		307.03	10.74	7.95	13.45	-11.16	8.67	3.08	-2.39
p		0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.021
s		2.46	2.23	2.04	2.04	1.63	1.10	1.05	1.01
R-square		27.32	41.07	51.66	69.89	86.52	87.91	89.17	
Tm (DSC) (C) =		163.5	+0.687*DR	+0.860*Conc.	-0.177*(Pigment*DR)				
t-ratio		1553.53	9.13	2.87	-2.17				
p		0.000	0.000	0.006	0.034				
s		0.878	0.811	0.765	0.765				
R-square		55.41	62.65	65.7					
n x 10⁻³ =		21.9	+3.18*DR	-0.788*Pigment	-1.69*Conc.	-0.290*(Pigment*DR)			
t-ratio		123.95	25.01	-4.24	-2.96	-2.11			
p		0.000	0.000	0.000	0.005	0.040			
s		1.8	1.43	1.36	1.32	1.32			
R-square		86.07	91.3	92.31	92.91	92.91			
Elongation (%) =		168	-127*DR	+42.3*Pigment					
t-ratio		9.06	-9.94	2.47					
p		0.000	0.000	0.017					
s		146	140	65					
R-square		61.04							
Tenacity (MPa) =		368	+71.5*DR	-39.4*Pigment	-11.8*(Pigment*DR)	-3.43*(DR*Draw Temp)	-36.0*(Pigment*Conc.)		
t-ratio		84.99	18.92	-8.43	0.000	0.004	0.009		
p		0.000	0.000	0.000	0.000	0.004	0.009		
s		43.9	32.6	29.2	27.3	25.8	25.8		
R-square		86.49	92.68	94.25	95.05	95.68			
Yield Strength (Mpa) =		292	+94.8*DR	-25.2*Pigment	-15.3*(Pigment*DR)				
t-ratio		71.17	32.17	-6.64	-4.81				
p		0.000	0.000	0.000	0.000				
s		43.4	36.3	30.6	30.6				
R-square		90.18	93.26	95.3					
Modulus (GPa) =		2.27	+0.674*DR	-0.206*Pigment	-0.120*(Pigment*DR)	-0.0104*(Draw Temp)			
t-ratio		39.94	16.45	-3.89	-2.73	-2.54			
p		0.000	0.000	0.009	0.009	0.014			
s		0.498	0.466	0.445	0.445	0.424			
R-square		77.37	80.62	82.59	84.51				

Table 13 Summary of the Key Results ;

INCREASING	Tm	X% (DSC)	X% (density)	n x 10 ³	Elongation	Tenacity	Yield Strength	Modulus
Pigment		↑	↑	↓	↑	↓	↓	↓
Pigment Conc.	↑		↓	↓				
DR	↑	↑	↑	↓	↓	↓	↓	↓
Draw Temp		↑	↑					↓
Pigment*DR	↓	↓		↓		↓	↓	↓
Pigment*Conc		↑	↑			↓		
Pigment*Draw Temp		↑						
Pigment* Draw Speed			↓					
Conc.*DR		↓						
DR*Draw Temp						↓		
Draw Temp * Draw Speed			↑					
Draw Speed								

Code:

0 = Pure PP, or 0.0% Pigment

1 = 1.0% Pigment

0.05 = 0.05% Pigment

2= Black Pigment

0.5 = 0.5% Pigment

3= Blue Pigment

CHAPTER 5

SUMMARY AND CONCLUSIONS

In this study, two pigments, one inorganic and one organic, were selected to produce colored spun and drawn polypropylene filaments with black and blue colors respectively. Wide angle x-ray diffraction (WAXS), differential scanning calorimetry (DSC), density, and birefringence were used in the analysis of structural characteristics for both pigmented and unpigmented PP drawn filaments. Uniaxial tensile tests were also carried out. The influence of pigment additions on the structure and properties of PP filaments in the drawing process, and the way that drawing process conditions influence the development of fine structure, as well as the mechanical properties of pigmented PP filaments, were investigated. An extensive statistical analysis is also provided to enhance a quantitative understanding of the effect of pigment types, pigment concentration, draw ratio, draw temperature and draw speed on the final structure and properties of pigmented drawn PP filaments. The studies resulted in the following conclusions:

- 1) Summarizing, it can be stated that drawing behavior is critically dependent on the properties of the as-spun filaments. The introduced pigments produce changes in the structure and properties

of the as-spun filaments which also carry over to affect the final structure and properties of drawn filaments. Pigmented PP filaments were found to have lower birefringence values and more crystallinity than natural, or unpigmented PP filaments. Moreover, under similar processing conditions the pigmented filaments possess lower tenacity, lower yield strength, lower modulus and larger elongation at break than natural PP filaments. The type and the scale of the variation of properties depends on the kind of pigments used and on the amount added. The two types of pigment additions produced unequal influence on the structure and properties. Apparently, the blue pigment has more impact on the development of structure and tensile properties of PP spun and drawn filaments than the black pigment. The drawability and drawn yarn mechanical properties are also greatly affected by the pigment concentration. Birefringence, tenacity, yield strength and modulus tend to decrease, and elongation increases, with the increase of pigment concentration from 0.05% to 0.5%, then to 1.0%. The maximum draw ratios calculated from the measured elongations of the as-spun filaments suggest that adding pigments considerably improves the drawability of pigmented PP filaments, especially at higher draw ratios.

2) The study of the effect of processing conditions on the structure development and mechanical properties of pigmented PP filaments has shown that the resulting structure and tensile

properties of pigmented PP filaments are extraordinarily sensitive to the drawing conditions used. The morphology developed during drawing is usually accompanied by significant mechanical property changes. The fiber mechanical properties tend to correlate with the orientation developed during the drawing. Changes of draw ratio and draw temperature may improve or damage fine structure of PP drawn filaments and therefore affect pigmented PP drawn properties. In particular, draw ratio and draw temperature have marked effect on the orientation and crystallinity of the pigmented PP filaments. The fiber crystallinities measured by the DSC and the density methods increase with the increases of draw ratio and draw temperature. Birefringence, tenacity, yield strength, modulus and DSC melting temperature increase with the increase of draw ratio. On the other hand, at a given draw ratio and draw temperature, increasing draw speed from 90 rpm to 180 rpm tends to lead to an increased elongation, and a reduced birefringence, tenacity, yield strength and modulus as well as DSC melting temperature. The significant relationships between the changes in the drawing behaviors and the changes in the pigmented PP structure developed during the drawing process are elucidated in Tables 12 and 13.

3) In addition to single valued function of pigment type, pigment concentration, and draw conditions, the structural and mechanical properties of pigmented PP filaments are also greatly influenced by the effects of their interactions. In particular, the combinations of

pigment type and pigment concentration, pigment type and draw ratio as well as draw ratio and draw temperature have statistically significant effect on the structural characteristics and mechanical properties of pigmented PP drawn filaments.

4) Finally, it can be said that the presence of pigments appears to have little negative effect on the drawing behaviors of pigmented PP filaments, except somewhat reduced tenacity and increased elongation observed. However, pigmented PP filaments can be physically drawn more at higher draw ratio due to a lower initial orientation in the as-spun filaments.

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APPENDIX

APPENDIX STATISTICAL DETAILS

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- i) Combined Effect of Draw Ratio, Draw Temperature and Draw Speed on the Structure and Properties of the Natural and Pigmented PP Filaments

Regression Analysis

The regression equation is

$$X\% \text{ (DSC)} = 44.8 + 1.92 \text{ DR} + 0.0681 \text{ D Temp} + 0.659 \text{ Pigment} + 1.41 \text{ Pigm*Con} \\ - 0.235 \text{ Pigm*DR} + 0.0184 \text{ Pigm*DT} - 0.470 \text{ Conc*DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	44.8304	0.1433	312.85	0.000
DR	1.91722	0.08383	22.87	0.000
D Temp	0.068079	0.008623	7.90	0.000
Pigment	0.6587	0.1562	4.22	0.000
Pigm*Con	1.4142	0.4422	3.20	0.002
Pigm*DR	-0.23531	0.09137	-2.58	0.013
Pigm*DT	0.018433	0.006700	2.75	0.008
Conc*DR	-0.4704	0.2024	-2.32	0.024

s = 0.8616 R-sq = 93.2% R-sq(adj) = 92.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	7	494.708	70.673	95.20	0.000
Error	49	36.377	0.742		
Total	56	531.085			

SOURCE	DF	SEQ SS
DR	1	420.641
D Temp	1	41.828
Pigment	1	10.438
Pigm*Con	1	6.614
Pigm*DR	1	5.868
Pigm*DT	1	5.309
Conc*DR	1	4.010

Unusual Observations

Obs.	DR	X% (DSC)	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	37.350	37.408	0.625	-0.058	-0.10 X
19	2.72	46.930	49.096	0.405	-2.166	-2.85R
25	3.22	49.040	50.737	0.477	-1.697	-2.37R
38	0.22	45.960	43.354	0.278	2.606	3.20R
46	0.22	47.470	46.718	0.686	0.752	1.44 X
48	0.22	50.460	50.003	0.600	0.457	0.74 X

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Regression Analysis

The regression equation is

$$Tm \text{ (DSC)} = 164 + 0.687 \text{ DR} + 0.860 \text{ P.Conc.} - 0.177 \text{ Pigm*DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	163.545	0.105	1553.53	0.000
DR	0.68704	0.07526	9.13	0.000
P.Conc.	0.8603	0.2997	2.87	0.006
Pigm*DR	-0.17737	0.08170	-2.17	0.034

s = 0.7846 R-sq = 65.7% R-sq(adj) = 63.8%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	3	62.493	20.831	33.84	0.000
Error	53	32.625	0.616		
Total	56	95.118			

SOURCE	DF	SEQ SS
DR	1	52.703
P.Conc.	1	6.889
Pigm*DR	1	2.901

Unusual Observations

Obs.	DR	Tm (DSC)	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	160.410	160.268	0.548	0.142	0.25 X
4	1.22	162.440	164.460	0.332	-2.020	-2.84R
38	0.22	165.400	163.765	0.109	1.635	2.10R
40	0.22	166.440	163.412	0.183	3.028	3.97R

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Regression Analysis

The regression equation is

$$\begin{aligned} \text{X\%-density} = & 51.7 + 0.986 \text{ DR-c} + 0.0770 \text{ DT-c} + 2.86 \text{ Pigm-c} - 5.04 \text{ Conc-c} \\ & + 4.66 \text{ Pigm*Con} + 0.0334 \text{ DT*DS} - 0.0525 \text{ Pigm*DS} \end{aligned}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	51.7354	0.1685	307.03	0.000
DR-c	0.98612	0.09183	10.74	0.000
DT-c	0.076995	0.009680	7.95	0.000
Pigm-c	2.8561	0.2124	13.45	0.000
Conc-c	-5.0372	0.4512	-11.16	0.000
Pigm*Con	4.6600	0.5372	8.67	0.000
DT*DS	0.03335	0.01084	3.08	0.003
Pigm*DS	-0.05245	0.02194	-2.39	0.021

s = 1.005

R-sq = 89.2%

R-sq(adj) = 87.6%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	7	407.741	58.249	57.64	0.000
Error	49	49.516	1.011		
Total	56	457.257			

SOURCE	DF	SEQ SS
DR-c	1	124.934
DT-c	1	62.884
Pigm-c	1	48.383
Conc-c	1	83.393
Pigm*Con	1	76.045
DT*DS	1	6.324
Pigm*DS	1	5.778

Unusual Observations

Obs.	DR-c	X%-densi	Fit	Stdev.Fit	Residual	St.Resid
43	0.22	56.470	53.976	0.361	2.494	2.66R
49	-0.78	50.530	50.780	0.749	-0.250	-0.37 X
55	-0.78	50.810	51.349	0.749	-0.539	-0.80 X

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Regression Analysis

The regression equation is

$$n \times 10^3 = 21.9 + 3.18 \text{ DR} - 0.788 \text{ Pigment} - 1.69 \text{ P.Conc.} - 0.290 \text{ Pigm*DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	21.9071	0.1767	123.95	0.000
DR	3.1837	0.1273	25.01	0.000
Pigment	-0.7877	0.1858	-4.24	0.000
P.Conc.	-1.6928	0.5712	-2.96	0.005
Pigm*DR	-0.2902	0.1378	-2.11	0.040

s = 1.317

R-sq = 92.9%

R-sq(adj) = 92.4%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	4	1182.56	295.64	170.44	0.000
Error	52	90.20	1.73		
Total	56	1272.76			

SOURCE	DF	SEQ SS
DR	1	1095.42
Pigment	1	66.55
P.Conc.	1	12.89
Pigm*DR	1	7.70

Unusual Observations

Obs.	DR	n x 10 ³	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	12.200	13.728	0.933	-1.528	-1.64 X
20	-2.78	11.150	13.701	0.587	-2.551	-2.16R
25	3.22	28.150	31.123	0.591	-2.973	-2.53R
50	-0.78	21.940	19.308	0.205	2.632	2.02R

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Regression Analysis

The regression equation is
 * Elong = 168 - 127 DR + 42.3 Pigment

Predictor	Coef	Stdev	t-ratio	p
Constant	167.85	18.52	9.06	0.000
DR	-126.54	12.73	-9.94	0.000
Pigment	42.28	17.11	2.47	0.017

s = 139.8 R-sq = 65.0% R-sq(adj) = 63.7%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	2	1960292	980146	50.13	0.000
Error	54	1055770	19551		
Total	56	3016062			

SOURCE	DF	SEQ SS
DR	1	1840877
Pigment	1	119415

Unusual Observations

Obs.	DR	Elong	Fit	Stdev.Fit	Residual	St.Resid
26	-2.78	874.6	560.5	44.9	314.1	2.37R
32	-2.78	898.0	560.5	44.9	337.5	2.55R

R denotes an obs. with a large st. resid.

* Elong = Elongation at break

Regression Analysis

The regression equation is

$$\text{Tenacity} = 368 + 71.5 \text{ DR} - 39.4 \text{ Pigment} - 11.8 \text{ Pigm*DR} - 3.43 \text{ DR*DT} - 36.0 \text{ Pigm*Con}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	368.195	4.332	84.99	0.000
DR	71.504	3.780	18.92	0.000
Pigment	-39.368	4.668	-8.43	0.000
Pigm*DR	-11.811	2.685	-4.40	0.000
DR*DT	-3.433	1.135	-3.03	0.004
Pigm*Con	-35.96	13.23	-2.72	0.009

s = 25.80

R-sq = 95.7%

R-sq(adj) = 95.3%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	5	751827	150365	225.92	0.000
Error	51	33943	666		
Total	56	785770			

SOURCE	DF	SEQ SS
DR	1	679640
Pigment	1	48639
Pigm*DR	1	12310
DR*DT	1	6322
Pigm*Con	1	4916

Unusual Observations

Obs.	DR	Tenacity	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	120.60	126.70	18.27	-6.10	-0.34 X
8	1.22	522.80	467.81	5.36	54.99	2.18R
19	2.72	519.30	590.44	8.32	-71.14	-2.91R

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Regression Analysis

* The regression equation is

$$Y \text{ Stress} = 292 + 94.8 \text{ DR} - 25.2 \text{ Pigment} - 15.3 \text{ Pigm*DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	291.935	4.102	71.17	0.000
DR	94.829	2.947	32.17	0.000
Pigment	-25.235	3.799	-6.64	0.000
Pigm*DR	-15.256	3.174	-4.81	0.000

s = 30.57

R-sq = 95.3%

R-sq(adj) = 95.0%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	3	1005412	335137	358.58	0.000
Error	53	49535	935		
Total	56	1054946			

SOURCE	DF	SEQ SS
DR	1	951348
Pigment	1	32472
Pigm*DR	1	21592

Unusual Observations

Obs.	DR	Y Stress	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	29.90	-6.73	21.61	36.63	1.69 X
4	1.22	532.00	496.77	14.66	35.23	1.31 X
8	1.22	478.50	409.10	5.66	69.40	2.31R
19	2.72	471.70	552.14	9.33	-80.44	-2.76R
48	0.22	365.20	285.15	5.42	80.05	2.66R

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

* Y. stress = yield strength

Regression Analysis

The regression equation is

$$\text{Modulus} = 2.27 + 0.674 \text{ DR} - 0.206 \text{ Pigment} - 0.120 \text{ Pigm*DR} - 0.0104 \text{ D Temp}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	2.27308	0.05692	39.94	0.000
DR	0.67398	0.04096	16.45	0.000
Pigment	-0.20565	0.05288	-3.89	0.000
Pigm*DR	-0.12032	0.04413	-2.73	0.009
D Temp	-0.010380	0.004091	-2.54	0.014

s = 0.4242

R-sq = 84.5%

R-sq(adj) = 83.3%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	4	51.039	12.760	70.91	0.000
Error	52	9.358	0.180		
Total	56	60.397			

SOURCE	DF	SEQ SS
DR	1	46.731
Pigment	1	1.963
Pigm*DR	1	1.187
D Temp	1	1.158

Unusual Observations

Obs.	DR	Modulus	Fit	Stdev.Fit	Residual	St.Resid
1	-2.78	0.9030	0.1639	0.2999	0.7391	2.46RX
8	1.22	4.1610	3.1345	0.0798	1.0265	2.46R
12	1.22	4.0590	3.1345	0.0798	0.9245	2.22R
46	0.22	2.0650	2.4014	0.2250	-0.3364	-0.94 X

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is X%-DSC on 14 predictors, with N = 57

Step	1	2	3	4	5	6	7
Constant	45.01	45.01	45.01	44.76	44.80	44.82	44.83
DR-c	1.852	1.835	1.796	1.809	1.887	1.900	1.917
T-Ratio	14.47	18.02	18.82	19.92	20.61	21.81	22.87
DT-c		0.0621	0.0642	0.0638	0.0623	0.0684	0.0681
T-Ratio		5.74	6.37	6.65	6.82	7.60	7.90
Pigm-c			0.40	0.74	0.69	0.68	0.66
T-Ratio			3.08	4.10	4.04	4.18	4.22
Pigm*Con				1.32	1.36	1.39	1.41
T-Ratio				2.58	2.80	3.02	3.20
Pigm*DR					-0.252	-0.272	-0.235
T-Ratio					-2.56	-2.90	-2.58
Pigm*DT						0.0179	0.0184
T-Ratio						2.56	2.75
Conc*DR							-0.47
T-Ratio							-2.32
S	1.42	1.13	1.05	0.996	0.947	0.899	0.862
R-Sq	79.20	87.08	89.05	90.29	91.40	92.40	93.15

More? (Yes, No, Subcommand, or Help)

SUBC> No

MTB > Regress 'X%-densi' 15 'Pigm-c'-'DT*DS';

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is Tm (DSC) on 15 predictors, with N = 57

Step	1	2	3
Constant	163.5	163.5	163.5
DR	0.655	0.634	0.687
T-Ratio	8.27	8.62	9.13
P.Conc.		0.98	0.86
T-Ratio		3.24	2.87
Pigm*DR			-0.177
T-Ratio			-2.17
S	0.878	0.811	0.785
R-Sq	55.41	62.65	65.70

More? (Yes, No, Subcommand, or Help)

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is X%-density on 14 predictors, with N = 57

Step	1	2	3	4	5	6	7
Constant	52.63	52.63	52.63	52.63	51.74	51.74	51.74
DR-c	1.009	0.989	0.906	0.933	0.986	0.986	0.986
T-Ratio	4.55	4.90	4.87	6.29	9.82	10.27	10.74
DT-c		0.0761	0.0807	0.0791	0.0770	0.0770	0.0770
T-Ratio		3.55	4.11	5.05	7.27	7.60	7.95
Pigm-c			0.85	1.48	2.86	2.86	2.86
T-Ratio			3.41	6.47	12.30	12.86	13.45
Conc-c				-3.93	-5.04	-5.04	-5.04
T-Ratio				-5.61	-10.21	-10.67	-11.16
Pigm*Con					4.66	4.66	4.66
T-Ratio					7.93	8.29	8.67
DR*DS						0.088	0.112
T-Ratio						2.39	3.08
Pigm*DS							-0.052
T-Ratio							-2.39
S	2.46	2.23	2.04	1.63	1.10	1.05	1.01
R-Sq	27.32	41.07	51.66	69.89	86.52	87.91	89.17
More? (Yes, No, Subcommand, or Help)							

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is $n \times 10^3$ on 15 predictors, with N = 57

Step	1	2	3	4
Constant	21.85	21.85	21.85	21.91
DR	2.99	3.08	3.09	3.18
T-Ratio	18.43	23.65	24.99	25.01
Pigment		-1.00	-0.75	-0.79
T-Ratio		-5.70	-3.93	-4.24
P.Conc.			-1.55	-1.69
T-Ratio			-2.64	-2.96
Pigm*DR				-0.29
T-Ratio				-2.11
S	1.80	1.43	1.36	1.32
R-Sq	86.07	91.30	92.31	92.91

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is Elong on 15 predictors, with N = 57

Step	1	2
Constant	167.9	167.9
DR	-122	-127
T-Ratio	-9.28	-9.94
Pigment		42
T-Ratio		2.47
S	146	140
R-Sq	61.04	65.00

More? (Yes, No, Subcommand, or Help)

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is Tenacity on 15 predictors, with N = 57

Step	1	2	3	4	5
Constant	356.9	356.9	359.2	361.4	368.2
DR	74.4	77.0	80.5	71.8	71.5
T-Ratio	18.77	25.93	28.61	17.92	18.92
Pigment		-27.0	-29.4	-30.2	-39.4
T-Ratio		-6.76	-8.10	-8.86	-8.43
Pigm*DR			-11.5	-12.1	-11.8
T-Ratio			-3.80	-4.24	-4.40
DR*DT				-3.5	-3.4
T-Ratio				-2.91	-3.03
Pigm*Con					-36
T-Ratio					-2.72
S	43.9	32.6	29.2	27.3	25.8
R-Sq	86.49	92.68	94.25	95.05	95.68
More? (Yes, No, Subcommand, or Help)					

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is Y Stress on 15 predictors, with N = 57

Step	1	2	3
Constant	288.8	288.8	291.9
DR	88.1	90.2	94.8
T-Ratio	22.47	27.29	32.17
Pigment		-22.0	-25.2
T-Ratio		-4.97	-6.64
Pigm*DR			-15.3
T-Ratio			-4.81
S	43.4	36.3	30.6
R-Sq	90.18	93.26	95.30

Stepwise Regression

F-to-Enter: 4.00 F-to-Remove: 4.00

Response is Modulus on 15 predictors, with N = 57

Step	1	2	3	4
Constant	2.248	2.248	2.272	2.273
DR	0.617	0.634	0.668	0.674
T-Ratio	13.71	14.95	15.56	16.45
Pigment		-0.171	-0.195	-0.206
T-Ratio		-3.01	-3.52	-3.89
Pigm*DR			-0.113	-0.120
T-Ratio			-2.45	-2.73
D Temp				-0.0104
T-Ratio				-2.54
S	0.498	0.466	0.445	0.424
R-Sq	77.37	80.62	82.59	84.51

More? (Yes, No, Subcommand, or Help)

- ii) Single Effect of Draw Ratio on the Structure and Properties of the Natural and Pigmented PP Filaments

Regression Analysis

The regression equation is

$$T_m = 161 + 0.615 \text{ DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	161.143	0.309	521.31	0.000
DR	0.61515	0.07195	8.55	0.000

s = 0.7752 R-sq = 68.3% R-sq(adj) = 67.3%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	43.930	43.930	73.09	0.000
Error	34	20.434	0.601		
Total	35	64.364			

Unusual Observations

Obs.	DR	T _m	Fit	Stdev.Fit	Residual	St.Resid
4	5.00	162.440	164.218	0.151	-1.778	-2.34R

R denotes an obs. with a large st. resid.

```
MTB > Name c24 = 'FITS4' c25 = 'RESI4'
MTB > Regress 'X%-DSC' 1 'DR';
SUBC> Fits 'FITS4';
SUBC> Constant;
SUBC> Residuals 'RESI4'.
```

Regression Analysis

The regression equation is

$$X\%-DSC = 37.9 + 1.80 \text{ DR}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	37.9300	0.4558	83.22	0.000
DR	1.8035	0.1061	17.00	0.000

s = 1.143 R-sq = 89.5% R-sq(adj) = 89.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	377.59	377.59	288.94	0.000
Error	34	44.43	1.31		
Total	35	422.02			

Unusual Observations

Obs.	DR	X%-DSC	Fit	Stdev.Fit	Residual	St.Resid
1	1.00	37.350	39.734	0.362	-2.384	-2.20R
19	6.50	46.930	49.653	0.335	-2.723	-2.49R

R denotes an obs. with a large st. resid.

Regression Analysis

The regression equation is
 $X\% - \text{densi} = 49.1 + 0.935 \text{ DR}$

Predictor	Coef	Stdev	t-ratio	p
Constant	49.0519	0.9927	49.41	0.000
DR	0.9347	0.2311	4.04	0.000

$s = 2.490$ $R\text{-sq} = 32.5\%$ $R\text{-sq}(\text{adj}) = 30.5\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	101.42	101.42	16.36	0.000
Error	34	210.75	6.20		
Total	35	312.17			

Regression Analysis

The regression equation is
 $n \times 10^3 = 9.57 + 3.09 \text{ DR}$

Predictor	Coef	Stdev	t-ratio	p
Constant	9.5708	0.7235	13.23	0.000
DR	3.0915	0.1684	18.36	0.000

$s = 1.815$ $R\text{-sq} = 90.8\%$ $R\text{-sq}(\text{adj}) = 90.6\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	1109.5	1109.5	336.97	0.000
Error	34	112.0	3.3		
Total	35	1221.5			

```
MTB > Name c30 = 'FITS7' c31 = 'RESI7'
MTB > Regress 'Elongati' 1 'DR';
SUBC> Fits 'FITS7';
SUBC> Constant;
SUBC> Residuals 'RESI7'.
```

Regression Analysis

The regression equation is
 $\text{Elongati} = 718 - 131 \text{ DR}$

Predictor	Coef	Stdev	t-ratio	p
Constant	717.88	63.12	11.37	0.000
DR	-131.03	14.69	-8.92	0.000

$s = 158.3$ $R\text{-sq} = 70.1\%$ $R\text{-sq}(\text{adj}) = 69.2\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	1993263	1993263	79.55	0.000
Error	34	851963	25058		
Total	35	2845225			

Unusual Observations

Obs.	DR	Elongati	Fit	Stdev.Fit	Residual	St.Resid
32	1.00	898.0	586.8	50.1	311.2	2.07R

Regression Analysis

The regression equation is
 Tenacity = 64.9 + 75.4 DR

Predictor	Coef	Stdev	t-ratio	p
Constant	64.93	19.05	3.41	0.002
DR	75.351	4.434	17.00	0.000

s = 47.77 R-sq = 89.5% R-sq(adj) = 89.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	659128	659128	288.84	0.000
Error	34	77589	2282		
Total	35	736717			

Unusual Observations

Obs.	DR	Tenacity	Fit	Stdev.Fit	Residual	St.Resid
4	5.00	558.50	441.68	9.33	116.82	2.49R

R denotes an obs. with a large st. resid.

```
MTB > Name c34 = 'FITS9' c35 = 'RESI9'
MTB > Regress 'Y. Stres' 1 'DR';
SUBC> Fits 'FITS9';
SUBC> Constant;
SUBC> Residuals 'RESI9'.
```

Regression Analysis

The regression equation is
 Y. Stres_y = - 39.8 + 86.3 DR

Predictor	Coef	Stdev	t-ratio	p
Constant	-39.81	18.62	-2.14	0.040
DR	86.290	4.334	19.91	0.000

s = 46.69 R-sq = 92.1% R-sq(adj) = 91.9%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
--------	----	----	----	---	---

Regression	1	864409	864409	396.47	0.000
Error	34	74129	2180		
Total	35	938538			

Unusual Observations

Obs.	DR	Y. Stres	Fit	Stdev.Fit	Residual	St.Resid
4	5.00	532.00	391.64	9.12	140.36	3.07R

R denotes an obs. with a large st. resid.

```
MTB > Name c36 = 'FITS10' c37 = 'RESI10'
MTB > Regress 'Modulus' 1 'DR';
SUBC> Fits 'FITS10';
SUBC> Constant;
SUBC> Residuals 'RESI10'.
```

Regression Analysis

The regression equation is
Modulus = 0.121 + 0.590 DR

Predictor	Coef	Stdev	t-ratio	p
Constant	0.1214	0.2053	0.59	0.558
DR	0.58979	0.04778	12.34	0.000

s = 0.5148 R-sq = 81.8% R-sq(adj) = 81.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	40.382	40.382	152.37	0.000
Error	34	9.011	0.265		
Total	35	49.393			

Unusual Observations

Obs.	DR	Modulus	Fit	Stdev.Fit	Residual	St.Resid
4	5.00	4.4080	3.0703	0.1005	1.3377	2.65R
8	5.00	4.1610	3.0703	0.1005	1.0907	2.16R

R denotes an obs. with a large st. resid.

- iii) Single Effect of Draw Temperature on the Structure and Properties of Natural and Pigmented PP Filaments

Regression Analysis

The regression equation is
 $X\%-DSC = 43.3 + 0.0527 \text{ DrawTemp}$

Predictor	Coef	Stdev	t-ratio	p
Constant	43.3283	0.8343	51.93	0.000
DrawTemp	0.05265	0.01219	4.32	0.002

$s = 1.180$ $R\text{-sq} = 65.1\%$ $R\text{-sq(adj)} = 61.6\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	25.991	25.991	18.67	0.002
Error	10	13.923	1.392		
Total	11	39.914			

```
MTB > Name c20 = 'FITS2' c21 = 'RESI2'
MTB > Regress 'Tm' 1 'DrawTemp';
SUBC> Fits 'FITS2';
SUBC> Constant;
SUBC> Residuals 'RESI2'.
```

Regression Analysis

The regression equation is
 $Tm = 164 - 0.0047 \text{ DrawTemp}$

Predictor	Coef	Stdev	t-ratio	p
Constant	164.457	0.824	199.66	0.000
DrawTemp	-0.00471	0.01203	-0.39	0.704

$s = 1.165$ $R\text{-sq} = 1.5\%$ $R\text{-sq(adj)} = 0.0\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	0.208	0.208	0.15	0.704
Error	10	13.569	1.357		
Total	11	13.777			

Regression Analysis

The regression equation is
 $X\%-densi = 49.1 + 0.0742 \text{ DrawTemp}$

Predictor	Coef	Stdev	t-ratio	p
Constant	49.083	1.043	47.08	0.000

DrawTemp 0.07420 0.01523 4.87 0.000

s = 1.474 R-sq = 70.4% R-sq(adj) = 67.4%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	51.615	51.615	23.74	0.000
Error	10	21.739	2.174		
Total	11	73.354			

```
MTB > Name c24 = 'FITS4' c25 = 'RESI4'
MTB > Regress 'n x 10^3' 1 'DrawTemp';
SUBC> Fits 'FITS4';
SUBC> Constant;
SUBC> Residuals 'RESI4'.
```

Regression Analysis

The regression equation is
 $n \times 10^3 = 24.0 - 0.0155 \text{ DrawTemp}$

Predictor	Coef	Stdev	t-ratio	p
Constant	24.0283	0.8650	27.78	0.000
DrawTemp	-0.01548	0.01263	-1.23	0.249

s = 1.223 R-sq = 13.1% R-sq(adj) = 4.4%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	2.247	2.247	1.50	0.249
Error	10	14.965	1.497		
Total	11	17.212			

Regression Analysis

The regression equation is
 $\text{Elongati} = 70.9 + 0.121 \text{ DrawTemp}$

Predictor	Coef	Stdev	t-ratio	p
Constant	70.92	11.40	6.22	0.000
DrawTemp	0.1213	0.1665	0.73	0.483

s = 16.12 R-sq = 5.0% R-sq(adj) = 0.0%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	138.0	138.0	0.53	0.483
Error	10	2598.6	259.9		
Total	11	2736.6			

Regression Analysis

The regression equation is
 Tenacity = 432 - 0.790 DrawTemp

Predictor	Coef	Stdev	t-ratio	p
Constant	432.47	22.99	18.81	0.000
DrawTemp	-0.7901	0.3358	-2.35	0.040

s = 32.51 R-sq = 35.6% R-sq(adj) = 29.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	5853	5853	5.54	0.040
Error	10	10569	1057		
Total	11	16422			

```
MTB > Name c30 = 'FITS7' c31 = 'RESI7'
MTB > Regress 'Y.Stress' 1 'DrawTemp';
SUBC> Fits 'FITS7';
SUBC> Constant;
SUBC> Residuals 'RESI7'.
```

Regression Analysis

The regression equation is
 Y.Stress = 328 + 0.068 DrawTemp

Predictor	Coef	Stdev	t-ratio	p
Constant	327.97	25.81	12.71	0.000
DrawTemp	0.0677	0.3770	0.18	0.861

s = 36.50 R-sq = 0.3% R-sq(adj) = 0.0%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	43	43	0.03	0.861
Error	10	13323	1332		
Total	11	13366			

Regression Analysis

The regression equation is
 Modulus = 3.00 - 0.00998 DrawTemp

Predictor	Coef	Stdev	t-ratio	p
Constant	3.0025	0.2771	10.84	0.000
DrawTemp	-0.009979	0.004047	-2.47	0.033

s = 0.3918 R-sq = 37.8% R-sq(adj) = 31.6%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	0.9335	0.9335	6.08	0.033
Error	10	1.5353	0.1535		
Total	11	2.4688			

Unusual Observations

Obs.	DrawTemp	Modulus	Fit	Stdev.Fit	Residual	St.Resid
4	50	3.271	2.504	0.124	0.767	2.06R

R denotes an obs. with a large st. resid.

- iv) Effect of Draw Speed and Pigments on the Structure and Properties of the Natural and Pigmented PP Filaments

Regression Analysis

The regression equation is

$$Tm = 163 + 1.44 \text{ P Conc.\%} - 0.00785 \text{ D. Speed}$$

Predictor	Coef	Stdev	t-ratio	p
Constant	163.073	0.481	339.35	0.000
P Conc.%	1.4433	0.5019	2.88	0.028
D. Speed	-0.007852	0.003220	-2.44	0.051

s = 0.3549 R-sq = 70.3% R-sq(adj) = 60.4%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	2	1.7907	0.8953	7.11	0.026
Error	6	0.7558	0.1260		
Total	8	2.5464			

SOURCE	DF	SEQ SS
P Conc.%	1	1.0416
D. Speed	1	0.7491

Regression Analysis

The regression equation is

Tenacity = 379 - 0.256 D. Speed - 35.7 Pigment + 85.2 P Conc. %

Predictor	Coef	Stdev	t-ratio	p
Constant	379.067	6.797	55.77	0.000
D. Speed	-0.25630	0.04554	-5.63	0.002
Pigment	-35.700	4.099	-8.71	0.000
P Conc. %	85.20	21.69	3.93	0.011

s = 5.020

R-sq = 98.2%

R-sq(adj) = 97.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	3	7062.3	2354.1	93.42	0.000
Error	5	126.0	25.2		
Total	8	7188.3			

SOURCE	DF	SEQ SS
D. Speed	1	798.1
Pigment	1	5875.3
P Conc. %	1	388.9

Regression Analysis

The regression equation is

Elongati = 37.2 + 0.555 D. Speed + 31.4 Pigment - 96.1 P Conc.%

Predictor	Coef	Stdev	t-ratio	p
Constant	37.150	8.532	4.35	0.007
D. Speed	0.55519	0.05717	9.71	0.000
Pigment	31.433	5.145	6.11	0.002
P Conc.%	-96.07	27.23	-3.53	0.017

s = 6.302

R-sq = 97.3%

R-sq(adj) = 95.6%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	3	7093.7	2364.6	59.55	0.000
Error	5	198.6	39.7		
Total	8	7292.2			

SOURCE	DF	SEQ SS
D. Speed	1	3745.0
Pigment	1	2854.3
P Conc.%	1	494.4

Regression Analysis

The regression equation is

$$Y. \text{ Stress} = 271 - 0.413 D. \text{ Speed} - 22.8 \text{ Pigment} + 64.5 P \text{ Conc.}\%$$

Predictor	Coef	Stdev	t-ratio	p
Constant	270.550	7.966	33.97	0.000
D. Speed	-0.41296	0.05337	-7.74	0.001
Pigment	-22.833	4.803	-4.75	0.005
P Conc.%	64.53	25.42	2.54	0.052

s = 5.883

R-sq = 95.9%

R-sq(adj) = 93.5%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	3	4085.8	1361.9	39.35	0.001
Error	5	173.0	34.6		
Total	8	4258.9			

SOURCE	DF	SEQ SS
D. Speed	1	2072.0
Pigment	1	1790.7
P Conc.%	1	223.1

Regression Analysis

The regression equation is

$$\text{Modulus} = 2.07 - 0.00440 \text{ D. Speed} - 0.213 \text{ Pigment} + 0.775 \text{ P Conc.}\%$$

Predictor	Coef	Stdev	t-ratio	p
Constant	2.06600	0.07208	28.66	0.000
D. Speed	-0.0044000	0.0004830	-9.11	0.000
Pigment	-0.21333	0.04347	-4.91	0.004
P Conc.%	0.7747	0.2300	3.37	0.020

s = 0.05324

R-sq = 96.1%

R-sq(adj) = 93.7%

Analysis of Variance

SOURCE	DF	SS	MS	F	P
Regression	3	0.34612	0.11537	40.71	0.001
Error	5	0.01417	0.00283		
Total	8	0.36029			

SOURCE	DF	SEQ SS
D. Speed	1	0.23522
Pigment	1	0.07875
P Conc.%	1	0.03215

- v) Regression Relationship between the Birefringence and
Tenacity of the Natural and Pigmented PP Filaments

Regression Analysis

The regression equation is

$$\text{Tenacity} = -174 + 24.3 \text{ n x } 10^3$$

Predictor	Coef	Stdev	t-ratio	p
Constant	-174.12	15.56	-11.19	0.000
n x 10 ³	24.3046	0.6962	34.91	0.000

s = 24.84 R-sq = 95.7% R-sq(adj) = 95.6%

Analysis of Variance

SOURCE	DF	SS	MS	F	P
Regression	1	751838	751838	1218.64	0.000
Error	55	33932	617		
Total	56	785770			

Unusual Observations

Obs.	n x 10 ³	Tenacity	Fit	Stdev.Fit	Residual	St.Resid
4	27.6	558.50	497.41	5.20	61.09	2.52R
9	11.1	110.20	95.17	8.19	15.03	0.64 X
14	10.5	107.90	80.35	8.58	27.55	1.18 X
20	11.1	109.30	96.87	8.14	12.43	0.53 X
26	10.9	100.70	89.58	8.33	11.12	0.48 X
29	25.9	395.20	454.15	4.31	-58.95	-2.41R
32	10.2	96.20	74.51	8.73	21.69	0.93 X

VITA

Changhong (James) Yin was born in Shanghai, P. R. China on September 23, 1959. He attended East China Institute of Textile Science and Technology, Shanghai, P. R. China in August 1978 and received the degree of Bachelor of Science in Polymer Engineering in July, 1982. During 1982 to 1984, he worked as a process engineer for Shanghai No. 7 Chemical Fiber Plant. He reentered China Textile University, renamed from East China Institute of Textile Science and Technology, in August, 1984 and in December, 1986 received a Master of Science degree in Polymer Material Science and Engineering. After graduation he worked as a research and development (R & D) engineer for China National Import and Export Commodity Inspection Bureau, Shanghai Branch. In January, 1990 he came to the United States and entered the University of Tennessee, Knoxville and in May, 1996 received a Master of Science degree in Polymer Engineering.

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