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# The effect of pigments on the development of structure and properties of polypropylene filaments

Yiqun Lin

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To the Graduate Council:

I am submitting herewith a thesis written by Yiqun Lin entitled "The effect of pigments on the development of structure and properties of polypropylene filaments." I have examined the final electronic 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:

Donald C. Bogue, Edward S. Clark

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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# THE EFFECT OF PIGMENTS ON THE DEVELOPMENT OF STRUCTURE AND PROPERTIES OF POLYPROPYLENE FILAMENTS

A Thesis
Presented for the
Master of Science
Degree
the University of Tennessee, Knoxville

Yiqun Lin
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# ABSTRACT

The effects of pigment additions on the development of structure and properties of melt spun polypropylene filaments were studied. Two polypropylene resins with melt flow rates (MFR) of 45 and 12 were evaluated and the main portion of the study was carried out on a set of samples containing four different pigments and have three different pigment concentrations. The investigation included the evaluation of the influence of pigments on spinline dynamics and crystallization kinetics during processing by the on-line experimental techniques, the characterization of the as-spun fibers with regard to orientation, crystallinity, birefringence and mechanical properties, the determination of the relative amount of smectic and crystalline monoclinic phases by x-ray diffraction, the observation of morphology of spherulites in polypropylene samples and the study of pigmented samples' thermal behavior by DSC technique.

Several different sets of melt spinning processing conditions were chosen in order to examine the effects of spinning conditions such as take-up velocity, mass throughput on final structure and properties of as-spun pigmented polypropylene filaments.

The results from this research indicated that the pigment additions act as nucleating agents and cause crystallization to occur at higher temperatures and at shorter distances from the spinneret during melt spinning. By nucleating the crystallization at higher temperatures the pigments 1) encourage the formation of monoclinic rather than smectic phase, 2) allow greater opportunity for crystals to grow during subsequent cooling, 3) result in higher levels of crystallinity for a given set of spinning conditions, and 4) reduce the as-spun molecular orientation due to lower molecular orientation in the melt at the point at which crystal nuclei are formed. However, the ability of pigments to act as nucleating agents varies among the pigments. The white and black pigments studied (inorganic pigments) have less effect on nucleating crystallization than the blue and red pigments (organic pigments).

Pigments that produce a marked effect on crystallization kinetics also affect the mechanical properties of the melt spun filaments. Increased nucleating power causes crystallization at higher temperatures in the spinline and causes the as-spun filaments to have lower tenacity and higher elongation to break. The change in mechanical properties increases as the concentration of pigment increases for each pigment.

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# CHAPTER I

# INTRODUCTION

Polypropylene is widely used in the production of fibers for textile and other applications. It is essential for these products to satisfy the aesthetic taste of the consumers in today's competitive markets. Therefore the addition of colors to polypropylene fibers is important. As polypropylene fiber has high crystallinity and contains no dyable sites, the most effective method for coloring polypropylene fibers is melt-pigmentation, in which the pigment is added to the polypropylene melt during the extrusion process. The pigments are organic or inorganic compounds in a finely divided particlate form. It is well known that many organic and inorganic compounds act as nucleating agents for crystallization of polypropylene (1, 2, 3, 4). To date, most of the researches reported in the literature on crystallization, structure and properties of polypropylene fibers have been carried out on natural resins (i. e. without coloration by the addition of pigments). Further, a few studies (5, 6) have indicated that certain pigments may act as nucleating agents during crystallization of polymers.

Since the addition of pigments to polypropylene is likely to affect crystallization behavior and other properties, this research project was carried out to study the effects of pigment additions on the development of structure and properties of melt spun polypropylene fibers.

The objectives of this study were:

1. to examine the influence of the pigment additions on structure formation and crystallization kinetics of melt spun polypropylene filaments;
2. to investigate the relative degree of influence among different pigments;
3. to compare the mechanical properties of pigmented and unpigmented polypropylene filaments;
4. to study the influence of resin molecular weight on the effects that pigments have on the structure and properties of polypropylene filaments;
5. to provide basic information to help control the processing and properties of pigmented polypropylene filaments.

The monofilament melt spinning process and on-line measurement techniques provided a unique way to study the relative crystallization kinetics of polypropylene resins during the process.

# CHAPTER II

# LITERATURE REVIEW

## 2.1 The Coloring and the Pigment Addition

As pointed by Stepek and Daoust (7) coloring is one of the processing steps in the production of many plastic materials. At the beginning of the plastics age, colorants were added to plastics mainly to hide the yellowish or brownish look caused by aging, but, at the present time, they are used mainly for aesthetic purposes. To color plastic material it is important to understand the coloring processes, which are subject to the appreciation of color shades, to the possible changes in the polymer properties during processing, and to the effects of other additives present in the plastic materials(8, 9).

When natural light strikes a piece of plastic material, it can interact with and be modified by the object in many different ways.

1. Absorption. Absorption is the process in which light is converted into heat. Most color effects arise from the absorption of different amount of the incident light at different wavelengths.

2. Scattering. Scattering is the process in which light is

redirected so that some fractions of it are traveling in new directions. Scattering causes objects to be translucent or opaque. Scattering can originate in the crystalline structure of the polymer itself, as well as from added pigment particles. The light emerging from a plastic as a result of the scattering processes inside it is said to be diffusely reflected or transmitted.

3. Reflection. A smooth surface can act as a mirror and the reflected light, following the laws of mirror reflection, leads to gloss. This is called specular reflection. The specular reflected light always has the same color as the light source, whereas the diffusely reflected light has the color of whatever is doing scattering-frequently a colored pigment.

For most polymers, about 4% of the incident light is reflected at each surface when the light is incident perpendicular to the surface, and about 7% when it hits at 45°. So a clear transparent plastic measured with perpendicular incident light can transmit no more than about 92%, the other 8% being reflected from its two surfaces.

If the material absorbs part of the light, it appears colored but may still be transparent; if all light is absorbed, the material appears black. When the light is only slightly scattered, the material is said to be translucent and its color is the result of the combination of the wavelengths going through it. If the scattering is so intense that no light is transmitted, it is said to be opaque. Absorption helps in achieving opacity, and as a limiting case black plastic can be opaque even without any scattering. In both cases the color of the material depends on the amount and kind of absorption present. If there is no absorption, a scattering material looks white; otherwise, it looks colored.

Most plastic materials have a high refractive index between 1.45 and 1.70 and the transmission is in the range of 80-90% of the incident light in the absence of light scattering (10). Because the refractive indexes of amorphous polymers is relatively uniform throughout the object, amorphous polymers have good light transmission. Since crystalline polymers are usually white opaque or translucent due to light scattering, the natural color of polymers varies from water clear for amorphous materials such as PS and PMMA, to white opaque in the case of highly crystalline polymers (HDPE, polyamides, polyformaldehyde, etc.) and yellow amber for those polymers derived from phenolic compounds (7).

## Colorants

Colorants are the substances which can modify the perceived color of objects. They can produce color by selectively absorbing and reflecting specific wavelengths of light energy from the wave bands which constitute natural light. Colorants are used in plastics in one of the following ways: (1) as compounds, where the amount of colorant in the final part (approximately 1.25%) is compounded into the resin and sold and used as such, (2) as dry color, where the colorants are sold as a dry powder consisting of one or more colorants and other additives and the end-user blends the appropriate amount of dry color with resin and produces the final colored part, (3) as pellet concentrates, where the colorants and other additives are compounded into a resin at relatively high percentages (25-50%) and are used in conjunction with virgin resin by the user, and (4) as liquid color, where the colorants become liquid or semiliquid fine dispersions that can automatically be dispensed to a processing machine consistently and efficiently (10). Traditionally, the colorants are divided into two broad classes, dyes and pigment.

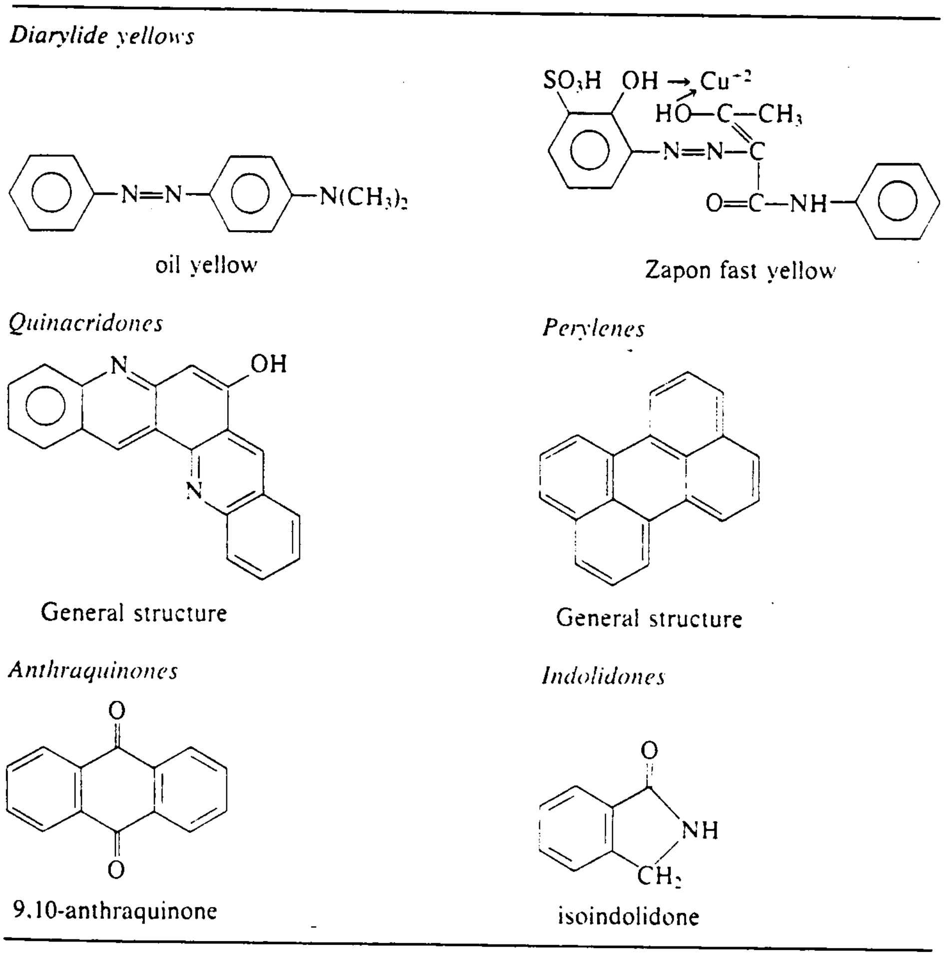
Dyes are synthetic organic chemicals containing one or more chromophores and are soluble in most solvents and in polymers without affecting their transparency (11). They impart color by absorption of selected wavelengths over the visible spectrum (400-700 nm). The solubility of dye gives a molecular dispersion of the dye in the polymer. This property is used to advantage in producing a wide range of transparent colors in some crystalline resins, such as polystyrene, polycarbonate and acrylics.

Pigments are colored substances in a powdered form and are not soluble. For any color other than black, scattering and reflection play an important role. So a main requirement for pigments used to impart color and opacity is that their particle size should be above the wavelength of the light and their refractive index should be much higher than that of plastics (9).

## Pigments

Pigments are divided according to their origin, as inorganic and organic pigments. Both types of pigments are compatible with most plastics. They can be used at loading necessary to produce a wide range of colored products.

Organic pigments usually are complex chemical compounds containing one or more benzene type structures. Some of the organic pigment structures are shown in Figure 2.1. They are characterized by small particle size (<0.1 micron), greater transparency and color strength. Due to the existence of one or more chromophores in their molecular structure, organic pigments have high absorption



*Diarylide yellows*

oil yellow

Zapon fast yellow

*Quinacridones*

General structure

*Perylenes*

General structure

*Anthraquinones*

9,10-anthraquinone

*Indolidones*

isoindolidone

Figure 2.1 Typical Organic Pigments Used in Plastics ( 7 ).

coefficient, but they do not scatter light efficiently due to their small particle size (9).

Organic pigments vary widely in their chemical structure, therefore, they have wide range of color and other properties. The commercially available organic pigments that can be considered for the coloration of plastics (listed in approximate order of the date of their introduction) are(7):

Phthalocyanines
Vats --Authraquinone
 --Thiondigoid
 --Perinone and Perylene
Azo
Dioxazine
Quinacridone
Isoindolinone

The azo pigment class is the largest of organics in terms of both volume of consumption and variety of products available. Their colors are in the yellow, orange and red hues. They are characterized chemically by the presence of an azo chromophore (-N=N-) in the molecule which connects the aromatic groups of varying complexity.

Phthalocyanines form the most important group of organic pigments. They may be divided into blue and green pigments. They have good light stability, good resistance to chemicals, and high tinctorial strength. Their cost is relatively low.

Compared to inorganic pigments, organic pigments are generally lower in specific gravity, higher in surface area, more transparent, clearer in shades, stronger in color and higher in price (although not necessarily more expensive to use) (9).

Inorganic pigments can be either natural or synthetic. They are usually metallic oxides, sulfides, lead salts, cadmium and mercury compounds, and carbon blacks. They are insoluble in common solvents. Compared to organic pigments they are larger in size (2 microns to 5 microns), lower in surface area and denser (specific gravities range from 3.5 to 5.0). They can function by scattering light due to their particle size and shape. They are in general superior to organic pigments in heat and light stability. They are relatively easy to disperse in plastics and are normally used in plastics where opaque or translucent colors are required. Table 2.1 lists some of the important inorganic pigments for the coloration of plastics (12).

The inorganic pigments used in this study to produce colored polypropylene filaments were carbon black and Titanium dioxide ($TiO_2$).

The production of carbon black exceeds that of any other pigments, but only 5 % is used as a pigment; the bulk

Table 2.1 Typical Inorganic Pigments in Plastics (12)

| Common Name | Chemical Cvomposition | Hue |
|---|---|---|
| Cadmium yellow | Mixture of Cds and ZnS | Yellow |
| Cadmium orange | CdSe | Orange |
| Mercadmium pigment | Mixed Cds-Hgs | Orange to maroon |
| Cadmium red | Mixed Cds-CdSE | Red |
| Red iron oxide | $Fe_2O_3$ | Red |
| Brown iron oxide | $Fe_2O_3$ | Buff, brown |
| Yellow iron oxide | $Fe_2O_3 .H_2O$ | Yellow |
| Black iron oxide | $Fe_3O_4$ | Black |
| Chromium oxide, anhyd. | $Cr_2O_3$ | Dull green |
| Cobalt alumium blue | $CoO.Al_2O_3$ | Redish blue to turquoise |
| Chrome yellow | PbCrO4, PbSO4 | Turquoise to lemon yellow |
| Chrome orange | (PbCrO4), (PbO)y | orange |
| Chrome green | Mixture of iron blue and chrome yellow | Green |
| Molybdate orange | PbCrO4, PbSO4, PbMoO4 | Orange |
| Zinc chromate | Basic zinc chromates | Yellow |
| Hititanium yellow | $NiO. 7IO_2$ | Yellow |
| Titanium brown | Titanate | Brown |
| Titanium blue | Titanate | Blue |
| Titanium green | Titanate | Green |

is used in the rubber industry (7). Carbon blacks have a high pigmentation power and they improve many of the physical properties of polymers, such as light stability, processibity, and mechanical properties. Carbon black is produced by two different methods: incomplete combustion of natural gas (channel black), or liquid hydrocarbons (lamp black and furnace black). Channel black has been banned in the United States since 1976. The carbon content of carbon black varies from 90 to 99%. The remainder consists of organic material, mainly hydrocarbon.

Titanium dioxide ($TiO_2$) is the most important white pigment used in plastics. It has well-blanced properties, such as high tinctorial strength, high covering power, good chemical resistance, good heat stability, and relatively low cost (7). Titanium dioxide pigments are produced either from anatase or from rutile grade $TiO_2$. Rutile $TiO_2$ pigments have fine particle size and uniform particle size distribution, so they are the most used for their higher covering power and their better stability for outdoor applications. Anatase $TiO_2$ is cheaper in cost, easier to disperse, but tends to precipitate out of the polymer matrix and has limited outdoor applications because of its tendency to turn yellow.

## 2.2 Structure Characteristics of Polypropylene

Polypropylene is a highly crystalline polymer melting at 165 °C and processed between 205 and 300 °C. It is formed by coordination catalysts of the Ziegler-Natta type. The structure of polypropylene is generally characterized by its molecular weight and its distribution, tacticity, crystalline structures, and morphology.

### Molecular Weight and Its Distribution

In general, commercial polymers are polydisperse in their molecular weight. The molecular weight is generally expressed in terms of number-average molecular weight, Mn, weight-average molecular weight, Mw, or viscosity-average molecular weight, Mv. The polydispersity can be defined as Mw/Mn, which is commonly used in the industry.

Molecular weight distribution is commonly measured by gel permeation chromatography, in which a polymer dissolved in solution, is eluted through a porous bed, with continuous monitoring of change in refractive index of the eluting solvent to obtain a differential curve of molecular size. On the other hand, the quantity $M_w/M_n$ can be used as a useful measure of the breadth of the molecular weight distribution curve. The range of values of $M_w/M_n$ is quite large. Typical values for polymer made with relatively simple polymerization kinetics have $M_w/M_n$ in the range 1.5 to 5 (13).

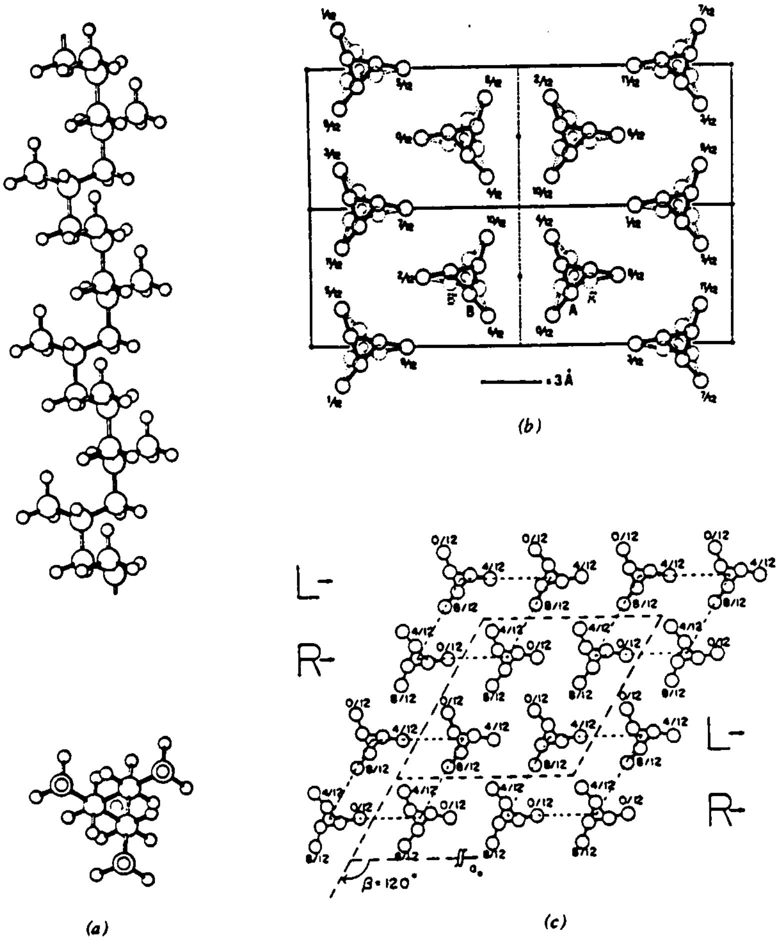
## Tacticity

Highly isotactic content of polypropylene is necessary for production of polypropylene fibers since higher crystallizability and better mechanical properties of the products are attributed to higher isotactic percentages. Commercial polypropylenes generally contain about 95% isotactic diads.

## Crystalline Structure and Crystallinity

The molecular chains of crystalline isotactic polypropylene exist in helical coils in the unit cell. Each repeat unit is 6.5 A long. It is found that lowest energy state is attained for a regular twist such that each chemical repeat unit is rotated by 120° around the helix; that is a 3/1 helix is formed. This symmetrical structure makes possible close-packed, monoclinic crystals, which by x-ray analysis show the following spacing: a=6.65 A, b=20.96 A, c=6.50 A, and $\beta$=99.3° (14, 15).

Polypropylene can exist in different crystal forms, monoclinic or within a limited temperature range and in the presence of certain foreign nuclei, hexagonal (Figure 2.2) (16). Rapidly quenched polypropylene is obtained in a



(a)

(b)

(c)

Figure 2.2 Diagram of (a) Single molecule Helix, and Unit Cells (b) Monoclinic and (c) Hexagonal of Polypropylene (16).

smectic or paracrystalline form, one in which each molecular segment is appropriately twisted but neighboring segments are only aligned rather than being packed well in a lattice. Smectic form converts to the monoclinic form when heated above 60 °C (17). The x-ray diffraction pattern of smectic structure consists of two broad peaks instead of the well known four major peaks of the monoclinic form.

The crystallinity of polypropylene is normally 45-70%.

## Morphological Structure of Polypropylene

The term morphology deals with the various levels of structure displayed by polymers and may be applied to both molecular and macroscopic levels of organization. X-ray diffraction is the preferred technique for investigating the spacing of individual atoms or chains within a crystal. Both transmission and scanning electron microscopy are valuable techniques for examining individual polymer crystals as well as surface topography of polymer samples.

Polymer molecules are several thousand angstroms long and the crystals are tens of thousands of angstroms in lateral dimensions but only 100 A thick. Electron diffraction patterns from individual crystals showed that the molecular chains are more or less perpendicular to the lamellar surface (18). In the single-lamellar crystals the chain then must fold back on itself and reenter the crystal at some other point. This feature of chain folding is characteristic of crystallizable polymers, even in multilamellar crystals and in spherulitic structures formed during crystallization from the melt.

Spherulites are three-dimensional aggregates of single-crystal lamellae. In an optical microscope between crossed polars they show a characteristic Maltese cross pattern in cross-polarized light. They form by nucleation at different points in the sample and grow as spherical entities. Analysis of the Maltese cross patterns has indicated that the molecules are normally aligned tangetially in polymer spherulites. The detailed structure of polymer spherulites can best be studied by electron microscopy because of the small size of the individual crystals.

Crystallization from a stressed-melt, such as in the melt spinning operation, produce a row-nucleated structure (19, 20). Linear nuclei are formed parallel to the strain direction. Secondary epitaxial nucleation on the surface of such linear row nuclei produces folded chain lamellae which are oriented perpendicular to the strain.

The study of structure development of isotactic polypropylene during melt spinning by Sheehan and Cole (21) and Nedella et al (22) showed that after melt spinning into ambient air, polypropylene filaments are highly crystalline and exhibit a monoclinic crystal structure, while by quenching polypropylene filaments into water at low stress levels (low take-up velocities), produces a paracrystalline smectic structure. The study of Lu and Spruiell (23) showed that under the spinning conditions of high cooling rates and low spinline stresses, the smectic structure occurs. The monoclinic crystal structure was formed under the processing conditions of lower cooling rates or higher spinline stresses at a given cooling rate. They observed a transition in the structure of the as-spun filament from smectic to monoclinic as take-up velocity increased for a given polymer. At a given take-up velocity, they observed the structure transition from smectic to monoclinic when the molecular weight of the polymer increased.

## 2.3 Theory of Crystallization Kinetics

### Rates of Nucleation and Growth

In the case of solid nucleating from a liquid, Turnbull and Fisher (17) obtained the rate of the nucleation as follows:

$$N = N_0 \exp[-\frac{(\Delta\phi + \Delta G_j)}{KT}] \qquad (2.1)$$

where $N_0$ is a constant dependent on molecular parameters; $\Delta\Phi$ is the activation energy of transport for a molecule across the phase boundary; $\Delta G_i$ is the critical free energy required to form the critical nucleus.

The overall nucleation rate is determined by the rate of transport of molecules to the nucleation site and the rate of formation of the nucleus. The two rates have opposite temperature dependence. The rate of nucleation increases with decreasing temperature just below the melting point, passes through a maximum, and then decrease with further decrease of temperature. The maximum reflects a competition between the driving force for crystallization, which increases with increasing undercooling, and the molecular mobility, which decreases with increasing undercooling.

The critical free energy term $\Delta G_i$ is expressed as (24, 25, 26, 27)

$$\Delta G_i = \frac{m r^2 r_e}{\Delta G_v^2} \tag{2.2}$$

where m is a constant which depends on the shape of critical nucleus; r is the side surface free enthalpy per unit area, $r_e$ that for the end surface; $\Delta G_v = \Delta h \Delta T / T_m$ is the free enthalpy per unit volume of crystal; $\Delta h$ is the heat of fusion per unit volume at the equilibrium melting temperature $T_m$ and $\Delta T$ is the supercooling.

Heterogeneous nucleation is the nucleation caused or enhanced by the presence of a second phase and occurring at the interface with it. The second phase could be impurities or nucleating agents on which crystallization takes place. It is necessary to introduce interfacial free energies of the heterogeneity in contact with the polymer melt and the crystal for the analysis of the heterogeneous nucleation. Price (26) and Turnbull (28) developed an expression for the rate of heterogeneous nucleation. Their expression may be written

$$N = C\exp[-\frac{\Delta\phi}{kT}]\exp[-\frac{16\pi r_e \Delta r T_m^2}{kT(\Delta h \Delta T)^2}] \qquad (2.3)$$

where C is a constant which is proportional to the critical cluster area, $\Delta r = r_{os} - r_s$, $r_{os}$ is the interfacial energy between the heterogeneity and polymer crystal, $r_s$ is the interfacial energy between the heterogeneity and polymer melt.

The theory of polymer crystallization developed by Hoffman and Lauritzen (25) pointed out that the growth processes in polymer crystallization are controlled by a mechanism of surface-coherent bi-dimensional nucleation.

The growth rate for regular chain folding (adjacent re-entry) and a smooth chain folded surface can be expressed by the equation (25):

$$G = G_0 \exp[-\frac{\Delta\phi}{kT}] \exp[-\frac{4b_0 \pi_e \Delta r T_m^0}{\Delta H_f \Delta T k T}] \qquad (2.4)$$

$\Delta\Phi$ is the activation energy for the transport of molecules across the crystal-liquid interface. Hoffman and Weeks (29) considered that $\Delta\Phi$ is related to segmental mobility of the polymer chain.

## Overall Crystallization Kinetics Under Isothermal Condition

The isothermal crystallization of a polymer can be described by the Avrami equation (30, 31):

$$X(t) = 1-\exp(-kt^n) \qquad (2.5)$$

where X(t) is the fraction crystallized; n is the Avrami index which usually has a value between 1 and 4, and the value of n is characteristic of the nucleation and growth mechanism of the crystalline phase (23, 24); k is the rate constant, largely dependent on the temperature of crystallization.

The overall rate of crystallization combines two aspects, the nucleation rate and growth rate which may be influenced by material characteristics and processing parameters.

## Crystallization Under Non-isothermal Conditions

The transformed weight fraction X(t) in non-isothermal crystallization can be treated by the following equation which resembles the Avrami equation (32, 33, 34):

$$X(t) = 1 - \exp[-(\int_0^t K(T)\,dt)^n] \qquad (2.6)$$

where $K(T)=k(T)^{1/n}$, and n and k(T) are the Avrami index and the isothermal crystallization rate constant, respectively.

The cooling rate may influence the degree of crystallinity and also has a marked effect on the crystalline structure of the fiber. The effect of cooling rate on the crystalline structure of polypropylene has been reported (35). At high quenching rate the polymer solidifies practically completely to a paracrystalline, thermodynamically less stable structure while at low quenching rate, the fiber structure develops into monoclinic order.

## 2.4 Crystallization Kinetics in Melt Spinning Process

In the melt spinning process crystallization takes place under stress and non-isothermal conditions. In the melt spinning process, temperature is a function of position along the spinline. The crystallization in the melt spinning is also very sensitive to molecular orientation in the amorphous phase and the molecular orientation in the spinning fiber is essentially a function of the spinning stress (22). So the rate of cooling and the spinning stress along the spinline may affect the morphology of as-spun fiber structure in a vary complex manner. Changes of material parameters, and the spinning conditions may have great influence on the structure development of polypropylene fibers in the melt spinning process.

Ziabicki and Kedjierska (36, 37, 38) were the earliest investigators to publish x-ray patterns and birefringence data of melt spun fibers and showed that orientation of molecules increased with spin stress. Spruiell and coworker (19, 22) conducted x-ray diffraction studies along the spinline of polypropylene and polyethylene filaments. They concluded that spinning variables such as polymer molecular weight, mass flow rate, melt temperature, and take-up velocity all affect the morphology of the spun filaments, but the combination of these effects on morphology can be traced to their effect on spinline stress. SAXS studies (20, 22, 39) of polypropylene filaments showed a continuous ring of nearly uniform intensity at low take-up velocities. As the take-up velocity increases, the SAXS patterns change to "two-point" patterns. Spruiell and coworkers (19, 39) have interpreted these features to indicate spherulitic morphology at very low spinning stress which undergoes a transition to a row-nucleated or cylindrical morphology as the spinning stress increases.

Oda, White and Clark (40) proposed that the birefringence is proportional to the stress. Nadella, Henson, Spruiell, and White (22) studied the structure development of melt-spun polypropylene. They found that the orientation factor increases steadily with the take-up velocity and that the value of $f_c$ increases with spinline stress, leveling off at 0.9, which indicates that the c-axes are tending to become more aligned with the fiber axis with increasing stress. Minoshima, White and Spruiell (41, 42) studied the influence of molecular weight distribution on the spinline elongational viscosity in isothermal melt spinning. They proposed that different melt spinning elongational viscosity functions will result in different spinline stress and that higher stress levels will lead to higher spinline birefringences and higher spun fiber birefringences and crystalline orientation.

## 2.5 Nucleating Agents and Their Effect on Crystallization

Nucleating agents are small crystalline particles that are dispersed in the crystallizing melt and remain solid at the crystallization temperature. Examples of nucleating agents are some inorganic or organic crystalline matter, which is finely dispersed in the polymer melt. They act as heterogeneous nuclei and increase the number of nuclei at a given crystallization temperature (1). During continuous cooling, such as occurs in many polymer processing operations, nucleating agents cause crystallization to start at lower supercooling. The spherulitic morphology resulting from nucleating agents is small in size, like the ones normally obtained at low crystallization temperature (without nucleating agent).

There are some practical reasons for the use of nucleating agents in polymer products. Some examples are described as follows.

1. Control of optical properties of products: In some processing of polymers, cooling results in lower surface temperature, thus produces grainy morphology, and higher

core temperature with larger spherulites. Nucleating agents make the core morphology more grainy, producing more uniform spherulitic size distribution. In this case, the optical uniformity can be obtained (2).

2. Control of mechanical properties: Grainy spherulitic structures are mechanically ductile and may have lower modulus because of the great number of molecular ties and amorphous regions between the small spherulites. Large spherulitic structures result in higher modulus and lower ductility (2,43).

3. Coloring of plastic products: If pigments were used for coloring, some pigments may act as nucleating agents (12).

Binsbergen (3) has carried out a detailed study of the chemical and physical nature of the nucleating agents. He indicated that the effectiveness of a given substance depends both on the nature of the heterogeneous surface and its dispersion in the polymer melt. He found that among the more effective nucleating agents are alkali metals or aluminum salts of aromatic or alicyclic carboxylic acids.

Inonue (1) studied the effect of nucleating agents on the kinetics of isothermal crystallization of nylon 6 in the temperature range of 180-205°C. Inoue found an increase in the crystallization rates associated with a decrease of the induction period of crystallization. The spherulites are homogeneously distributed and are smaller in size. He also found that the size of spherulites varied depending on the crystallization temperature (crystallization at high temperature produced large spherulites, whereas at low temperature small spherulites are obtained; however, the size of the spherulite was almost independent of crystallization temperature in the nucleated polymer (1).

Beck and Ledbetter (4) reported that in polypropylene the degree of supercooling, polymer morphology, clarity and tensile properties may be altered by the presence of deliberately added heterogeneous foreign agents. Increase in the concentration of nucleating agent increases the nucleation rate with greatest effects occurring at low concentration of nucleating agent.

Wlochowicz et al (5) used IR-absorption technique to investigate the influence of pigments on the crystallization process of melt-pigmented polypropylene films. The results showed that the crystallization half-time had a considerable change depending on the type of pigment applied and they concluded that the crystallization process of colored PP is mainly determined by the time-dependent occasional formation of crystal nuclei.

Tueturro et al (6) studied crystallization kinetics and morphology of high density polyethylene containing organic and inorganic pigments. The experimental results showed that only organic pigments increase the crystallization rate, by acting as nucleating agents. And in these cases, moreover, the crystalline spherulite was smaller in size and the morphology of polyethylene was changed due to the addition of the pigments.

# CHAPTER III

# MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURES

## 3.1 Materials and Preparation

The resins used in this study were isotactic polypropylenes, provided by Exxon chemical Company. Two isotactic polypropylene resins were studies, one with a melt flow rate (MFR) of 45 (the code we gave was PP-1) and the other with a melt flow rate of 12 (with the code of PP-2). Some characteristics of these resins are summarized in Table 3.1 (44). The primary color concentrates studied were supplied by Standridge Color Corporation. Four pigments having the colors white, black, red and blue were supplied. The red and blue pigments were organic pigments and the white and black pigments were inorganic pigments. The loading of pigments in the color concentrates ranged from 25% to 50%. Some information about these color concentrates is given in Table 3.2 (45). An attempt was made to prepare these concentrates using only the same MFR polypropylene resin used in our study as a carrier resin. This apparently was not possible in the case of the phthalyl blue pigment as subsequent examination by DSC and infrared spectroscopy indicated the presence of small amounts of polyethylene wax

Table 3.1 Polypropylene Resin Information

| Code | PP-1 | PP-2 |
|---|---|---|
| MFR | 45.6 | 12 |
| Intrinsic Viscosity | 1.036 | |
| $M_w$ | 138993 | 179200 |
| $M_n$ | 65241 | 67400 |
| $M_w/M_n$ | 2.16 | 2.66 |

Table 3.2 Pigment Master Batch Information

| Color | Loading (%) | Comments |
|---|---|---|
| White | 50 | $TiO_2$ rutile |
| Black | 25 | Cabot 660 furnace black |
| Red-brn | 25 | Ciba Geigy |
| Phthalyl blue | 25 | Red shade |

in this color concentrate master batch. Sixteen additional pigment samples were supplied. These later samples were not studied as extensively, but were used to examine the generality of the results found for the primary color concentrates.

Materials for melt spinning were prepared according to a major experimental plan illustrated in Figure 3.1. For each of the four color concentrates studied, three samples were prepared with the pigment concentrations of 0.05%, 0.5%, and 1.0% by weight, these samples were each spun into colored filaments. Also natural PP samples were directly fed into the extruder through the hopper of the spinning machine to obtain natural PP filaments.

## 3.2 Melt Spinning

### Melt Spinning Equipment

The melt spinning was carried out using a melt spinning machine designed and manufactured by Fourne Associates of west Germany (Figure 3.2). The Fourne extruder has a single screw of 13 mm diameter and 300 mm length. The extruder is equipped with a nitrogen purged hopper with a seven liter capacity. Along the barrel there are two independently controlled band-type heaters. The spinning head also has two independently controlled band

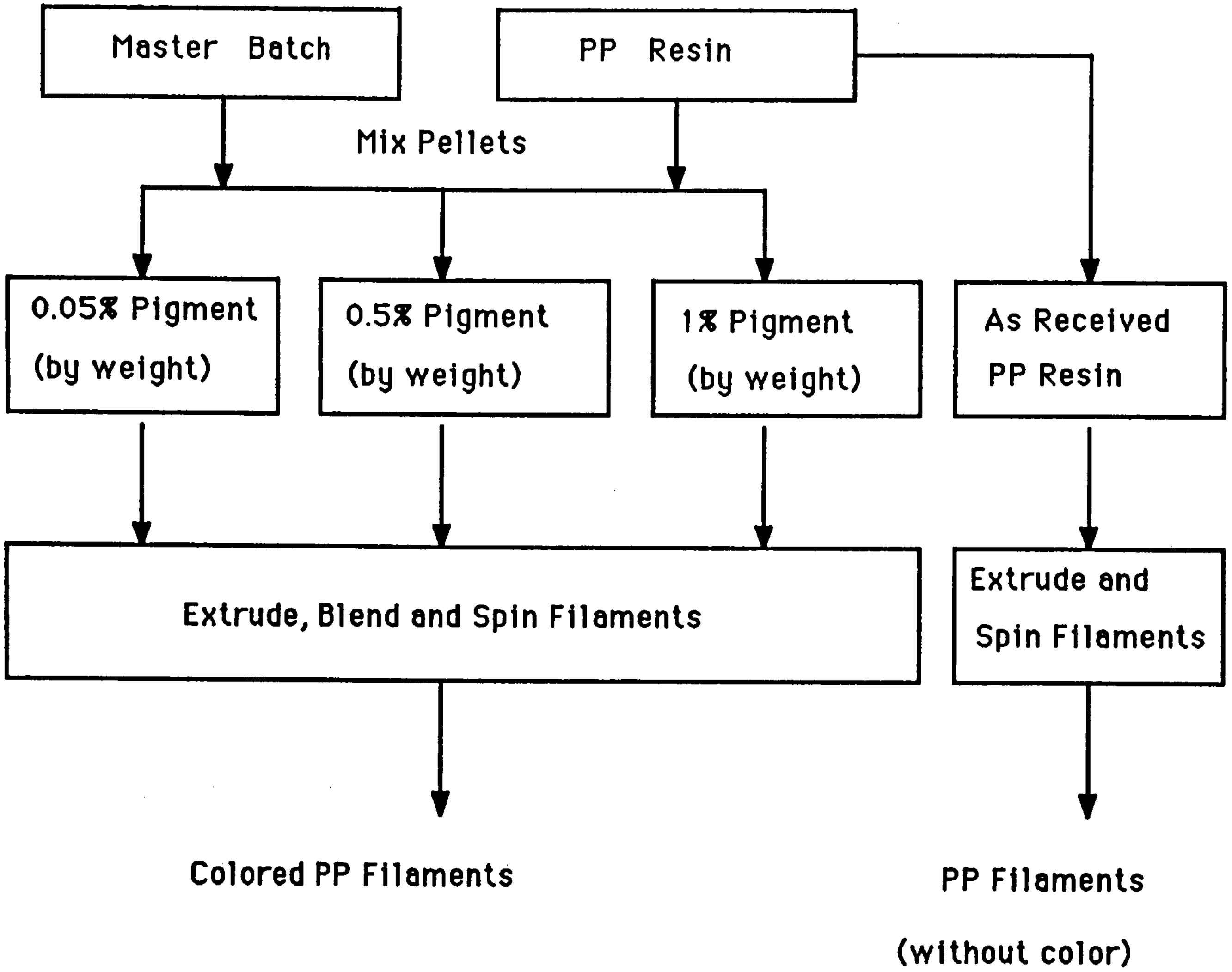


Figure 3.1 Major Experimental Plan for Making Pigmented and Natural Polypropylene Filaments in This Study.

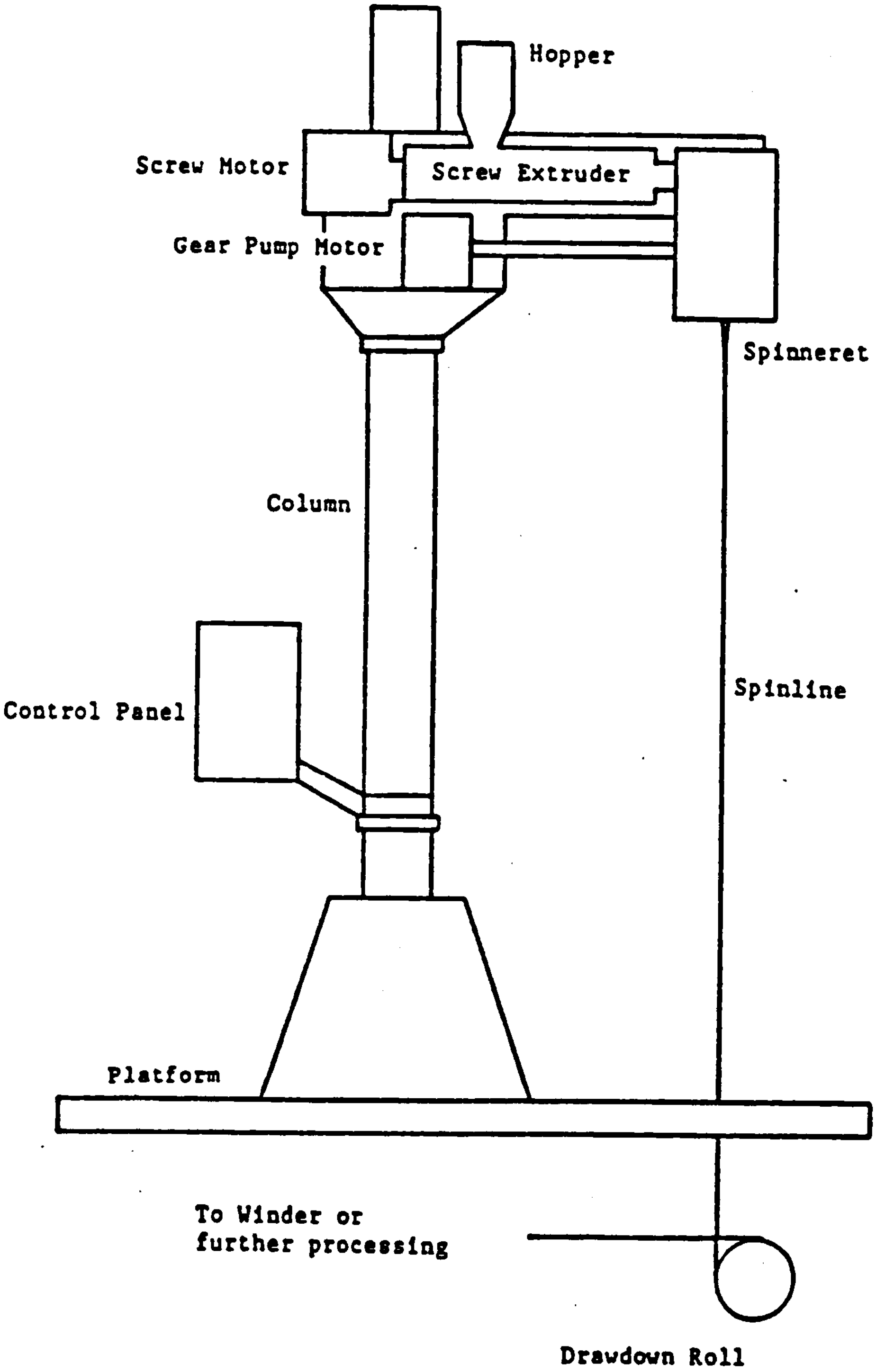


Figure 3.2 Schematic of the University of Tennessee's melt spinning equipment.

heaters similar to those on the barrel. The extruder receives polymer pellets by gravity and supplies molten polymer at a pressure of $1.0 \times 10^3$ to $3.0 \times 10^3$ psi to a gear pump (Zenith) which maintains a constant mass flow rate through the spinneret. The throat of the extruder was cooled by running water to prevent molten polymer from backwashing into the hopper feed section. The discharged polymer stream from the gear pump is forced to pass through a 325 mesh filter screen and through a single capillary die which has a diameter of 0.762 mm and a L/D ratio of 5.0.

The polymer temperature in the discharged stream was measured by two platinum-resistance thermometers which are placed in the polymer stream. The temperature readings are indicated on a meter on the control panel. The melt pressure is indicated by a Dyanisco pressure gauge. To obtain the desired mass flow output of the polymer melt, the gear pump speed is manually adjusted by means of a variable speed gear box. Once set, the flow rate remains constant.

The entire assembly of the screw extruder and spinning head block is mounted on a vertical steel column. The spinline length can be easily changed by moving the assembly up and down along the column.

The filament exiting the die is cooled by air and drawn down by a take up device (godet, provided by

Monsanto) which has the capability of producing take-up velocities up to 5,000 m/min. The filament is then wound-up onto a bobbin under constant tension using a Leesona winder.

Melt Spinning Processing Conditions

The general spinning conditions selected in this research are listed in Table 3.3 and Table 3.4. These conditions were chosen in order to be quite similar to commercial spinning conditions and resulting fiber deniers (12 denier).

To investigate the effects of processing conditions on the structure and properties of both natural and pigmented PP filaments, the effects of changing mass throughput and take-up velocity were studied in this project.

1. Filaments of natural PP-1, natural PP-2, 0.5% red pigmented PP-1, 0.5% red pigmented PP-2 and 0.5% black pigmented PP-2 were melt spun with the mass throughput of 1.5, 2.0, 2.5 and 3.0 g/min at a constant take-up velocity (1400 m/min). All the other conditions were kept constant as described in Table 3.3 for PP-1 filaments and Table 3.4 for PP-2 filaments.
2. Filament of natural PP-1, natural PP-2, 0.5% red PP-1, 0.5% red pigmented PP-2 and 0.5% black PP-2 were melt spun with the take-up velocities of 700, 1400, and 1700 m/min.

Table 3.3 Processing Conditions for the Melt Spinning of PP-1 Filaments

| | |
|---|---|
| Take-up velocity | 1400 m/min |
| Mass throughput | 2.0 g/min/hole |
| Spinline cooling | static ambient air |
| Extrusion temperature | 210 °C |
| Spinline length | 4.3 m |
| Spinneret hole diameter | 0.762 mm |

Table 3.4 Processing Conditions for the Melt Spinning of PP-2 Filaments

| | |
|---|---|
| Take-up velocity | 1400 m/min |
| Mass throughput | 2.0 g/min/hole |
| Spinline cooling | static ambient air |
| Extrusion temperature | 220 °C |
| Spinline length | 4.3 m |
| Spinneret hole diameter | 0.762 mm |

In this case the mass throughput was adjusted whenever necessary to keep constant filament diameter (12 denier). All the other conditions were kept constant as described in Table 3.3 for PP-1 filaments and Table 3.4 for PP-2 filaments.

### Melt Spinning Procedure

Trial spinning runs were carried out to determine the optimum processing parameters. Experimental parameters to be decided included: temperature settings for each of the four heated zones, correct metering pump speed to achieve the desired mass throughput, correct screw speed to maintain melt pressure at the chosen metering pump setting, and godet speed required to produce a chosen filament velocity.

A typical run began with the loading of the polypropylene pellets or the mixture of PP and pigment concentrate pellets into the hopper. The heaters and the cooling water were turned on nearly two hours before equipment operation to reach the desired processing condition. Before starting the extruder and the gear pump motors, both the extruder screw and gear pump were checked for free, unhindered rotation. Then the gear pump motor was turned on first, followed by turning on the screw motor. With the gear pump speed setting in the desired value the screw speed was gradually increased until the pressure between the extruder and the gear pump was in the range of 1,000 to 2,000 psi. The mass throughput was checked by cutting the threadline at certain time interval and weighing the output on a balance. Once the spinline was set the machine was allowed to run for several hours to get a stable spinline before the winding of the bobbins.

The take-up velocity was contolled by adjusting the speed of the take-up device.

## 3.3 On-line diameter Measurement

The on-line diameter measurement, developed by Bheda (46), was carried out by using a Zimmer system (Diameter monitor model 460/2, digital controller model 466/2) manufactured by Zimmer OHG, West Germany. A schematic of the Zimmer and its operating principle is presented as Figure 3.3. Its operation is based on a non-contact back illumination principle which permits measurement of both opaque and semitransparent materials. Illumination was provided by light emitting diode which generated light at the wavelength of 390 nm. The Zimmer diameter monitor can measure diameters ranging from 0 to 2 millimeters, with a resolution of 0.5 micrometers. The displayed diameter is a reading averaged over 11 millimeters of filament length.

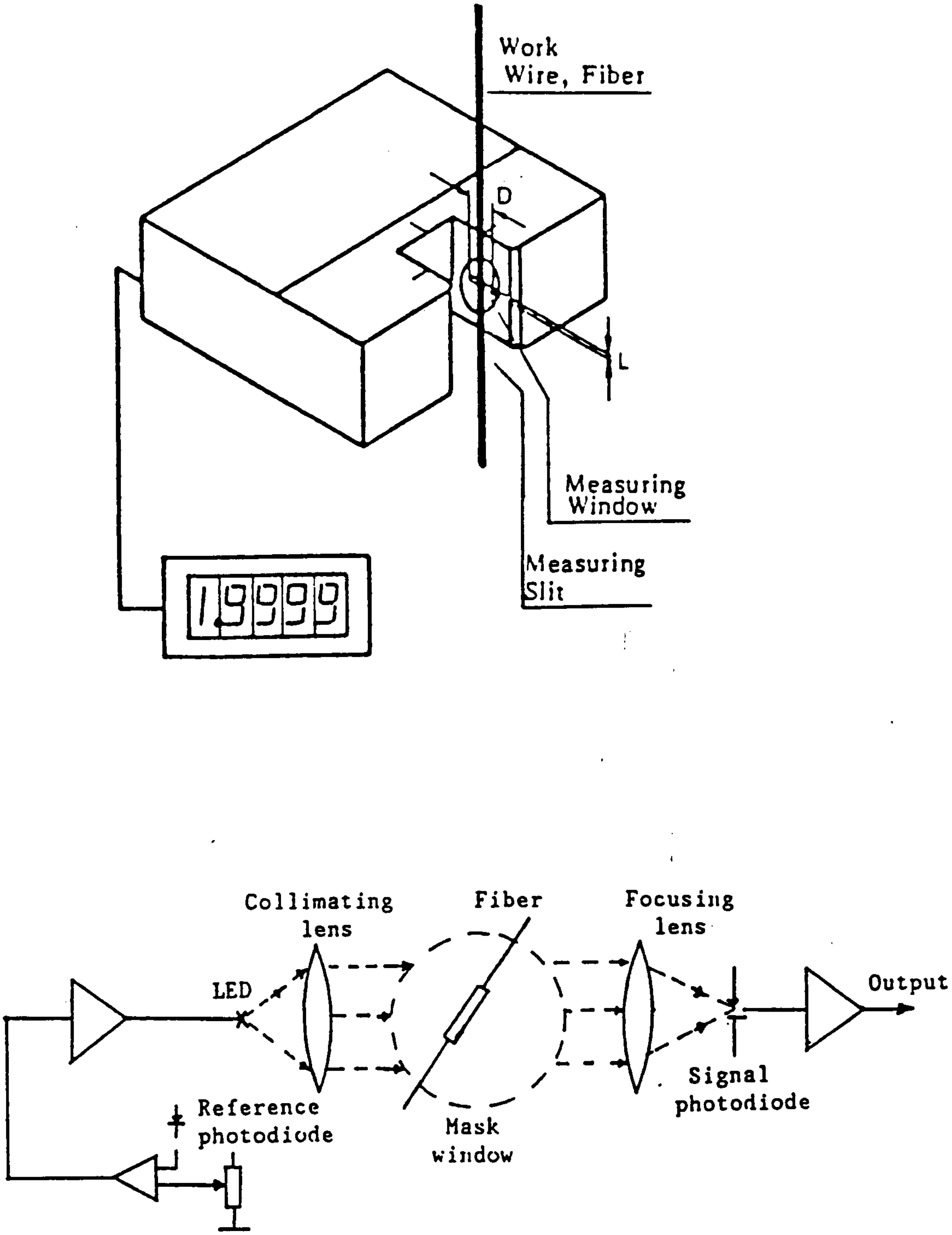


Figure 3.3 The Zimmer diameter monitor and its operating principle.

Because the diameter value on the spinline was a function of the variations in the melt spinning process, such as the variation in throughput rate, take-up tension, extrusion temperature, etc., an IBM-XT personal computer was interfaced with the Zimmer system to collect and store data over a certain period of time. Typically, two thousand diameter values ware collected by the computer within twenty seconds at each position at 10 centimeter intervals along the spinline. To process the data a computer program was used in which the operator must specify the diameter range and minimum number of occurrences required per diameter for that diameter to be included in the overall averaging process. Since the neat polypropylene and pigmented polypropylene filaments were semitransparent, the mean diameter, once calculated, was then corrected for fiber transparency. A transparency correction equation was formed which gave the relation between the diameter values measured by an Olympus microscope and by the Zimmer system. From the correction equation the transparency correction factor can be determined.

In the experiments the Zimmer monitor was mounted on a movable stand which can be moved to any position along the spinline. Before the measurement the instrument was zeroed and then calibrated with wire standards (purchased from Zimmer OHG). The measurement started at the bottom position of the spinline close to the take-up device, and moved up at intervals of 10 centimeters until reaching the position 10 centimeters from the spinneret.

## 3.4 Property Characterization

### Density and Crystallinity

The density of the as-spun filament was determined using a density gradient column prepared in the laboratory. Standard laboratory procedure was followed in preparing the column. (Consult Appendix A of Wust's Ph. D. dissertation (47) for a step-by-step outline of density gradient column preparation.) The solution in the density gradient column was prepared by mixing water and isopropyl alcohol at 23 °C according to ASTM standard D1505-68. The column was calibrated using glass beads of known density. Density readings of the samples were taken 24 hours after the samples were put into the column so that the samples had reached their equilibrium position.

It was assumed that there were three phases existing in pigmented filament, namely crystalline, amorphous and pigment, and that each had a distinct density. In calculation of crystallinity of the samples the following equation was derived assuming the existance of distinct phases.

$$\theta = \frac{\frac{1}{\rho} - \frac{1}{\rho_a} - c_p\left(\frac{1}{\rho_p} - \frac{1}{\rho_a}\right)}{(1 - c_p)\left(\frac{1}{\rho_c} - \frac{1}{\rho_a}\right)} \qquad (3.1)$$

where $\vartheta$ is the crystallinity of the filament sample, $\rho_a$ is the density of amorphous phase (for polypropylene, $\rho_a = 0.854$ g/cm$^3$), $\rho_c$ is the density of crystalline phase (for polypropylene, $\rho_c = 0.932$ g/cm$^3$), $\rho_p$ is the density of the pigment, $c_p$ is the pigment concentration and $\rho$ is the measured density of the sample. Since we do not have information of the exact chemical content for the pigments, we estimated the density of the pigments by searching some literature (5) as follows: $\rho_p = 1.5$ g/cm$^3$ for red pigment, $\rho_p = 1.8$ g/cm$^3$ for blue pigment, $\rho_p = 1.8$ g/cm$^3$ for black pigment and $\rho_p = 3.9$ g/cm$^3$ for white pigment.

## Wide Angle X-ray Diffraction

Wide angle x-ray diffraction scans of the filament samples were obtained using a Rigaku diffractometer with nikel filtered CuK$\alpha$ radiation of wavelength 1.542 A. the X-ray unit was operated at 40 kV and 20 mA. The filament was wound on a glass plate so that all fibers were parallel. The glass plate was then mounted on the x-ray diffractomer unit so that the fiber axis was normal to the x-ray beam.

## Birefringence and Orientation

The total birefringence of the filament was measured using an Olympus polarizing microscope (Model No. 206080) and Olympus 4 order Berek compensator (Model No. CTPI-200105). Birefringence measurements were taken with the polars crossed and the axis of the fiber oriented perpendicular to the insertion direction of the compensator. At the zero reading on the compensator a black band was observed across the field of view. When a birefriengent fiber was brought into view the black band within the fiber 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 retardation was calculated from the compensator reading and the brifringence was calculated by dividing the retardation by the fiber diameter. Thus

$$\Delta n = R/d \qquad (3.2)$$

where $\Delta n$ is the fiber brifringence, R is the retardation reading, d is fiber diameter.

## Differential Scanning Calorimetry

A Perkin-Elmer DCS 7 Thermal Analysis Difference Scanning Calorimeter was used to measure the quiescent crystallization kinetic behavior of the polypropylene resins and pigmented PP samples collected after extrusion. 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 non-isothermal DSC experiments the samples were heated to 210 °C and held for ten minutes to allow the samples to become completely molten; then they were cooled to 80 °C at rate of 20 °C/min.

## Observation of Morphology of Spherulites

Observation of morphology of spherulites for natural unpigmented PP and pigmented PP samples were made using a Mettler FP-82 hot stage, mounted on a Olympus microscope equiped with a 35 mm camera, with heating and cooling being contolled by a Mettler FP-82 unit. The microscope was used in the polarizing mode and the 35 mm camera was used for photographic recording. The extrudate samples were preheated at 210 °C for 10 min prior to cooling to the chosen isothermal crystallization temperature. The observation of spheruilites under isothermal crystallization was made at 132 °C and 140°C, respectively.

Non-isothermal crystallization was also carried out by cooling from 210 °C to room temperature at a rate of 20 °C/min.

### Instron Tensile Tester

The mechanical properties of natural unpigmented and pigmented as-spun fibers were measured by using a table model Instron Tensile Tester at 21 °C and 65 % RH. Fifteen tensile tests were carried out for every filament type and condition tested. This provided sufficient data to obtain a reliable average value of the calculated properties. According to ASTM standard D3382, a gauge length of 25.4 mm and crosshead velocity of 50 mm/min were used.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Effect of Pigments on the Structure of As-spun Polypropylene Filaments

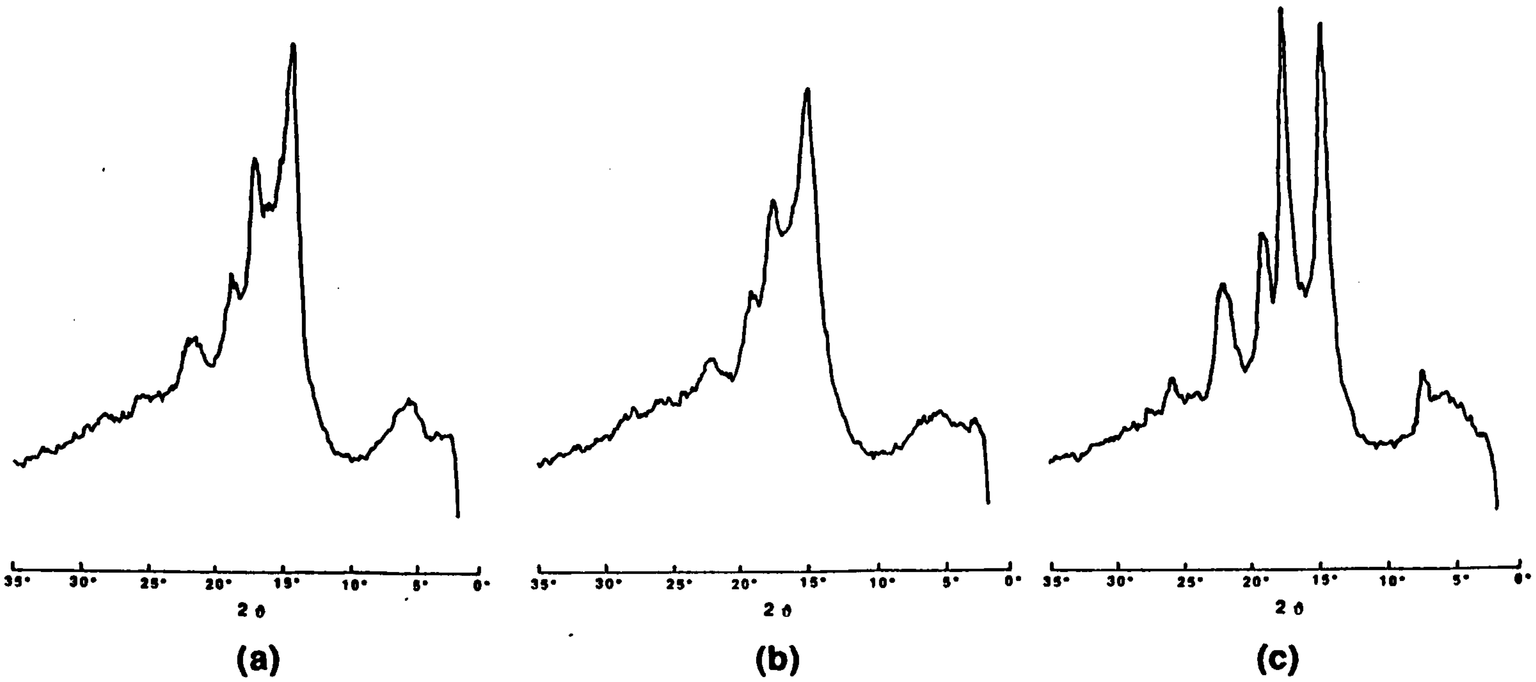
The effects of pigments on the structure of as-spun PP filaments were studied by the techniques of wide angle x-ray diffraction, density, birefringence, optical microscopy, differential scanning calorimetry, on-line measurement and mechanical tests.

### Wide Angle X-ray Diffraction

Wide angle x-ray diffractometer scans of as-spun PP filament samples are shown in Figure 4.1 to Figure 4.10.

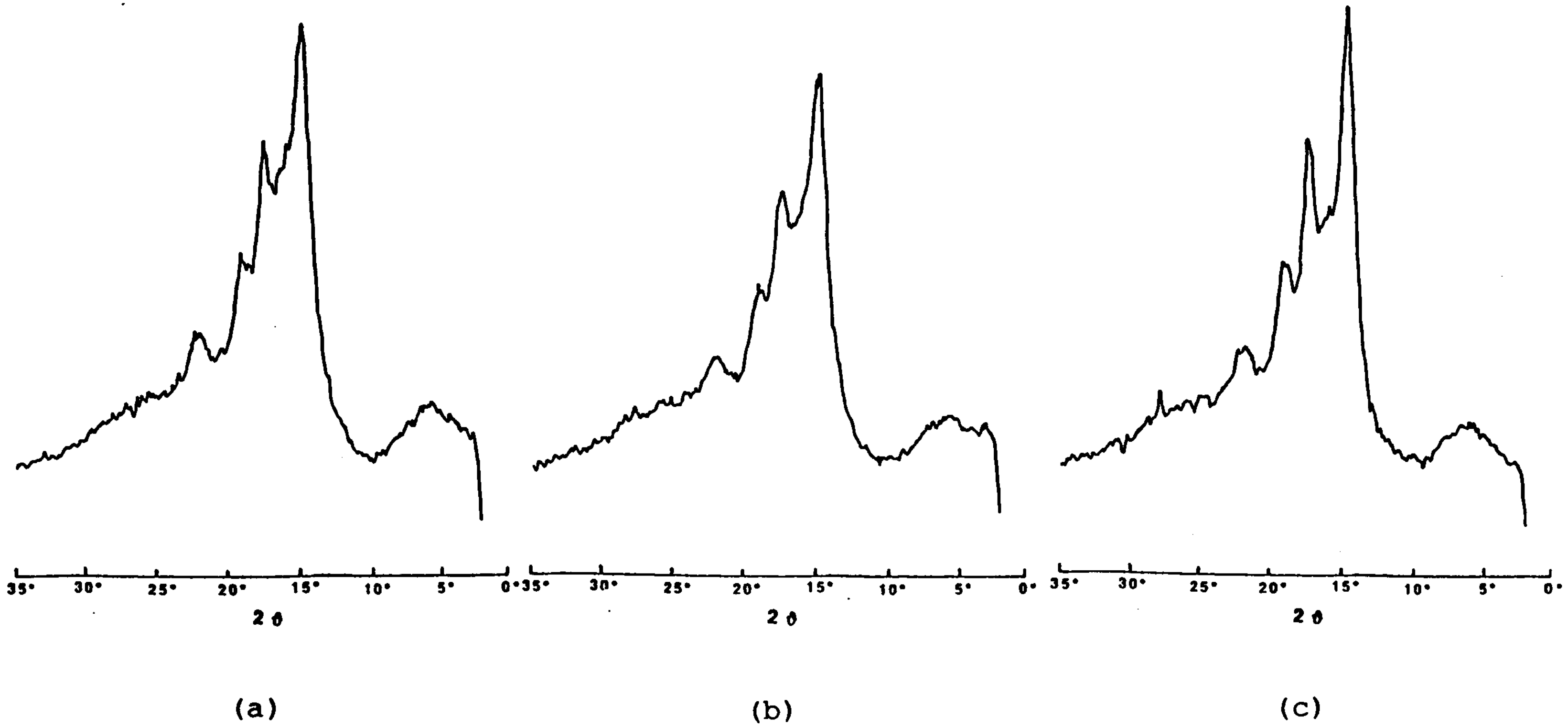
It is known that a metastable smectic phase is formed on fast quenching of isotactic polypropylene from melt to solid state (21) and in some melt spun samples of unpigmented, natural polypropylene homopolymers (23, 48) spun under conditions similar to those used in the present study. The presence of smectic phase is detected by broadened, poorly developed x-ray reflections (21, 23, 49). Such broadening of the x-ray reflections is evident in the diffractometer scans for the unpigmented natural polypropylene with MFR =45 (PP-1) and the white pigmented polypropylene (PP-1-White) samples as shown in Figures 4.1a and 4.1b. The blue pigmented filament (PP-1-Blue) shows more distinct diffraction peaks from the (110), (040) and (130) reflections of the monoclinic phase, Figure 4.1c. Red pigmented (PP-1-Red) samples exhibited diffraction patterns (Figure 4.4) similar to those of the blue pigmented samples (Figure 4.3), while the x-ray patterns from the black pigmented (PP-1-Black) samples (Figure 4.5) were more similar to those of the white pigmented samples (Figure 4.2). This indicates an increase in monoclinic phase and, probably a decrease of smectic phase with increased pigment concentration. The above results suggest that the pigment acts as a nucleating agent for crystallization during the spinning processing and the structural formation of the filament is influenced by the pigment. Also, these results suggest that different pigments have different nucleating power for crystallization. In this case blue and red pigments have more nucleating power than that of white and black ones. In the remainder of this thesis we will examine the available data for consistency with this hypothesis.

There was also an effect of pigment concentration on the structure of the filaments as shown in Figures 4.2 through 4.5. For example, the pattern of 0.05% red



(a) (b) (c)

Figure 4.1 Wide Angle X-ray Diffractometer Scans of (a) Natural PP-1, (b) 0.5% White Pigmented PP-1 and (c) 0.5% Blue Pigmented PP-1 Filaments.



(a) (b) (c)

Figure 4.2 Wide Angle X-ray Diffractometer Scans of (a) 0.05% White Pigmented PP-1, (b) 0.5% White Pigmented PP-1 and (c) 1.0% White Pigmented PP-1 Filaments.

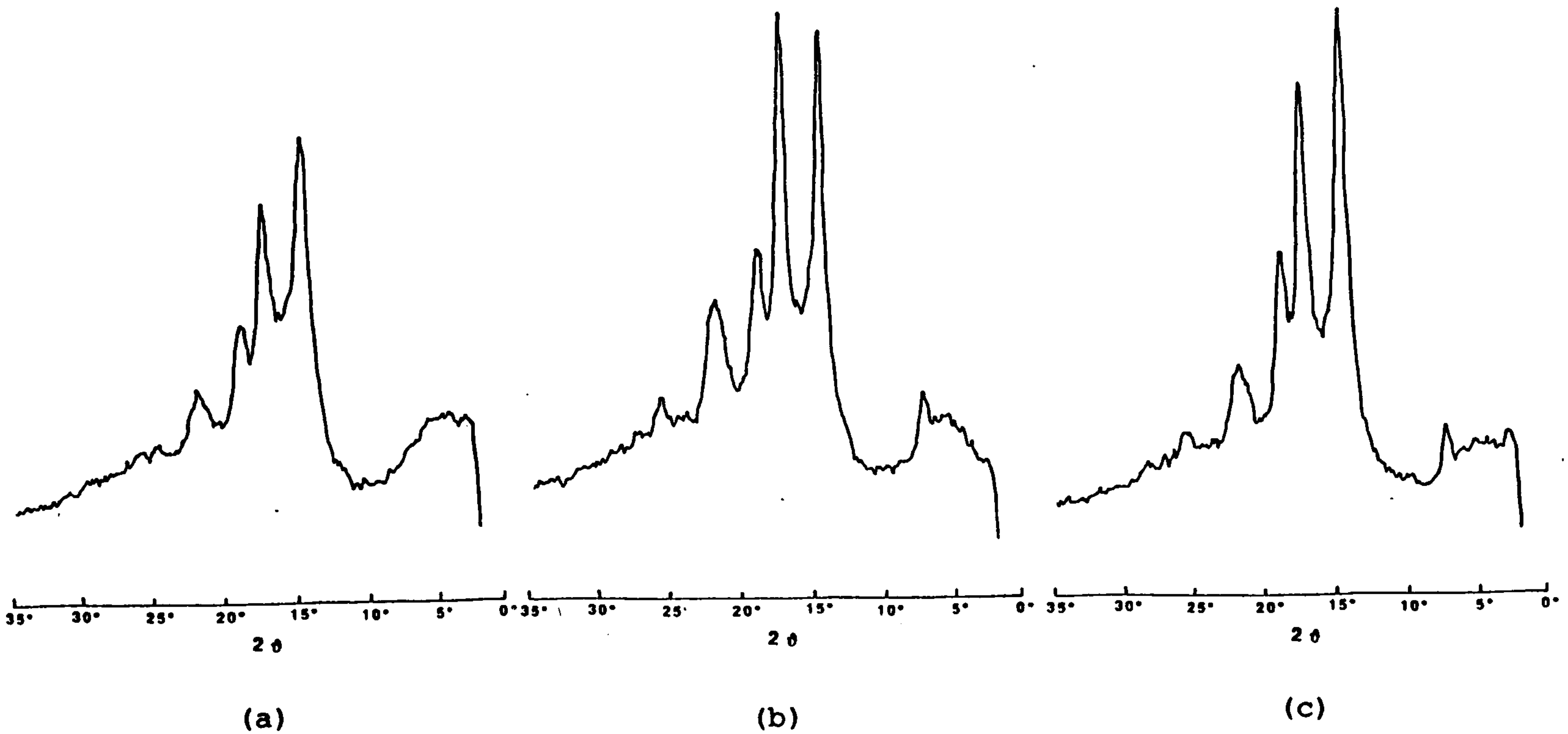
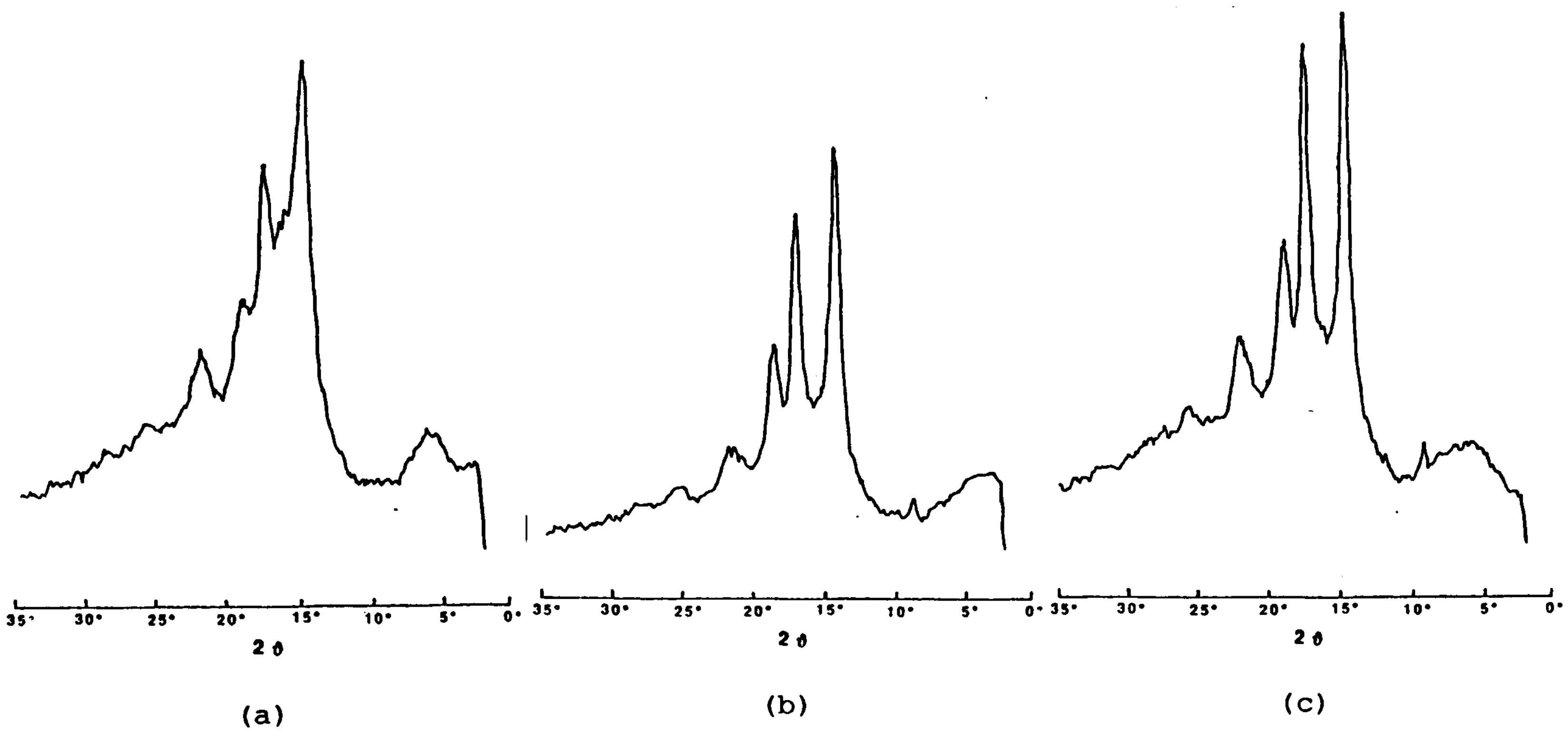


Figure 4.3 Wide Angle X-ray Diffractometer Scans of (a) 0.05% Blue Pigmented PP-1, (b) 0.5% Pigmented PP-1 and (c) 1.0% Blue Pigmented PP-1 Filaments.

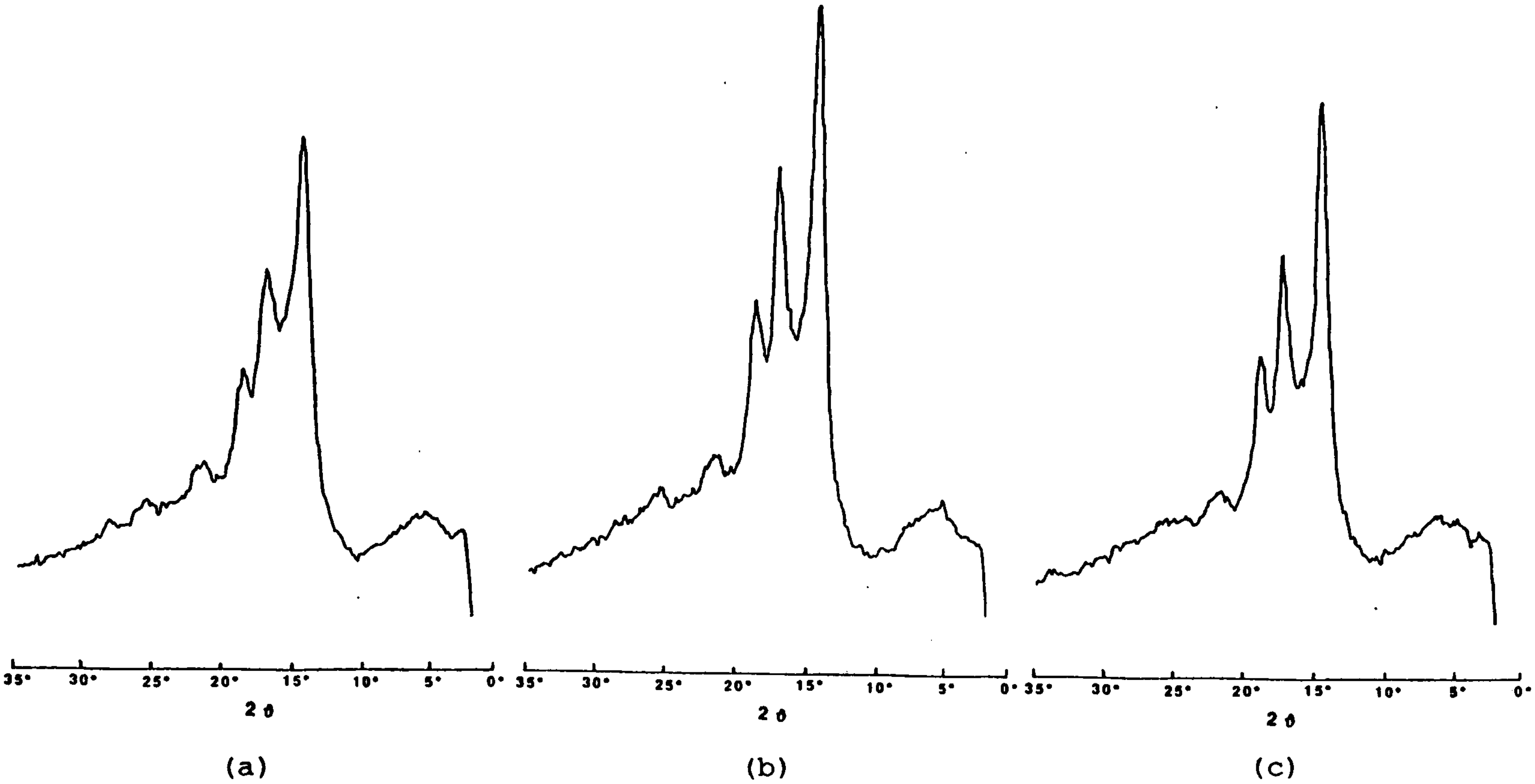


(a)

(b)

(c)

Figure 4.4 Wide Angle X-ray Diffractometer Scans of (a) 0.05% Red Pigmented PP-1, (b) 0.5% Red Pigmented PP-1 and (c) 1.0% Red Pigmented Filaments.



(a) (b) (c)

Figure 4.5 Wide Angle X-ray Diffractometer Scans of (a) 0.05% Black Pigmented PP-1, (b) 0.5% Black Pigmented PP-1 and (c) 1.0% Black Pigmented Filaments.

pigmented filament (PP-1-Red-0.05) (Figure 4.4a) shows little difference from that of natural unpigmented PP (PP-1) (Figure 4.1a), but as concentration of red pigment increases the patterns tended to change from the pattern in Figure 4.1a toward that in Figure 4.1c as pigment concentration was increased.

Figure 4.6 presents wide angle x-ray diffractometer scans for natural unpigmented PP-1 filaments spun under different mass throughput (at constant take-up velocity of 1400 m/min). Figure 4.6 clearly shows that the ratio of smectic phase to monoclinic phase increases with an increase of mass throughput. Since the stress level in the spinline increases with decrease of mass throughput, the increase of the amount of monoclinic phase with decreasing mass throughput is likely due to the effect of stress induced crystallization and the increase of temperature of crystallization accompanying the increased stress levels as previously discussed by Lu and Spruiell (48) and Zhou and Spruiell (50). Figure 4.7 shows that the structure of 0.5% red pigmented PP filament is largely composed of monoclinic crystal phase and changes little with varying mass throughput. Again, this suggests that the 0.5% red pigmented PP (PP-1-Red-0.5) is less sensitive to effect of stress induced crystallization because the pigment causes

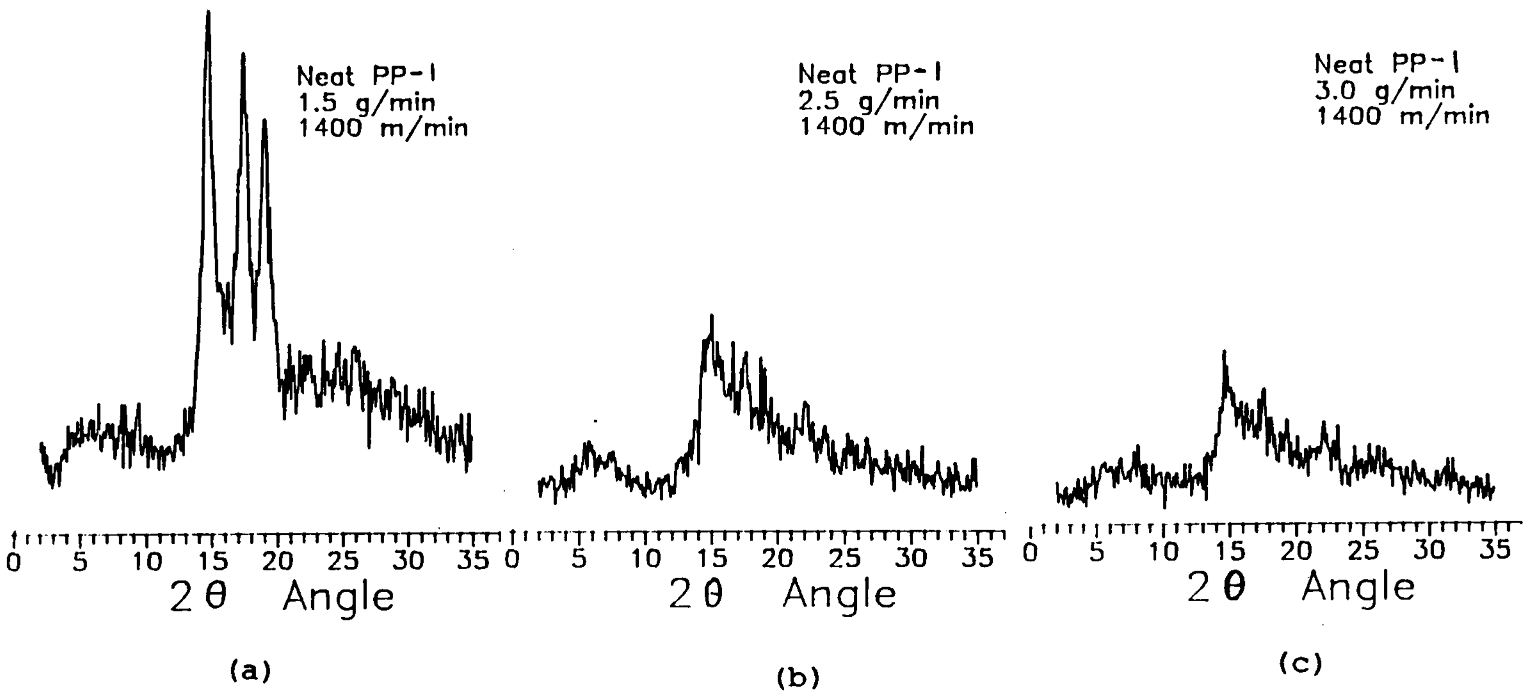


Figure 4.6 Wide Angle X-ray Diffractometer Scans of Natural PP-1 Filaments Spun under Mass Throughput of (a) 1.5 g/min, (b) 2.5 g/min and (c) 3.0 g/min at Constant Take-up Velocity of 1400 m/min.

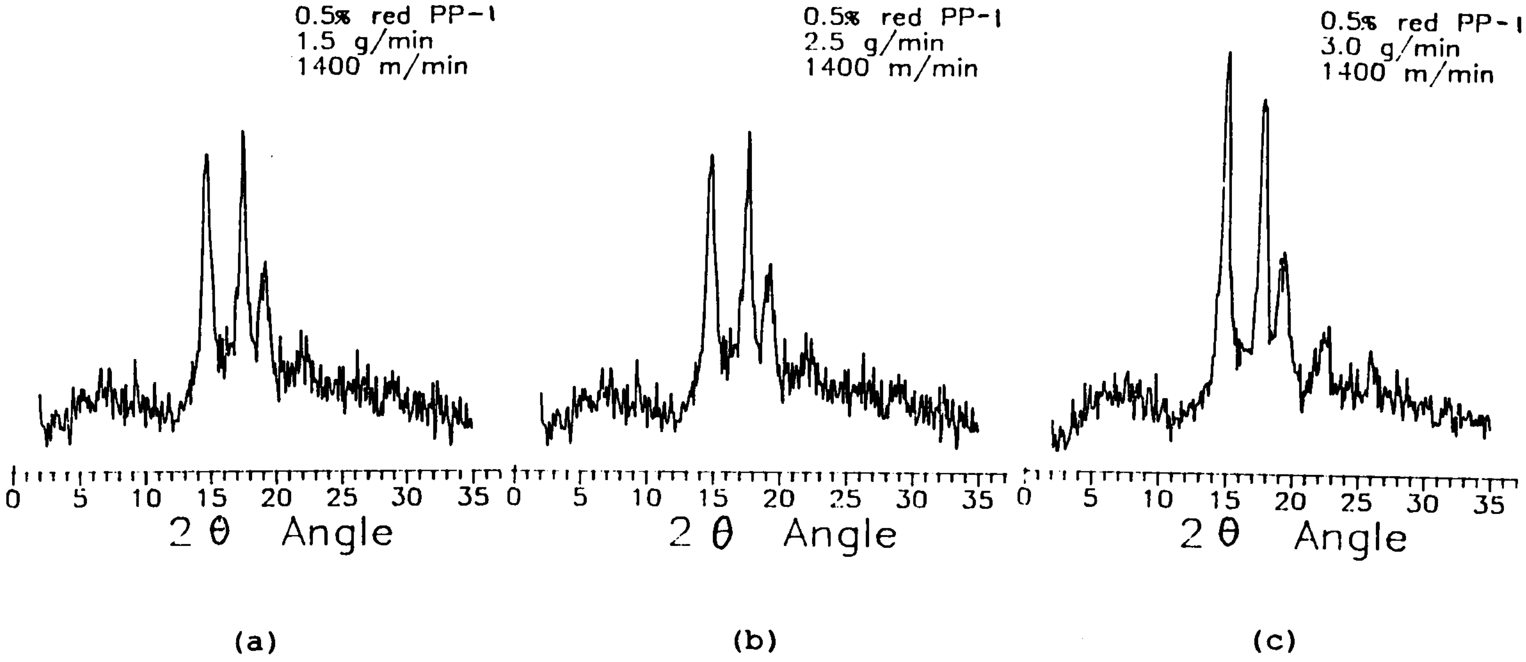


Figure 4.7 Wide Angle X-ray Diffractometer Scans of 0.5% Red Pigmented PP-1 Filaments Spun under Mass Throughput of (a) 1.5 g/min, (b) 2.5 g/min and (c) 3.0 g/min at Constant Take-up Velocity of 1400 m/min.

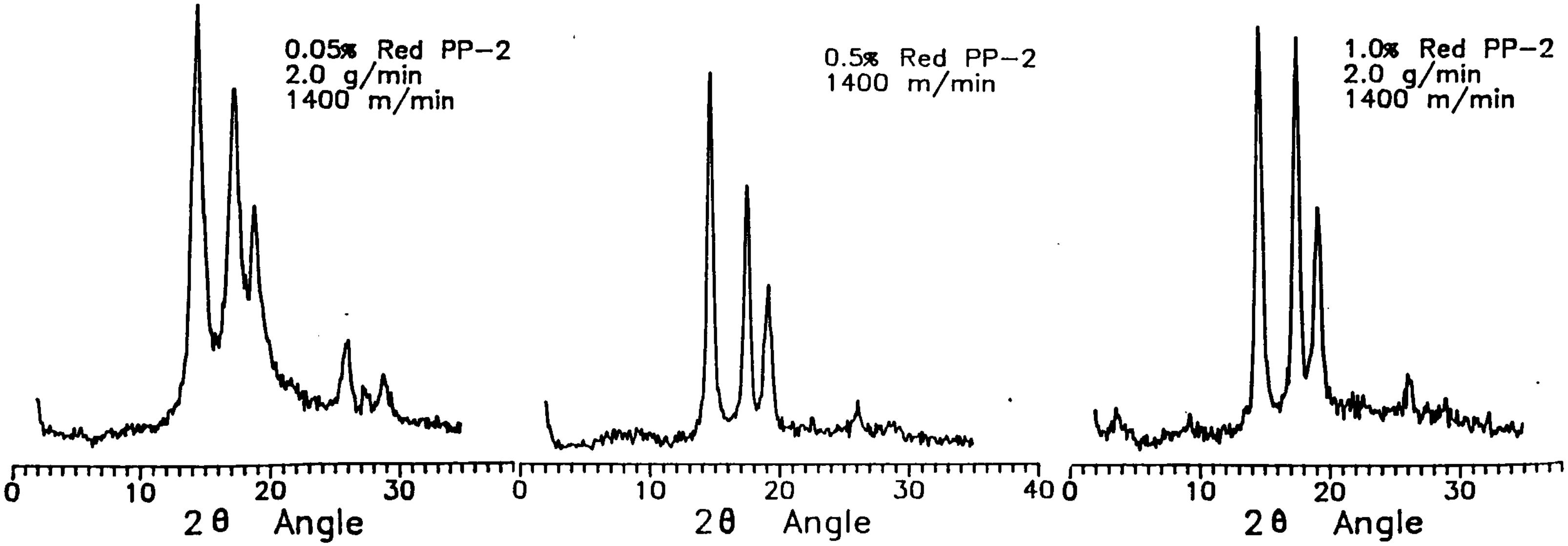
the crystallization to occur at higher temperature due to its nucleating ability.

Figures 4.8 through 4.10 present the wide angle x-ray scan patterns for PP-2 filaments. Under the present spinning conditions, it was observed that very distinct diffraction peaks of (110), (040) and (130) exist in all filament samples of PP-2. This suggests that a large amount of monoclinic crystal was formed in the structure of PP-2 filaments due to its higher viscosity and larger effect of stress induced crystallization, compared with PP-1 resin.

## Density and Crystallinity Index

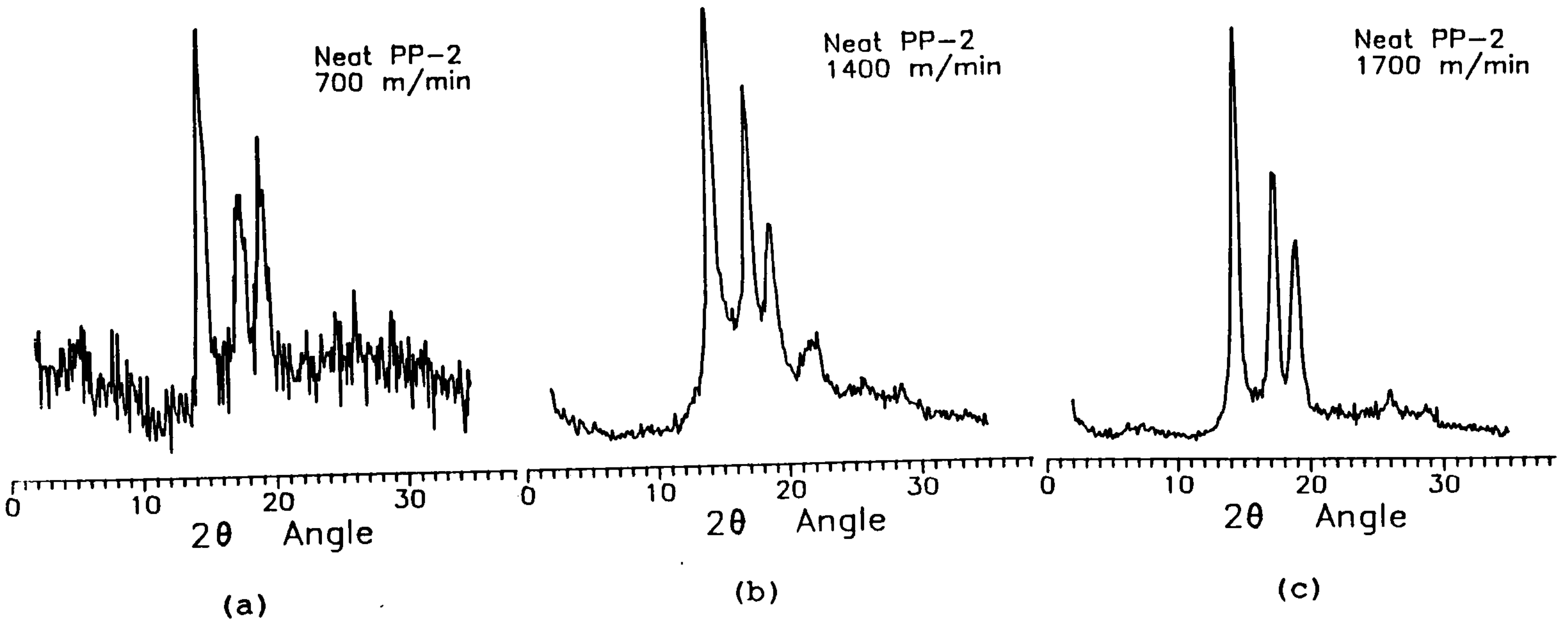
The degree of crystalline order in a semicrystalline polymer is often measured by a numerical measurement of crystallinity index. The crystallinity index of fiber can be calculated from density measurement, x-ray diffraction and differential scanning calorimetry (DSC), and other techniques. The density method is most commonly used to determine the crystallinity of fiber. The method of computing the crystallinity index and correcting for the presence of pigments was discussed in the section on experimental techniques.

Tables 4.1 and 4.2 show measured density and crystallinity index for the as-spun PP-1 and PP-2 filaments at each pigment concentration. Samples with greater amounts



(a) (b) (c)

Figure 4.8 Wide Angle X-ray Diffractometer Scans of Red Pigmented PP-2 Filaments with Pigment Concentration of (a) 0.05%, (b) 0.5% and (c) 1% by Weight.



(a) (b) (c)

Figure 4.9 Wide Angle X-ray Diffractometer Scans of Natural PP-2 Filaments under Take-up Velocity of (a) 700 m/min, (b) 1400 m/min and (c) 1700 m/min.

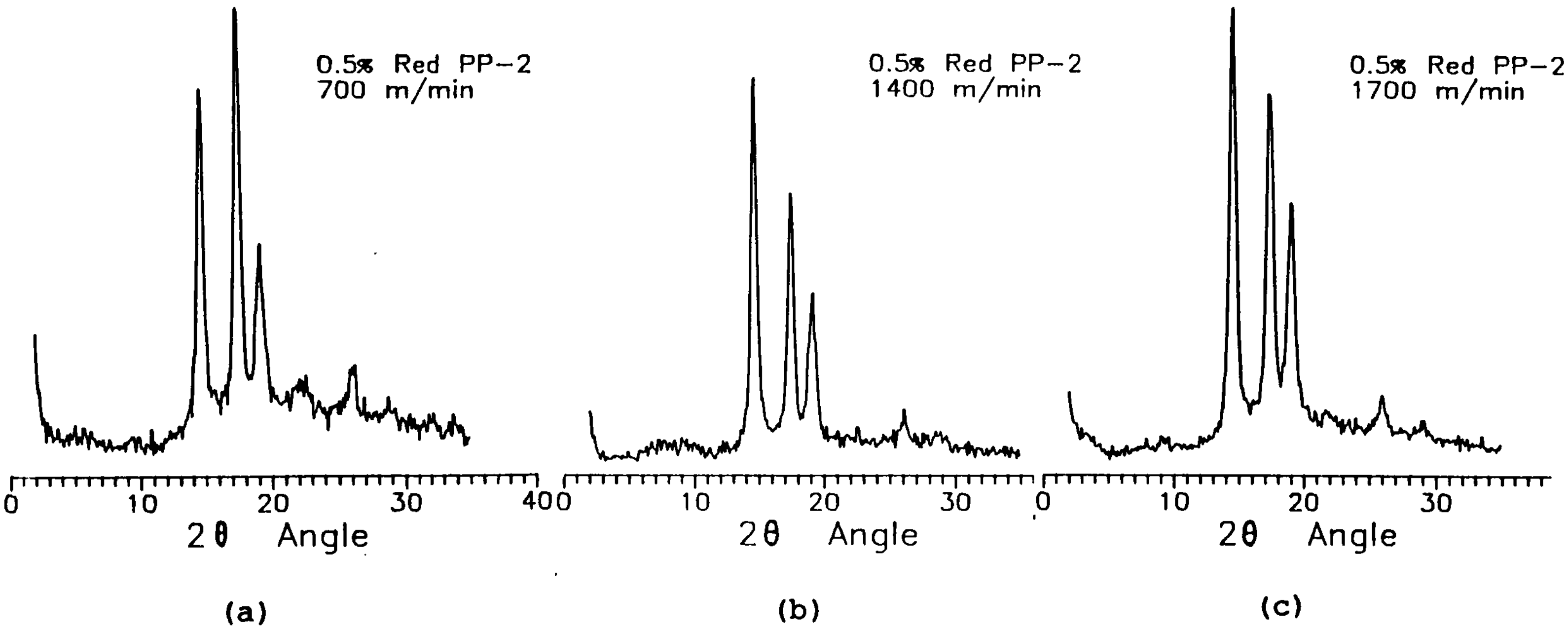


Figure 4.10 Wide Angle X-ray Diffractometer Scans of 0.5% Red Pigmented PP-2 Filaments under Take-up Velocity of (a) 700 m/min, (b) 1400 m/min and (c) 1700 m/min.

Table 4.1 Density and Crystallinity Index for PP-1 Filaments

| Sample | Measured Filament Density (g/cm$^3$) | Deduced Polymer Density (g/cm$^3$) | Crystallinity Index (%) |
|---|---|---|---|
| Natural PP-1 | 0.8936 | 0.8936 | 52.99 |
| 1 % Blue PP-1 | 0.9048 | 0.9003 | 61.47 |
| 0.5 % Blue PP-1 | 0.9035 | 0.8962 | 62.68 |
| 0.05 % Blue PP-1 | 0.8986 | 0.8984 | 59.06 |
| 1 % Red PP-1 | 0.9019 | 0.8983 | 58.95 |
| 0.5 % Red PP-1 | 0.9016 | 0.8998 | 60.86 |
| 0.05 % Red PP-1 | 0.8939 | 0.8937 | 53.14 |
| 1 % Black PP-1 | 0.9013 | 0.8968 | 57.04 |
| 0.5 % Black PP-1 | 0.8991 | 0.8968 | 57.12 |
| 0.05 % Black PP-1 | 0.8943 | 0.8941 | 53.60 |
| 1 % White PP-1 | 0.9022 | 0.8962 | 56.30 |
| 0.5 % white PP-1 | 0.8985 | 0.8955 | 55.41 |
| 0.05 % White PP-1 | 0.8933 | 0.8930 | 52.23 |

Table 4.2 Crystallinity Index for PP-2 Filaments*

| Sample | Crystallinity Index (%) |
|---|---|
| Natural PP-2 | 61.07 |
| 0.05% Red PP-2 | 62.33 |
| 0.5% Red PP-2 | 63.33 |
| 1.0% Red PP-2 | 66.09 |
| 0.05% Black PP-2 | 61.83 |
| 0.5% Black PP-2 | 62.46 |
| 1.0% Black PP-2 | 63.78 |

*Processing conditions were the same for all the filaments: take-up speed = 1400 m/min, mass throughput = 2.0 g/min.

of monoclinic phase such as red and blue pigmented samples would be expected to have higher densities and higher values of the crystallinity index. The crystallinity indices of all pigmented filaments are higher than that of the natural unpigmented PP filament. With the pigmented concentration increasing from 0.05% to 0.5%, the crystallinity of the pigmented filaments increases while the degree of increasing depends on the nature of the pigment. But there is little change of crystallinity when the pigment concentration changes from 0.5% to 1.0% which agrees with the trend of the wide angle x-ray diffraction scan pattens for pigmented filaments. The blue and red pigmented filaments have higher levels of crystallinity index than the white and black ones for a given set of spinning conditions.

Tables 4.3 and 4.4 present the density and crystallinity of both natural and 0.5% red pigmented filaments spun with different mass throughputs. For PP-1 filaments all of the 0.5% red pigmented samples have higher level of crystallinity than the natural PP-1 samples. Note, however, that the crystallinity increases somewhat with increase of mass throughput for the 0.5% red pigmented samples, due to the decreased cooling rate, while the opposite trend is observed for the natural unpigmented PP-1 due to its sensitivity to the increased spinline stress.

Table 4.3 Density and Crystallinity Index for PP-1 Filaments at Different Mass Throughput

| Sample | Mass Throughput (g/min) | Measured Filament Density ($g/cm^3$) | Deduced Polymer Density ($g/cm^3$) | Crystallinity Index (%) |
|---|---|---|---|---|
| 0.5% Red PP-1 | 1.5 | 0.8995 | 0.8977 | 58.17 |
| 0.5% Red PP-1 | 2.0 | 0.9000 | 0.8982 | 58.79 |
| 0.5% Red PP-1 | 2.5 | 0.9013 | 0.8995 | 60.44 |
| 0.5% Red PP-1 | 3.0 | 0.9019 | 0.9001 | 61.20 |
| Natural PP-1 | 1.5 | 0.8963 | 0.8963 | 56.39 |
| Natural PP-1 | 2.0 | 0.8931 | 0.8931 | 52.31 |
| Natural PP-1 | 2.5 | 0.8930 | 0.8930 | 52.18 |
| Natural PP-1 | 3.0 | 0.8930 | 0.8930 | 52.18 |

Table 4.4 Crystallinity Index for PP-2 Filaments at Different Mass Throughput

| Sample | Mass Throughput (g/min) | Crystalliniity (%) |
|---|---|---|
| Natural PP-2 | 1.5 | 63.59 |
| Natural PP-2 | 2.0 | 61.07 |
| Natural PP-2 | 2.5 | 61.07 |
| Natural PP-2 | 3.0 | 57.28 |
| 0.5% Red PP-2 | 1.5 | 63.59 |
| 0.5% Red PP-2 | 2.0 | 63.33 |
| 0.5% Red PP-2 | 2.5 | 62.33 |
| 0.5% Red PP-2 | 3.0 | 62.33 |
| 0.5% Black PP-2 | 1.5 | 63.40 |
| 0.5% Black PP-2 | 2.0 | 62.01 |
| 0.5% Black PP-2 | 2.5 | 62.03 |
| 0.5% Black PP-2 | 3.0 | 61.81 |

Compared with PP-1 resin the effect of pigment on crystallinity for PP-2 is less. All of the natural PP-2 samples have higher level of crystallinity than the natural PP-1 samples. With the addition of pigments, crystallinity slightly increases. Table 4.4 presents the crystallinities of the filaments spun at different mass throughput for natural, 0.5% red and 0.5% black pigmented PP-2 samples. The variation of crystallinity with mass throughput is smaller than for the PP-1 samples. The change of crystallinity with increase of mass throughput for natural unpigmented PP-2 samples shows similar pattern as that of natural PP-1. The crystallinity for 0.5% red pigmented PP-2 is higher than that of natural unpigmented PP-2 except at the mass throughput of 1.5 g/min, but the crystallinity level for 0.5% red pigmented filaments changes little with varying mass throughput, which also may be explained by the assumption that the ratio of monoclinic phase in the red pigmented PP fiber reaches saturation due to the higher viscosity and larger effect of stress induced crystallization at all mass throughput levels.

Tables 4.5 and 4.6 show the density and crystallinity index of filaments of natural PP-1, PP-2 and 0.5 % red pigmented PP-1, PP-2 spun at three different take-up velocities, 700 m/min, 1400 m/min and 1700 m/min. To keep

Table 4.5 Density and Crystallinity Index for PP-1 Filaments at Different Take-up Velocities

| Sample | Take-up Speed (m/min) | Measured Filament Density (g/cm$^3$) | Deduced Polymer Density (g/cm$^3$) | Crystallinity Index (%) |
|---|---|---|---|---|
| 0.5% Red PP-1 | 700 | 0.9013 | 0.8995 | 60.44 |
| 0.5% Red PP-1 | 1400 | 0.9000 | 0.8982 | 58.79 |
| 0.5% Red PP-1 | 1700 | 0.8995 | 0.8977 | 58.17 |
| Natural PP-1 | 700 | 0.8907 | 0.8907 | 49.23 |
| Natural PP-1 | 1400 | 0.8914 | 0.8914 | 50.13 |
| Natural PP-1 | 1700 | 0.8938 | 0.8938 | 53.21 |

Table 4.6 Crystallinity Index for PP-2 Filaments at Different Take-up Velocities

| Sample | Take-up Speed (m/min) | Crystalliniity (%) |
|---|---|---|
| Natural PP-2 | 700 | 57.28 |
| Natural PP-2 | 1400 | 61.07 |
| Natural PP-2 | 1700 | 61.09 |
| 0.5% Red PP-2 | 700 | 64.84 |
| 0.5% Red PP-2 | 1400 | 63.33 |
| 0.5% Red PP-2 | 1700 | 63.33 |
| 0.5% Black PP-2 | 700 | 60.35 |
| 0.5% Black PP-2 | 1400 | 62.01 |
| 0.5% Black PP-2 | 1700 | 62.20 |

constant diameter of the filament, the mass throughput was adjusted during the melt spinning. The crystallinities of all 0.5% red pigmented filaments for PP-1 are higher than that of natural PP-1 filaments because of the nucleating effect on crystallization by the red pigment. The effect of changing take-up velocity (keeping constant diameter of as-spun fiber) on the crystallinity of natural unpigmented PP filaments differs from that of 0.5% red pigmented PP filaments. The crystallinity level of natural PP filaments increases with increasing take-up velocity while the crystallinity level of the 0.5% red pigmented samples decrease with increasing take-up velocity. The differences may be explained as follows. There are two major factors which will influence the crystallization on the spinline: crystallization rate and cooling rate. Increasing the spinning speed increases the cooling rate and, in the absence of other effects, would result in reduced crystallinity. This is the effect being observed for the pigmented samples. Because of the strong nucleating effects of the pigment, the crystallization rate is high and crystallization begins at a relatively high temperature in the spinline. Increased spinning speed merely suppresses the crystallization somewhat due to the increased cooling rate. In the absence of the pigment the natural PP crystalizes at a lower temperature and in the presence of somewhat greater molecular orientation. Increased take-up velocity further increases this molecular orientation. This causes an increase of crystallization rate which offsets the effect of increased cooling rate, resulting in increased crystallinity. The latter effect is well known in the case of natural PP(48). This leads to higher levels of crystallinity with increasing take-up velocity so long as the influence of molecular orientation on crystallization kinetics can override the influence of increased cooling rate in retarding the development of crystallinity.

## Birefringence

The addition of pigments also had effects on the molecular orientation of the filaments. Figures 4.11 and 4.12 show the birefringence of the natural PP-1 and PP-2 and pigmented filaments at the three levels of pigment concentration. The birefringence reflects the total orientation of molecules, i.e. in both the crystalline and the amorphous phases. In general, the birefringence and thus the orientation of the pigmented filaments are lower than the unpigmented filament. This may be explained by the fact that the pigmented samples crystallize at higher temperature and from a melt with lower molecular orientation at the beginning of the crystallization which will be discussed in detail in the section describing the

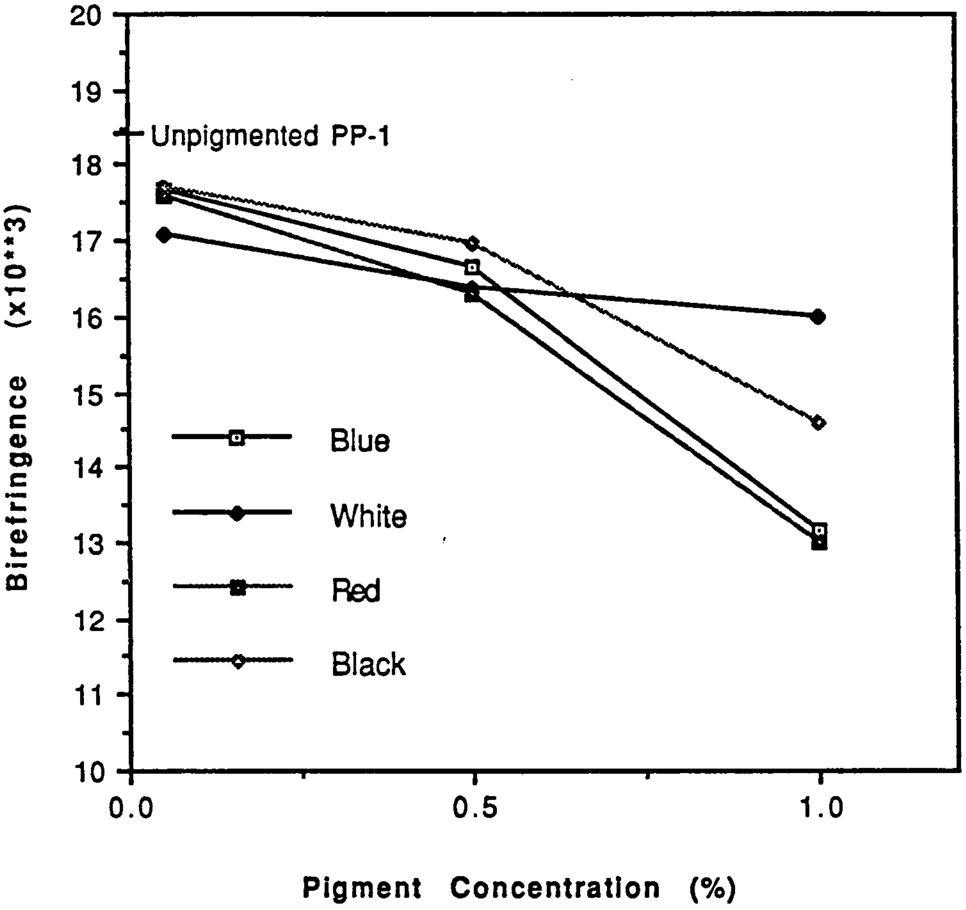


Figure 4.11 Birefringence vs. Pigment Concentration for PP-1 filaments.

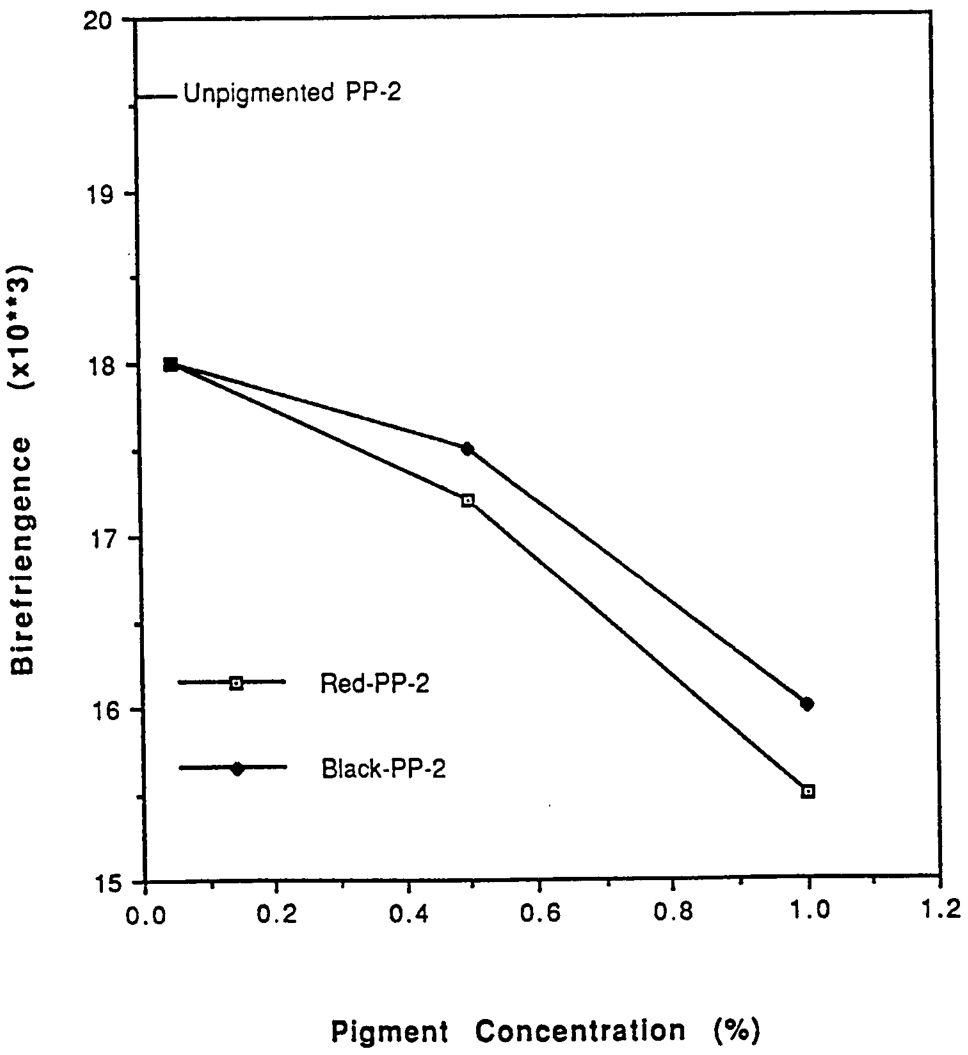


Figure 4.12 Birefringence vs. PIgment Concentration for PP-2 Filaments.

on-line measurement. The birefringence value of PP-2 filaments is higher than that of PP-1 for both the natural PP and red pigmented PP samples due to higher spinline stress developed by the higher viscosity of PP-2 resin. The variation of birefringence of PP-2 filaments with pigment concentration is smaller than that of PP-1 filaments because the structure of PP-2 filament has already reached saturation state in the pigment concentration range used in this study.

Figures 4.13 and 4.14 present the birefringence of the natural PP-1, PP-2 and 0.5% pigmented filaments at three take-up velocities. The birefringence exhibits a complex behavior for PP-1 filaments. In general, the orientation of the red pigmented samples are lower due to the reason explained above. A reversal of this trend at the lowest take-up velocity is likely due to the higher level of crystallinity in the pigmented samples. Orientation in the crystalline phase is likely to be substantially higher than in the amorphous phase in both red pigmented and unpigmented filaments due to oriented nucleation and crystal growth; this produces the reversal. The birefringence of fibers from PP-2 resin increases with spinning speed. The PP-2 filaments have higher birefringence values than PP-1 samples at every take-up velocity due to high spinline stress. The variation of

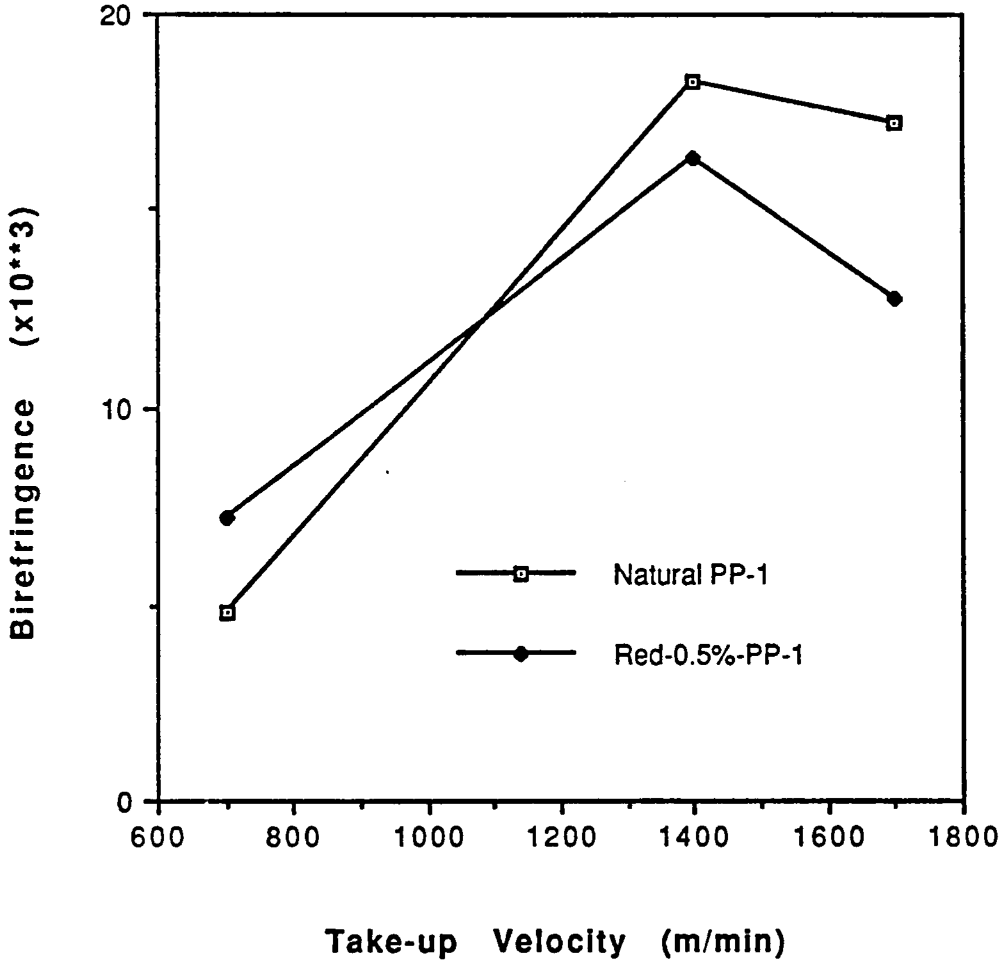


Figure 4.13 Birefringence vs. Take-up Speed for PP-1 Filaments.

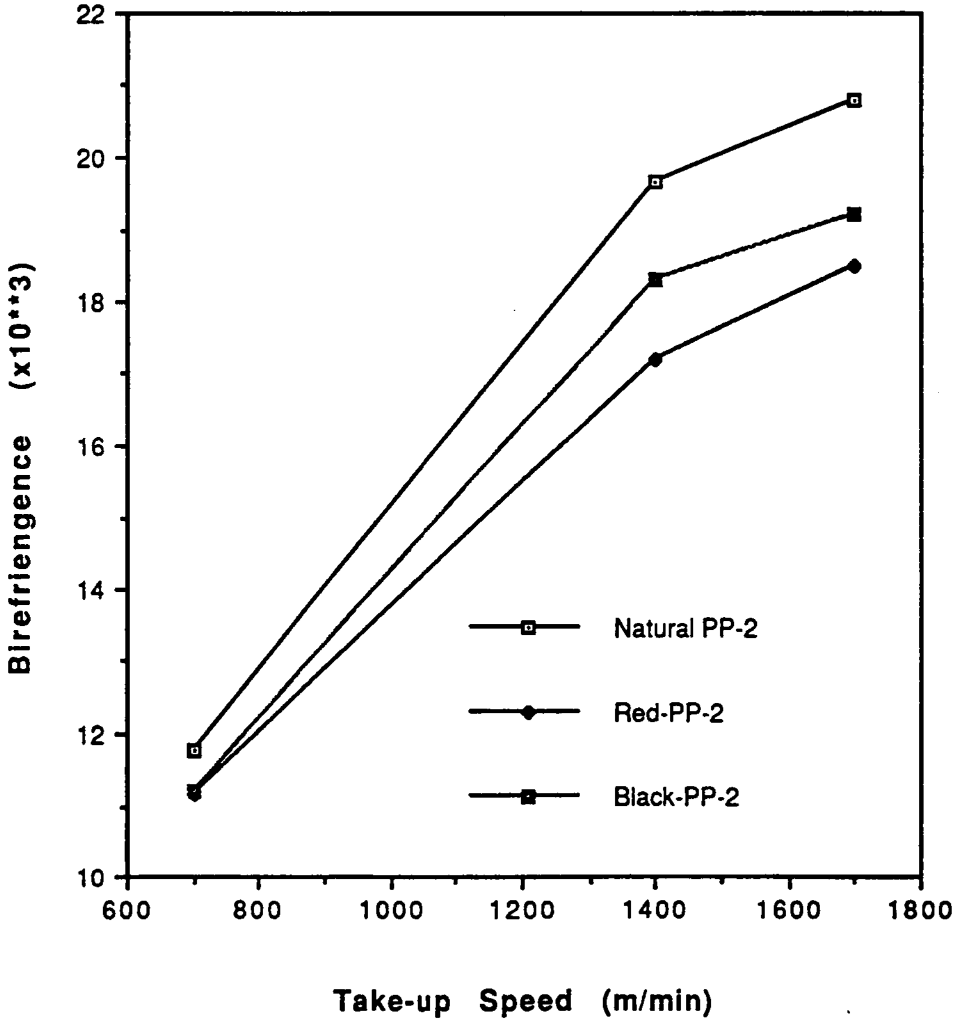


Figure 4.14 Birefringence vs. Take-up Speed for PP-2 Filaments.

birefringence of PP-2 filaments with take-up velocity is much smaller than PP-1. This may also be explained by assuming that the structure of PP-2 filaments has already reached saturation state in the take-up speed range used in this study.

Figure 4.15 clearly shows that the birefringence (orientation) of the PP-2 filaments decreases as the mass throughput increases. Drawing ratio and stress level on spinline decrease with increasing the mass throughput at the constant take-up speed. The decreasing of orientation of filaments with increasing mass throughput is likely due to the decreasing of the stress level on spinline.

## 4.2 Morphology of Spherulites in Polypropylene Samples

We have deduced from previous experimental results that the pigment in PP may act as a nucleating agent. further evidence can be obtained from observation by optical microscopy during crystallization. Figure 4.16 presents micrographs of spherulites observed at room temperature after selected extrudate samples which were cooled from 210 °C to room temperature at a rate of 20 °C/min. Blue pigmented polypropylene, Figure 4.16c, contains many more spherulites per unit volume and a

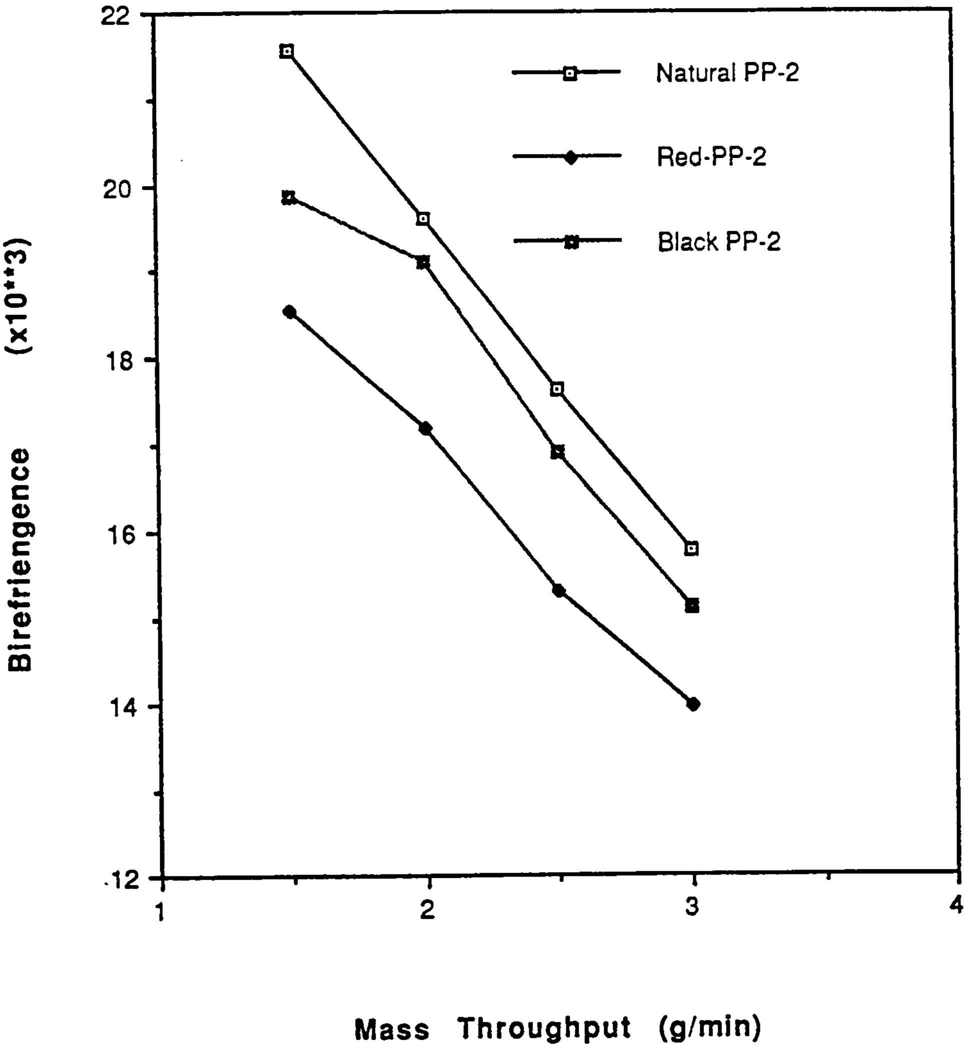
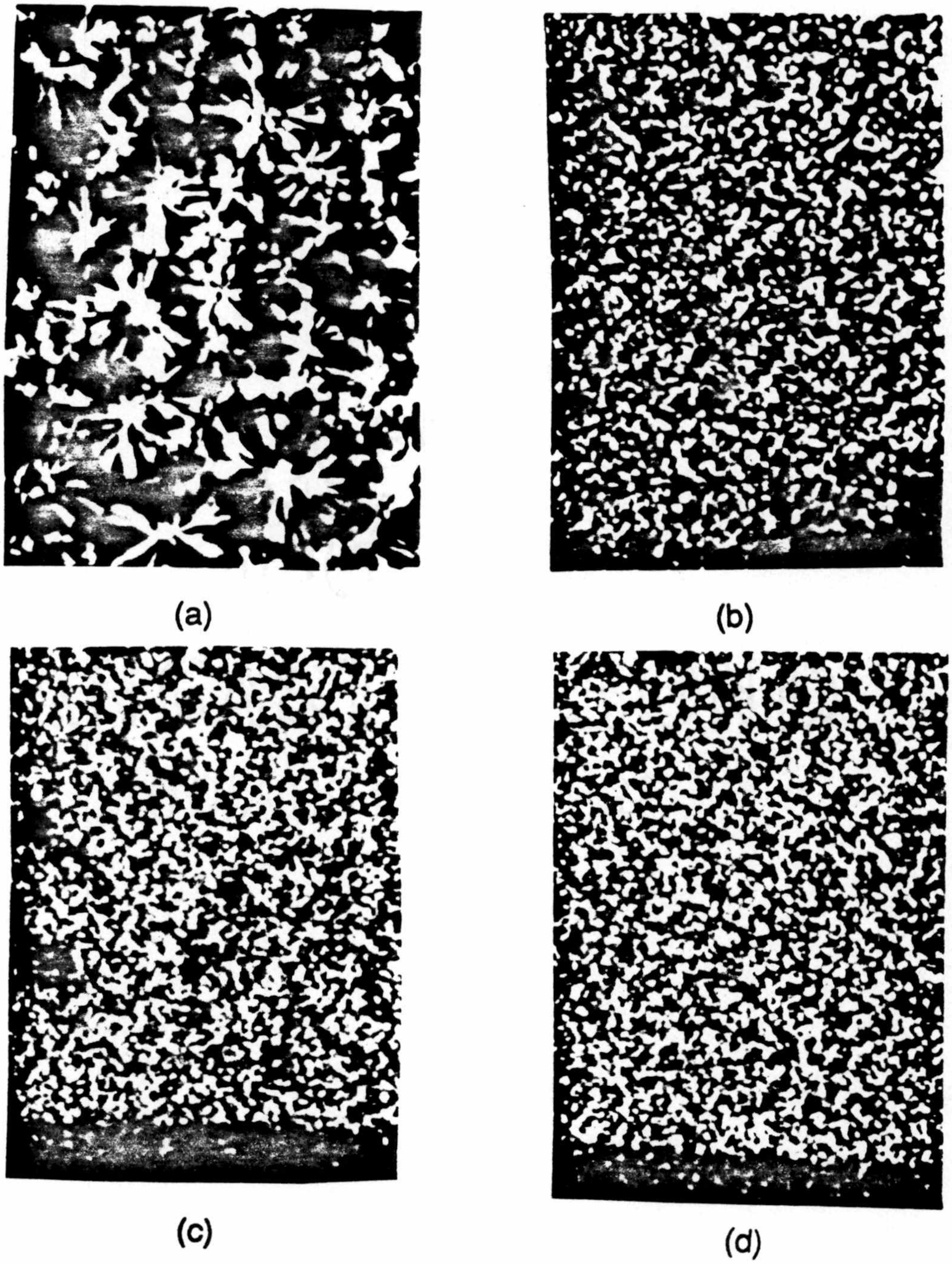


Figure 4.15 Birefringence vs. Mass Throughput for PP-2 Filaments.

(a) (b) (c)

Figure 4.16 Spherulites of (a) Natural PP-1, (b) 0.5% White PP-1, (c) 0.5% Blue PP-1 after Coolingfrom 210 °C to 25 °C at Rateof 20 °C/min..



(a) (b)

(c) (d)

Figure 4.17 Spherulites of (a) Natural PP-1, (b) 0.05% Blue PP-1, (c) 0.5% Blue PP-1 and (d) 1% Blue PP-1 after Cooling from 210 °C to 25 °C at Rate of 20 °C/min.

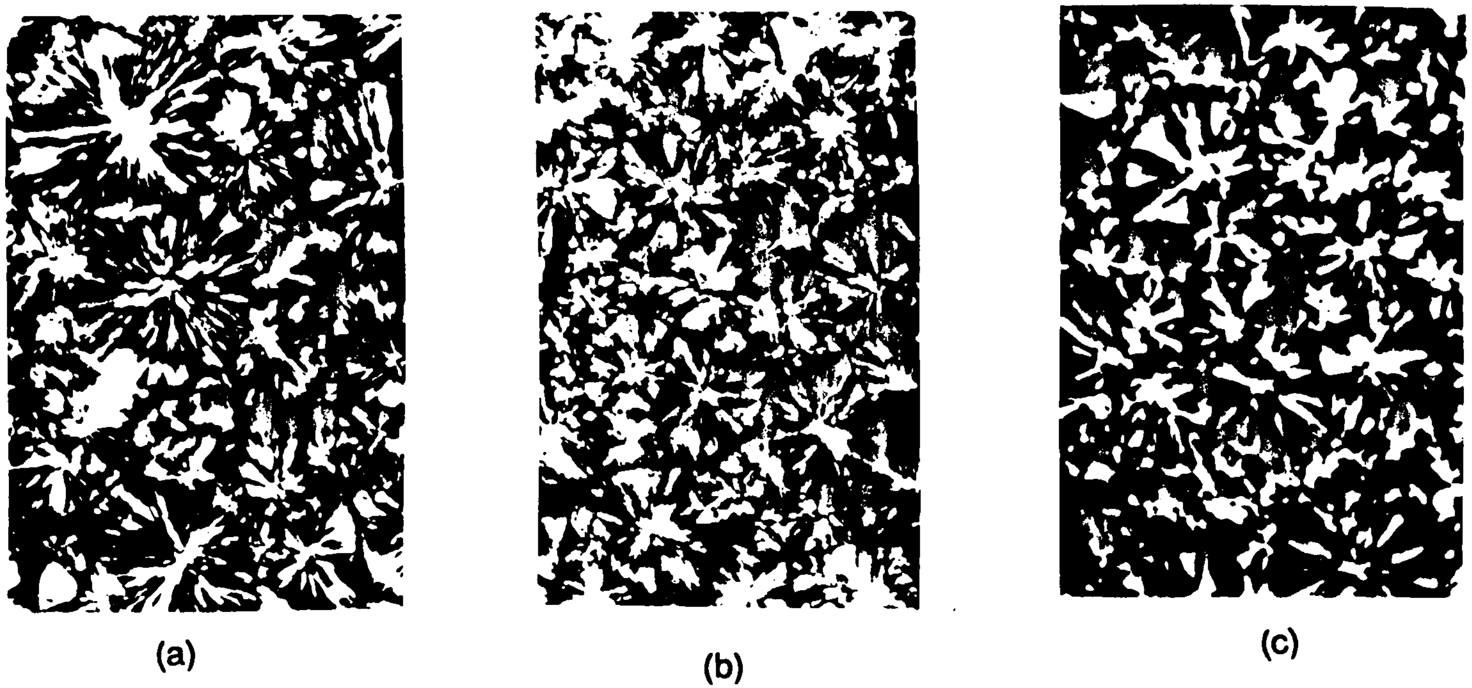
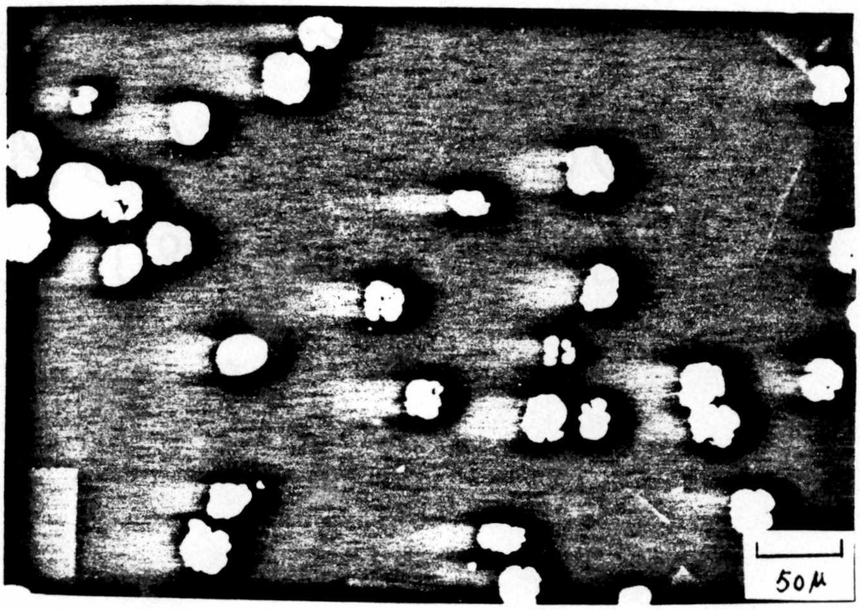
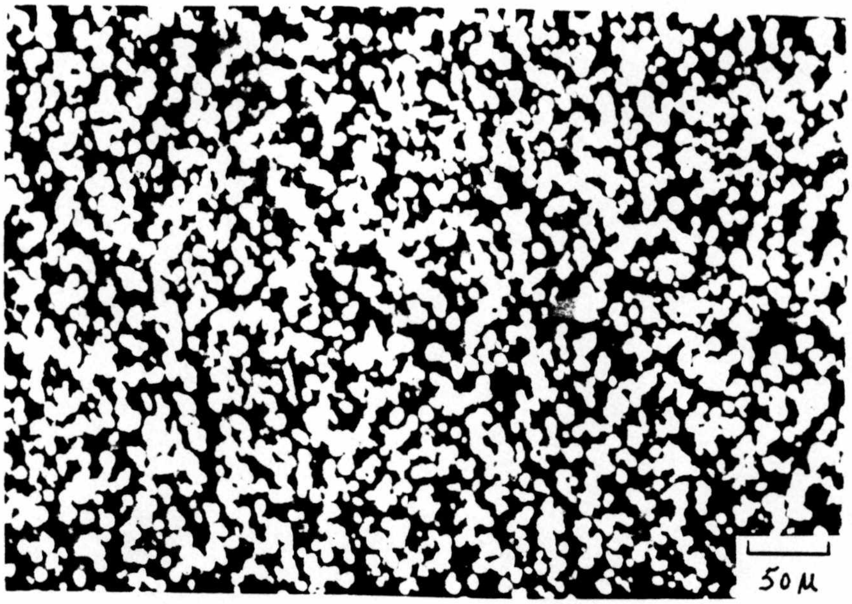

(a) (b) (c)

Figure 4.18 Spherulites of (a) 0.05% white PP-1, (b) 0.5% White PP-1 and (c) Natural PP-1 after Cooling from 210 °C to 25 °C at Rate of 20 °C/min..



(a)



(b)

Figure 4.19 Spherulites of (a) Natural PP-1 after Growth for 5 min, (b) 0.05% Blue PP-1 after Growth for 2 min, Both at 132 °C.

smaller spherulite size than the unpigmented polypropylene control, Figure 4.16a. On the other hand, the spherulites of the specimen containing white pigment, Figure 4.16b, are very similar in size and number density to those of the unpigmented polypropylene. Moreover, the spherulite size and number density of spherulites in the blue pigmented samples varies with the concentration of the pigment. Figure 4.17 shows that as the blue pigment concentration increases, the spherulite number density increases and the spherulite size decreases. Figure 4.18 shows that the spherulite number density and the spherulite size have no significant change as the white pigment concentration increases. The effect of the blue pigment as nucleating agent can also be observed after partial isothermal crystallization as shown in Figure 4.19. These observations suggest that the blue pigment acts as a powerful nucleating agent while the white pigment has relatively little effect on the crystallization kinetics and morphology of polypropylene.

## 4.3 Differential Scanning Calorimetry

The crystallization kinetics of natural PP-1 and pigmented PP-1 samples were studied by using a Perkin-Elmer DSC 7. Cooling thermograms of pigmented and unpigmented PP-

1 samples are presented in Figure 4.20 and Figure 4.21. The exothermal peaks result from crystallization of the samples. It is observed in Figure 4.20 that the blue pigmented PP-1 sample begins to crystallize at much higher temperature than the natural unpigmented PP-1 sample. With the increase of the concentration of the blue pigment in the sample, the temperature of crystallization increases. At 1% blue pigment, this increase of crystallization temperature during cooling amounts to about 12 to 13 Celsius degrees. This clearly indicates that the blue pigment acts as a strong nucleating agent for polypropylene and substantially increases its crystallization kinetics. Figure 4.21 shows that the crystallization temperature of white pigmented PP-1 is only slightly different from that of the unpigmented PP-1. Hence, the white $TiO_2$ pigment is not a strong nucleator of crystallization in polypropylene. The onset and peak temperature of crystallization for natural and red , blue, white and black pigmented PP-1 are tabulated in Table 4.7. All pigmented PP-1 samples start crystallization at higher temperature than natural unpigmented PP. At a given pigment concentration level, the crystallization temperatures of the four pigments studied in this investigation increased in the order

White < black < Red< Blue

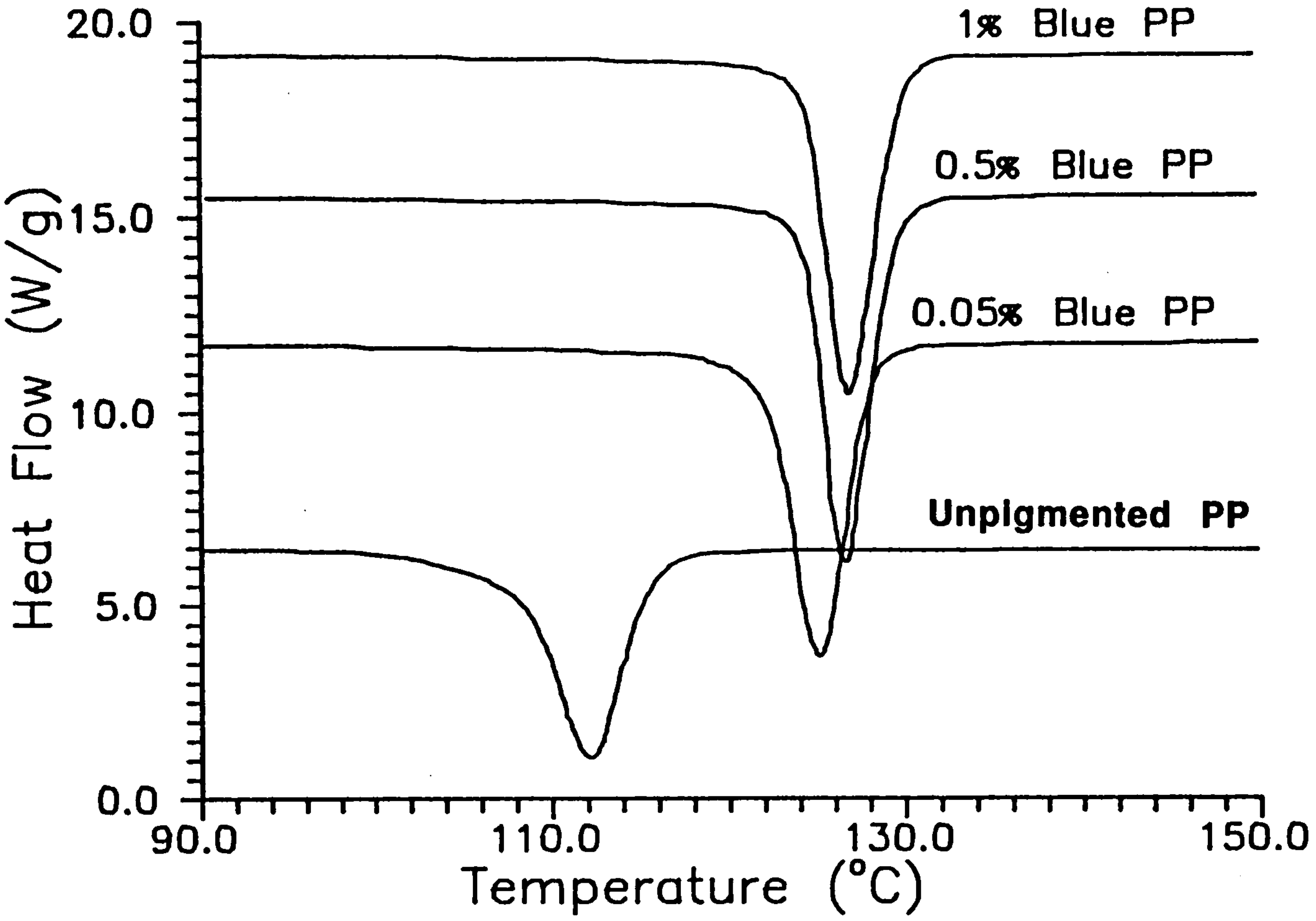


Figure 4.20 DSC thermograms of Natural and Blue Pigmented PP-1 with Cooling Rate of 20 °C/min.

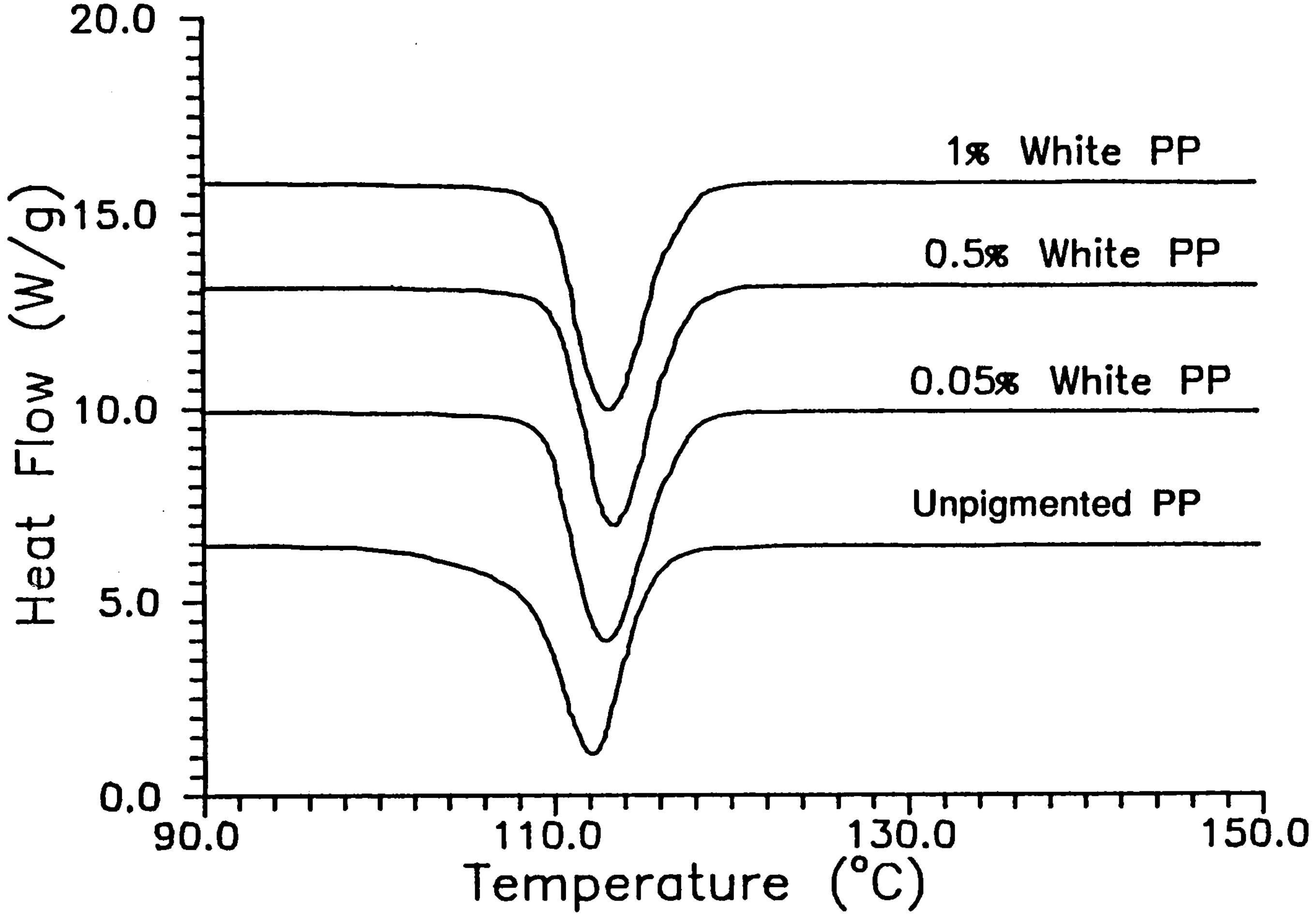


Figure 4.21 DSC Thermograms of Natural and White Pigmented PP-1 with Cooling Rate of 20 °C/min.

Table 4.7 Non-isothermal Crystallization Temperature for PP-1 Samples

| Sample | Onset Temperature ($^{o}C$) | Peak Temperature ($^{o}C$) |
|---|---|---|
| Natural PP-1 | 115.8 | 111.5 |
| 0.05% REd PP-1 | 123.1 | 120.3 |
| 0.5% Red PP-1 | 127.4 | 124.8 |
| 1.0% Red PP-1 | 127.6 | 125.1 |
| 0.05% Blue PP-1 | 129.0 | 126.0 |
| 0.5% Blue PP-1 | 129.6 | 126.9 |
| 1.0% Blue PP-1 | 130.0 | 127.1 |
| 0.05% Black PP-1 | 119.7 | 115.3 |
| 0.5% Black PP-1 | 120.7 | 116.8 |
| 1.0% Black PP-1 | 121.1 | 117.2 |
| 0.05% White PP-1 | 117.4 | 113.0 |
| 0.5% white PP-1 | 117.7 | 113.6 |
| 1.0% white PP-1 | 117.6 | 113.2 |

* It was carried out by using DSC under the cooline rate 20 °C/min.

with the black pigment being slightly more effective as a nucleating agent than the white pigment, and the red pigment being slightly less effective than the blue pigment.

Another sixteen pigments were evaluated for the effect on the crystallization of Exxon polypropylene PP-1 (MFR = 45) under non-isothermal condition. These sixteen master batches of color concentrates with different loading percentage were provided through Exxon Chemical. Samples with 0.5% pigment by weight were made using a single stage mixing extruder (Brabender). The temperature of extrusion was 210 °C. Table 4.8 presents the temperature of crystallization for pigment master batches. The temperature of crystallization covers quite broad range (92 °C to 132 °C) among the pigment master batches. In general all inorganic master batches have lower crystallization temperature. This may be explained on the basis that the inorganic pigment possesses much less nucleating power than its counterpart organic pigment. The other effect which might be considered is the nature of the carrier resin since some master batches have quite low crystallization temperature.

Table 4.9 shows the temperature of crystallization for 0.5% pigmented polypropylene samples. The table is sorted

Table 4.8 Crystallization Temperature for Pigment Master Batches

| Name | Loading | Peak Temp. (°C) | Onset Temp. (°C) |
|---|---|---|---|
| D1059 Rutile $TiO_2$ | 50% | 91.85 | 94.90 |
| Moly Orange | 50% | 92.17 | 95.04 |
| D1937 PE black | 35% | 109.50 | 112.71 |
| D1159 Chrome Yellow | 50% | 110.59 | 114.18 |
| SEC6759 Cabot 660 Furn. Black | 25% | 112.16 | 117.22 |
| SEC6758 Rutile $TiO_2$ | 50% | 114.08 | 117.34 |
| D1137 Chromophtal Yellow | 25% | 119.79 | 122.70 |
| D1346 $Fe_2O_3$ Red 101 | 25% | 119.90 | 123.70 |
| D1367 Perylene scarlet red | 25% | 121.57 | 124.87 |
| D1822 Phthalocyamine green | 25% | 123.22 | 126.58 |
| D1724 Phthalocyamine blue 8 | 25% | 123.54 | 127.17 |
| D1620 Carbazol violet | 25% | 123.66 | 127.58 |
| SEC6761 Phthalyl Blue | 25% | 123.75 | 127.55 |
| D1229 Chromophtal orange 4B | 25% | 124.69 | 127.75 |
| SEC6760 Ciba Geigy Red-brn | 25% | 125.43 | 128.52 |
| D1340 Berylene red | 25% | 125.94 | 129.35 |
| D1345 Chromophtal red-br | 25% | 127.06 | 129.70 |
| D1726 Phthalocyamine Blue B | 25% | 128.04 | 131.62 |
| D1621 Quinacridone red 192 | 25% | 128.87 | 132.46 |
| D1624 Quinacridone violet 19 | 25% | 132.17 | 135.01 |

Table 4.9 Crystallization Temperature for 0.5% Blend PP-1 Samples

| Name | Loading | Peak Temp. (°C) | Onset Temp. (°C) |
|---|---|---|---|
| D1159 Chrome Yellow | 50% | 107.79 | 113.11 |
| Moly Orange | 50% | 108.13 | 114.19 |
| D1937 PE black | 35% | 108.24 | 113.73 |
| D1059 Rutile $TiO_2$ | 50% | 111.72 | 115.99 |
| SEC6758 Rutile $TiO_2$ | 50% | 113.60 | 117.70 |
| SEC6759 Cabot 660 Furn. Black | 25% | 116.80 | 120.70 |
| D1137 Chromophtal Yellow | 25% | 116.87 | 120.66 |
| D1346 $Fe_2O_3$ Red 101 | 25% | 116.91 | 121.34 |
| D1367 Perylene scarlet red | 25% | 118.96 | 123.47 |
| D1620 Carbazol violet | 25% | 119.50 | 124.13 |
| D1822 Phthalocyamine green | 25% | 121.51 | 125.94 |
| D1229 Chromophtal orange 4B | 25% | 121.89 | 125.81 |
| D1724 Phthalocyamine blue 8 | 25% | 121.93 | 126.64 |
| D1345 Chromophtal red-br | 25% | 122.81 | 126.49 |
| D1340 Berylene red | 25% | 122.82 | 127.09 |
| D1726 Phthalocyamine Blue B | 25% | 124.45 | 128.64 |
| SEC6760 Ciba Geigy Red-brn | 25% | 124.80 | 127.40 |
| D1621 Quinacridone red 192 | 25% | 125.03 | 129.80 |
| SEC6761 Phthalyl Blue | 25% | 126.90 | 129.60 |
| D1624 Quinacridone violet 19 | 25% | 127.38 | 131.49 |

ascendantly according to the peak temperature of crystallization of the samples. All inorganic pigmented PP samples have lower crystallization temperature than the ones with organic pigments. The range of crystallization temperature (peak) among the samples is from 108 °C to 127 °C. The crystallization temperature of some inorganic pigmented samples is even lower than that of the natural unpigmented PP-1 (111.5 °C). This may be caused by the influence of the carrier resin.

## 4.4 On-line Diameter Profiles and Structure Development During Melt Spinning

On-line diameter measurements were carried out by using a Zimmer diameter monitor interfaced with an IBM-AT personal computer. The diameter profiles along the spinline for natural unpigmented PP-1, red and blue pigmented PP-1 samples are presented in Figure 4.22 and Figure 4.23. The University of Tennessee Melt Spinning Modeling Program (51, 46) was used to produce a master temperature profile along the spinline (Figure 4.24) based on the melt spinning processing conditions used in the experiment. Using this master temperature curve along with the on-line diameter profile it is possible to estimate the solidification

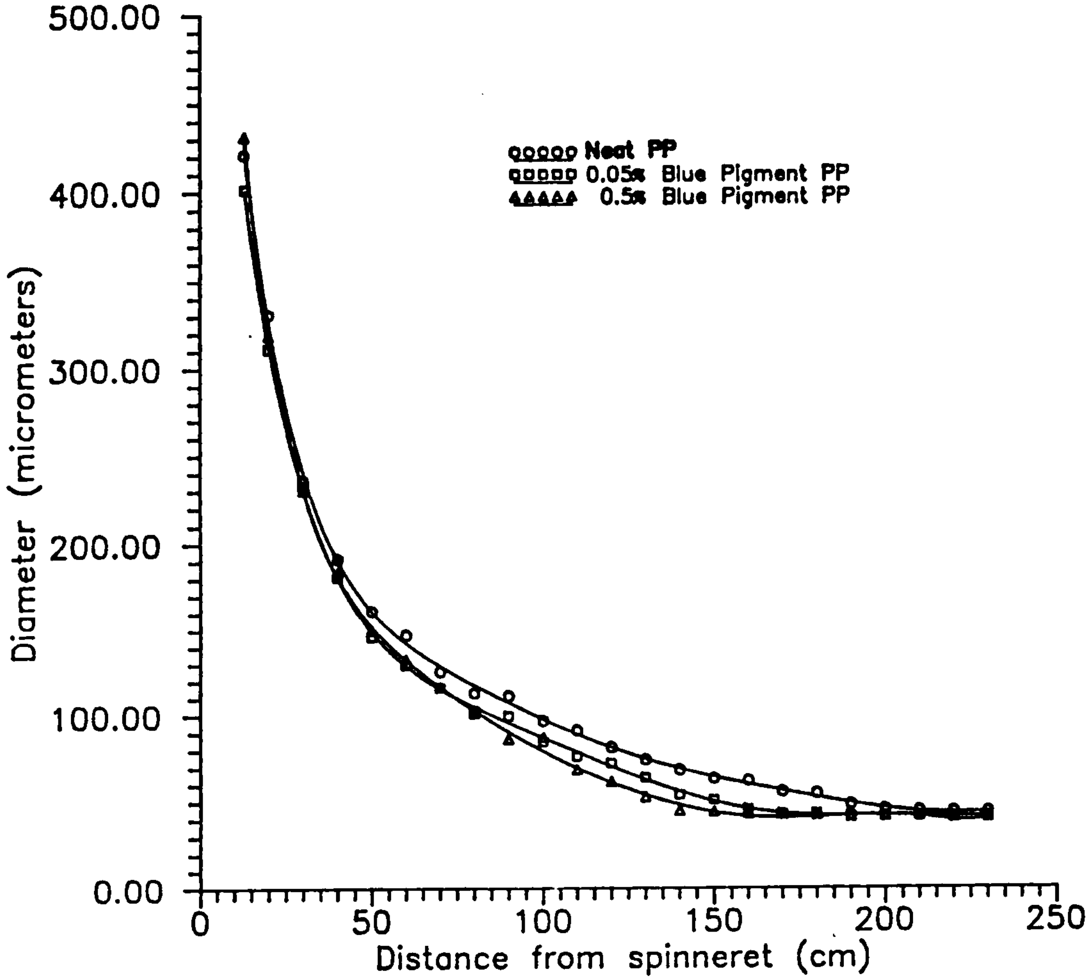
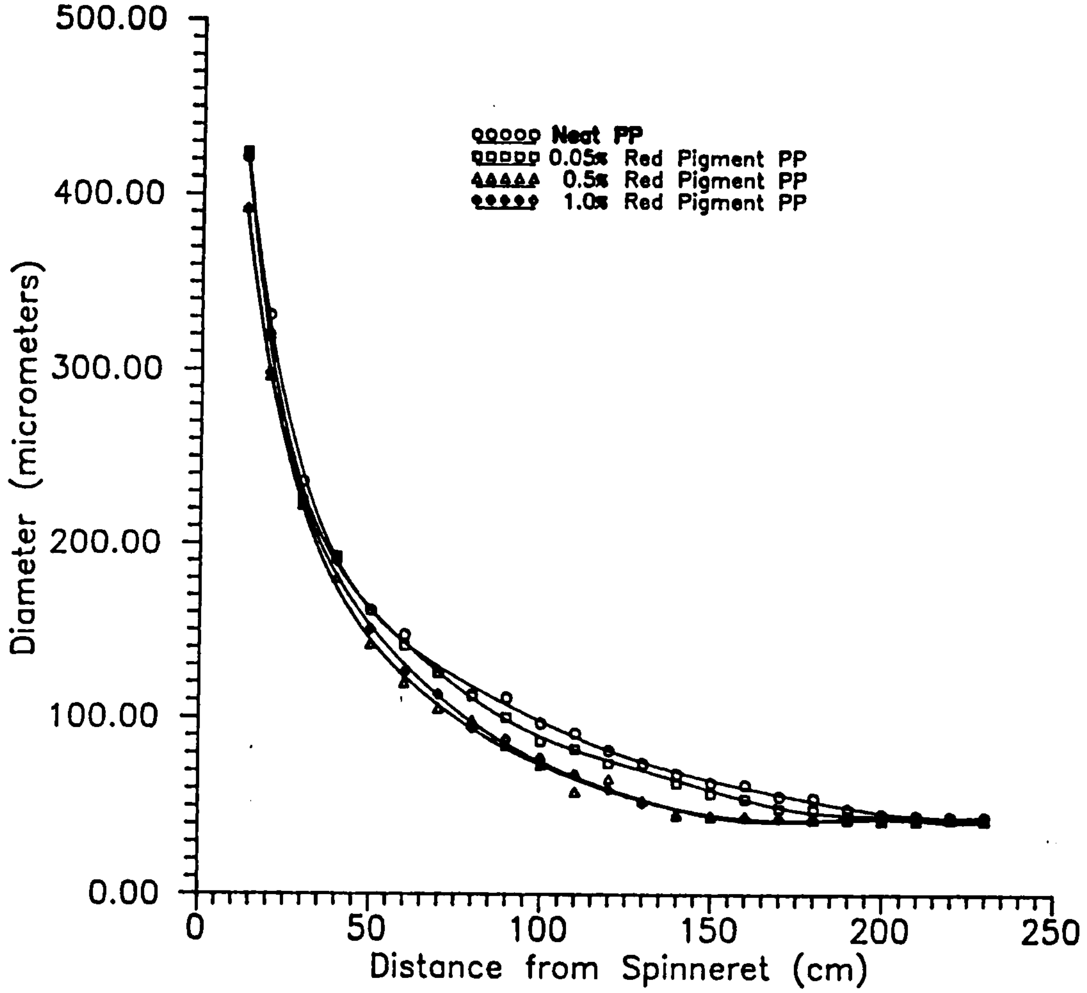


Figure 4.22 On-line Filament Diameter Profiles for Natural and Blue Pigmented PP-1.



Figutr 4.23 On-line Filament Diameter Profiles for Natural PP-1 and Red Pigmented PP-1.

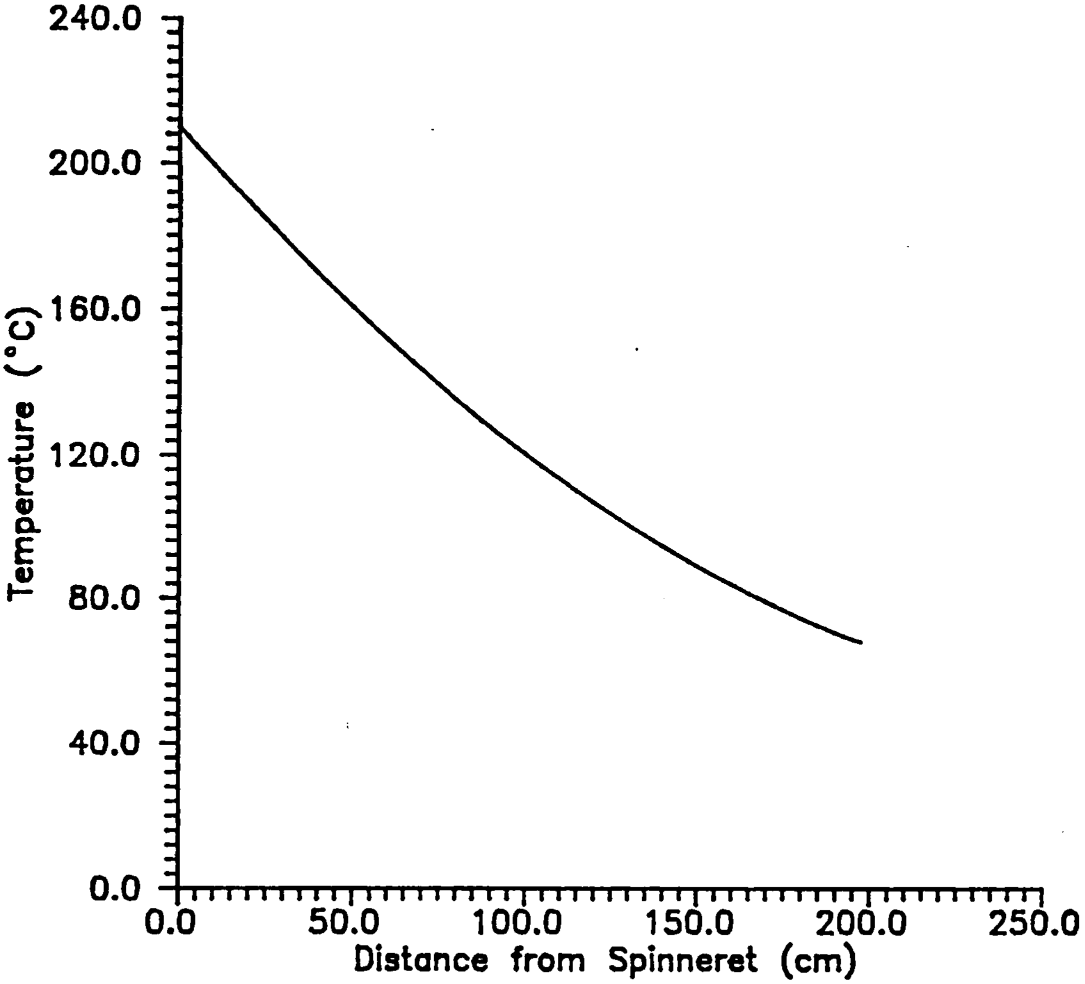


Figure 4.24 Master On-line Temperature Profile generated by Melting Spinning Modeling Program.

position and temperature (crystallization temperature on spinline) for each sample. The values of the solidification position were assumed to correspond to the point on the spinline at which the diameter levels out. This distance and the corresponding crystallization temperature are reported in Tables 4.10 and 4.11 as a function of pigment identity and concentration. It was found that the temperature of crystallization for Pigmented PP-1 is higher than that of natural unpigmented PP-1. However, the effect of pigments on the on-spinline crystallization temperature is different among the pigments. The blue and red pigments cause crystallization to occur at higher temperatures and shorter distances from the spinneret during melt spinning. The white and black pigments have less effect on the on-spinline crystallization temperature than the blue and red pigments. These results are in agreement with the DSC results and indicate that the pigments are capable of nucleating crystallization during melt spinning as well as under quiescent conditions. They readily explain the observed differences in crystallinity index and molecular orientation in the filaments. By nucleating the crystallization at higher temperatures, the pigments encourage the formation of monoclinic rather than smectic phase, allow greater opportunity for crystals to grow during subsequent cooling, and they reduce the as-spun

Table 4.10 Solidification Position and Onset Temperature of Crystallization on Spinline for PP-1 Filaments

| Filament | Solidification Position (distance from spinline) (cm) | Onset Temperature of Crystallization (°C) |
|---|---|---|
| Natural PP-1 | 180 | 74 |
| 0.05 % Red PP-1 | 160 | 84 |
| 0.5 % Red PP-1 | 130 | 100 |
| 1.0 % Red PP-1 | 130 | 100 |
| 0.05 % Blue PP-1 | 150 | 89 |
| 0.5 % Blue PP-1 | 130 | 100 |
| 1.0 % Blue PP-1 | 130 | 100 |
| 0.05 % White PP-1 | 175 | 77 |
| 0.5 % white PP-1 | 175 | 77 |
| 1.0 % White PP-1 | 175 | 77 |
| 0.05 % Black PP-1 | 165 | 80 |
| 0.5 % Black PP-1 | 162 | 83 |
| 1.0 % Black PP-1 | 162 | 83 |

Table 4.11 Solidification Position and Onset Temperature of Crystallization on Spinline for PP-2

| Filament | Solidification POsition (distance from spinline) (cm) | Onset Temperature of Crystallization (°C) |
|---|---|---|
| Natural PP-2 | 140 | 94 |
| 0.5% Red PP-2 | 130 | 100 |
| 0.5% black PP-2 | 140 | 94 |

molecular orientation due to lower molecular orientation in the melt at the point at which crystal nuclei are formed.

Table 4.11 shows solidification positions and onset temperatures for PP-2. The extrusion temperature was 220 °C, the mass throughput was 2.0 g/min, and the take-up velocity is 1400 m/min. Compared to natural PP-1, natural PP-2 has solidification point closer to the spinneret and therefore has higher onset crystallization temperature. This is due to the high viscosity of the resin and, therefore, high rheological stress in the spinline and high crystallization rate. On the other hand, the effect of pigments on the on-spinline crystallization temperature of PP-2 is less then that of PP-1. That means PP-2 is less sensitive to the effect of nucleating crystallization because the high rheological stress in the spinline causes stress induced crystallization to be dominant in the crystalization process.

## 4.5 Effect of Pigments on Mechanical Properties of As-spun Polypropylene Filaments

Figure 4.25 and Figure 4.26 present the results of tensile tests for the filaments of the natural PP-1 at the three levels of pigment concentration. It was found that

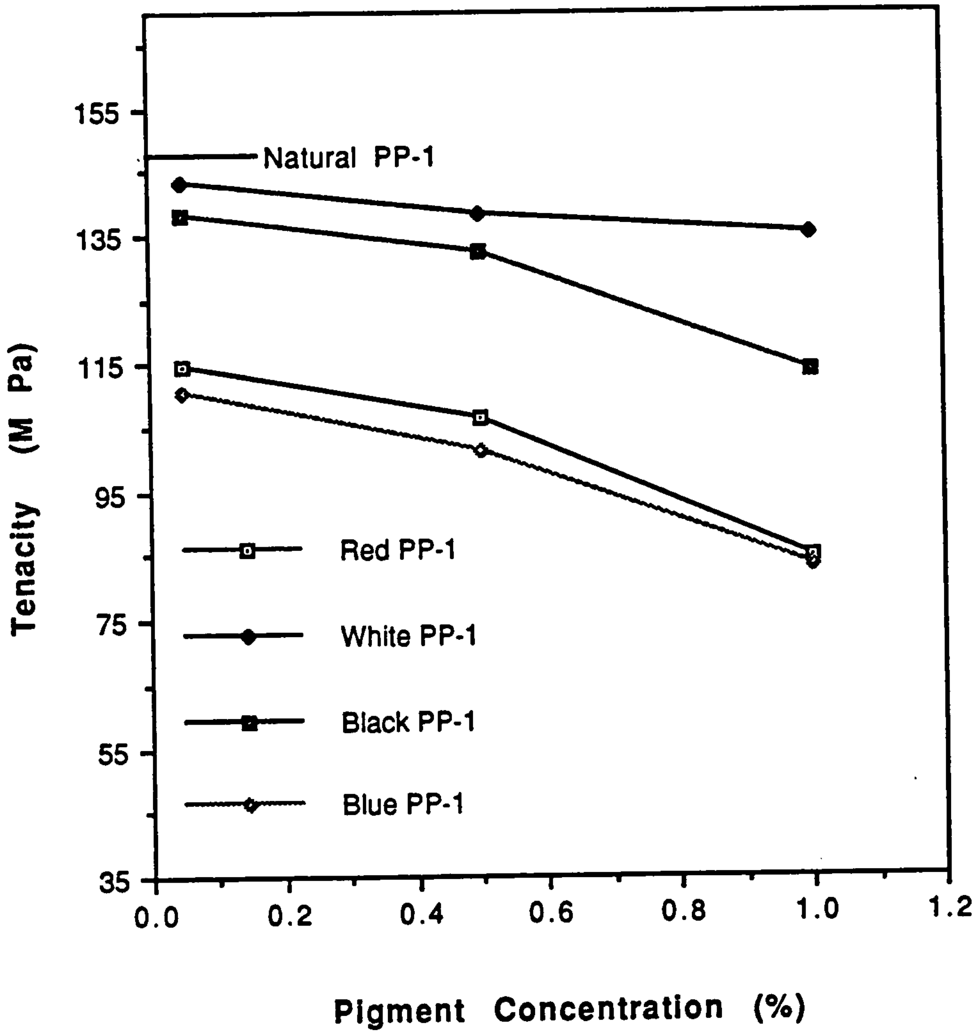


Figure 4.25 Tenacity vs. Pigment Concentration for PP-1 Filaments

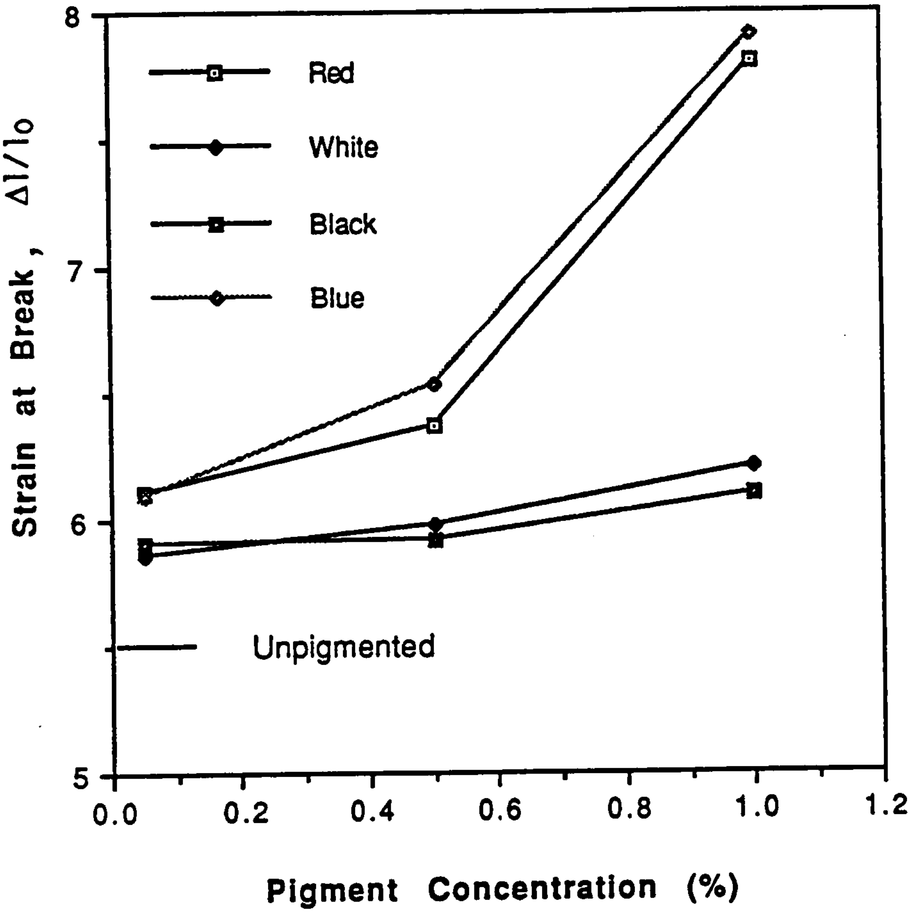


Figure 4.26 Strain at Break vs. Pigment Concentration for PP-1 filaments.

natural PP-1 filament has higher tenacity and lower elongation at break than all pigmented PP-1 filaments spun at the same processing conditions. The change in mechanical properties increases as the concentration of pigment increases for each pigment. The blue and red pigments had greater influence on tenacity and elongation at break than the white and black pigments. The difference between natural and pigmented PP-1 filaments is possibly due to the different morphology. The difference among the pigmented sample appears to reflect the differences of nucleating power previously established among the different pigments. The red and blue pigments are highly active as nucleating agents which causes crystallization at higher temperatures and results in fewer tie molecules and lower molecular orientation with the result of lower breaking stress. Higher elongations result from greater unfolding of lamellae in the spherulites formed in the pigmented samples.

Figure 4.27 and Figure 4.28 show the results of tensile tests for natural, 0.5% red and 0.5% white pigmented PP-1 filaments at different take-up velocities. The tenacity of all the PP-1 samples increases with increase of take-up velocity while the elongation to break exhibits the reverse trend. At the same take-up velocity the natural PP-1 filament has higher tenacity and lower

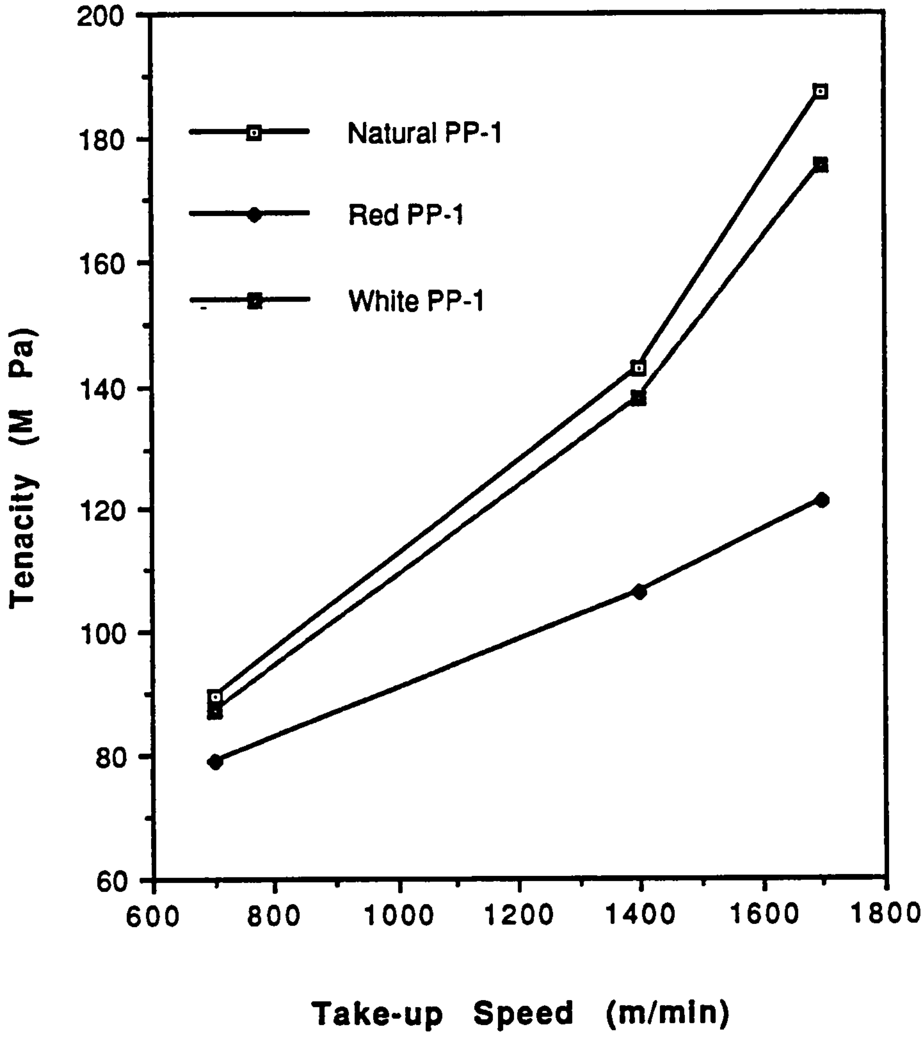


Figure 4.27 Tenacity vs. Take-up Speed for PP-1 Filaments

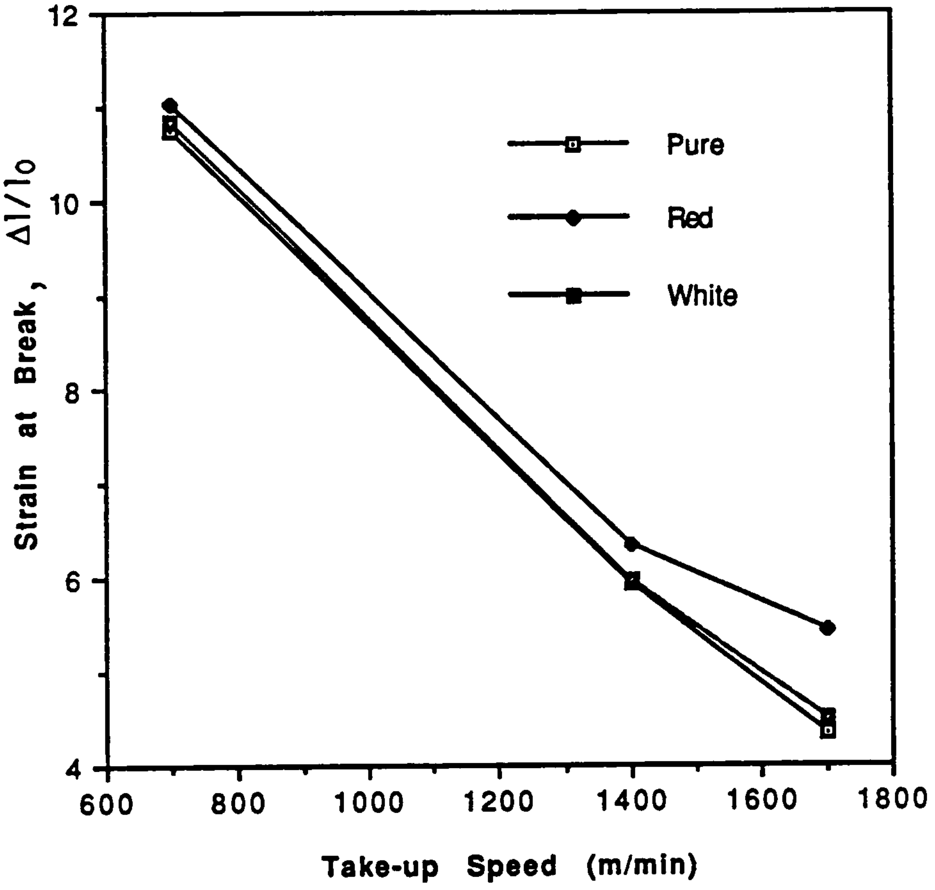


Figure 4.28 Strain at Break vs. Take-up Velocity for PP-1 Filaments

elongation at break than either red or white pigmented PP-1 filaments. However, the mechanical properties of white pigmented PP-1 fiber are much closer to those of the natural PP-1 fiber than are those of the red pigmented PP-1 fiber, which is probably due to the fact that the white pigment has much smaller nucleation effect on crystallization of polypropylene. These results appear to reflect the observed differences in orientation of the filaments as measured by the birefringence values discussed in previous section.

Figure 4.29 and Figure 4.30 present the mechanical properties for natural and 0.5% red pigmented PP-1 at different mass throughput. The red pigmented PP-1 filaments possess lower tenacity and higher elongation at break than the natural PP-1 filaments under all mass throughput conditions. Tenacity decreases with increasing of the mass throughput while the elongation at break increases, which is due to the fact that the stress level in the spinline increases with decrease of mass throughput.

Figure 4.31 to Figure 4.36 present the mechanical properties of the filaments of natural, red and black pigmented PP-2 with varying pigment concentration, take-up velocity and mass throughput. The tenacity and elongation at break of these filament samples show similar tendencies with change of processing conditions to those observed for

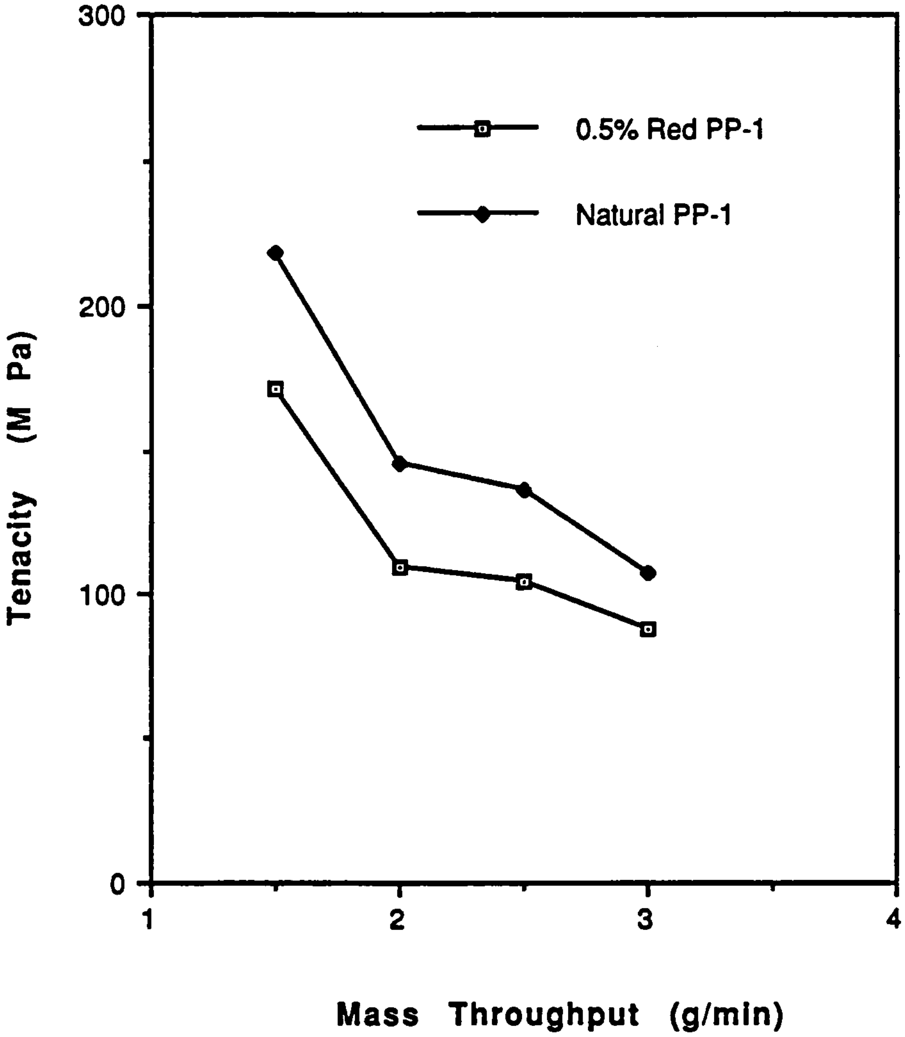


Figure 4.29 Tenacity vs. Mass Throughput for PP-1 Filaments

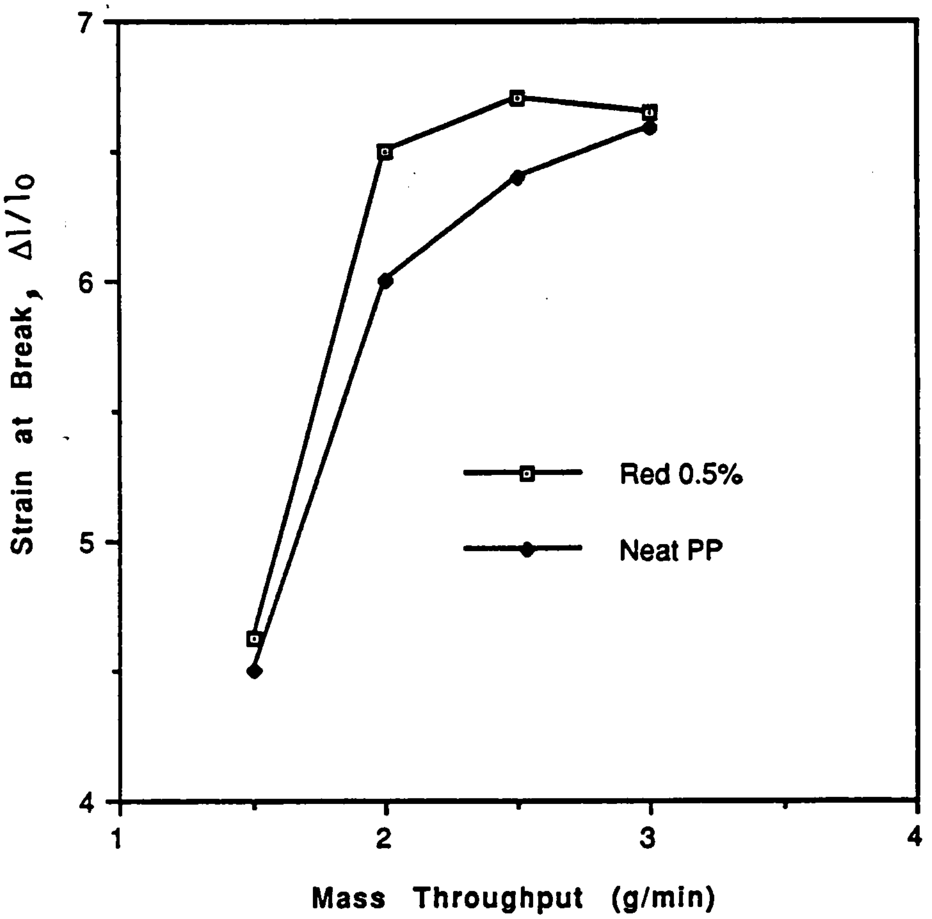


Figure 4.30 Strain at Break vs. Mass Throughput for PP-1 Filaments

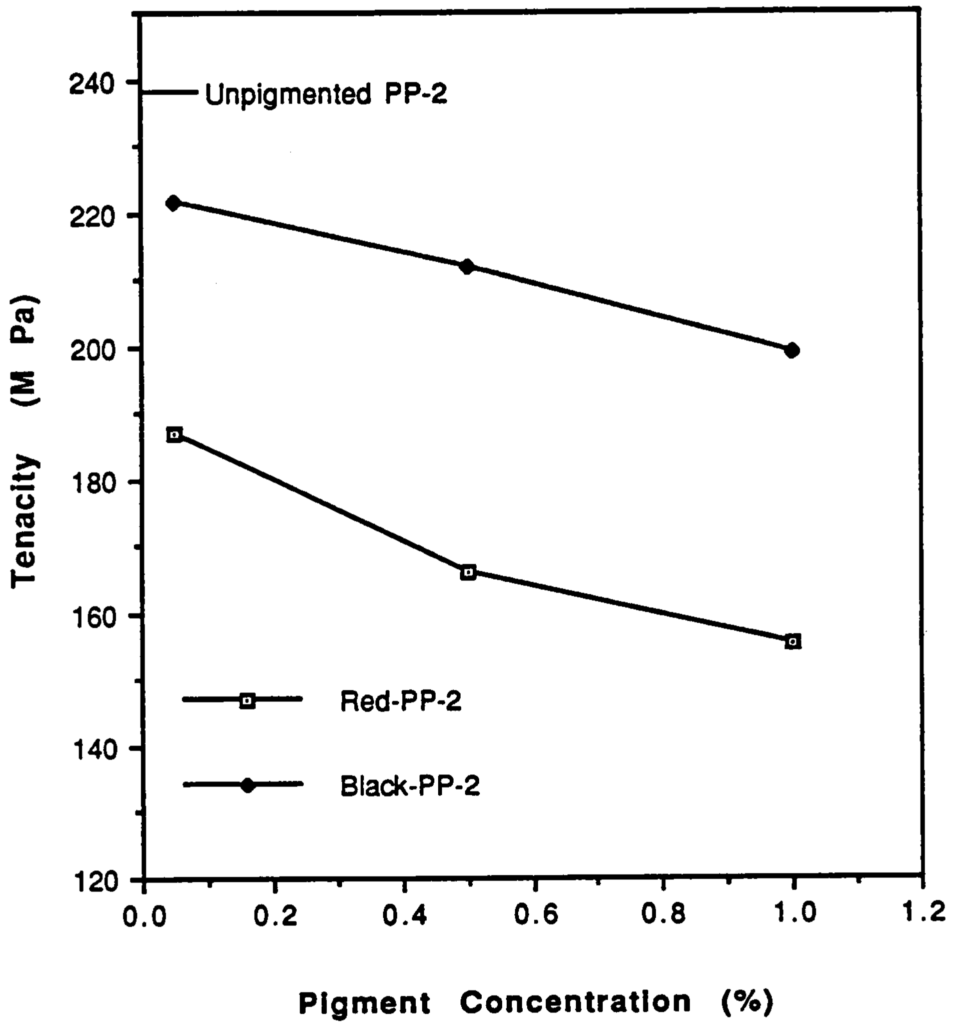


Figure 4.31 Tenacity vs. Pigment Concentration for PP-2 Filaments.

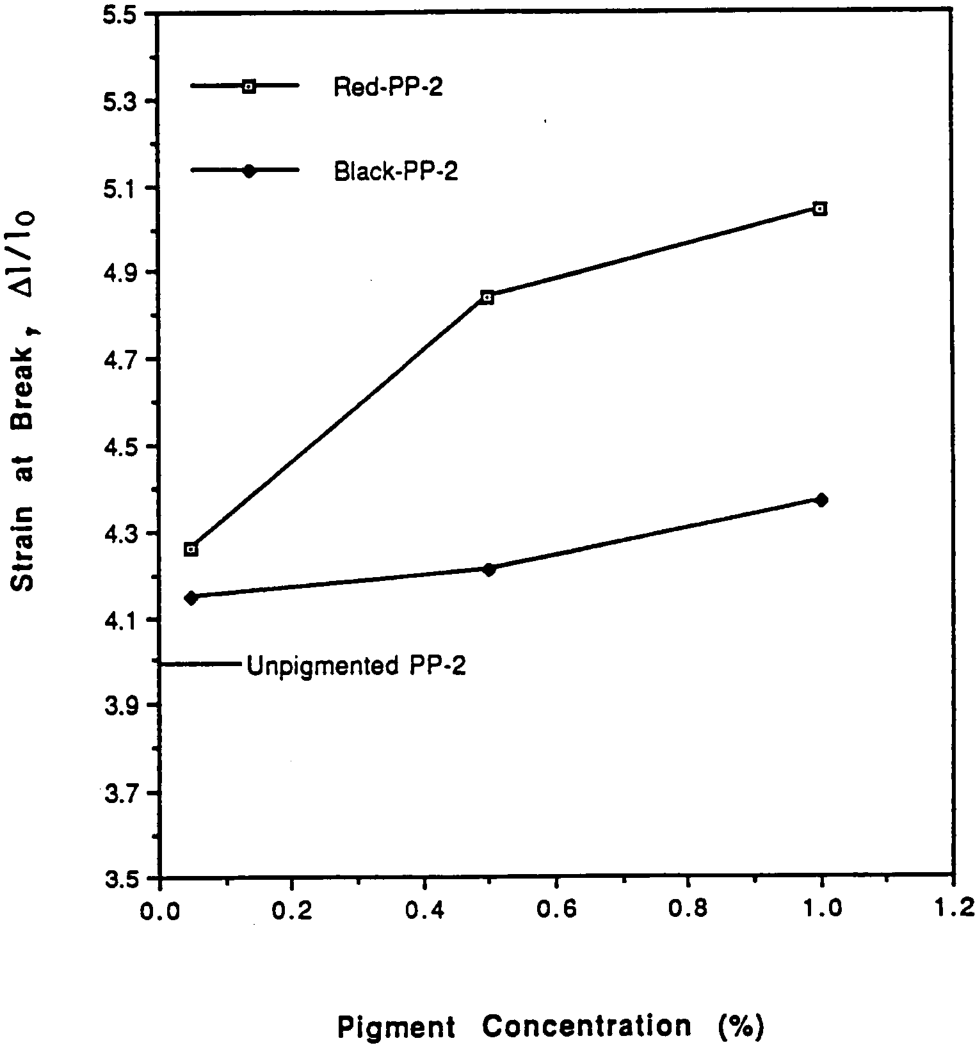


Figure 4.32 Strain at Break vs. Pigment Concentration for PP-2 Filaments.

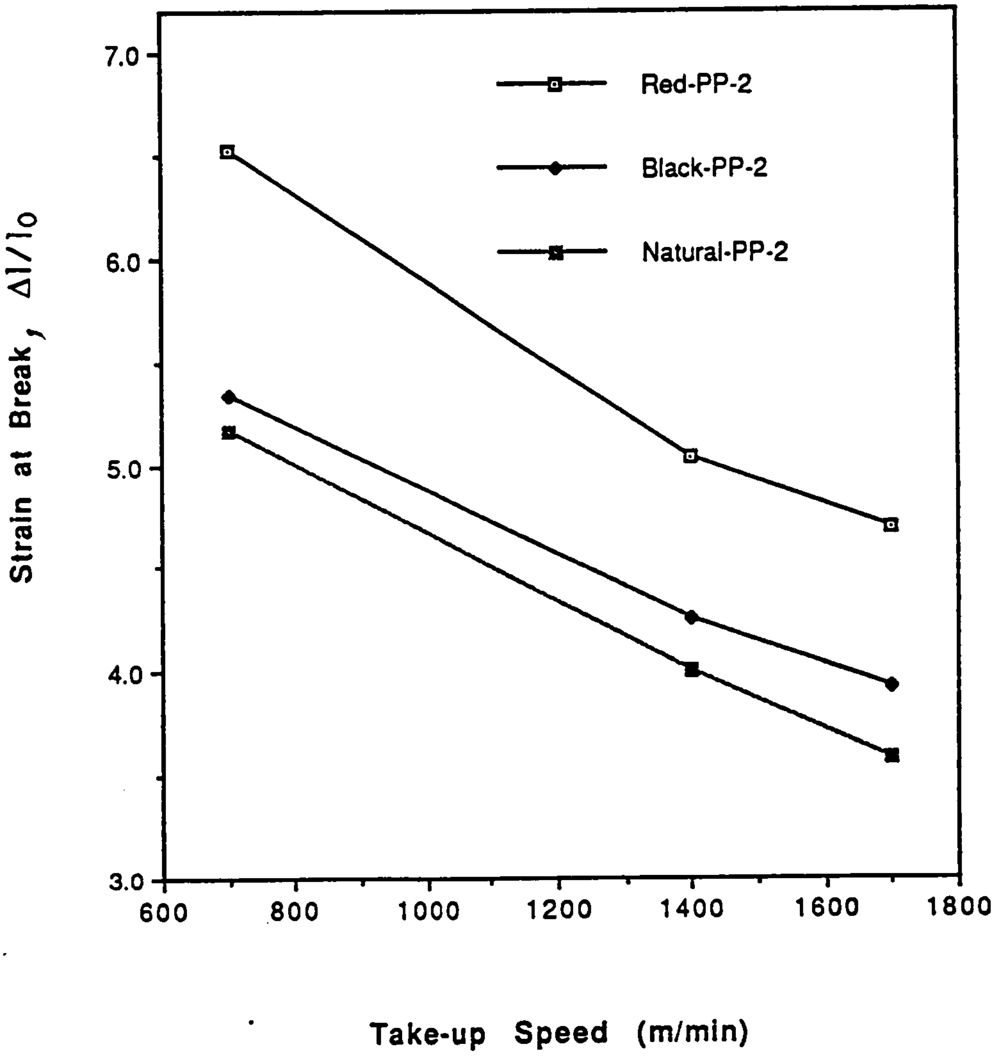


Figure 4.33 Strain at Break vs. Take-up Speed for PP-2 Filaments.

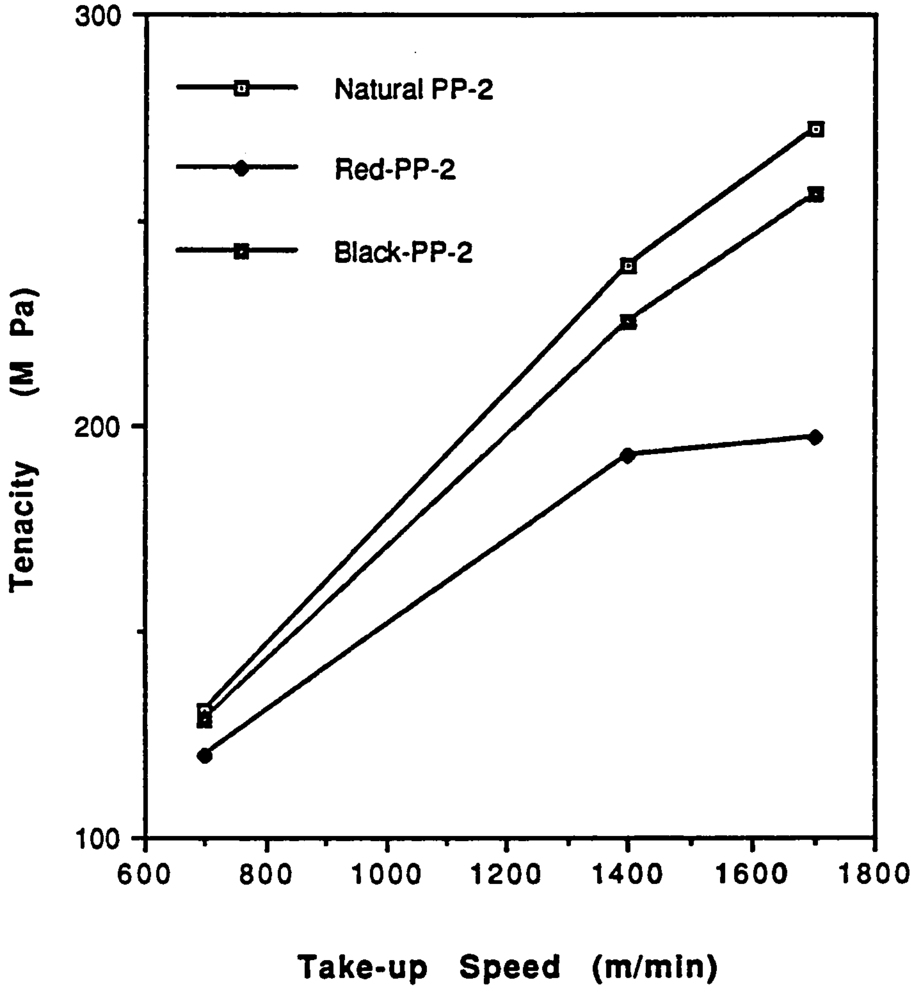


Figure 4.34 Tenacity vs. Take-up Speed for PP-2 Filaments.

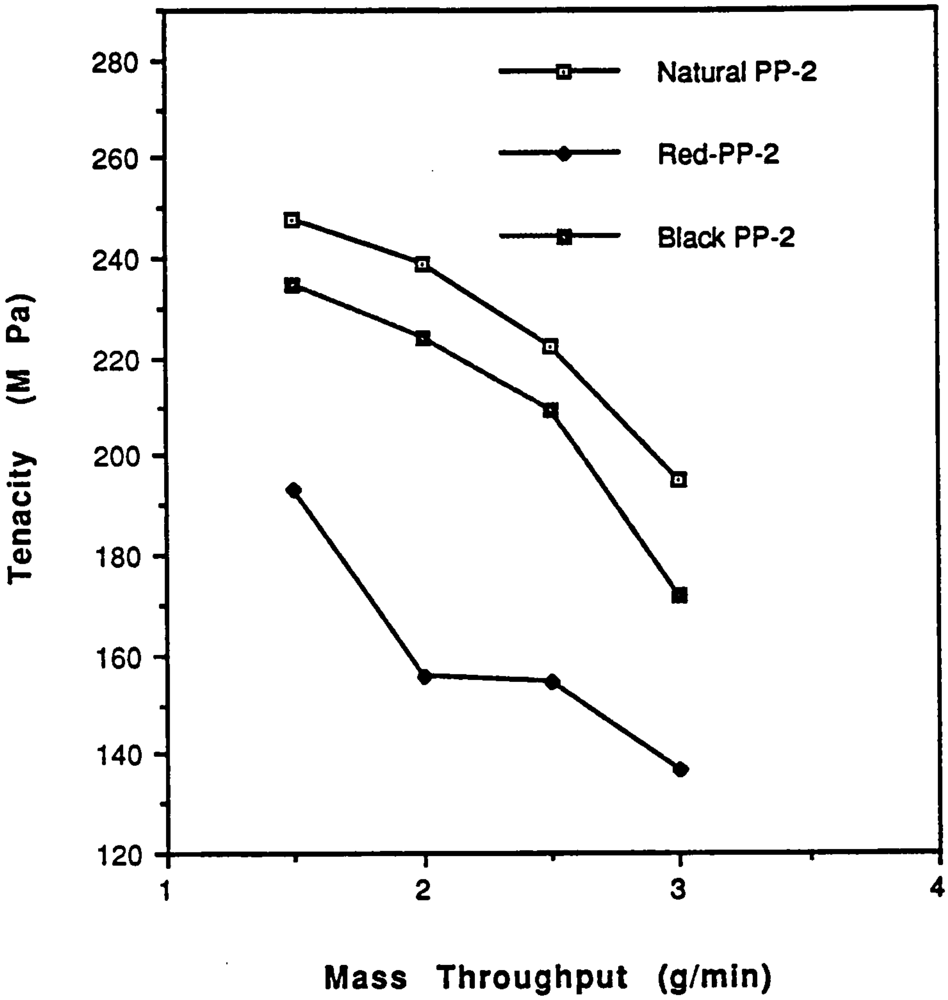


Figure 4.35 Tenacity vs. Mass Throughput for PP-2 Filaments.

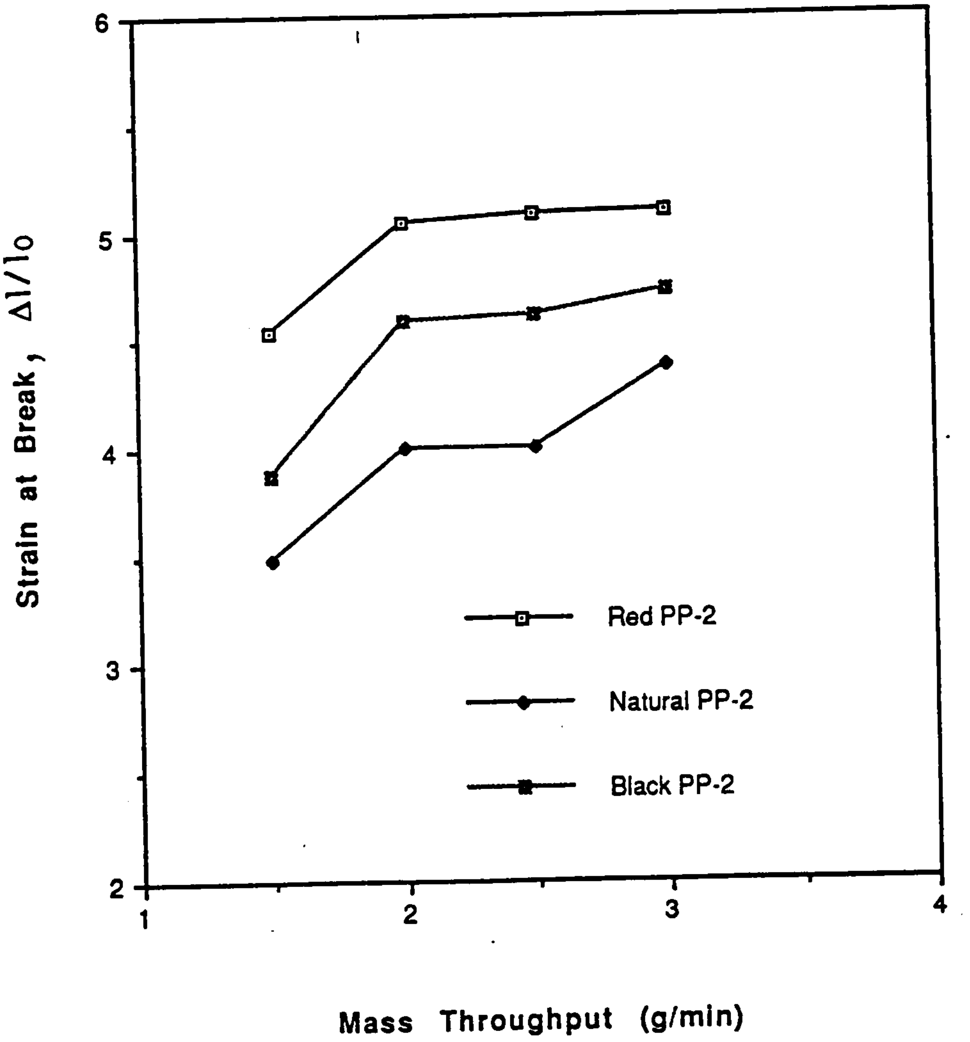


Figure 4.36 Strain at Break vs. Mass Throughput for PP-2 Filaments.

the PP-1 samples, but the PP-2 filaments have higher tenacity and lower elongation at break than the PP-1 filaments, given the same pigment concentration level and processing conditions. These results also reflect the observed differences in orientation of the PP-1 and PP-2 filaments discussed in the section on birefringence. Tables 4.12 through 4.15 show the standard deviation data of mechanical property testing. They were calculated based on fifteen tensile tests and according to the equation

$$S=\sqrt{\frac{1}{(n-1)}\sum_{i=1}^{n}(x_i-\overline{x})^2} \qquad (4.1)$$

Figure 4.37 and Figure 4.38 present plots of the tenacities of filaments versus birefringence values (orientation). Figures 4.39 and 4.40 show plots of the strain at break versud birefringence values. Each point at a curve correspoundents to a certain pigment concentration level. The figures show that the tenacity of pigmented PP filament does not correlate well with the birefringence value as observed in previous studies on natural PP filaments (52, 53, 23). This may indicate that for pigmented polymers the orientation of the filament is not the only variable that determines the tenacity of the filament. These results suggest that the pigment size and pigment concentration in the filament might also play

Table 4.12 Sample Standard Deviation of Mechanical Property Testing for PP-1 Filaments

| Sample | S for Tenacity (MPa) | S for Strain at Break |
|---|---|---|
| Natural PP-1 | 1.3 | 0.19 |
| 0.05% Blue PP-1 | 6.6 | 0.35 |
| 0.5% Blue PP-1 | 4.7 | 0.26 |
| 1.0% Blue PP-1 | 6.7 | 0.21 |
| 0.05% Red PP-1 | 4.1 | 0.32 |
| 0.5% Red PP-1 | 5.0 | 0.29 |
| 1.0% Red PP-1 | 3.8 | 0.29 |
| 0.05% Black PP-1 | 4.7 | 0.18 |
| 0.5% Black PP-1 | 5.1 | 0.14 |
| 1.0% Black PP-1 | 8.0 | 0.31 |
| 0.05% White PP-1 | 4.5 | 0.12 |
| 0.5% White PP-1 | 6.9 | 0.23 |
| 1.0% white PP-1 | 0.6 | 0.21 |

Table 4.13 Sample Standard Deviation of Mechanical Property Testing for PP-1 Filaments with Different Take-up Velocity

| Sample | Speed (m/min) | S for Tenacity (MPa) | S for Strain at Break |
|---|---|---|---|
| Natural PP-1 | 1700 | 6.3 | 0.25 |
| Natural PP-1 | 1400 | 1.3 | 0.19 |
| Natural PP-I | 700 | 6.6 | 0.49 |
| 0.5% Red PP-1 | 1700 | 4.8 | 0.29 |
| 0.5% Red PP-1 | 1400 | 5.0 | 0.29 |
| 0.5% red PP-1 | 700 | 7.0 | 0.44 |

Table 4.14 Sample Standard Deviation of Mechanical Property Testing for PP-1 Filaments with Different Mass Throughput

| Sample | Mass Throughput (g/min) | S for Tenacity (MPa) | S for Strain at Break |
|---|---|---|---|
| Natural PP-1 | 1.5 | 4.2 | 0.18 |
| Natural PP-1 | 2.5 | 7.0 | 0.20 |
| Natural PP-1 | 3.0 | 3.8 | 0.22 |
| 0.5% Red PP-1 | 1.5 | 4.8 | 0.19 |
| 0.5% Red PP-1 | 2.5 | 5.0 | 0.24 |
| 0.5% red PP-1 | 3.0 | 7.0 | 0.19 |

Table 4.15 Sample Standard Deviation of Mechanical Property Testing for PP-2 Filaments

| Sample | S for Tenacity (MPa) | S for Strain at Break |
|---|---|---|
| Natural PP-2 | 4.8 | 0.22 |
| 0.5% red PP-2 | 3.2 | 0.18 |
| 0.5% Black PP-2 | 2.9 | 0.24 |

important roles in determining the value of the tenacity of the filament.

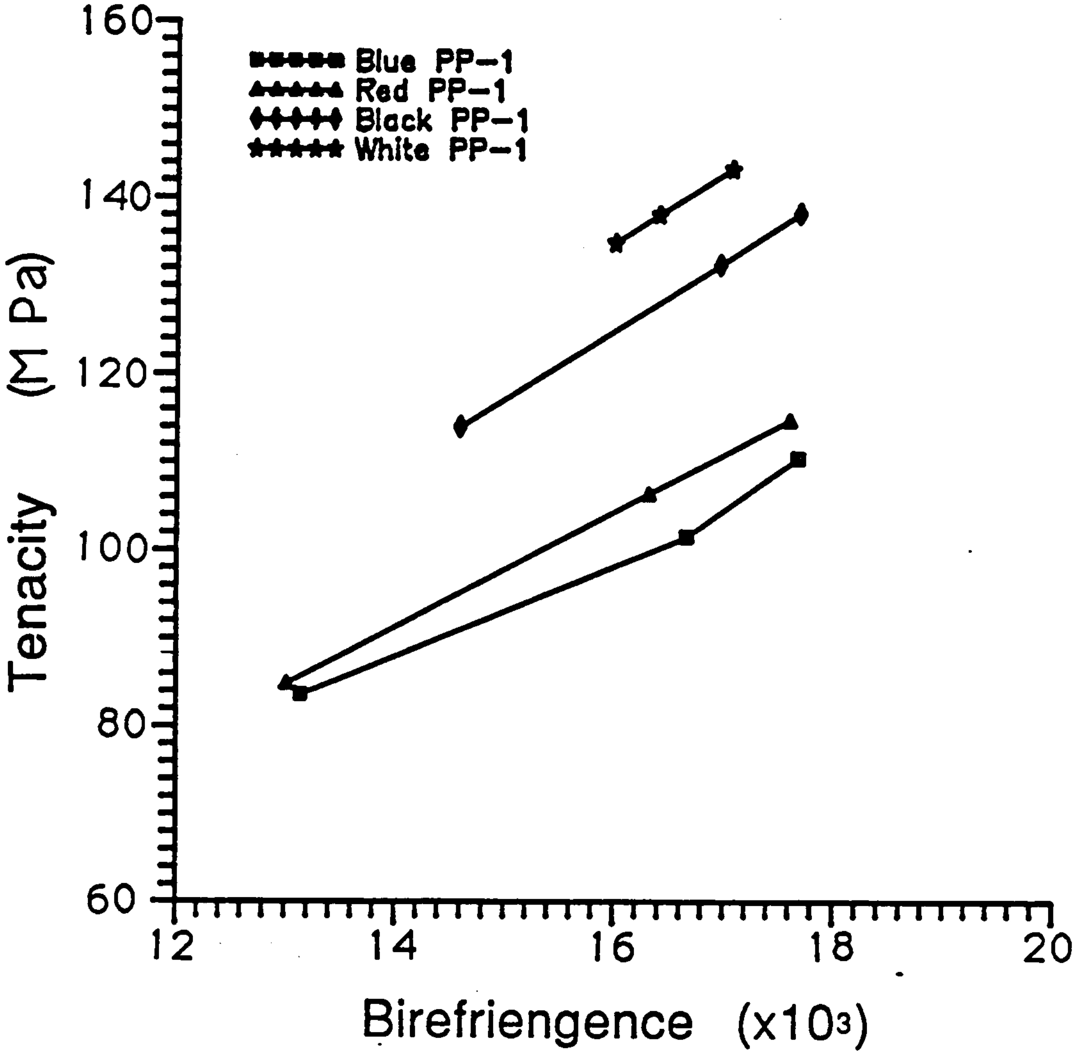


Figure 4.37 Tenacity vs. Birefringence for Pigmented PP-1 Filaments.

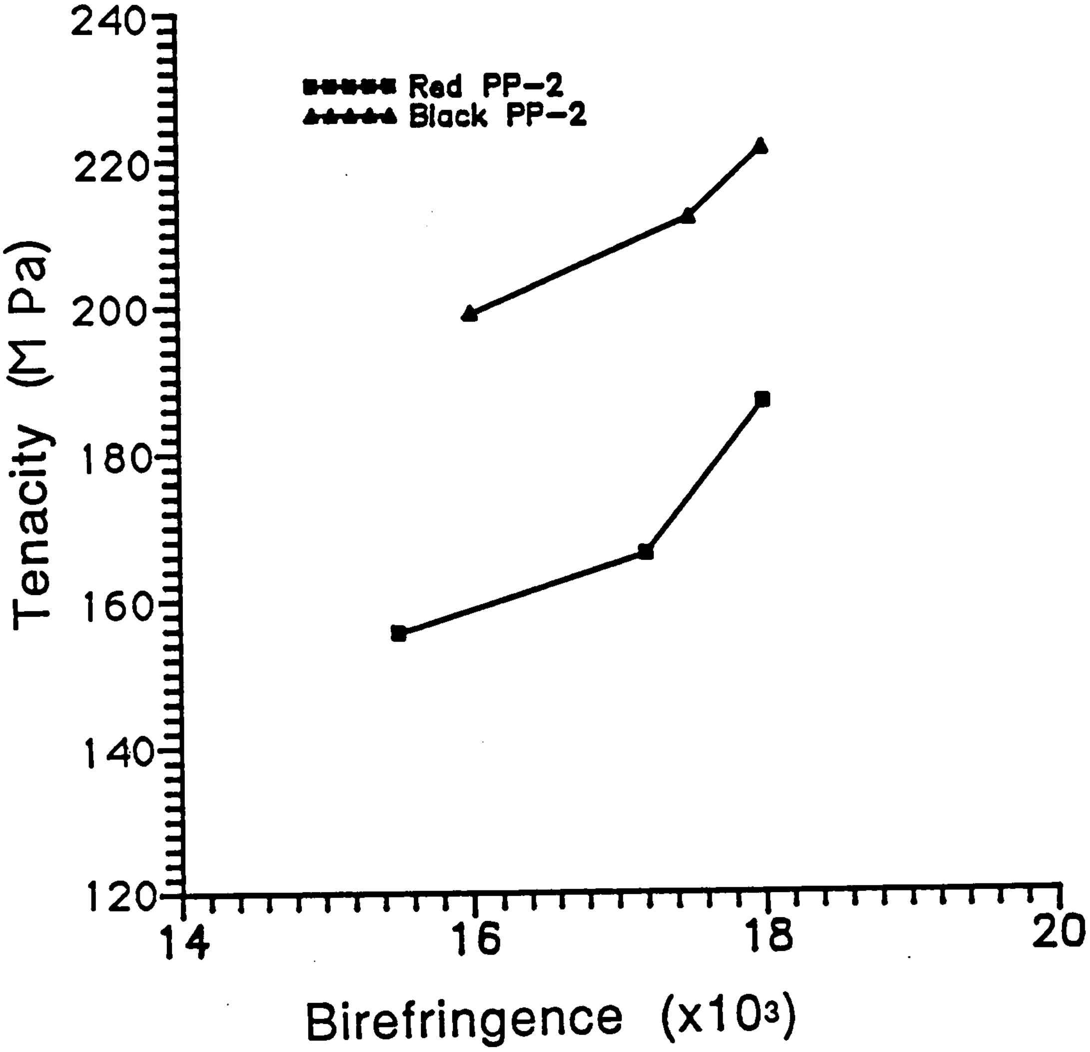


Figure 4.38 Tenacity vs. Birefringence for Pigmented PP-2 Filaments.

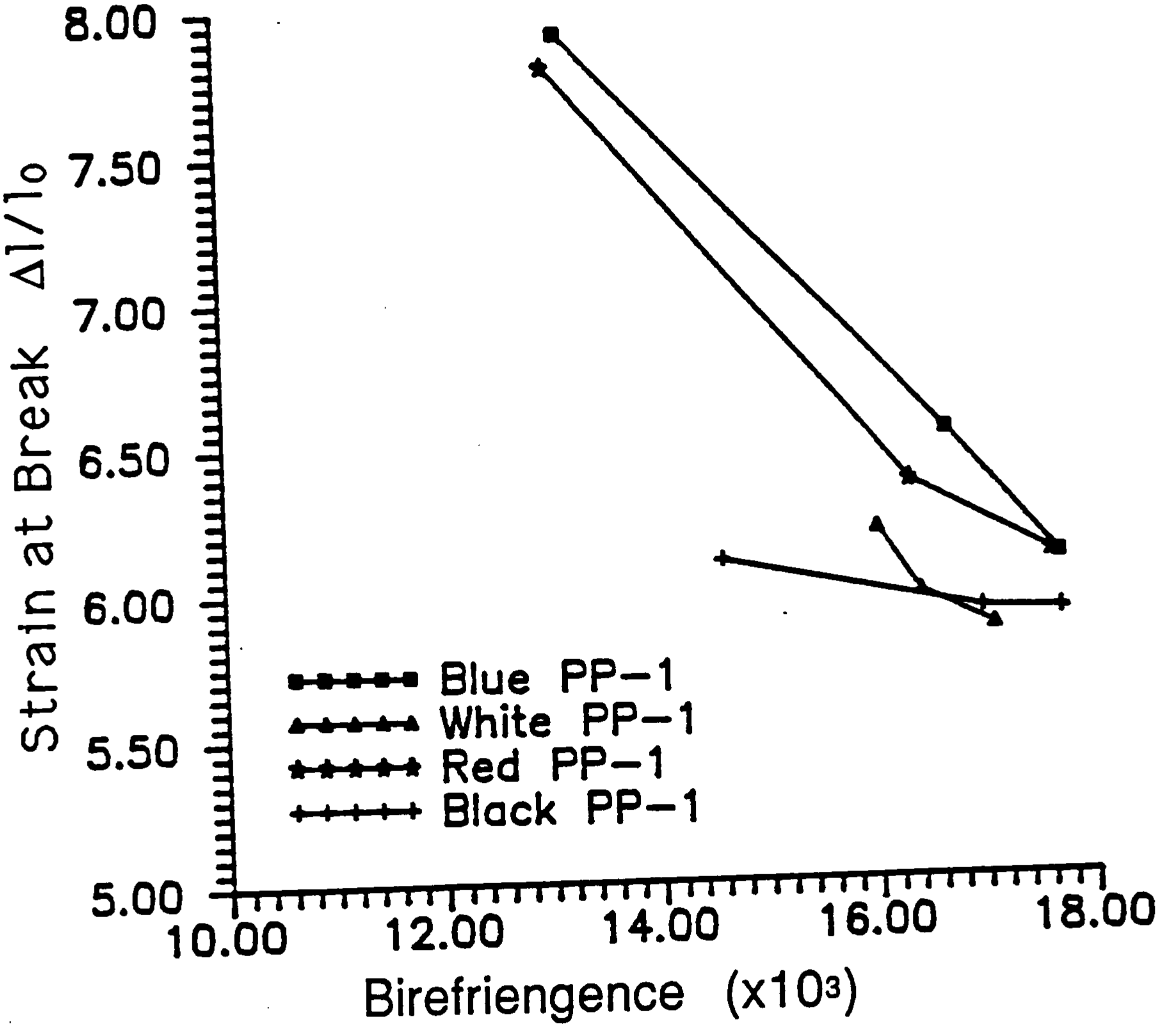


Figure 4.39 Strain at Break vs. Birefringence for Pigmented PP-1 Filaments.

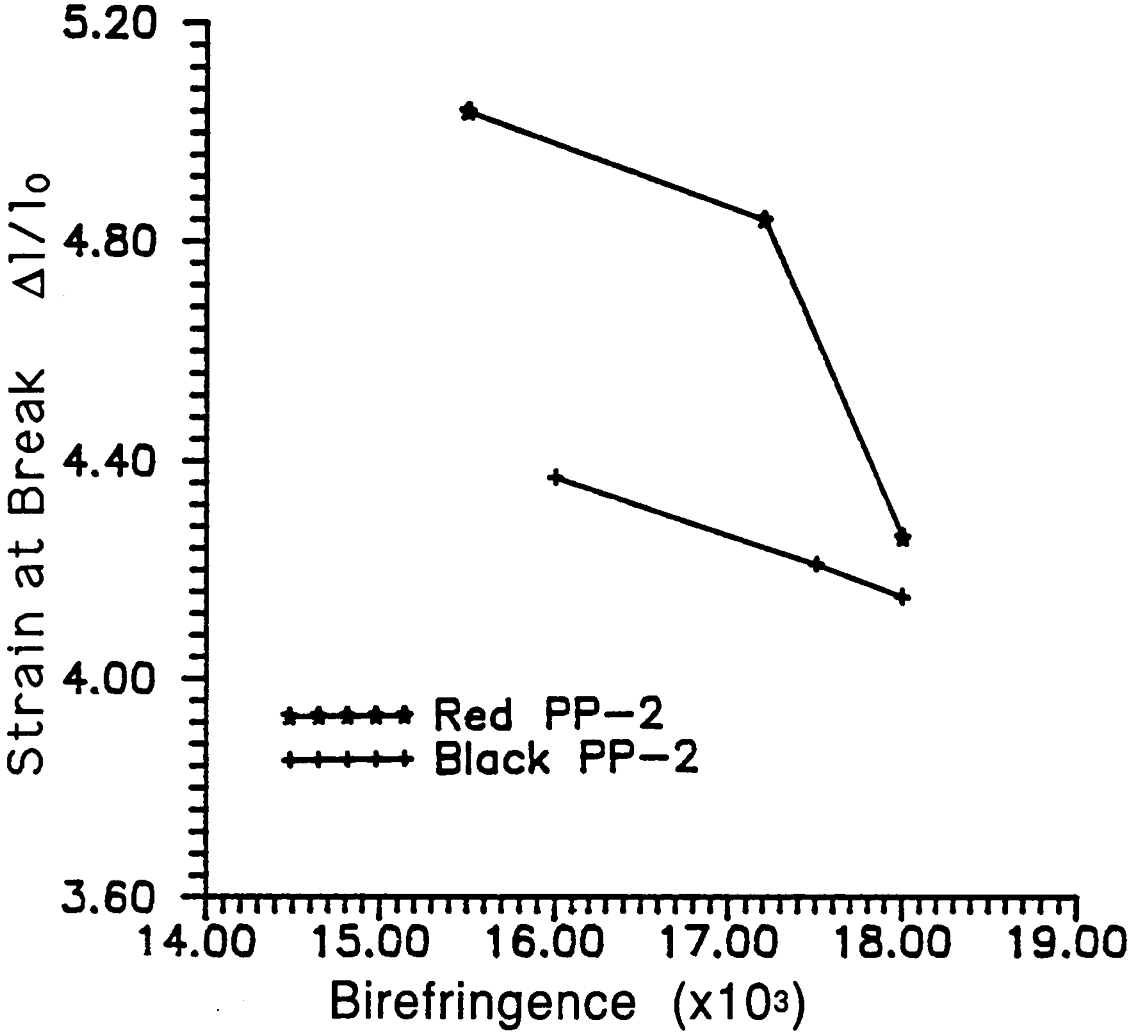


Figure 4.40 Strain at Break vs. Birefringence for Pigmented PP-2 Filaments.

# CHAPTER V

# CONCLUSIONS AND RECOMMENDATIONS

The main purpose of this study was to investigate the influence of various pigment additions on two types of polypropylene base resins. It has provided much useful information concerning the effect of pigment additions on the development of structure and properties of melt spun polypropylene filaments.

The following conclusions were drawn from this study:

1. The pigment additions act as nucleating agents and change the crystallization kinetics. The crystalline spherulite is smaller in size and the morphology of polypropylene is changed due to the addition of the pigments.
2. Because of their effects on crystallization kinetics, the pigments also have a marked influence on the way in which the filament draw down during the spinning process. They cause crystallization to occur at higher temperatures and at shorter distances from the spinneret during melt spinning. They also result in higher levels of crystallinity for a given set of spinning conditions, and they reduce the as-spun molecular orientation due to lower

molecular orientation in the melt at the point at which crystal nuclei are formed.

3. The pigments vary in their ability to influence crystallization kinetics as follows:

White < Black < Red < Blue

Of these pigments, the white and black are inorganic pigments and red and blue are organic pigments. The blue pigment is highly active as a nucleating agent while the white pigment has only a minor influence.

4. Pigments that produce a marked effect on crystallization kinetics also affect the mechanical properties of the melt spun filaments. Increased nucleating power causes crystallization at higher temperatures in the threadline and causes the filament to have lower tenacity and higher elongation at break.

5. Polypropylene resins with different molecular weights respond differently to the effect of pigments additions. Compared to PP-1 sample PP-2 (melt flow rate 12), a resin with higher molecular weight is less sensitive to the effect of nucleating crystallization because the high rheological stress in the spinline causes stress induced crystallization to be dominant in the crystallization process.

In order to provide a fundamental understanding of the effect of pigment package on the development of structure and properties of polypropylene fiber it would be beneficial to conduct a few more studies.

1. It would be desirable to study the effect of pigments on the rheology of the polymer. Both off-line (basic rheology measurements) and on-line measurement are needed to fully evaluate the influence of the pigments on the processing behavior.
2. Examination of the influence of a wide range of pigment package is desirable, as it has been established that pigments vary substantially in their effect on the spun filaments.
3. Influence of carrier resin on crystallization, structure and mechanical properties of pigmented PP might be investigated.
4. A model could be developed to study the contribution or effect of spinline stress and pigment nucleation on crystallization kinetics on spinline, the ratio of these two contributions and their interaction.

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In September of 1986 she began graduate studies at the University of Tennessee, Knoxville. While attending graduate school, she worked as a research assistant for the Agricultural Experimental Station from 1987 to 1988. She was nominated as a member of Phi Kappa PHi Honor Society in 1987. She received her M. S. degree in Textile and Apparel in May 1989. In Jan. 1989 she transferred to the Department of Material Science & Engineering in the University of Tennessee, Knoxville. She worked as a research assistant from Jan. 1989 to Dec. 1990.