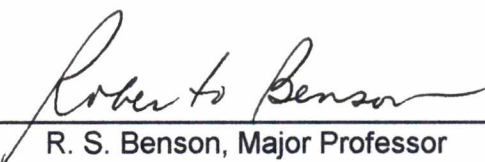


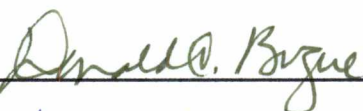
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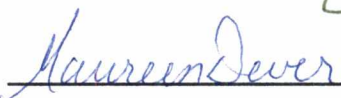
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CHARACTERIZATION OF POLYPROPYLENE/POLY(VINYL ALCOHOL) BLENDS.

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Liliana Mendez

August, 1994

*To my parents,
Esau Mendez Garcia
and
Monica Muhlemann de Mendez,
and the special person in my life,
Rafael Sanmiguel Blanco
with love...*

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ABSTRACT

Polypropylene (PP) and poly(vinyl alcohol) (PVOH) resins of varying degree of hydrolysis were mechanically blended. A (90/5) composition was blended with 5 and 10 % polypropylene-grafted-maleic anhydride copolymer (g-PP). The blends were characterized by Differential Scanning Calorimetry (DSC), Tensile Testing, Dynamic Mechanical Analysis (DMA), Fourier Transform Infrared Spectroscopy (FTIR), and X-Rays Diffraction. Additionally, study of the morphology and examination of water uptake of the blended systems were conducted.

The study of thermal properties of the blended systems show a shift in the crystallization temperature (T_c) of PP towards higher temperatures. This change in the T_c of PP along with the growing of PP spherulites surrounding PVOH particles implies that the PVOH acts as a nucleating agent.

A change of PVOH content in PP/PVOH blends and the presence of water, affects both the mechanical and dynamic mechanical properties. The tensile strength and elongation to break of PP/PVOH blend systems, as well as the modulus for wet samples decrease with PVOH content, while an increase in the modulus of dry samples is observed with increasing PVOH content. Results of tensile tests and DMA suggest that water acts as a plasticizer in the blends.

The addition of g-PP promotes an enhancement of the mechanical properties of the blends and a finer dispersion of the PVOH particles in the PP matrix, which indicates that g-PP acts as a compatibilizing agent. FTIR spectra of the blends indicate formation of hydrogen bonding when g-PP is present in the systems.

Due to the fact that PVOH is a water-soluble polymer, blends of PP/PVOH have shown the ability to absorb water for certain periods of time, before partial or complete dissolution of PVOH occurs.

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I. INTRODUCTION.

Polymer blends play an increasingly important role in industry. This is because of the ability to tailor their properties to specific end use at low cost. By blending two or more polymers having different molecular characteristics, new materials with a combination of properties can be obtained (1). This study used blends of polypropylene and poly(vinyl alcohol) to improve the wettability of polypropylene.

Polypropylene (PP) is a material which is extensively used in numerous technical applications due to its low specific weight, adaptability to complicated structures, excellent solvent resistance, and availability at low cost. However, the poor wettability of polyolefin surfaces gives rise to problems when absorption of water is required. To overcome this difficulty, various solutions have been proposed: addition of fillers capable of absorbing water, and surface treatments such as plasma treatment, flame treatment, corona treatment, and chemical acid etching, among others. These surface treatments introduce polar groups in to the PP surface making possible the adhesion of PP to polar surfaces or the absorption of water (2).

In general, modifications of PP are intended to impute different, desired properties to a new modified resin, such as enhanced thermal stability; multiphase physical responses; biological resistance; compatibility; degradability; impact response; flexibility or rigidity; wettability, etc. (3).

Poly(vinyl alcohol) (PVOH) is a crystalline polymer which is biodegradable and soluble in water. Different commercial grades of PVOH depending on the percentage hydrolysis and degree of polymerization can be found. The properties of PVOH depend on the hydrogen bonds acting between hydroxyl groups and the involute state of the molecule (4). PVOH is usually produced from polymerization of vinyl acetate. It can be molded, cast into films, and spun into yarns. The main applications of PVOH

include warp sizing and processing of textile fibers, paper manufacture, adhesives, and optical films (4).

Compatibilization agents are generally used for bridging the phases of immiscible blends. The bridging by compatibilizers is analogous to the role of surfactants in oil-oil emulsions (5). Compatibilizing agents may reduce interfacial tension and increase adhesion between the phases, allowing a finer dispersion and more stable morphology to be created. The morphology and properties also depend on parameters such as composition and processing conditions during mixing (5). For example, the size of the dispersed droplets becomes smaller as the interfacial tension is reduced.

Polypropylene-grafted-maleic anhydride (PP-g-MAH), a block copolymer, was chosen as a compatibilizing agent for PP/PVOH blends. Grafting of unsaturated monomers such as maleic anhydride (MAH) and acrylic acid to olefins are the most common free-radical grafting reactions. Grafting of MAH to polyolefins has been used to improve adhesion of the polyolefin to polar phases (6). While the highly absorbant fillers may tend to leach-out, and the completeness of the homogeneity of surface modification cannot be guaranteed. The blending of a water-soluble polymer (PVOH) in the presence of a compatibilizer (PP-g-MAH) should lead to a stable water absorbant material.

II. BACKGROUND.

2.1. POLYPROPYLENE.

Polypropylene (PP) is a semi-crystalline thermoplastic polyolefin resin. The excellent combination of good mechanical properties and favorable economics, have made polypropylene one of the most important commercial thermoplastics.

2.1.1. MANUFACTURING OF POLYPROPYLENE.

Shortly after the discovery of High Density Polyethylene (HDPE), it was found by Natta, that propylene and higher α -olefins could also be polymerized by the use of coordination catalysts, such as $\text{TiCl}_3\text{-Al}(\text{CH}_2\text{CH}_3)_3$ (7). The polymerization of propylene produces two kinds of polypropylene resins: an essentially amorphous, rubbery, and soluble fraction and a highly crystalline, hard, and insoluble fraction.

The first step in the production of PP is based on the procurement of its monomer, propylene. Over 90 % of the propylene consumed today is polymerized to high-octane gasoline (8). Polypropylene, however, requires substantially pure propylene, and this demands extra processing steps.

Several methods have been suggested for the production of propylene (8), but the most common and practical involves the dehydration of *n*-propanol and 2-propanol. The latter, yields a highly pure propylene (99 %) which is suitable for manufacturing of PP. In any case, the preparation of propylene requires the use of sulfuric acid and an aluminum sulfate catalyst.

Catalytic cracking of petroleum is performed in order to produce gasoline and heating oil as the main products; just 2-5 % of propylene is attained, but if the raw material is subjected to several separations at 380-530 °C for 5-120 seconds under a

pressure of 250-300 kPa, 50-75 % of propylene can be obtained. The principal impurities are H_2S , and CO_2 (9).

The purification of propylene is essential in order to avoid poisoning of the catalyst and variation in polymer properties. In some cases, purification of propylene is carried out in a rectifying column with selective absorption of some impurities (8). Once the pure gas is obtained, two different paths can be followed. The first, which is the most common, is similar to the Ziegler process to polyethylene, since the catalyst is produced *in situ*. Nevertheless, in the case of PP, the catalyst is formed in a separate vessel just before the reaction is carried out. These catalyst are generally formed from transition metal salts and organometallic compounds. The preferred catalyst system for the production of isotactic polypropylene (iPP) consists of titanium trichloride and aluminum triisobutyl (8).

The manufacturing of PP can be divided in three steps: polymerization, separation of the catalysts and solvents from the polymer, and pelletizing of the polymer. Suspension polymerization is preferred because relatively low temperatures (50-80 °C) are required. High temperatures in the polymerization process tend to produce soft, atactic materials rather than the desired isotactic form. In the suspension polymerization, the monomer is added to an agitated reactor containing a dispersion of the catalyst in a liquid hydrocarbon at a pressure of about 100 atm. The temperature is maintained below the softening temperature of the polymer, and polymer granules form around the catalyst particles. The polymer granules are kept in suspension by the agitator.

The solvent-polymer granules-catalyst slurry is then pumped to a flash drum where a reduction in pressure removes the unreacted monomer, which is then recycled.

The slurry is run into a centrifuge or filter to remove the diluent, and then, the solvent is distilled to separate it from the atactic and low-molecular weight material.

The polymer is re-slurried with an extractant which usually consists of weak HCl in methanol, to decompose the catalyst and afterwards, it is removed in another centrifuge or filter. The polymer is then washed with water to remove the HCl, steam-distilled to remove final traces of solvent, dried, extruded, and formed into pellets. In order to obtain a colorless polymer, it has to be treated with suitable clays, silica gel, or other decolorizing agents. It is also necessary to add antioxidants to the polymer before it is exposed to air. The properties of the resulting polymer can be greatly influenced by the catalyst composition, physical form of the catalyst, aging of the catalyst, and gas composition.

2.1.2. STRUCTURAL ORDER OF POLYPROPYLENE.

Various degrees of order can be distinguished in polypropylene. The arrangement of the monomer repeat units in the polymer chain indicates the tacticity or degree of order of the polymer. The tacticity of the polymer is controlled by the manner in which the addition of the monomer unit takes place, and this in turn depends on the interaction between the terminal chain and the approaching monomer molecule. The arrangement is not random or accidental, and it has a great influence on the properties of the polymer. A polymer with no steric order in which the monomer units are randomly disposed in space relative to each other is called "atactic". The most important form of PP is the "isotactic" in which the monomer units are arranged in a regular succession. The ability of isotactic polypropylene to crystallize is what makes it of commercial importance. Another spatial arrangement of monomers which may be encountered for PP is called "syndiotactic". The term syndiotactic corresponds to the

polymer in which the side groups alternate up and down along the main chain. Figure 2-1 shows a schematic representation of the atactic, syndiotactic, and isotactic forms of PP.

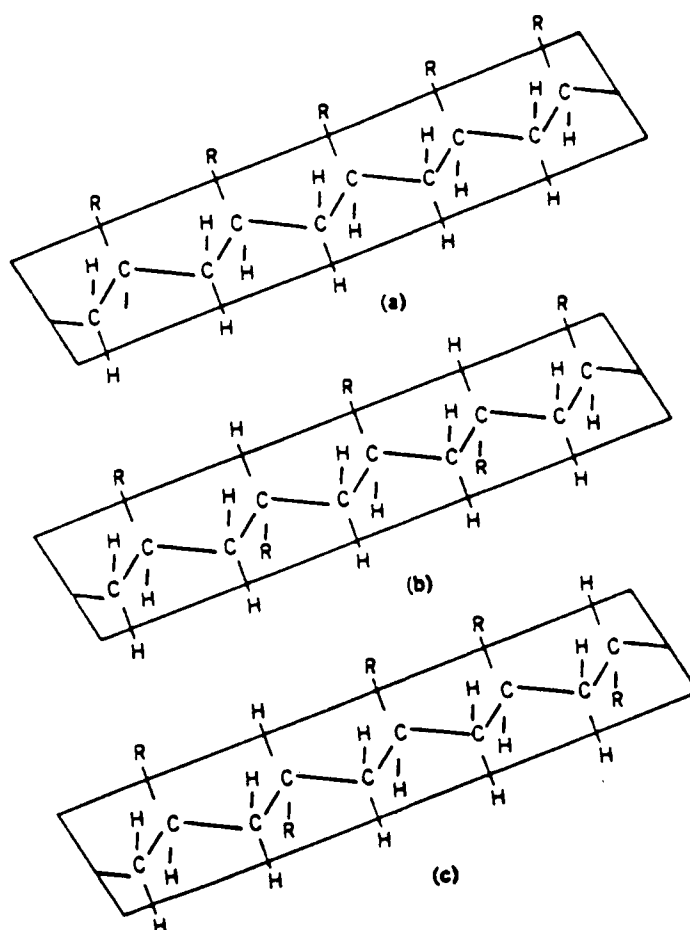


Figure 2-1. Polypropylene stereoisomers ($R = -CH_3$): (a) isotactic, (b) syndiotactic, (c) atactic (9).

The probability of isotactic placement with respect to the last unit is:

$$\sigma_i = k_i / (k_i + k_s) \quad (2-1-1)$$

and for syndiotactic placement

$$\sigma_s = k_s / (k_i + k_s) = 1 - \sigma_i \quad (2-1-2)$$

where k_i and k_s are the rate constants for the corresponding placements (10). The ratio k_s / k_i determines the degree of stereoregulation:

$$k_s / k_i = \exp (\Delta F^\ddagger / RT) \quad (2-1-3)$$

$$\Delta \Delta F^\ddagger = \Delta F^\ddagger_s - \Delta F^\ddagger_i \quad (2-1-4)$$

k_s / k_i is zero for isotactic placement, unity for atactic placement, and infinite for syndiotactic placement. $\Delta \Delta F^\ddagger$ is the free energy of activation difference between syndiotactic and isotactic placement; $\Delta \Delta F^\ddagger$ has been calculated to be of the order of 1 kcal/mole in favor of syndiotactic placement, that is, of the same order of magnitude as RT at common polymerization temperatures. Consequently, both placements are nearly equally probable under normal polymerization conditions, thus leading to essentially atactic polymers. However, the use of Ziegler Natta catalysts favors the formation of a stereoregular structure because a high degree of control of the approach and attack of monomer molecules onto the growing chain is promoted (7,10).

The arrangement of the methyl groups is not as simple as shown in Figure 2-1, because if all the methyl groups are located in the same side of the chain, they crowd each other. Due to the steric interaction of the methyl groups, the isotactic chain

assumes a helical configuration and ternary symmetry; that is, it repeats itself after three monomeric units and an identity period of 65 nm. Figure 2-2 shows the chain conformation of isotactic polypropylene. The spiral molecule interlocks with other spiral molecules to form the crystals. The upper part of the figure represents a side view of a short segment of polymer chain. Each monomer unit is rotated 120 degrees from the next one, so that the fourth one is placed identically with the first; this sequence will continue indefinitely until the tacticity of the molecule is changed or something else interferes. This means that crystalline isotactic PP assumes the form of 3_1 helices. The lower part of the figure represents an end view of the same segment of the molecule, showing very clearly how the unisymmetrical carbon atoms are located to give the least interference.

There are two possible spiral arrangements for a polypropylene molecule, one right-handed and one left-handed. In the crystals, the two enantiomorphous spirals are present in equal proportions. There are two possible orientations for each of them, one with the CH-CH bond in the up direction, and the other with the CH-CH bond in the down direction. Isomorphous spirals differing in the orientation of the CH-CH bond occupy about the same space and can substitute for each other in the crystal. In Figure 2-2, a diagram of the position of the carbon atoms of isotactic propylene in space (when crystallized) can be seen.

2.1.3. CRYSTAL STRUCTURE.

General requirements for the crystallizability of polymer molecules are geometrical regularity of the molecular structure (high degree of tacticity), sufficient packing efficiency of the polymer chains, and abundant favorable conditions for the kinetics of crystallization (11). Even under the most favorable conditions polymers will

never achieve full crystallinity because of chain entanglements, structural imperfections, and insufficient rate of crystallization. The physical properties of a polymer are determined by its crystal structure (12). Particularly in the case of crystalline polymers, X-ray diffraction methods are the most important tools in elucidating property-structure relations.

Polymer molecules with a particular molecular structure (e.g. iPP) aggregate to form crystals, and these in turn, aggregate to form spherulites. The manner of aggregation of molecules determines the crystal structure, and the aggregation of the crystals produces the morphological structure (spherulitic or single crystal) (8,12).

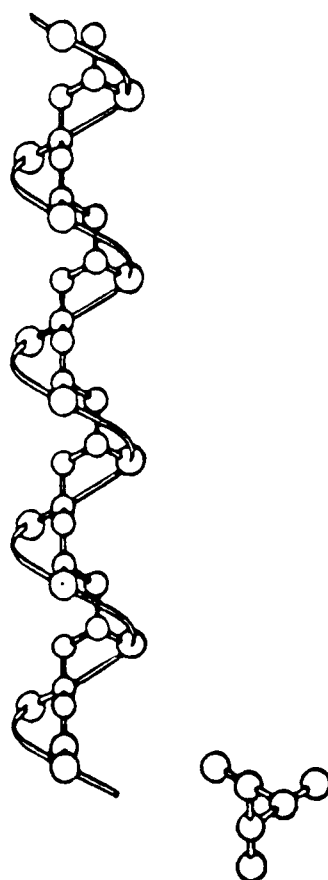


Figure 2-2. Chain conformation of isotactic Polypropylene (9).

The crystal structure of isotactic PP was clarified by Natta (13). The unit cell of isotactic polypropylene is monoclinic, with a crystallographic density of 0.936 g/cm^3 and contains 12 monomeric units; while the unit cell of syndiotactic polypropylene is orthorhombic. The crystallographic density of syndiotactic PP is 0.91 g/cm^3 , and arranges 48 monomeric units. The unit cell constants for the isotactic and syndiotactic PP are given in Table 1.

Isotactic PP can crystallize in three different polymorphic forms, α , β , γ , and smetic. The occurrence of these forms depends upon many factors, among which the most important are the thermal treatment, molecular weight and degree of isotacticity of the sample.

Table 1. Unit cell constants for isotactic and syndiotactic Polypropylene.

Constants	Isotactic	Syndiotactic
a , nm	0.664	1.45
b , nm	2.096	0.58
c , nm	0.650	0.74
β	$99^{\circ}22'$	90°

The principal isotactic form of PP is the α form. The α crystalline form of PP consists of a monoclinic crystal structure in which the chains assume a helical conformation. The β form is generally formed in mixture with the α form by quenching the melt at temperatures between 100° and $120^{\circ} \text{ }^{\circ}\text{C}$. The analysis of the crystal

structure of the β form of isotactic PP suggests that the unit cell is hexagonal (14,15). The γ form of isotactic PP has been obtained by melt crystallization under conditions of elevated pressure (16). The most likely unit cell for the γ form is triclinic. The smetic form of isotactic PP is a phase of intermediate order (between amorphous and crystalline) that is obtained when isotactic PP is rapidly quenched from the melt. Figure 2-3 shows the X-ray diffraction θ scan for the α , β , smetic, and amorphous forms of isotactic PP.

Polyolefins are only partially crystalline and the determination of the degree of crystallinity by X-ray diffraction, Density Gradient Column (DGC), and Differential Scanning Calorimetry (DSC) is of great importance. The X-ray diffraction method (17) relates the intensity of the main crystalline peaks to that of the amorphous halo. The theory behind the density gradient method (18) assumes that the polymer consists of crystalline zones with a theoretical (X-ray) density of 0.936 g/cm^3 and amorphous zones with a density of 0.855 g/cm^3 ; the degree of crystallinity is derived by linear interpolation. DSC data (19) may be used to determine the degree of crystallinity by comparison of the heat of fusion per unit weight with the heat of fusion of a purely crystalline PP.

2.1.4. MORPHOLOGY OF POLYPROPYLENE.

It is important to know that crystalline polymers may occur in two different morphological forms: crystallization from a very dilute solution leads to the formation of lamellar single crystals whereas crystallization from the melt leads to the formation of spherulites (7). Single crystals obtained from dilute solutions of crystallizable polymers are composed of lamellae with a thickness of the order of $100 \text{ \AA}$ and with lateral dimension of at least one micron. The simplest crystals are monolayers, more

complicated ones (i.e. spherulites) may contain 10 to several hundred lamellae, all originating from the same nucleus. Spherulites are a birefringent assemblage of crystals starting usually from a heterogeneous nucleus and spreading out in a spherical fashion until they fill practically the entire volume of the bulk crystallized polymer (7,8). When observed in a polarizing microscope between crossed polarizers spherulites display a dark Maltese Cross.

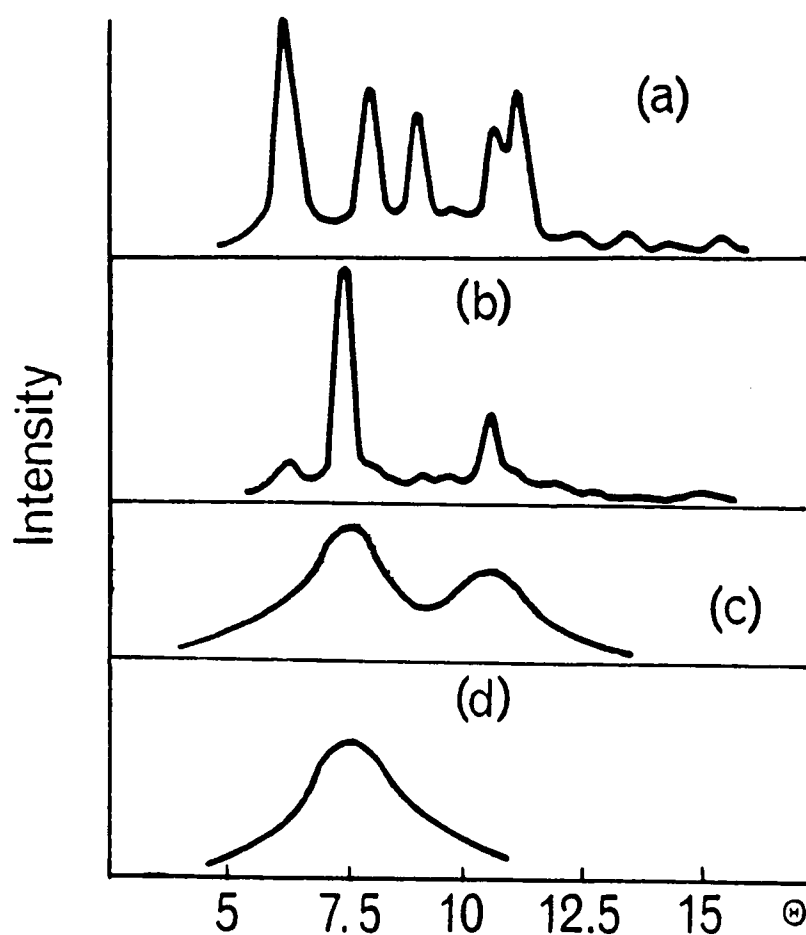


Figure 2-3. X-rays Diffraction Diagrams of (a) Monoclinic, (b) Hexagonal, (c) Smetic and (d) Amorphous Form of isotactic PP (7).

Unlike other crystalline polymers, polypropylene exhibits at least four different types of spherulites which differ not only in amount but even in the sign of their birefringence. Mixed types of crystalline forms within the same spherulite can also be observed (8). When a sample of polypropylene is partially crystallized and then rapidly quenched, a feathery growth of crystals is attained, among which is a considerable amount of amorphous material. The dimensions of the spherulites of isotactic PP can vary from a few to 100 μm . Rapidly cooled polypropylene has smaller crystallites than slowly cooled samples. Certain treatments, such as gamma radiation, tend to accelerate the growth of crystallites (20). Under certain conditions spherulites can be grown to quite large sizes; this could induce cracks formation between the spherulites, and also within them.

2.2. POLY(VINYL ALCOHOL):

Poly(vinyl alcohol) (PVOH), is a polyhydroxy polymer, which turned out to be the largest volume, synthetic, water-soluble resin produced in the world (9). It was the first totally synthetic colloid ever produced.

The first important use of PVOH was as a fiber, introduced in the market in Japan as "Vynlon" (4). Vynlon was first developed before the Second World War, but it was not commercialized until after the war, when it was extensively studied by academic and commercial laboratories. The major emphasis in research on PVOH was placed on the improvement of Vynlon fiber, including a search for polymers with higher degrees of polymerization, with more uniform distribution and with higher degrees of crystallinity to improve mechanical strength and water resistance needed for fiber applications. With the gradual reduction in cost, other end uses began to be exploited,

and various grades of PVOH were developed depending on the needs of the manufacturer.

The basic properties of PVOH depend on its degree of polymerization and hydrolysis (4). Table 2 summarizes the commercial grades of different manufacturers. Figure 2-4 shows the most common commercial grades, classified by percentage hydrolysis and degree of polymerization, which leads to the definition of two major groups: (a) a fully hydrolyzed group with a degree of hydrolysis above 98 percent, and (b) a partially hydrolyzed group with 87 to 89 percent hydrolysis. The partly hydrolyzed group includes grades with hydrolysis values lower than 80 percent.

Table 2. Poly(vinyl alcohol) - Commercial Grades of Different Manufacturers.

Trade Name	Manufacturer
Alcotex	Revertex
Elvanol	Du Pont Co.
Gelvatol	Shawinigan, Inc.
Gohsenol	Nippon Gohsei
Lemol	Borden Chemical and Plastics
Moviol	Hoechst Celanese Corp.
Polyviol	Wacker Chemicals, Inc.
Poval	Kuraray
Rhodoviol	Rhone-Poulenc
Vinex	Air Products and Chemicals, Inc.
Vinol	Airco Chemicals

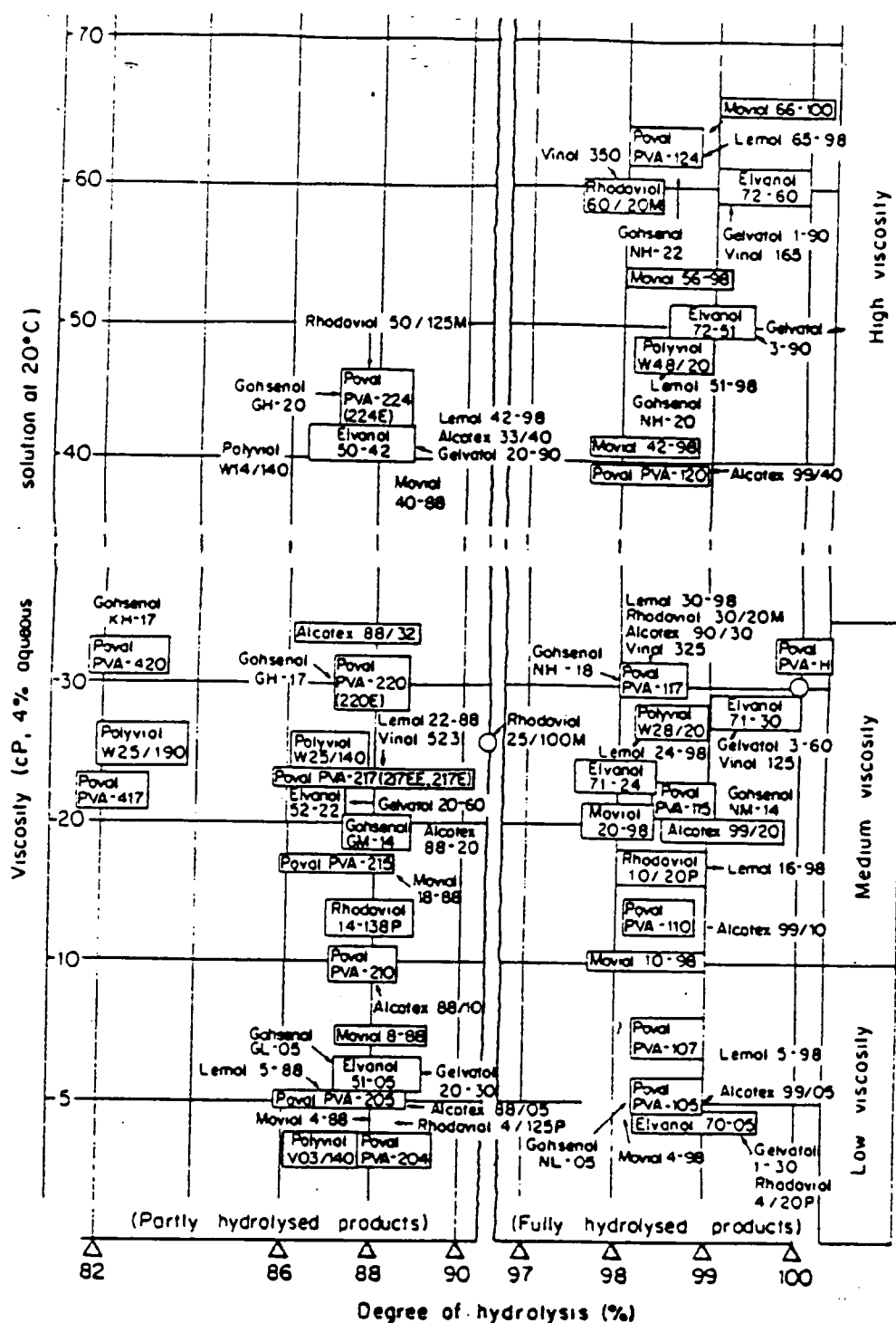


Figure 2-4. Poly(vinyl alcohol)-Commercial Grades of Different Manufacturers (4).

2.2.1. MANUFACTURING OF POLY(VINYL ALCOHOL).

Poly(vinyl alcohol) is a very special synthetic polymer that cannot be prepared by polymerization of the corresponding monomer, but from vinyl acetate, which is the ester of vinyl alcohol (21).

In 1898, in the laboratory studies of Erdmann and Kottner, and in two German patent applications by Wunderlich (1907), the conversion of carbide acetylene into acetaldehyde was carried out (4). In 1932, the Consortium fur Elektrochemische Industrie under the direction of Mugdan, suggested a method in which recycling of acetylene in a circuit with acetaldehyde, with return of the unconsumed acetylene in the process (4). This process was the first employed for the direct oxidation of acetylene to acetaldehyde. By the same token, the production of acetic acid by the oxidation of acetaldehyde was successfully established by Mugdan and Galitzenstein in 1911, which meant the production of vinyl acetate monomer (for use as a starting material for the manufacture of PVOH). The process is summarized in Figure 2-5 (4,21). The development took some years, but finally, in 1924, Baum, Deutsch and Herrmann established a method by which a technically satisfactory synthesis of the monomer was possible, by the use of a mercury containing catalyst. In 1927, the same workers improved the method with a mercury-free system, which was known as the "thermal-vinylation" method. It was soon employed in Germany and other countries (4,21).

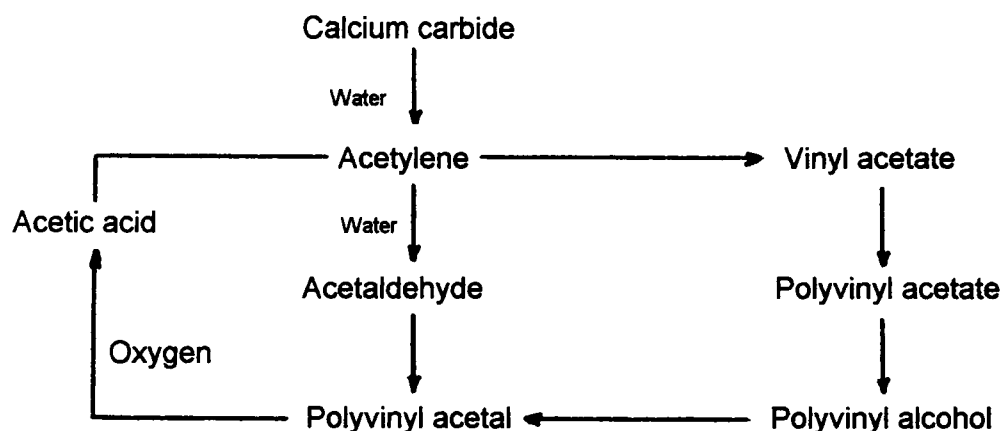


Figure 2-5. Schematic representation of the synthesis of PVOH.

The polymerization reactions for the preparation of the esters required for production of PVOH are exothermic. The addition of large quantities of monomer leads to a build up of heat which is sometimes uncontrollable, and can be explosive. However, the use of a catalytically initiated polymerization process was not understood at first, so that thermal polymerization reactions were carried out in light glass vessels, with reaction times up to a week (21). These polymerization processes were plagued with several problems that made necessary the development of different techniques. Experiments considering the use of autoclaves, the catalytic effects of peroxides and the regulating effect of acetaldehyde were developed (4,21,22).

The importance of the purity of the starting material was not realized, and several attempts to produce high-molecular-weight polymers from impure monomers were unsuccessful. By using high purity monomer, Haenel and Hermann in 1925, were able to develop a method for safe polymerization of large quantities of vinyl acetate (Figure 2-6).

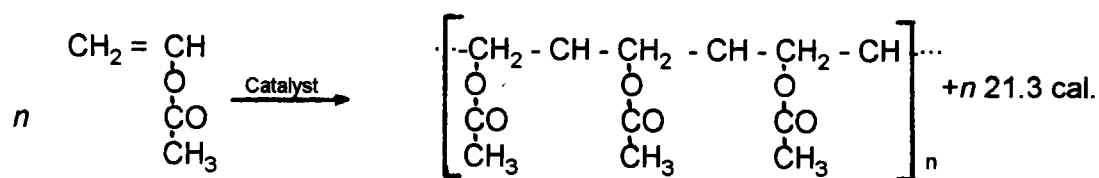


Figure 2-6. Polymerization reaction of vinyl acetate (4).

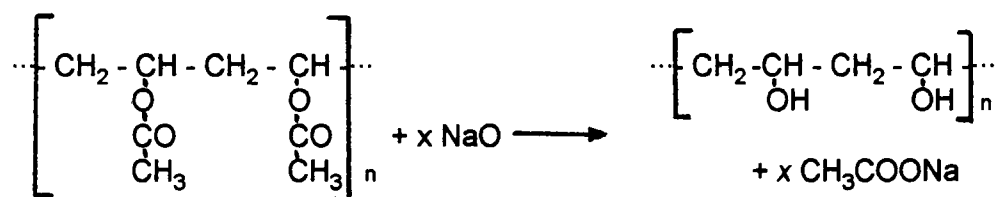
In 1932, Haehnel, Hermann and Berg published a formula in which acetic acid is split off, and the classical saponification reaction proceeds, taking less than the calculated amount of acetate salt. By means of ester interchange, acetic acid is obtained, and the nature of the ester can be determined from the alcohol employed (Figure 2-7). Since the esters are good solvents, it is possible to remove them from the alcohol by simple distillation, thus providing an economical process for the production of PVOH (4,21).

Today, the methods for the production of PVOH are all based on the complete or partial hydrolysis of polyvinyl esters. Most methods start from a homogeneous alcoholic polyvinyl ester solution. In continuous processes, the alcoholic polyvinyl ester solution is mixed with the catalyst continuously to a homogeneous mixture before the reaction sets in, with the homogeneous mixture being brought from the mixing zone into the reaction zone.

In the case of discontinuous process, the catalyst also has to be homogeneously distributed in the alcoholic ester solution. As the viscosity increases, gelling of the batch can be obtained. The viscosity increase requires much more energy for kneading or stirring, which limits the size of the batch. The alternative of making the addition of the catalyst at a regulated rate, such that the viscosity increase remains

within acceptable limits, requires such a great extended reaction time that the capacity of the plant is diminished.

Saponification:



Ester interchange:

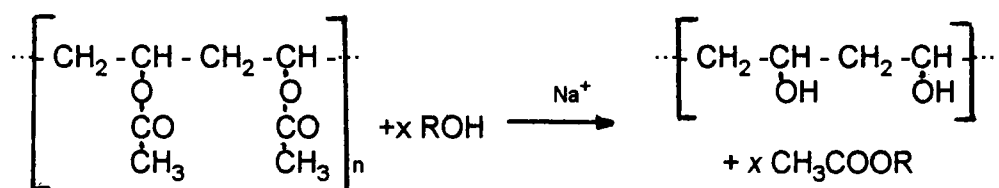


Figure 2-7. Saponification and ester interchange reactions in the production of PVOH (4).

In the large production plants using continuous polymerization in operation today, the polymerization is carried out in an ester-interchange system. The solution, premixed with the catalyst, is conveyed through the ester-interchange system without the introduction of further mixing. The reaction product is removed from this process unaltered, but after a short period of time, gel formation is observed, indicating the formation of PVOH, which is then separated from the ester produced, and from the residual solvent.

vinyl bromoacetate, and vinyl trifluoroacetate), vinyl aliphatic acid esters (vinyl formate, vinyl propionate, vinyl butyrate, vinyl pivalate), vinyl benzoate, vinyl ethers (benzyl vinyl ether, tert-butyl vinyl ether, and trimethylsilyl vinyl ether), divinyl compounds (divinyl oxalate, divinyl malonate, divinyl succinate, divinyl formal, among others), and acetaldehyde. All these routes from monomers other than vinyl acetate have been used in the production of PVOH, but the most economic commercial process is the one from vinyl acetate.

Among the characteristics of the derived PVOH, two important points must be considered:

1- The proportion of 1,2-glycol structures in the PVOH obtained varies with the structure of the parent vinyl ester (Table 3).

2- The effects of stereoregularity are related to syndiotacticity, which changes with the precursor vinyl ester.

2.2.2. STRUCTURAL ORDER OF POLY(VINYL ALCOHOL).

The highly crystalline nature of PVOH was first noted in 1935 by Halle and Hofmann (4). In 1955, Natta and his collaborators using X-ray diffraction patterns postulated three structures (isotactic, syndiotactic, and atactic) for PVOH. Figure 2-8 shows these stereoregular forms of fully hydrolyzed PVOH.

FTIR has been successfully used to study the tacticities of PVOH resins by measuring the ratio of the intensities of the infrared spectral bands at 916 and 849 cm^{-1} (4,21,23,24). The relation is represented by the equation:

$$\text{syndiotacticity} = (72.4 + 1.09) (D_{916} / D_{849})^{0.43 \pm 0.006} \cdot 100 \quad (2-2-1)$$

Table 3. 1,2-glycol content in Poly(vinyl alcohol) obtained from different parent vinyl esters ($\text{CH}_2 = \text{CHOCOR}$) (4).

R	1,2-glycol content (mole %)		Polymerization Temperature(°C)	E (kcal/mole)
	Δ^a	Δ^b		
H	0.89		30	
CH ₃	1.79	1.17	60	1.3 -1.5
CH ₃	1.49		30	
C ₃ H ₇	1.39		30	
C ₃ H ₇		0.95	60	
C ₄ H ₉		0.95	60	
CClH ₂	1.21	0.85	30	
CCl ₃	1.3		30	
CF ₃	0.6		30	
C ₄ H ₅ F ₄ ^c		(0-0.25)	20	
C ₆ H ₇ F ₆ ^d		(0-0.25)	20	
C ₆ H ₅	1.22	0.72	60	2.8
C ₆ H ₅		0.80	60	2.0

^a From consumption of periodate.

^b From Flory's method.

^c Vinyl 2,2,4,4-tetrafluoropentanoate.

^d Vinyl 2,2,4,4,6,6-hexafluoroheptanoate.

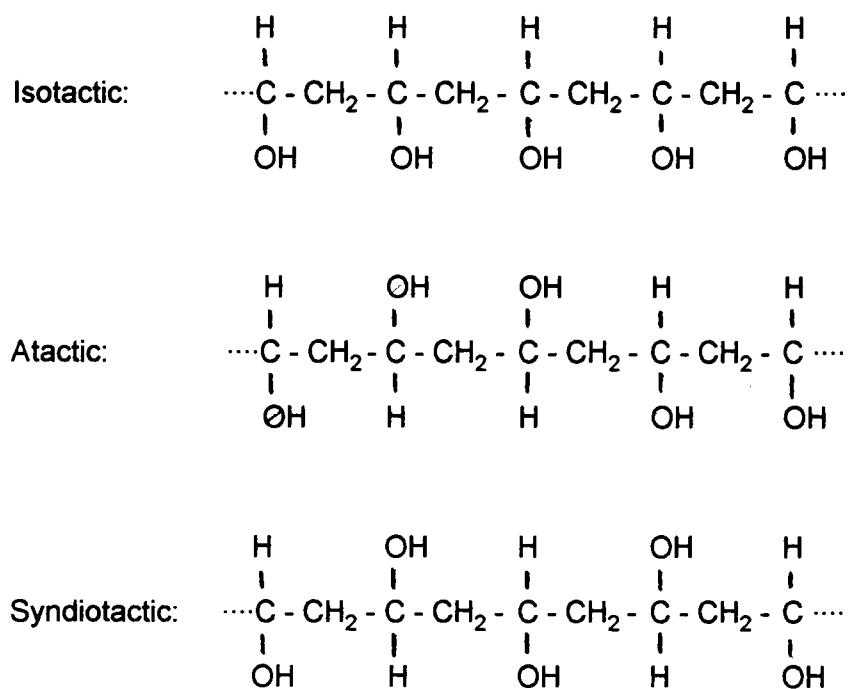


Figure 2-8. Stereoregular forms of fully hydrolyzed Poly(vinyl alcohol) (4).

Halle and Hofmann (22), and Fuller (25), deduced that the structure of PVOH consists of 1,3-glycol linkages and that all the hydroxyl groups are arranged along the same side, namely in the *d,d,d,...*, or *l,l,l,...* position, apparently independent of the structure of poly(vinyl acetate). On the other hand, Mooney (4) proposed a model for the crystalline parts of PVOH on the basis of the described arrangement of the hydroxyl groups along the PVOH chains. Nevertheless, Sakurada and Fuchino proposed that the hydroxyl groups were alternatively arranged in the left- and right-hand positions along the chains, and were responsible for the high softening point and strong mechanical strength of PVOH fibers. Later on, Bunn (4,26) proposed a model in which the hydroxyl groups were randomly arranged along the chains. The model was deduced from the fact that the volume taken up by the hydroxyl groups in PVOH is so small that the polymer can crystallize despite the irregular arrangement of the hydroxyl groups. The crystal structure of atactic PVOH proposed by Bunn (27) is generally accepted (Figure 2-9), although some alterations in the parameters of the unit cell have been suggested since this structure was first published (4). The proposed unit cells are all monoclinic, and the dimensions are shown in Table 4. One unit cell comprises two monomer units of vinyl alcohol. The density of the unit cell is calculated to be 1.345 g/cm³.

2.3. POLYMER BLENDS.

The historical development of polymer blends is not well defined, although the rapid growth of polymer blends was evident during the 1980's. By 1987, it was estimated that 60 to 70 percent of polyolefins and 23 percent of other polymers were sold as blends even though they were not identified as such (28). In the early 90's, the use of unmodified resins was reduced to less than 50 percent and manufacturers think

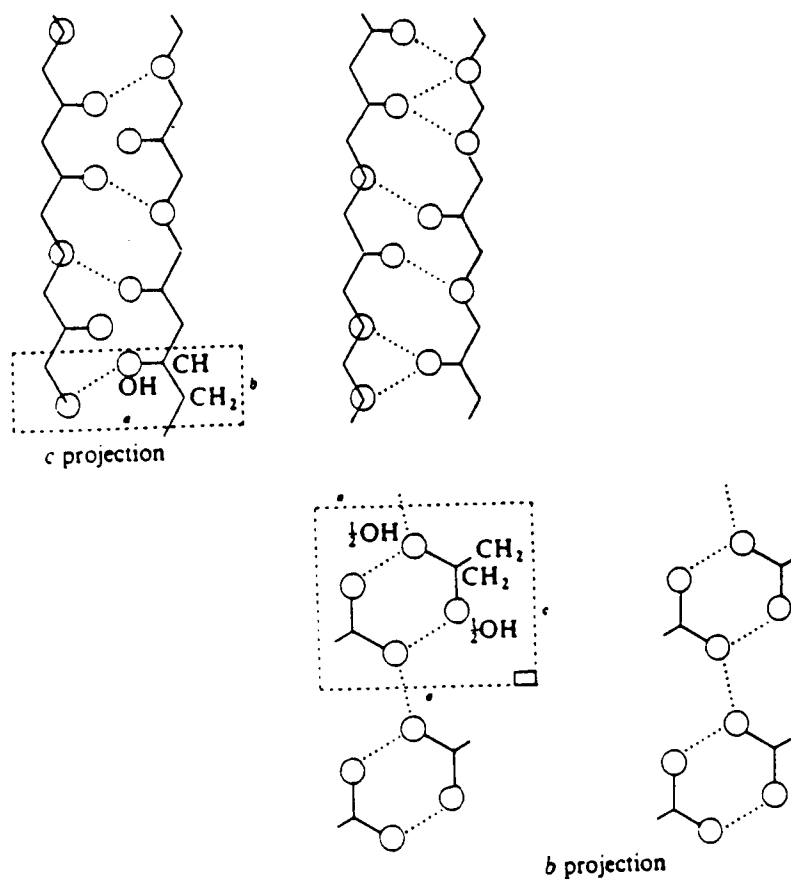


Figure 2-9. Crystal structure of atactic PVOH (the dotted lines indicate hydrogen bonds) (4).

Table 4. Dimensions of the unit cell of PVOH (4).

Technique	a(A)	b(A)	c(A)	β	Author
X-ray diffraction	7.81	2.52	5.51	91°42'	Bunn
	7.82	2.52	5.60	90°	Mooney
	7.83	2.52	5.53	87°	Sakurada
	7.83	2.52	5.51	91°42'	Nitta et. al
	7.82	2.53	5.49	92°10'	Mochizuki
Electron diffraction	7.81	-	5.43	91°30'	Tsuboi and Mochizuki

this trend will further increase in the future because of the fact that the plastics industry is moving toward more complex systems in order to satisfy more demanding needs at lower cost.

The first attempts in blending of commercial resins were related to the blending of natural rubber (NBR) with gutta percha by Hancock in 1886. This experiment led to a mixture which was easily applied for water-proofing cloth. The poly(vinyl chloride)/NBR blend was the first commercial thermoplastic blend in 1942 along with the development of mechanical mixtures of NBR with poly(styrene-co-acrylonitrile), SAN, known as ABS. The next important commercial blends consisted upon mixing of poly-2,6-dimethyl-1,4-phenylene ether (PPE) and polystyrene (PS). The PPE/PS systems help to introduce the term "miscible blend". Later on, blends with polyamides, polycarbonate (PC), poly(vinyl chloride) (PVC), and polyolefins gained commercial interest.

The main reason for blending, compounding, and reinforcing is economics. The goal is to generate materials with "good properties" at low cost. The following economy-related reasons have been proposed:

- 1- Extension of the engineering resin performance by diluting it with a low cost polymer,
- 2- Development of materials with a full set of desired properties.
- 3- Formation of a high performance blend from synergistically interacting polymers,
- 4- Adjustment of the composition of the blend to customer specifications,
- 5- Recycling industrial and/or municipal plastic scrap (29-31).

2.3.1. TYPES OF POLYMER BLENDS.

From a thermodynamic point of view, binary blends can be divided into miscible, partially miscible, and immiscible.

Miscible blends are those polymer blends which are homogeneous down to the molecular level. The miscibility or solubility of the components of the blend in one another, is associated with the negative value of the energy of mixing:

$$\Delta G_m = \Delta H_m \leq 0$$

where ΔG_m is the free energy of mixing, and

ΔH_m is the heat of mixing.

The miscible blends exhibit a single phase and a single T_g between those of the constituents. Because polymers will never achieve full crystallinity, there will always exist an amorphous phase within them. In miscible blends, the amorphous phase of each component is soluble in the other.

The partially miscible blends are those in which miscibility may be observed at certain compositions. Phase separation in partially miscible systems becomes more evident as the mixture approaches a composition of 50/50. Also in these blends, two different T_g s can be distinguished between the glass transition temperatures of the two homopolymers.

The immiscible blends, are those in which the polymer constituents exist as separate phases with poor attraction between them. The component polymer at lower concentration forms a discrete phase while the polymer present in a higher concentration constitutes the continuous phase. When two polymers form an immiscible blend, two different glass transition temperatures (T_g), similar to those of the

homopolymers can be detected. The existence of distinct T_g s is one of the most determinant indications of immiscibility in blends.

From a morphological point of view, polymer/polymer blends can be divided into amorphous, semi-crystalline/amorphous, and semi-crystalline blends. The amorphous blends consist of the blending of two amorphous polymers. These blends may be immiscible, partially miscible, or miscible. The best example of an amorphous blend is the partially miscible Polycarbonate/Acrylonitrile-Butadiene-Styrene blend (PC/ABS). The PC/ABS blends consist of three separate phases because ABS is in itself a two-phase mixture consisting of an impact rubber modified styrene acrylonitrile (SAN), and are considered to be partially miscible because there is some intermixing of the PC and SAN domains. In this case, the resultant material exhibits better mechanical and thermal properties than ABS because of the presence of PC; there is good interfacial adhesion between PC and ABS due to the partial solubility of ABS in the PC phase, and for instance, an efficient transference of mechanical stresses across the boundaries is possible, yielding to a tough material.

The semi-crystalline/amorphous blends consist of the blending of a semi-crystalline and a amorphous polymer. If processing occurs above the T_g of the amorphous polymer, and above the melting point (T_m) of the crystalline constituent, both the phase equilibrium at the processing temperature and crystallization on cooling must be considered. At the processing temperature the system is either miscible or immiscible, but at temperatures lower than the melting temperature, the semi-crystalline polymer may super-cool or crystallize.

Semi-crystalline polymers improve the chemical resistance and stiffness of amorphous resins, while amorphous polymers improve the toughness, creep resistance and dimensional stability of crystalline polymers. Examples of semi-

crystalline/amorphous blends are the following: the cis/trans-polyisoprene blends studied by Carter and its collaborators (32) in which a single T_g for a series of blends of cis/trans-polyisoprene, and compatibility at all compositions were reported. Crystallinity of the cis/trans-polyisoprene blends decreased with crystallizable trans content and the spherulite growth rate decreased as the non-crystallizable cis content of the blends increased. The mechanical properties of the blends were also studied, and a decrease in the tensile modulus with crystallinity was observed. The polystyrene/polyolefin blends have been reported as a prototype of a class of binary blends consisting of a glassy amorphous (at room temperature) and a crystalline polymer (32). Incompatibility between polyolefins and PS in the molten state has been evident, although various interesting morphologies can be obtained according to their different viscosities at the processing conditions, and to their relative amounts (33,34). A very slight decrease in crystallinity as well as that of the melting point with increasing the atactic PS content has been reported (35). The Polycarbonate/Polyethyleneterephthalate blends (PC/PET) are partially miscible, which is reflected in its enhancement of mechanical properties. A single T_g is evident for 75/25 blends, but above a 25 percent PC level, the blends exhibit two T_g s. Partial solubility of PC in PET has been concluded because of the increase in the T_g of the latter. The yield strength and modulus of PC/PET blends is relatively constant while the percent elongation exhibits a maximum at approximately 75 percent PET.

The semi-crystalline blends consist of blending of two semi-crystalline resins. Semi-crystalline blends are of great commercial importance because most of the engineering polymers crystallize. Initially, semi-crystalline systems were considered of no interest as the crystallization intrinsically indicated immiscibility, but nowadays, these kinds of blends have received increased attention and it has been found that the two

components may influence each other giving rise to very interesting effects such as depression of the melting point, decrease or increase of the crystallinity and the rate of crystallization, and change of morphological features.

Semi-crystalline blends which are miscible are very rare, but Polybutyleneterephthalate/Polyethyleneterephthalate blends (PBT/PET) have shown miscibility. Other examples of miscible semi-crystalline blends include: the PP/Ethylene vinyl-alcohol copolymer blends (PP/EVOH) studied by Lohfink et. al (36), in which the development of a laminar structure of EVOH dispersed phase in a PP matrix was shown to be possible. Morphological studies revealed that the laminar structure was a result of die design. Oxygen permeation tests showed that PP/EVOH systems exhibit lower oxygen permeability than pure PP, when EVOH is incorporated as a dispersed phase into the system. Other examples of miscible semi-crystalline blends include studies reported by Berghmans and Overbergh on isotactic Polystyrene/Poly(2,6-dimethyl phenylene oxide) systems (37); Sato and Takahashi on linear and branched PE blends (38); Greco et. al on PE/PP blends (1); Inoue and Grebowicz (39) and Pakula (32) on Nylon 6/ Nylon 11 and Nylon 66/Nylon 6 blends; Valenza and Spadaro (40) and LaMantia and Curto (41) on Nylon 6/Linear Low Density Polyethylene, among others.

2.3.2. DETERMINATION OF POLYMER/POLYMER MISCIBILITY.

Polymer blends are physical mixtures of chemically distinct polymers. The methods used to study blends miscibility can be divided into three groups: phase equilibria methods, determination of the polymer/polymer interaction parameter, χ_{ik} , and indirect compatibility tests. The latter category includes glass transition temperature determination, spectroscopic techniques, and others.

The polymer/polymer interaction parameter and phase diagrams are important items for further discussion. For polymer blends, the free energy of mixing can be expressed as:

$$\Delta G_m / RTV = \chi_{12}' \phi_1 \phi_2 \quad (2-3-1)$$

where ΔG_m is the free energy of mixing,

R is the gas constant,

T is the temperature,

ϕ_1 and ϕ_2 are the volume fractions of the constituents of the blend, and

χ_{12}' is the polymer/polymer interaction parameter.

Equation (6) is a fundamental equation for studying the miscibility of polymer blends. The miscibility of polymer blends, in terms of the equilibrium thermodynamics, must be considered within a range of certain parameters (temperature, pressure, chain structure, molecular weight), under which the free energy of mixing is negative. For ΔG_m to be negative, the binary polymer/polymer interaction parameter must be negative. There are three contributions to χ_{12} : the specific interactions between the polymers, the dispersion forces, and free volume. Figure 2-10 shows a schematic representation of the variation of the interaction parameter (solid line) for solutions and polymer blends (28).

The graph (a) represents interactions encountered mostly in solutions with upper and lower critical solution temperatures, UCST and LCST respectively. For polymer blends, the miscibility vanishes on heating above the LCST.

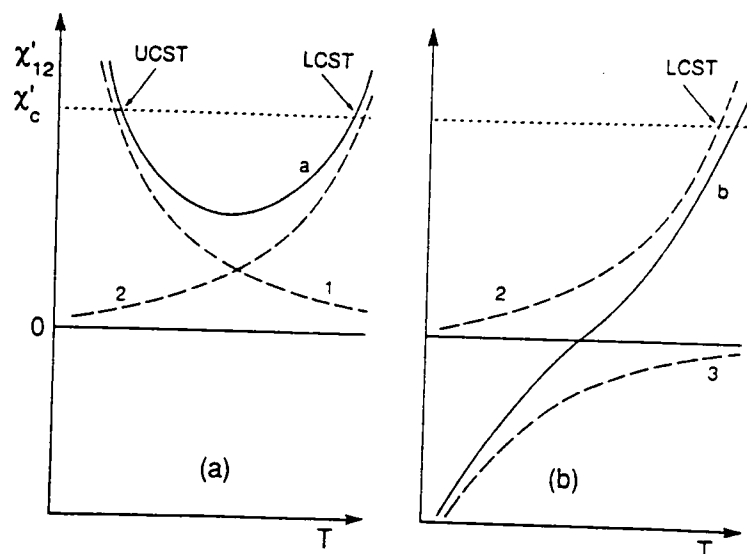


Figure 2-10. Schematic representation of the temperature variation of the interaction parameter, χ_{12} , for polymer solutions (a) and polymer blends (b): 1. dispersion forces, 2. free volume, and 3. specific interactions (28).

The temperature-composition phase diagrams of polymer blends are of extreme importance for the characterization of the interactions between the components of the blend, as well as the solubility of one polymer in the other (42,43). The most common phase diagrams of binary polymer blends of high molecular weight are shown in Figure 2-11 (42). The diagram (A) in Figure 2-11 is called "tree trunk"; about 95 % of all binary blends have a phase diagram of this type. It is characteristic of incompatible blends in which mutual solubility of the components is not observed. On the other hand, Figure 2-11 (B) shows the typical phase diagram for compatible blends. Although the components of compatible blends are miscible in each other, there is phase separation

at elevated temperature (43). Other types of phase diagrams can be observed in polymer blends (28,42-44), but generally, the LCST is more frequent than UCST.

The interfaces between the constituents of a polymer blend are responsible for the kinetics of phase separation and mechanical mixing of molten polymers (42). The mechanical properties of binary polymer blends are directly related to the interfacial energies and the interactions between both phases. The thermodynamic criterion for two phases at equilibrium is that the chemical potential μ of each component be the same. The study of phase behavior of polymer blends can be very complex and it is beyond the scope of this work.

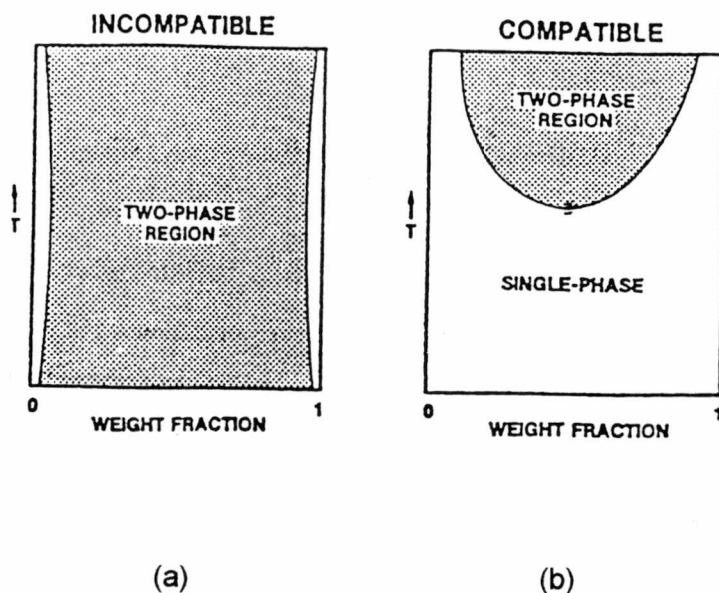


Figure 2-11. Phase Diagrams of Binary Polymer Blends (42).

2.3.2.1. Determination of the Polymer/Polymer Interaction Parameter (χ_{ik}).

1. Empirical Determination of the Polymer/Polymer Interaction Parameter.

According to Flory-Huggins theory, the interaction parameter, χ_1 , can be calculated using the following equation:

$$\chi_1 = \{ (V (\delta_1 - \delta_2)^2) / RT \} > 0 \quad (2-3-2)$$

where δ_1 and δ_2 are the solubility parameters for the components of the blend, and V is the molar volume.

Usually, the solubility parameters of each homopolymer are known, which makes possible the determination of the interaction parameter by:

$$\chi_1 = \rho \left(\sum_{i=1}^n F_i / M \right) \quad (2-3-3)$$

where $\sum_{i=1}^n F_i$ is the sum of the molar attraction constant for all the chemical groups in

the polymer repeat unit,

M is the molecular weight of the repeat unit, and

ρ is the density of the polymer.

In any case, if the calculated χ_1 is close to zero, the polymer blend is likely to be miscible leading to a negative value of the free energy of mixing (thermodynamic equilibrium).

2. Direct Methods for determining the χ_{ik} .

The term "direct" is referred to methods of χ_{ik} determinations in which the addition of a test medium (e.g. a low molecular weight liquid) is not necessary. Direct methods include SANS and SAXS experiments which are used to measure the depression of the melting point which is one of the signs of compatibility. The relation is expressed as:

$$(1/T_m) - (1/T_m^0) = - (R V_2 / \Delta H_2 V_1) [(\ln \phi_2) / m_2 + (m_2^{-1} - m_1^{-1}) \phi_1 + \chi_{12} \phi_1^2] \quad (2-3-4)$$

where subscripts 1 and 2 indicate both polymers,

m is the number of units in the molecule (degree of polymerization),

V is the molar volume, and

ΔH is the heat of fusion.

For polymer blends in which m_1 and m_2 are approximately the same and tend to infinite, the equation (9) can be simplified to:

$$(T_m / T_m^0) = 1 + B (V_2 / \Delta H_2) \phi_1^2 \quad (2-3-5)$$

where B is a measure of the characteristic interaction density for the polymer pair:

$$B = \chi_{12} RT / V_1 \quad \text{at } T = T_m \quad (2-3-6)$$

3. Indirect Methods.

Indirect methods are those in which a test medium is needed for indirectly calculating the χ_{ij} . These include glass transition determinations, Nuclear Magnetic Resonance, and Infrared Spectroscopy.

Glass Transition Temperature (T_g).

The glass transition temperature is the temperature at which the polymer goes from the glassy to the rubbery state. The glass transition temperature, T_g , is determined mainly by the chemical structure of the chain units (12). The presence of polar groups, which cause high dipolar forces both intermolecularly and intramolecularly, raises T_g . The most important factor is however the geometric shape and size of the side groups along the chains. Steric hindrances to the rotation of the chain segments are a powerful influence in raising the value of T_g ; the effect of the chain length on T_g is quite secondary. The determination of the glass transition temperature of the components of the blend is one of the most commonly method used to predict miscibility of polymer blends. Immiscible blends exhibit two glass transition temperatures, while miscible blends possess a single T_g . Nevertheless, some studies show disagreement with the fact that a single T_g is a true measurement of miscibility (44).

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) are the most popular methods of T_g determination; heat capacities are evaluated as a function of temperature. Dynamic mechanical measurements of complex modulus as a function of temperature is another accurate technique for measuring T_g . There are numerous reports indicating agreement between DSC and dynamic mechanical results (45-47). On the other hand, other authors have reported disagreement (48).

There are several equations which can be used to predict the variation of the glass transition temperature, T_g . Most of these equations are empirical (49,50-53).

Couchmann Equation (49):

In 1978, Couchmann proposed the following expression for miscible blends:

$$\ln T_g = \left[\sum_i w_i \Delta C_{p_i} \ln T_{g_i} \right] / \left[\sum_i w_i \Delta C_{p_i} \right] \quad (2-3-7)$$

where w_i and T_{g_i} are the weight fraction and glass transition temperature of polymer i in the blend respectively, and ΔC_{p_i} designates the glass transition increment of the heat capacity of the specimen, originally assumed to be independent of T .

From Couchmann Equation several empirical equations can be derived:

Gordon - Taylor equation (50,54):

In 1952, Gordon and Taylor suggested a general expression for predicting the variation of the glass transition temperature:

$$\sum_i w_i \Delta C_{p_i} (T_{g_i} - T_g) = 0 \quad (2-3-8)$$

for two component systems the equation is written in the form:

$$w_1 (T_{g1} - T_g) + K w_2 (T_{g2} - T_g) = 0 \quad (2-3-9)$$

where K , equal to $\Delta C_{p2} / \Delta C_{p1}$, can be used as an empirical parameter which is considered as a measure of miscibility.

Fox equation (51):

$$\sum_i w_i (1 - T_g / T_{g_i}) = 0 \quad (2-3-10)$$

Utracki and Jukes equation (28):

In 1984, Utracki and Jukes derived an equation assuming $T_{g_i} \Delta C_{p_2} = \text{constant}$:

$$(\ln T_g) / T_g = \sum_i (w_i \ln T_{g_i}) / T_g \quad (2-3-11)$$

This equation was found to follow the T_g vs w_i dependencies for miscible blends, as well as plasticized systems. However, in partially miscible blends the introduction of an empirical parameter describing deviation from the assumed negligibility of the entropy of mixing was necessary. Consequently, for a two component system the following expression was suggested:

$$w_1 \ln (T_g / T_{g_1}) + K w_2 \ln (T_g / T_{g_2}) = 0 \quad (2-3-12)$$

Recently, a two-parameter empirical relation was proposed by Kwei (52,53):

$$T_g = (w_1 T_{g_1} + K w_2 T_{g_2}) / (w_1 + K w_2) + q w_1 w_2 \quad (2-3-13)$$

The first term on the right hand side of the equation is equivalent to the Gordon-Taylor equation, whereas the second one represents the polymer-polymer interaction contribution.

Nuclear Magnetic Resonance Spectroscopy.

NMR is a very useful technique when the microstructure of polymers is to be deduced (17). Relevant applications of NMR in polymer blends include the determination of composition and structure of the homopolymers present in the blend, the study of phase separation processes by determination of polymer/polymer miscibility by the half-life of the spin relaxation times (55), the study of the individual environment of the carbon atoms in a blend by ^{13}C NMR, and the relative strength of interaction between a specific group of the solute and solvents when the polymer is in a binary mixture of interacting and non-interacting solvents (56).

Infrared Spectroscopy.

Infrared spectroscopy is a molecular vibration spectroscopic method, very simple from an experimental point of view (17). The analysis of the wavelength of the absorption bands is a very useful tool to characterize polymer blends. Information regarding the miscibility of blends may be obtained by studying the spectral shifts. If the blend is immiscible, the adsorption spectrum of the blend will be the sum of those for the components. If the blend is miscible, the interaction between the two components will perturb the bonding between atoms, and differences would lead to shifts in the position to certain absorption bands. A widely studied interaction which contributes to miscibility and is easily detected by infrared spectroscopy is hydrogen bonding (57).

2.3.3. POLYMER BLENDS CRYSTALLIZATION.

2.3.3.1. Crystallization in Miscible Polymer Blends.

Crystallization of miscible blends is more complex than that of immiscible blends because the presence of the second component considerably affects the T_g , T_m and crystallization rate. Nishi and Wang (58) developed an expression that relates the melting temperature to the homopolymer melting point (Equation 2-3-5). From equations 2-3-5 and 2-3-6, miscibility of crystallizable polymer blends can be evaluated.

Equation 2-3-5 is only valid when: crystals in the polymer blend are in equilibrium, melting is conducted under close to equilibrium conditions, the presence of the second component does induce change in the crystal system, its lattice spacing, or lamellar thickness, and the second component does not undergo a phase transition. Unfortunately, these conditions are very rare. Changes in melting temperature of a miscible blend may be carefully used as a parameter to determine miscibility. Evidently, both T_m and T_g are affected by the blend constituents, which means that the rate of crystallization is also affected.

The crystallization and morphology of the blends depend on the crystallization conditions. In semi-crystalline polymer blends the kinetics of crystallization, the phase equilibria, and the morphologies are difficult to interpret.

In 1979, Paul and Barlow identified five patterns of crystallization upon addition ϕ_2 of a crystallizable polymer (crystallizable diluent) to a blend (Figure 2-12) (59).

2.3.3.2. Crystallization of Immiscible Blends.

The crystallization of immiscible polymer blends follows the crystallization kinetics of homopolymers provided that crystallization takes place within a domain of a neat

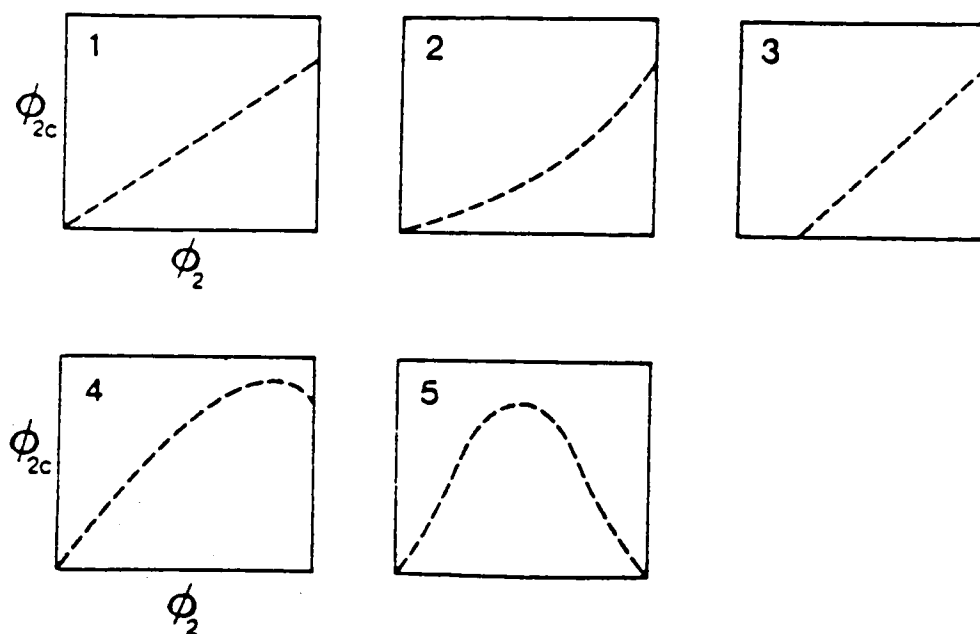


Figure 2-12. Patterns of crystallization in polymer blends containing a semi-crystalline polymer-2 (28,59). ϕ_2 is the volume fraction of the crystallizable polymer, and ϕ_{2c} is the mole fraction of crystals in the blend.

- (1) the diluent does not affect crystallization,
- (2) the diluent retards the crystallization rate,
- (3) the diluent prevents crystallization at its high loading,
- (4) the diluent accelerates crystallization, and
- (5) the diluent provides enough thermal stability to cause crystallization of normally non-crystalline polymer.

polymer with no interference by the other resin. When the system is cooled below the equilibrium melting point, T_m^0 , crystallization occurs. Three mechanisms of nucleation have been reported (28): spontaneous homogeneous nucleation in the super cooled homogeneous melt (this mechanism rarely occurs), orientation induced nucleation caused by alignment of the polymer chains, and heterogeneous nucleation originated by the presence of a foreign particle or phase.

The crystallization process goes through several steps: nucleation, lamellar growth, spherulitic growth, and aggregate growth. The two main steps are nucleation and crystal growth.

The rate of nucleation can be expressed as (60):

$$N = N_0 \exp (- (E_0 + \Delta G_0^*) / RT) \quad (2-3-14)$$

where N_0 is a measure of the concentration of the polymer segments,

E_0 is the energy of activation, and

ΔG_0^* is the free energy for forming a nucleus.

The Hoffman-Lauritzen theory predicts the variation of the melting point, T_m , with the thickness of the formed lamellae during crystallization, L :

$$T = T_m^0 (1 - 2 \gamma_e / \Delta H_f L) \quad (2-3-15)$$

where T_m^0 is the maximum value of T_m determined for the equilibrium crystal having the maximum lamellar thickness, $L_{\max}$ and γ_e is the interfacial energy.

The results of several investigations (61,62) indicate that crystallization generates an ordered structure not only in the crystalline phase, but in the amorphous phase as well. The study of crystallization kinetics and morphology of polymer blends are of extreme importance in the elucidation of the polymer-polymer interaction and the ultimate properties of the blend.

2.3.4. MECHANICAL PROPERTIES OF POLYMER BLENDS.

In general, mechanical properties depend upon the inter- and intramolecular interactions of the polymer, changes in thermal and mechanical history, and viscoelastic quantities (63). Friction, abrasion, and wear are properties that depend on certain parameters, such as, temperature, load, and the environmental surroundings of the resin.

The techniques employed for testing mechanical properties of polymer blends are the same used for the study of homopolymers. The most common include the stress-strain and dynamic mechanical testing (64).

Various models have been developed to explain the viscoelastic behavior of polymers. Some of the most common models include the Maxwell Model, Voigt Model, and the Standard Linear Solid, which is a combination of the two models.

Stress-Strain Testing:

The stress-strain behavior of polymers is similar to that of conventional materials, except for the fact that polymers show a marked time or rate dependence. Stress-strain curves of polymers can be readily obtained by subjecting a specimen to a tensile force applied at a constant rate of testing. Determination of the stress-strain behavior

of polymers is particularly useful as it gives information concerning important mechanical properties such as Young's modulus, yield strength, and brittleness.

During a stress-strain experiment, the sample is elongated at a constant strain rate, and important changes are promoted at both, micro- and macromolecular levels. For a ductile polymer, as the sample is being deformed, energy is absorbed, and slipping of the chains is induced; this is known as "yield point" and corresponds to the point at which permanent plastic deformation takes place. The value of the yield strain for polymers is typically of the order of 5-10 percent which is very much higher than that of metals and ceramics. For a tough polymer, the yield point is followed by extensive elongation at almost constant stress leading to "necking" of the sample. When stress is applied to a polymer sample, energy is absorbed within the sample by the viscoelastic deformation of the polymer chains and by the creation of new surface areas (craze and crack), and finally it breaks.

The stress-strain tests are of great help in the characterization of polymer blends. By the addition of a rubbery phase to a brittle polymer, an increase in toughness and elongation to break of the brittle polymer can be achieved (65). Small amounts of the rubbery phase lead to materials in which yielding and necking are easily observed, while large amounts of rubber induce large elongation, an indistinct yield point, and probably, cavitation. The introduction of block and graft polymers also affect the stress-strain behavior of polymer blends. In the cases in which the grafted chains and the matrix are similar, good adhesion between the phases is promoted, and improvement of the mechanical properties is achieved. Figure 2-13 shows the variation of the stress-strain behavior of PE/atactic PS at different atactic PS percentages.

2.3.4.1. Theories for Predicting Mechanical Properties of Blends.

Polymer blends in which one of the components is present at very small concentrations, can be treated as particulate-filled systems. Several theories have been proposed for predicting the mechanical behavior of polymer blends and particulate-filled systems (66-71). Important factors that have been taken into account are the type of dispersion present in the blend, the amount of particle agglomeration, and the character of the adhesion between the phases. Several calculations concerning the mechanical properties of polymers filled with spherical or ellipsoidal particles, composites, and polymer blends have been reviewed.

Most theories are based on spherical shaped filler particles in spite of the fact that only few fillers are spherical in shape. Nevertheless, many particles such as cubes, have nearly the same dimensions in all directions. Therefore, the theories based on spheres can be applied to shapes other than spheres yielding to only small or no deviations of the experimental results. The major source of errors in the application of these theories is due to the fact that the theories assume perfect adhesion between the phases conforming the system, and the dispersion of the particles of the minor component is perfect. The errors described above are usually difficult to measure experimentally (71).

Einstein's Equation (66).

This equation is used for predicting the modulus of elasticity of a system with perfect adhesion between the filler, which has to be at low concentrations, and the matrix. Einstein's equation can only be applied when the filler is more rigid than the matrix. An important variable in Einstein's equation is the volume occupied by the filler

particles, but the equation does not contemplate any dependence of the reinforcing ability of the filler on its particle size.

Einstein's equation is given by the following expression:

$$G = G_1 (1 + 2.5 \phi_2) \quad (2-3-16)$$

where G is the resultant shear modulus of the system,

G_1 is the shear modulus of the matrix, and

ϕ_2 is the volume fraction of the filler or minor component of the blend.

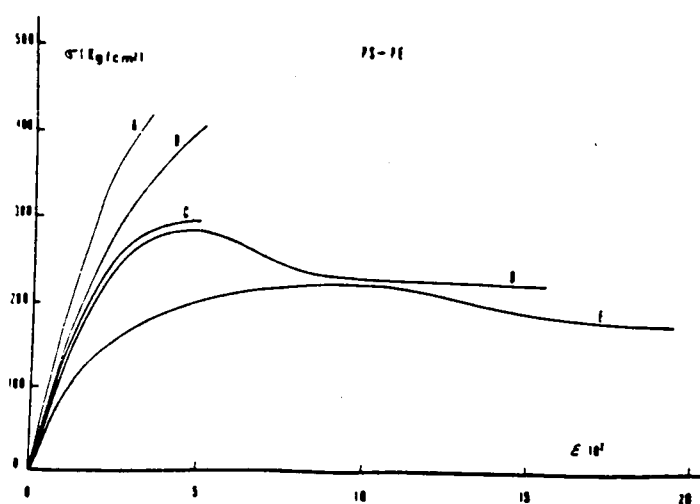


Figure 2-13. Variation of Stress-Strain behavior of Polyethylene/atactic-Polystyrene blends at different atactic-Polystyrene percentages (A, 100 %; B, 65 %; C, 40 %; D, 30 %; E, 0 %) (32).

In reality, polymeric blends do not exhibit perfect adhesion between the phases. This fact inspired Einstein to develop a theory in terms of viscosity that initially was used for predicting the behavior of systems in which spherical particles were imbedded in a liquid; slipping of the liquid by the spheres was observed. This equation can also be interpreted in terms of the shear modulus as follows:

$$G = G_1 (1 + \phi_2) \quad (2-3-17)$$

Where there is no adhesion between the two phases, the reinforcing action will not be effective, and even decreasing of the modulus can be observed.

Guth and Smallwood's Equation (66,67,69).

An extension of Einstein's theory is the Guth and Smallwood's equation. The equation was first developed for the study of the effect of suspended colloidal carbon black spheres into a continuous rubber matrix in which the ellipsoidal filler particles were stiffer than the matrix causing an increase in modulus:

$$G = G_1 (1 + 2.5 \phi_2 + 14.1 \phi_2^2) \quad (2-3-18)$$

This relation holds also for the Young's modulus E, because of the relation:

$$G = E / 3 \quad (2-3-19)$$

Kerner's Equation.

This equation was first developed as an attempt to describe the elastic constants, shear modulus and bulk modulus, of an macroscopically isotropic and homogeneous composite, in terms of the moduli and concentrations of its components. The components of the system were assumed to be in the form of grains suspended in and bonded to an uniform suspending medium. The grains were also assumed to be spherical and perfectly distributed in the medium. No restriction on the sizes of individual grains was contemplated (66).

Kerner's equation is one of the most versatile predictions and it is given by (72):

$$G = \frac{G_1 [(\phi_2 G_2 / (7 - 5 \nu_1) G_1 + (8 - 10 \nu_1) G_2) + (\phi_1 / (15 - 15 \nu_1))]}{[(\phi_2 G_1 / (7 - 5 \nu_1) G_1 + (8 - 10 \nu_1) G_2) + (\phi_1 / (15 - 15 \nu_1))]} \quad (2-3-19)$$

where ν_1 is the Poisson's ratio of the matrix.

When the filler is more rigid than the matrix, as is assumed by Einstein and Guth and Smallwood in their predictions, Kerner's relation can be simplified to (66,72):

$$G = G_1 \{ 1 + (\phi_2 / \phi_1) [(15 - 15 \nu_1) / (8 - 10 \nu_1)] \} \quad (2-3-20)$$

Kerner's equation also considers the cases in which the filler or minor components of the blend has smaller modulus than the continuous phase, and it even deals with the phase inversion phenomenon.

Sato and Furukawa's Equation.

This equation considers an adhesion factor, T , which is zero for perfect adhesion and 1.0 for no adhesion between the phases:

$$E = E_1 \{ [1 + 0.5 (y^2 / (1 - y))] [1 - (y^3 T / 3) ((1 + y - y^2) / (1 - y + y^2))] - [(y^2 T / (3 - 3y)) ((1 + y - y^2) / (1 - y + y^2))] \} \quad (2-3-21)$$

where $y = \phi_2^{0.33}$.

Some equations have been modified in order to predict the modulus of systems where the filler particles are not spheres but rod-shaped or plate-like particles.

Kuhn and Kuhn's Equation.

The relation proposed by Kuhn and Kuhn for predicting the modulus of systems which filler particles are rod-like and randomly oriented in the matrix (66). This equation indicates the influence of the filler particle shape on the modulus:

$$\ln (G / G_1) = (2.5 \phi_2 + 0.407 (P - 1)^{1.508} \phi_2) / (1 - S \phi_2) \quad (2-3-22)$$

where P is the axial ratio of the rigid ellipsoidal or rod-like particles, and S is the sedimentation volume, which is 1.35 for spheres and 1.91 for rods.

Modified Mooney Equation.

For plate-like particles, an increase in modulus over that expected for spheres has been reported (66). The modified Mooney equation is expressed as:

$$\ln (G / G_1) = \{ [2.5 \phi_2 + (32 / 15 \pi) (1 / P - 1) \phi_2] - [0.628 ((1 / P - 1) \phi_2) / (1 / P) - 0.075)] \} / (1 - S \phi_2) \quad (2-3-23)$$

Figure 2-14 shows The prediction of the modulus of particulate-filled systems as a function of concentration of filler for various theories (66).

Even though a number of theories of the elastic modulus of filled polymers have been proposed, not too much information regarding other mechanical properties, e.g. tensile strength and elongation to break can be found in the literature.

Motivated by the lack of information in this field, some authors (66,71) have used simple models of filler polymers for developing approximate equations for the elongation to break, tensile strength, and impact strength. These equations have been combined with equations for the modulus (assuming Hookean behavior, and all the stress-strain properties can be derived as a function of the filler concentration for the two cases of perfect adhesion and no adhesion between the filler (or minor component of the blend) and the matrix (71).

Perfect Adhesion between Filler and Polymer.

Nielsen has published several simple models based on perfect adhesion between the filler and polymer (71). The actual microscopic elongation of the matrix relative to the observed elongation of the filled system is given by the following expression:

$$\varepsilon' / \varepsilon = 1 / (1 - \phi_2^{1/3}) \quad (2-3-24)$$

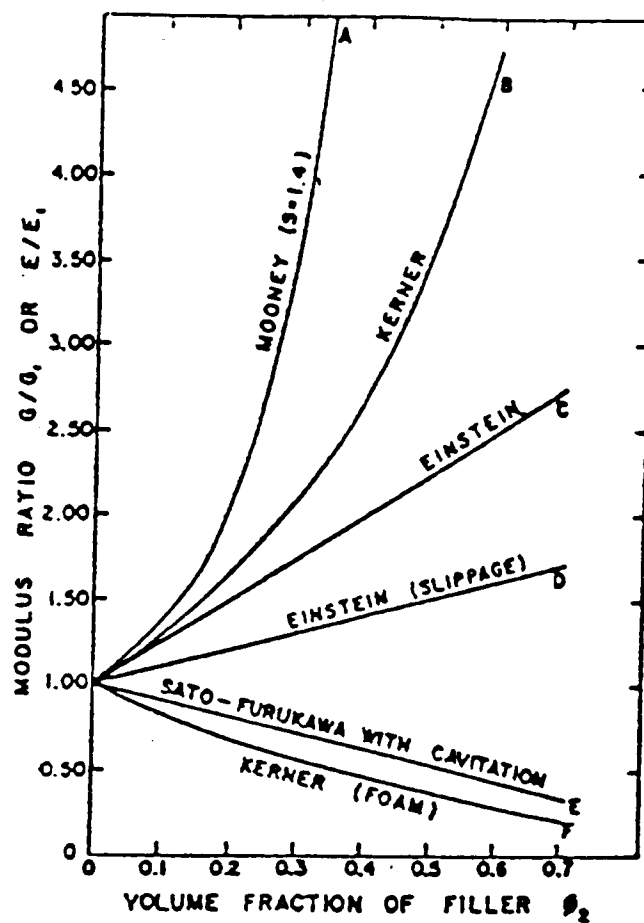


Figure 2-14. Modulus as a function of concentration of filler.

where ϵ' is the actual elongation of the matrix, and

ϵ is the overall elongation of the filled system.

Figure 2-15 shows the simplest model in which the filler particles are attached to the polymer in a series of arrangements.

The assumption that the polymer that constitutes the matrix in the filled system breaks at the same elongation as it does when no filler is present, can be made. In this case, the elongation to break of the system will be (71):

$$\epsilon_B \text{ (filled)} / \epsilon_B \text{ (unfilled)} = 1 - \phi_2^{1/3} \quad (2-3-25)$$

For calculating the tensile strength, the model shown in Figure 2-15 cannot be assumed because the simple model does not allow for the filler particles to carry part of the load. By combining equation (2-3-25) with equations for the modulus of filled systems with spherical filler particles (e.g. Kerner's equation), the tensile strength, σ_B , is given by:

$$\sigma_B = E \epsilon_B \quad (2-3-26)$$

where E is the Young's modulus of the filled polymer.

Passmore and Bisset (66) proposed an equation for the cases in which porosity has a great influence in the tensile strength of the filled system :

$$\sigma_B = \sigma_{B0} e^{-aP} \quad (2-3-27)$$

where σ_B is the tensile strength of the system,

σ_{B0} is the tensile strength when the system is non-porous,
 P is the porosity, and
 a is a constant.

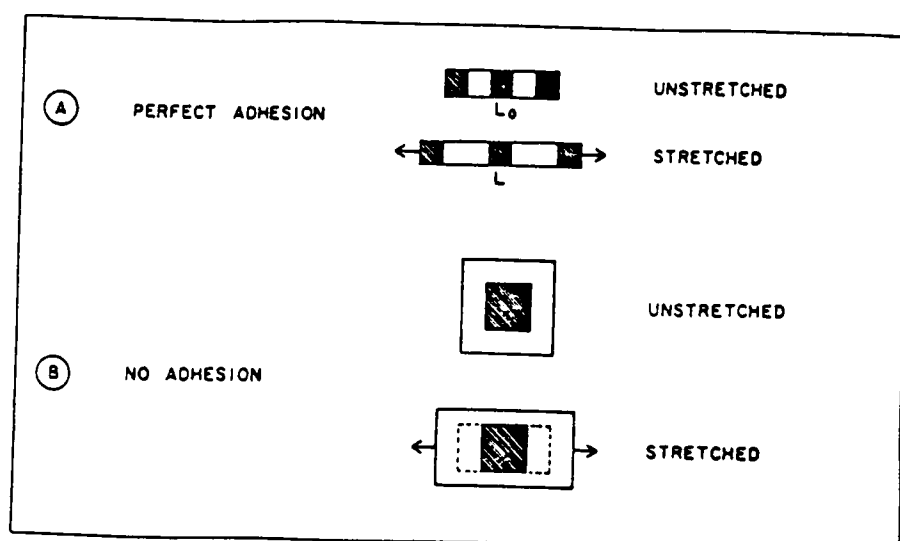


Figure 2-15. Models for filled polymers (71).

No Adhesion between Filler and Polymer.

In the case of no adhesion between the phases conforming the system, the load has to be entirely carried by the matrix. However, the filler particles tend to distort the stress fields, so that, when the specimen breaks, the fracture travels from one filler particle to another (Figure 2-15 (B)). The equation proposed by Nielsen for predicting the tensile strength of filled polymer systems is given by:

$$\sigma_B (\text{filled}) / \sigma_B (\text{unfilled}) = (1 - \phi_2)^{2/3} S \quad (2-3-28)$$

where S is the stress concentration function. Generally, S is expected to have a value of 0.5.

Figures 2-16 and 2-17 show the theoretical curves for the elongation to break and tensile strength of filled systems assuming different theoretical equations for the modulus.

Rule of Mixtures.

The rule of mixtures has been widely used to predict the mechanical properties of polymer blends (9,28,32,73-75). In the simplest cases, for miscible blends, with excellent thermodynamic compatibility of the components and additive characteristics, the prediction of mechanical properties can be done by using the following expression:

$$P = P_1 \phi_1 + P_2 \phi_2 + I P_1 P_2 \quad (2-3-29)$$

where P is the property to be evaluated, the subscripts 1 and 2 correspond to the two polymer components, and I is the interaction coefficient which describes the level of synergism. If $I=0$, the blend is additive; if $I<0$, the blend is non-synergistic, and for $I>0$, the blend is synergistic. Figure 2-18 shows the representation of the rule of mixtures for miscible blends.

In reality, the experimental data do not adhere to the rule of mixtures because several parameters are not taken into account by this theory. The parameters which are not included in the rule of mixture are: the variation of the property-composition relation with the nature of the components (amorphous, semi-crystalline, rubbery), the

kind of interactions between the constituents, the thermodynamic state of the blend (immiscibility or miscibility), mechanical state of the blend, presence of stress-concentrations, voids, or any other imperfections, etc.

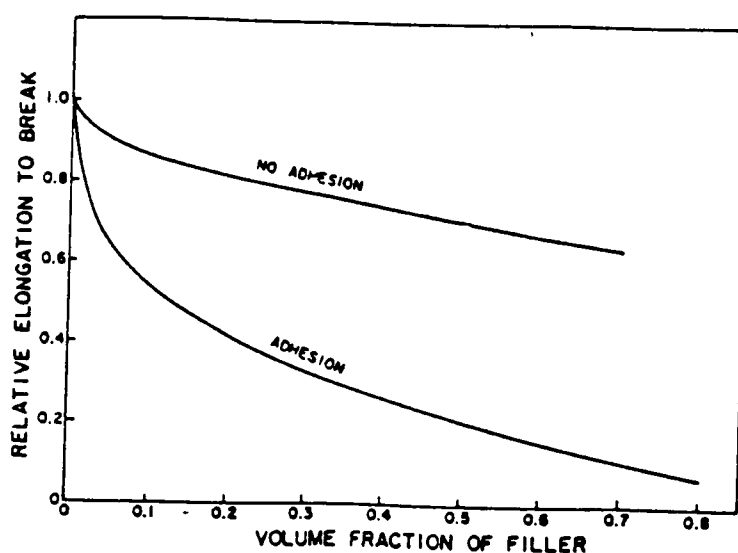


Figure 2-16. Theoretical curves for the elongation to break for the case of perfect adhesion and no adhesion between the filler and polymer phases.

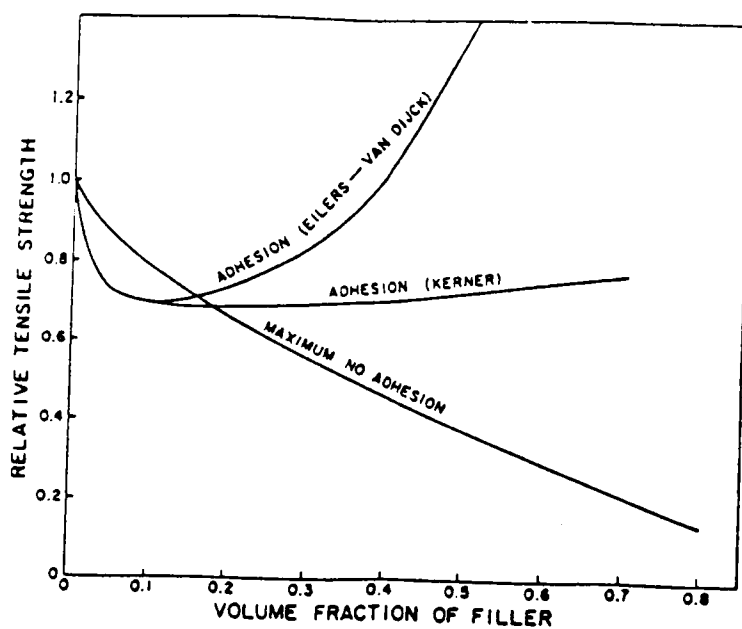


Figure 2-17. Theoretical curves for the tensile strength of filled polymers.

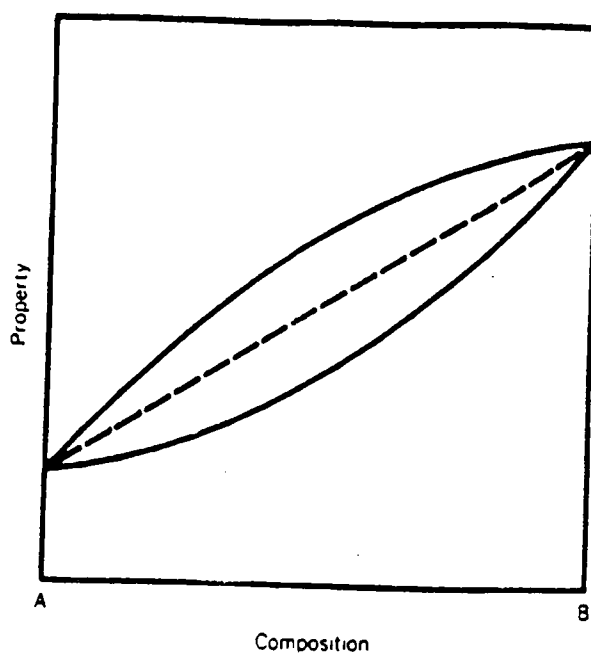


Figure 2-18. Typical property vs. composition relations for miscible blends of polymers.

Dynamic Mechanical Analysis:

As a result of the dynamic mechanical analysis of the dynamic mechanical properties of polymers, the relationships between the dynamic properties and the structural parameters (i.e. crystallinity, molecular weight, molecular orientation, crosslinking, copolymerization and plasticization), and external variables (temperature, pressure, time, frequency, humidity, etc.) can be explained (76). When oscillating sinusoidal load is applied to a specimen at a particular frequency, the variation of stress and strain with time can be given by:

$$\begin{aligned}\varepsilon &= \varepsilon_0 \sin \omega t, \text{ and} \\ \sigma &= \sigma_0 \sin (\omega t + \delta)\end{aligned}\tag{2-3-30}$$

where δ is the phase angle or the relative angular displacement of the stress and strain, and ω is the angular frequency. A complex notation is often favored for the representation of the dynamic mechanical properties of viscoelastic materials. The stress and strain are given by:

$$\begin{aligned}\varepsilon &= \varepsilon_0 \exp i\omega t, \text{ and} \\ \sigma &= \sigma_0 \exp i(\omega t + \delta)\end{aligned}\tag{2-3-31}$$

The overall complex modulus, $E^* = \sigma / \varepsilon$ is then given by the following equation:

$$E^* = (\sigma_0 / \varepsilon_0) \exp i\delta = (\sigma_0 / \varepsilon_0) (\cos \delta + i \sin \delta)\tag{2-3-32}$$

from this expression, the real (E') and imaginary (E'') parts of the modulus, better known as storage and loss modulus respectively, are derived:

$$E^* = E' + iE'' \quad (2-3-33)$$

The phase angle is given by:

$$\tan \delta = E'' / E' \quad (2-3-34)$$

The dynamic mechanical instruments measure the deformation of a material in response to vibrational forces (76). Some of the representative instruments for measuring dynamic mechanical properties of polymers include the Rheovibron, the torsion pendulum, the torsional braid analyzer, the vibrating reed or cantilever, the mechanical spectrometer, the dynamic mechanical analyzer, and the complex-modulus apparatus (76).

Typical modulus-temperature curves of miscible, partially miscible, and immiscible polymer blends are shown in Figures 2-19, 2-20, and 2-21, respectively (65). Miscible polymer blends exhibit a steep break in the modulus curves. Figure 2-19 also shows a shift of the modulus on the temperature scale as the relative concentration of the components of the blend increases. Partially miscible blends show a not so steep break in modulus as miscibility of the two constituents of the blend is reduced (Figure 2-20). Finally, immiscible blends exhibit two steps in the modulus-temperature curves (Figure 2-21), as well as two peaks in the damping-temperature curve, each peak being characteristic of the glass transition temperature of the components of the blend. The

magnitude of the peaks is relatively characteristic of the concentrations of the components.

The modulus-temperature and damping-temperature curves of polymer blends give valuable information regarding the molecular motion of its components. The glass transition of the constituents of the blend can be determined from the position of the main chain relaxations.

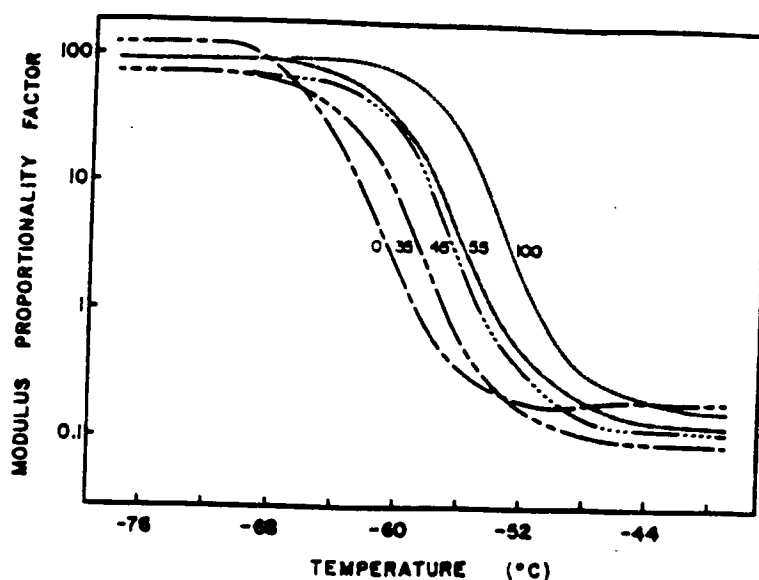


Figure 2-19. Modulus proportionality factor (relative elastic modulus) of mixtures of miscible blends of two different styrene-butadiene copolymers of similar styrene content (16% and 23.5%).

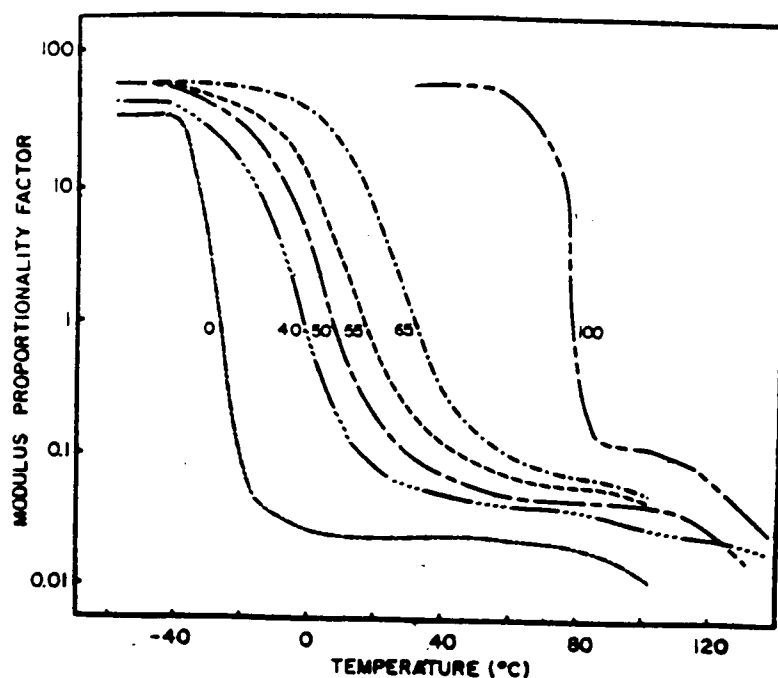


Figure 2-20. Modulus proportionality factor or relative elastic modulus of partially miscible blends of two styrene-butadiene copolymers (37.5% and 50%).

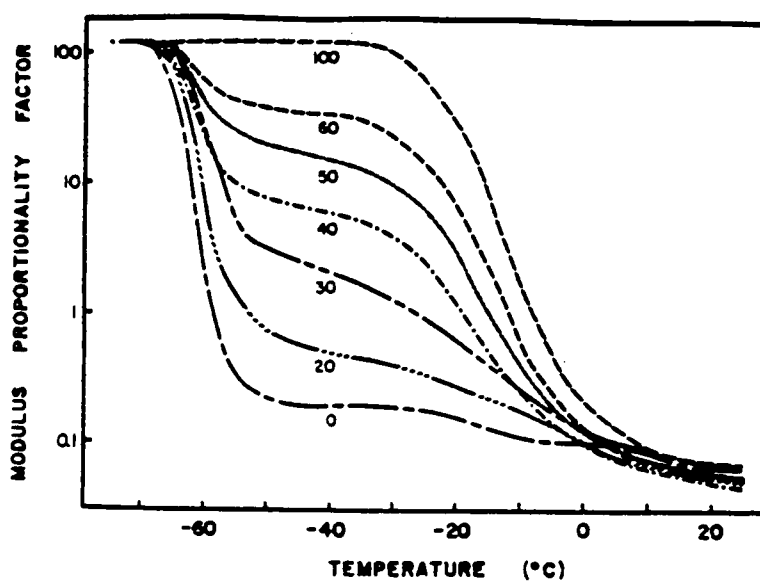


Figure 2-21. Relative elastic modulus of immiscible blends of two styrene-butadiene copolymers of different styrene content (16% and 50%).

2.3.5. COMPATIBILIZATION OF POLYMER BLENDS.

Polymer blends play an increasingly important role in industry. Generally, simple blends of different polymers result in immiscibility which can generate an heterogeneous system. This may not be a problem because sometimes it is desirable to have a two-phase structure. However, if there is high interfacial tension and poor adhesion between the two resins, the dispersion will be extremely poor, leading to separation of the phases or stratification during later processing or use of the blend. Consequently, poor mechanical properties are evident, as well as highly coarse unstable phase morphologies.

These problems have been mitigated in many cases by the introduction of small quantities of additive, generally known as "compatibilizing agents". The use of compatibilizing agents in polymer blends dates to the 1960's. However, serious considerations of their influence on phase morphologies as well as mechanical properties dates to the 1970's with the work of Heikens and co-workers (77-79) on the use of graft copolymers of poly(ethylene-styrene) and block copolymers of poly(ethylene-buthylene-styrene) on PE/PS blends.

Compatibilizing agents are graft-and-block copolymers of chemically reactive species. The desired effect may be attained if one of the arms of the block or graft polymer is miscible with or adheres to one of the phases. Figure 2-22 shows a schematic representation of the ideal location of block-and-graft copolymers at the interface between the constituents of a blend (80).

For the compatibilizing agents to be effective, the interfacial energy between the phases must be reduced, a finer dispersion during mixing must be possible, stability against gross separation must be provide, and an improvement in the interface

adhesion must be observed (80,81). The block or graft copolymer must then have the propensity to segregate into two phases.

Another important consideration is that usually block-and-graft copolymers are expensive, which makes of interest the maximization of their efficiency so that only small quantities are required. The following equation express the amount of block copolymer of molecular weight, M , required to saturate all of the interface in a blend (80):

$$\frac{\text{Mass of block copolymer}}{\text{Original volume of blend}} = 3 \phi_A M / a R N \quad (2-3-35)$$

where ϕ_A is the volume fraction of polymer A as spherical particles of radius R in a matrix of polymer B, a is the area that each block copolymer molecule occupies in the interface, and N is the Avogadro's number.

It is evident that materials with high molecular weight are preferred, because the longer the segments the higher the cohesive forces needed to anchor them firmly into the domains they penetrate.

One of the most studied applications of graft copolymers is in impact-modified plastics (82,83). It is well known that glassy polymers are brittle by nature which results in poor capability to absorb energy, that is poor impact strength. The addition of rubbery materials to PS has been widely studied, and several reports indicate that by grafting styrene on to rubber, and by adding the graft copolymer to PS, significant increase in impact strength is produced. The detailed mechanisms by which the proper combination with rubber acts to improve the impact strength of glassy polymers is very complex, but definitely, the regulation of phase morphology is determinant.

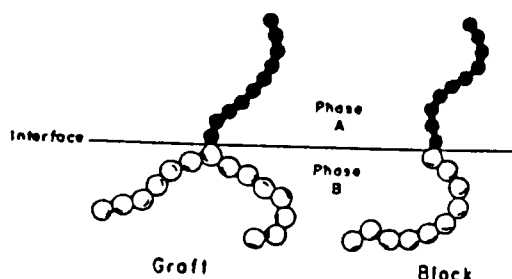
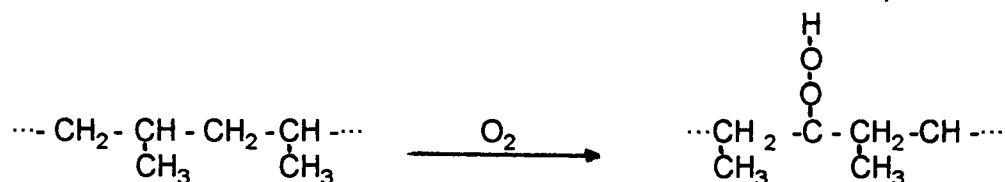


Figure 2-22. Ideal location of block-and-graft copolymers at the interface between polymer phases A and B.

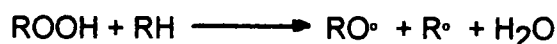
2.3.5.1. Graft and block copolymers of α -olefins.

Block copolymers of different types are prepared by polymerization of α -olefins or by modification of polymeric products. The most common method for preparing block copolymers of α -olefins is by using catalyst systems which maintain their activity for a long time. However, graft copolymers are the most utilized in blends involving polyolefins.

Oxidation of polyolefins results in the formation of hydroperoxy groups, followed by decomposition, i.e. thermal decomposition, and this leads to the generation of free radicals that can be employed as initiators of the formation of grafted chains. If the polyolefin contains tertiary carbons, as PP does, hydroperoxidation is quite simple. For PP, the process follows the reaction:



Heterogeneous hydroperoxidation of PP occurs mostly in the amorphous regions and in the outer surfaces of crystalline regions, that is why the structural ordering of PP is retained even after intensive grafting (3). The decomposition of hydroperoxy groups is a bimolecular reaction which essentially involves the interaction between a hydroperoxy group and a hydrogen atom which is attached to a tertiary carbon atom in the macromolecular chain:



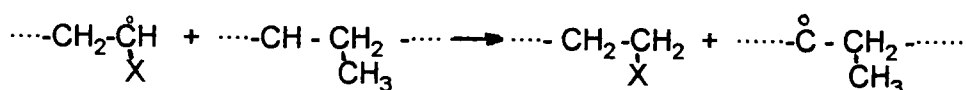
both radicals ($\text{RO}^\bullet$ and $\text{R}^\bullet$) are capable of initiating the growth of grafted chains (82). The decomposition of hydroperoxy groups can also go through mono-molecular mechanism:



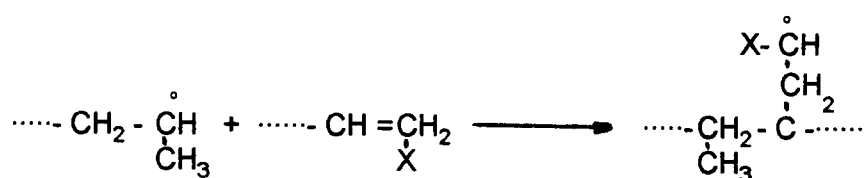
the ${}^\bullet\text{OH}$ radical, along with the polymeric free radicals, is also capable of initiating the polymerization of the monomer, in the presence of which, the hydroperoxy groups are decomposed. The polymerization initiated by ${}^\bullet\text{OH}$ radicals leads to the formation of the homopolymer.

Chain transfer onto the polymer can be used to prepare graft copolymers even without a preliminary oxidation. The process consist on the polymerization of the

monomer in the presence of a free-radical primer and the polyolefin, e.g. PP, yielding to the formation of macroradicals:



the macroradical acts as the initiator of the grafting reaction:



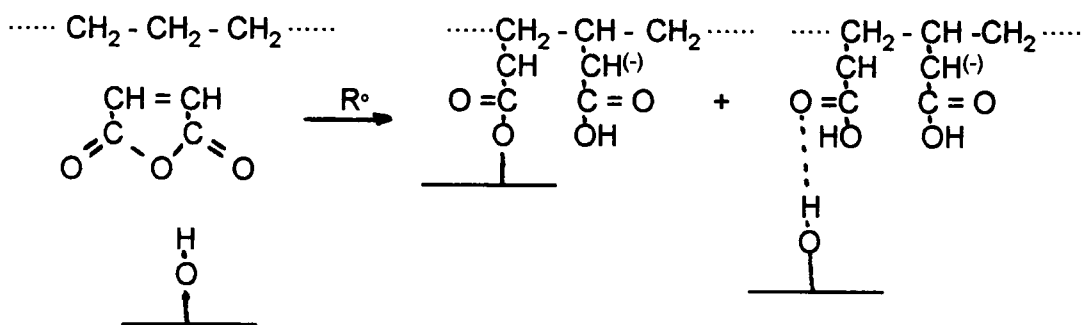
the product will consist of a mixture of the graft copolymer and the homopolymer.

The most common free-radical grafting reactions involves saturated monomers such as maleic anhydride (MAH) and polyolefins, e.g. PP and PE. The main purpose of grafting MAH to polyolefins is to improve adhesion of the polyolefins to polar phases.

Gaylord et al. (3), studied the graft copolymerization of MAH onto PE, concluding that the heterogeneous radical-catalyzed reaction of MAH and PE in the presence of a radical catalyst undergoing rapid decomposition, leads to the formation of Poly-MAH chains, and individual MAH units to the PE, accompanied by crosslinking. Additionally, their reports indicate that the reaction of MAH and PE consists of two basic reactions: homopolymerization of MAH accompanied by crosslinking of PE and graft polymerization of MAH onto PE, and the appendage of individual MAH onto PE by the addition of PE radicals to MAH.

Gaylord and Takhashi (3) prepared PE-clay composites through *in situ* graft copolymerization of MAH, using a radical catalyzed polymerization, which yielded PE-g-MAH-clay composites having better mechanical properties than unfilled PE or PE-clay

mixtures prepared in the absence of MAH or a radical catalyst. Crosslinking also took place during the graft polymerization process, and it was demonstrated that it plays an important role in the enhancement of the mechanical properties of the composite. Important remarks can be made from this study: the compatibilization involves the reaction of MAH with PE to form a MAH-g-PE that is followed by the reaction of the pendant anhydride groups with the hydroxyl groups of the clay, and the bonding between the MAH moieties and clay hydroxyls takes the form of covalent ester linkages and/or hydrogen bonds:



Improvement of the adhesion between the polymer phases and the mechanical properties of Polyamide/PP blends with MAH grafted styrene-ethylene-butylene-styrene block copolymer (SEBS-g-MAH) have also been reported by Holsti-Miettinen and Seppala (5). By the same token, Armat and Moet (84) reported that SEBS-g-MAH plays a dual interfacial function in PE/Nylon 6 systems.

2.3.5.2. Other compatibilized systems.

Interactions between Linear Low Density Polyethylene/Poly(Octadecene-co-Maleic Anhydride) blends (LLDPE/ C_{18} -MAH) have been observed (85), and the presence of the C_{18} -MAH in the LLDPE melt increases the nucleation rate for LLDPE

crystallization; suppression of side-chain crystallization of the C₁₈-MAH component has been observed, and the mechanical properties of the blends, is essentially a sum of the pure components properties (Rule of Mixtures). The blends are miscible in both the melt and solid state.

Jones and Wielinski (86) have reported the significant improvements in adhesion that the incorporation of MAH onto the Ethylene-Vinyl acetate (EVA) matrix can provide. Different methods for "maleating" EVA have been investigated in an effort to control its physical properties while optimizing its adhesion to other materials. The heat stability and compatibility of MAH-modified EVA polymers have been shown improve by the chemical modification. Modified EVA polymers have also shown excellent adhesion to aluminum and Nylon, indicating that they are suitable for use in applications that require bonding between non-porous substrates.

III. EXPERIMENTAL.

3.1. MATERIALS.

Two poly(vinyl alcohol) resins were obtained from Air Products and Chemicals, Inc., Allentown, PA. The resins' trade names are VinexTM 1003 (percent of hydrolysis higher than 98%) and VinexTM 2019 (88% hydrolyzed). Table 5 shows the typical physical data for Air Products' PVOH resins provided by the manufacturer.

A polypropylene resin (PP3445) with a MFR of 35, and a polypropylene/grafted-maleic anhydride (Exxelor PO-1015) resin were supplied by Exxon Chemical Company.

Table 5. Physical Properties of PVOH resins.

Color	White to Off-white
Odor	Odorless
pH	4-8 4% aqueous solution
Vapor Pressure (mm Hg)	Not applicable
Vapor Density (Air = 1)	40 lbs/cu ft
Boiling Point	Not applicable
Freezing/Melting Point	170-230 °C
Solubility in Water	Soluble in either hot or cold water
Specific Gravity (Water = 1)	1.25-1.27 g/cu cm
Evaporation Rate (Butylacetate = 1)	No data
Viscosity (CPS)	No data
Molecular Weight	Mixture

3.2. PREPARATION OF BLENDS.

Mechanical blends were prepared as follows: both components were weighed to get the desired composition and then, the components of each composition were mechanically mixed for 8 hours at room temperature in a blender. The mechanical blends were dried in a vacuum oven at 80 °C for 8 hours. Pellets of Exxelor were pulverized in a Hammer mill, and subsequent mechanical mixing of the resulting white powder with the PP and PVOH was carried out. The blends were extruded using a Brabender screw Extruder. The Brabender extruder possesses a circular die of 3.18 mm in diameter. The screw extruder's temperature zones are given in Table 6. A code name was assigned to each blend to facilitate its identification. The processing conditions for the samples are listed in Table 6. Each blend was extruded twice to achieve better mixing of the constituents (homogeneous blends). The extruded blends were dried in a vacuum oven at 80 °C for 8 hours, and placed in a desiccator to keep them dry for further studies.

3.3. PREPARATION OF FILMS.

Samples for water adsorption determination, X-rays diffraction, tensile testing, Fourier Transform Infrared Spectroscopy, and dynamic mechanical analysis, were prepared as films, using a Wabash Model 12-12-2TB 12-ton melt press. The blend pellets were placed between two clean sheets of Teflon film which in turn were placed between two stainless steel ferrotype platens. The resulting platens-teflon film-resin sandwich was then inserted between the press plates. The pellets were allowed to melt at 230 °C for at least 2 minutes before the press was completely closed. A pressure of about 5 tons was applied for 1 minute, and then it was increased up to 9 tons. High pressure was applied for 2 minutes. The pressed films were quenched in

Table 6. Code Names and Processing conditions for the studied samples.

Material	Sample Code	Temperature (°C)			Extrusion Rate(RPM)
		Zone 1	Zone 2	Zone 3	
Pure Polypropylene	PP3445	-	-	-	-
Pure PVOH2019	PVOH2019	-	-	-	-
Pure PVOH1003	PVOH1003	-	-	-	-
Pure PP/g-MAH	g-PP	-	-	-	-
PP/PVOH2019 (95/5)	PP/PV2 (95/5)	190	180	160	20
PP/PVOH2019 (90/10)	PP/PV2 (90/10)	190	180	160	20
PP/PVOH2019 (80/20)	PP/PV2 (80/20)	190	180	160	20
PP/PVOH2019 (70/30)	PP/PV2 (70/30)	190	180	160	20
PP/PVOH1003 (95/5)	PP/PV1 (95/5)	200	190	170	20
PP/PVOH1003 (90/10)	PP/PV1 (90/10)	200	190	170	20
PP/PVOH1003 (80/20)	PP/PV1 (80/20)	200	190	170	20
PP/PVOH1003 (70/30)	PP/PV1 (70/30)	200	190	170	20
PP/PP-g-MAH/PVOH2019					
(90/5/5)	PGV2 (90/5/5)	190	180	160	20
(85/10/5)	PGV2 (85/10/5)	190	180	160	20

liquid Nitrogen immediately after they were removed from the press. The films were saved in a desiccator for subsequent experiments.

3.4. STUDY OF MORPHOLOGY.

A light microscope Olympus BF22 (connected to a Sony 12 inch and a JVC VCR) was used to record and study the morphology of the pure materials and their blends. Thin sections of the samples were obtained by cutting pellets with an American Optical Spencer Rotary Microtome (model 820) with glass knives. The thin sections were placed in a Mettler FP-80 central processor with hot stage in order to melt them for subsequent study under the microscope.

3.5. THERMAL ANALYSIS.

A Perkin-Elmer Series 7 Thermal Analysis Differential Calorimeter was used for thermal analysis of the blends and pure components. A Perkin-Elmer 7500 Professional Computer and a TAS7 Instrument Controller were also used. The DSC7 calorimeter was calibrated for temperature according to the procedure described in the user's manual using pure indium as a standard ($T_m^\circ = 156.60\text{ }^\circ\text{C}$). The baseline calibration was done by using two empty sample holders. A nitrogen flow was maintained through the sample chamber. Pellets of the blends were cut to size and weighed on a Mettler analytical balance (Model 760), and crimp-sealed in Aluminum DSC pans. The sample weights ranged from 4 to 7 mg. All DSC scans were performed as follows: the initial temperature was $40\text{ }^\circ\text{C}$; the samples were held at $40\text{ }^\circ\text{C}$ for 1 minute after which, the temperature was raised up to $250\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$. Temperature was held at $250\text{ }^\circ\text{C}$ for 1 minute, and subsequent cooling at a rate of 10

°C/min was carried out. When the sample reached a temperature of 40 °C, it was held at that temperature for 1 minute and finally heated up to 250 °C at 10 °C/min.

3.6. WATER ADSORPTION MEASUREMENTS.

Films of the blends and pure materials were dried in a vacuum oven for 8 hours at 80 °C. The dried films were cut to squares and weighed before being immersed in water. The weights of the samples were taken after 1, 2, 5, 7, 14, 22, and 36 hours of immersion. A Mettler analytical balance (Model 760) was used for this purpose. The variation of weight as a function of immersion time was determined.

3.7. TENSILE TESTING.

Mechanical tensile testing was carried out according to the ASTM D882-83 standard tensile test procedure using an Instron Tensile Test Equipment (Table Model 1122). Samples dried in a vacuum oven for 24 hours at 80 °C (dry samples), and samples subjected to controlled humidity conditions (65 % r.h. and 20 °C) in a conditioning room for the same period of time (wet samples) were tested. The sample size was 5 mm x 70 mm. The gage length was 50 mm, the maximum load 2,000 gm, the crosshead speed 100 mm/min, and the chart speed 500 mm/min. Mechanical properties such as tensile modulus, tensile strength, and elongation to break were determined from the mechanical test data. The modulus was typically measured at about 10% elongation.

3.8. DYNAMIC MECHANICAL ANALYSIS (DMA).

Dynamic mechanical analysis was performed using an automated Autovibron Dynamic Viscoelastometer (IMass, Inc., Accord, Mass). The "dry" and "wet" samples

were cut to 5 mm width and 30 mm in length. The tension applied was 20 grams. The temperature range used in the experiment was -100 ° to 140 °C. All data were obtained at 1.1, 11, and 110 Hz. Only the 11 Hz curves are presented in this work. The T_g was determined from the loss modulus-temperature curve at 11 Hz.

3.9. X-RAYS DIFFRACTION.

A Rigaku X-rays Diffractometer was used to collect the X-ray scattering curves for pressed films of the blends and pure materials. Samples were cut to squares of 15 mm x 15 mm that were analyzed according to the conditions shown in Table 7. Some conditions were common to all the studied samples: the voltage dial was fixed at 35 kV; the ampere dial was at 20 mA; the Mode was set at the continuous scan condition; the number of cycles was adjusted to 1; the drive axis was equal to $2\theta / \theta$; the time constant was kept at 5 seconds; the scan speed was equal to 1 degree/minute; the start angle was 10°, and the stop angle was 35°. The crystallinity of the samples was determined by this technique.

3.10. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR).

A Digilab FTS-40 Fourier Transform Infrared Spectrometer (Cambridge, MA) was used to collect infrared spectra of the studied samples. A resolution of 8 cm⁻¹ and 256 scans were used to collect the spectra. The FTIR was used to study the miscibility of the blends, to establish a comparison between the two PVOH resins, and to explore the nature of the interactions between the studied resins and the Exxelor in the presence of the compatibilizing agent (g-PP).

Table 7. Count rate and Chart speed conditions for the X-rays diffraction tests.

Sample	Count Rate (CPS)	Chart Speed (mm/min)
PP3445	1000	20
PVOH2019	1000	20
PVOH1003	1000	40
g-PP	1000	20
PV2 (95/5)	1000	20
PV2 (90/10)	1000	40
PV2 (80/20)	2000	40
PV2 (70/30)	2000	40
PV1 (95/5)	2000	20
PV1 (90/10)	1000	40
PV1 (80/20)	2000	40
PV1 (70/30)	2000	40
PGV2 (90/5/5)	2000	20
PGV2 (85/10/5)	4000	20

IV. RESULTS.

4.1. THERMAL BEHAVIOR OF PRESSED FILMS.

Figures 4-1 to 4-6 show the thermal behavior of the three blended systems. The data of the thermal properties of the blends, are listed in Tables 8 to 10. In Figures 4-1 to 4-6 one can see that in most cases, the crystallization and/or melting peaks of the constituents of the blends are easily identifiable.

In the case of the blends of PP with PVOH 1003, crystallization of PP occurs at higher temperatures as the concentration of PVOH increases, while the crystallization temperature of PVOH in the blends is not discernible at low concentrations. However, the crystallization peak of blends with PVOH 1003 concentrations greater than 20 % the crystallization temperature of PVOH is at higher temperatures than that of the pure homopolymer (Figure 4-1).

Figure 4-2 shows the crystallization curves of blends of PP with PVOH 2019 at different compositions of PVOH. From Figure 4-2 a significant increase in the crystallization temperature of PP is observed for blends with 5%PVOH. As the concentration of PVOH increases, a slight depression of the crystallization peak of PP can be observed. The crystallization peak of PP in the blends is always located at higher temperatures than that of the pure homopolymer. The PVOH crystallization peak in the thermograms of the blends is not observable, and even in the curve for pure PVOH, the crystallization peak is very small because PVOH 2019 does not exhibit a high degree of crystallinity.

From Figure 4-3 one can see that there is a decrease in the crystallization temperature of PP as the concentration of g-PP increases for blends with 5%PVOH

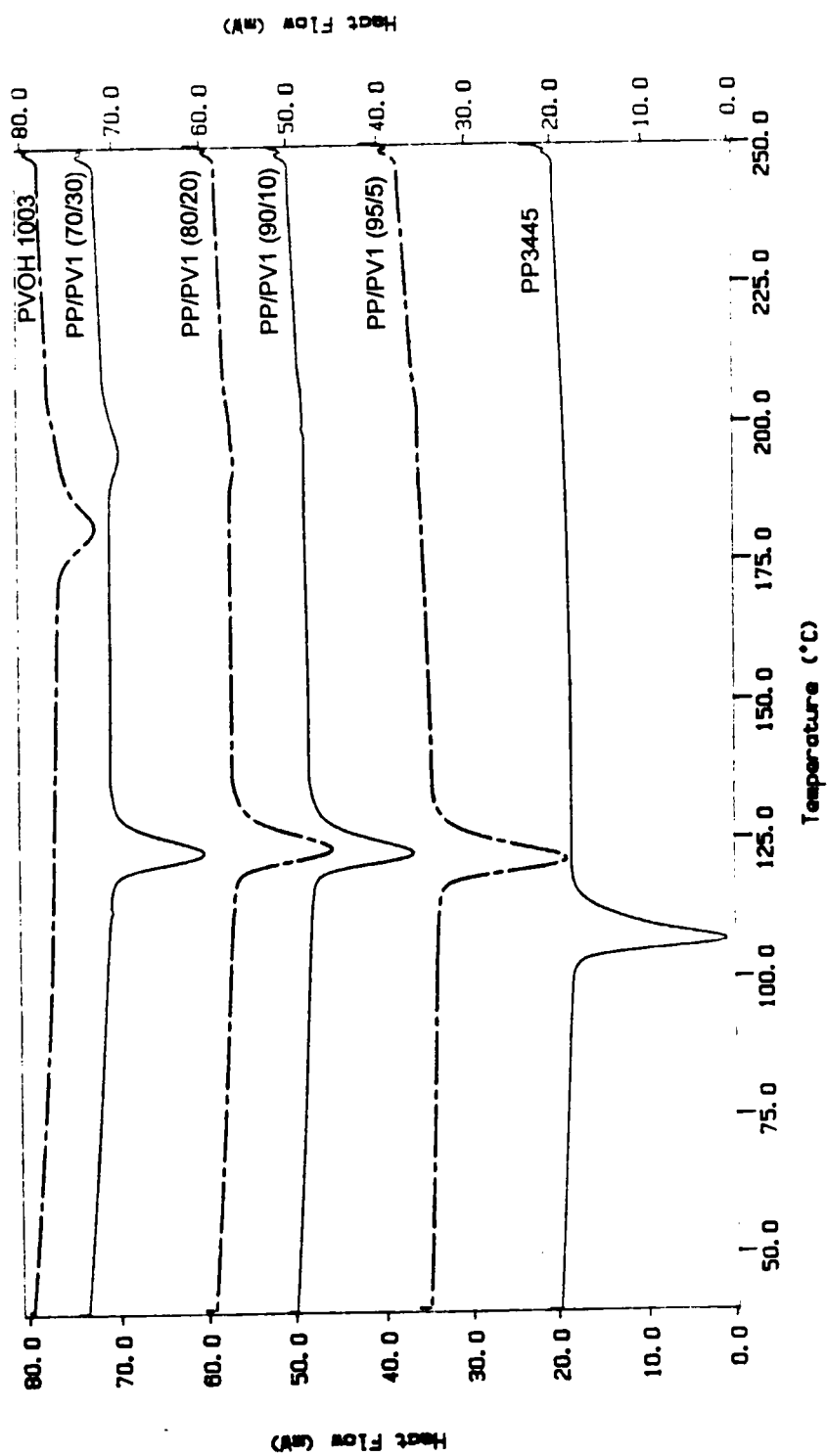


Figure 4-1 . Crystallization Behavior of PP/PVOH 1003 Blends.

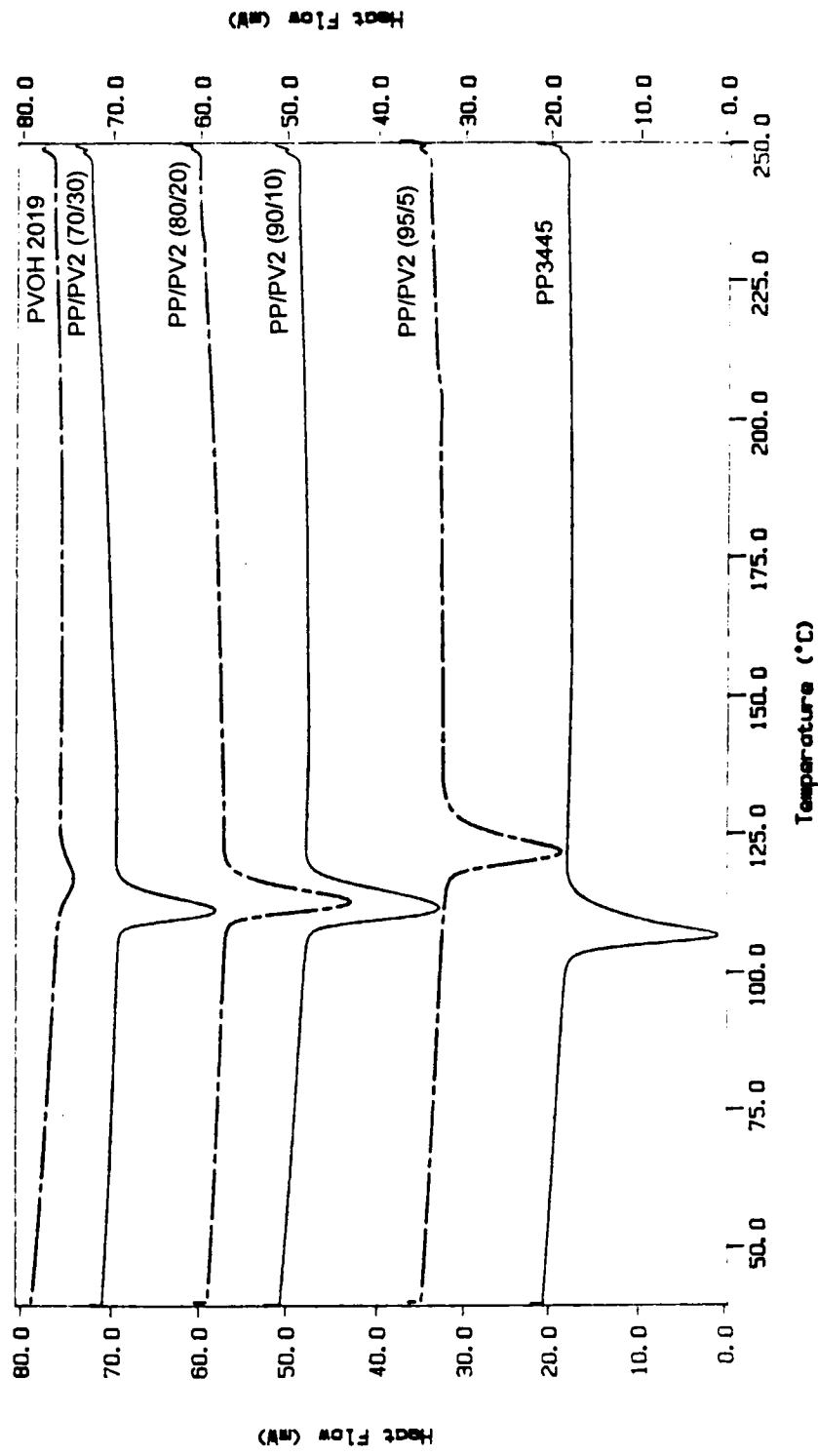


Figure 4-2 . Crystallization Behavior of PP/PVOH 2019 Blends.

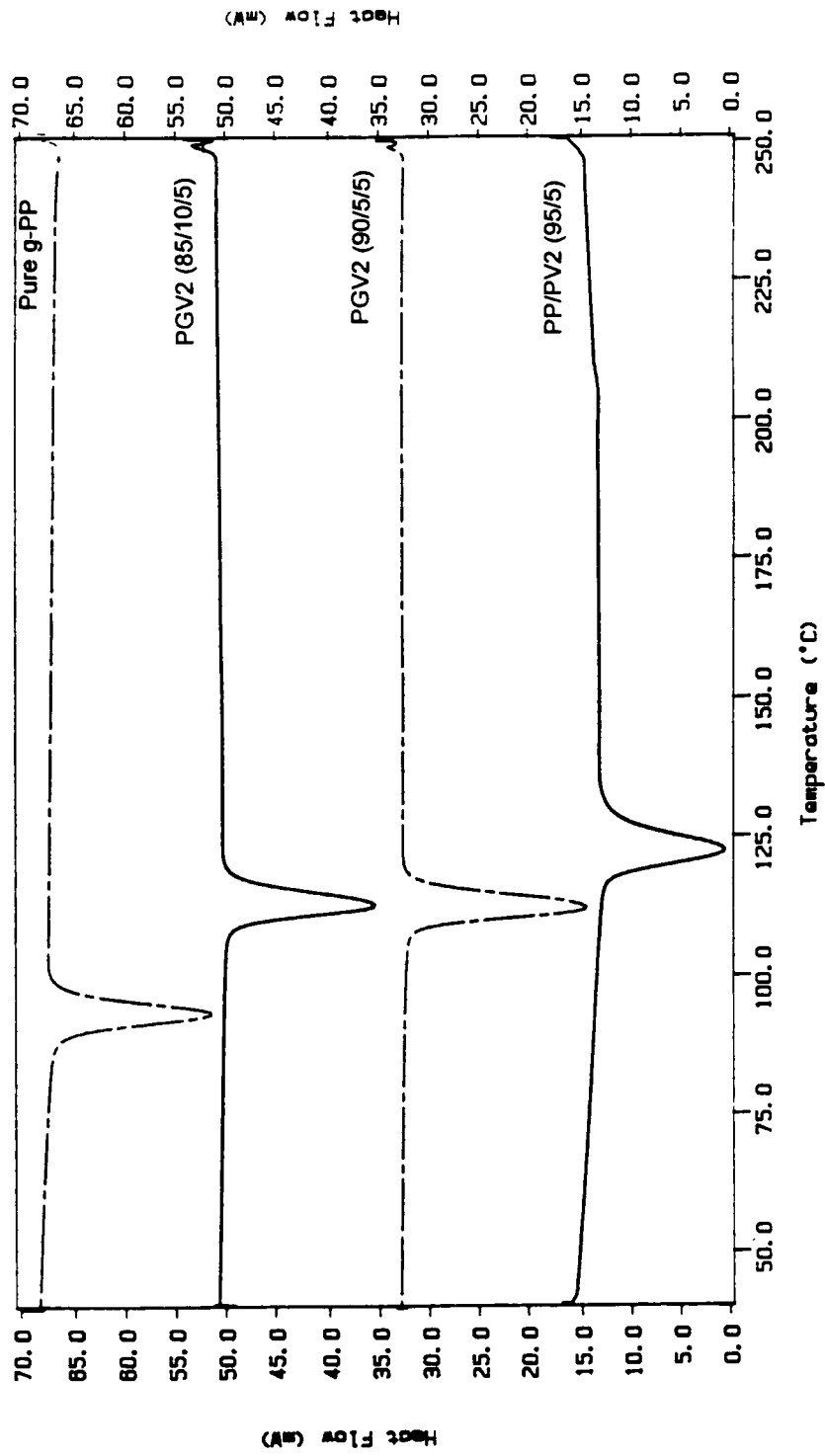


Figure 4-3 . Crystallization Behavior of PP/g-PP/PVOH 2019 Blends.

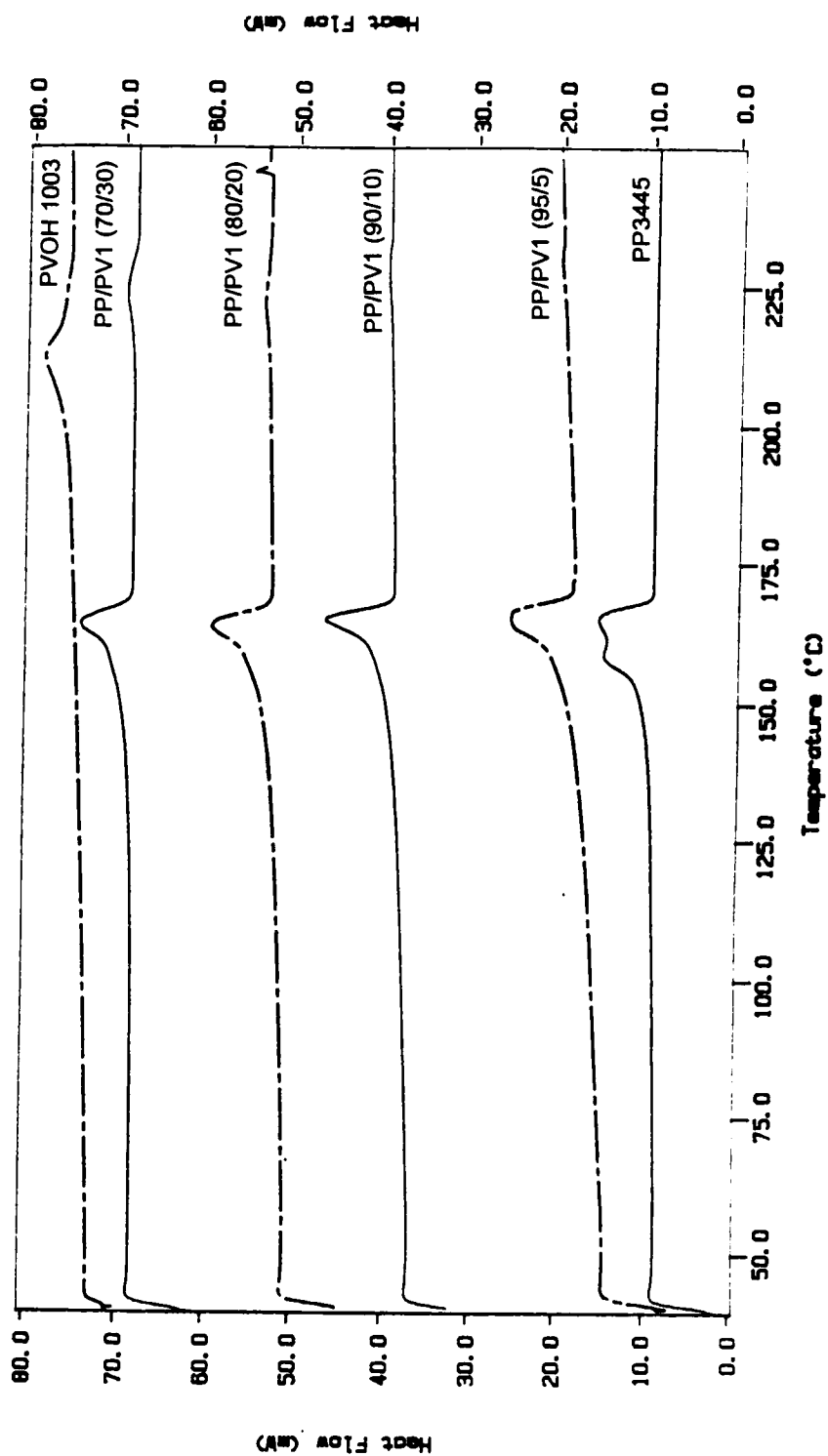


Figure 4-4 . Melting Behavior of PP/PVOH 1003 Blends.

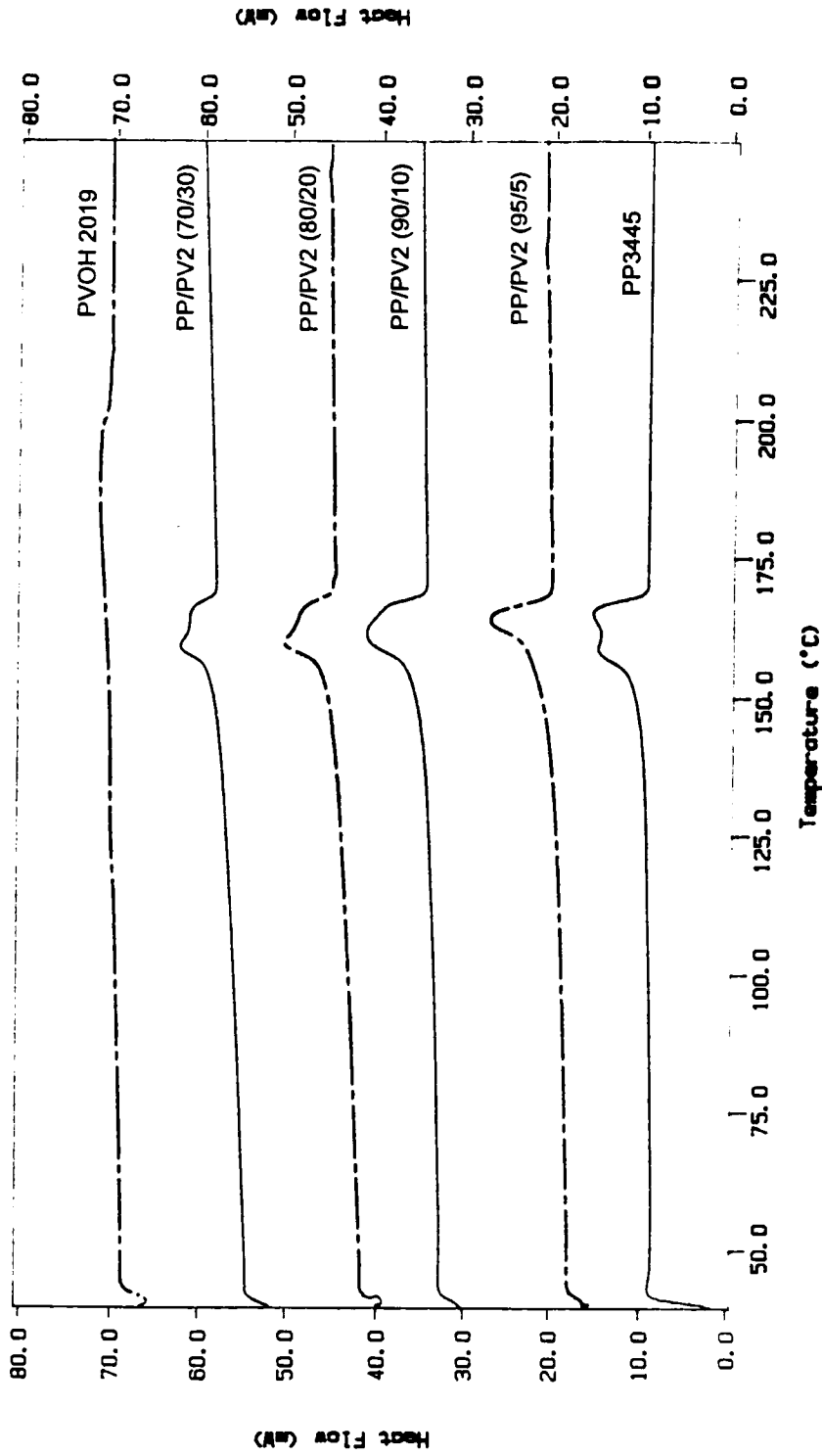


Figure 4-5 . Melting Behavior of PP/PVOH 2019 Blends.

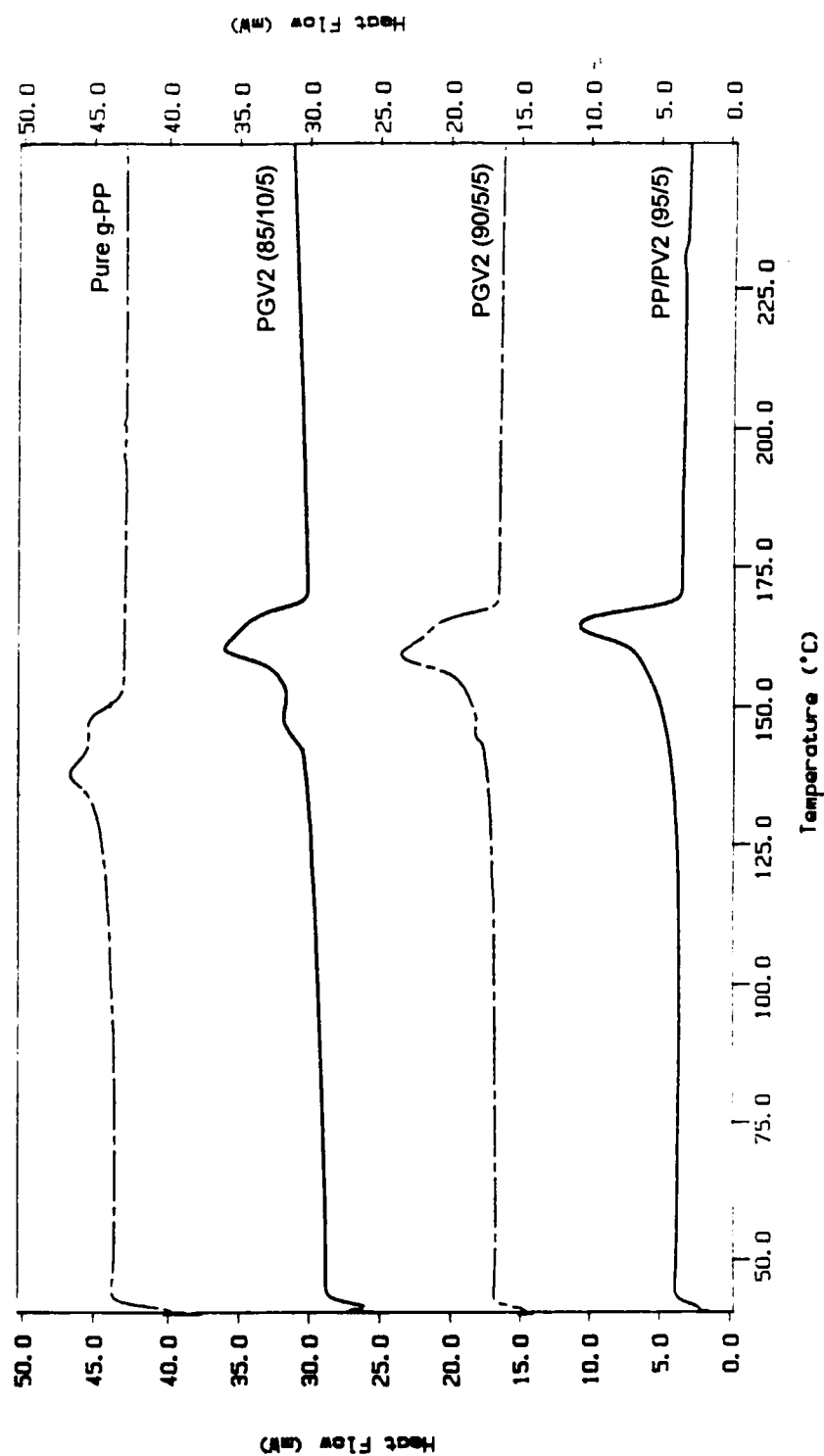


Figure 4-6 . Melting Behavior of PP/g-PP/PVOH 2019 Blends.

Table 8. DSC Data for PP/PVOH 1003 Blends

Blend Composition	PP		PVOH 1003	
	T _m (°C) (±2)	T _c (°C) (±2)	T _m (°C) (±2)	T _c (°C) (±2)
Pure resin	164	108	214	184
(95/5)	162	121	231	182
(90/10)	161	122	229	197
(80/20)	160	124	222	193
(70/30)	159	124	225	193

Table 9. DSC Data for PP/PVOH 2019 Blends

Blend Composition	PP		PVOH 2019	
	T _m (°C) (±2)	T _c (°C) (±2)	T _m (°C) (±2)	T _c (°C) (±2)
Pure resin	164	108	182	117
(95/5)	163	123	-	-
(90/10)	163	114	-	-
(80/20)	162	113	183	-
(70/30)	161	113	183	-

Table 10. DSC Data of PP/g-PP/PVOH 2019 Blends.

Blend	PP		g-PP		PVOH 2019	
Composition	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)
	(±2)	(±2)	(±2)	(±2)	(±2)	(±2)
Pure resin	164	108	141	93	182	-
(95/5)	163	123	-	-	-	-
(90/5/5)	160	114	144		-	-
(85/10/5)	160	113	144	-	-	-

2019. The crystallization peak of g-PP is located at a lower temperature with respect to that of pure PP.

Figure 4-4 shows the melting behavior of blends of PP with PVOH 1003. The melting peak of PP in the blend systems is shifted to slightly lower temperatures compared with the pure homopolymer. The melting peak of PVOH 1003 is evident at concentrations higher than 20%, and it is located at higher temperatures than that of the pure resin. The melting peak of pure PVOH 1003 is higher than that of pure PP.

In the case of PP/PVOH 2019 blend systems (Figure 4-5), a slight depression of the melting temperature of PP is observed. PVOH 2019 exhibits a higher melting temperature than the blends as well as pure PP. The melting peak of PVOH 2019 in the blends is not distinguishable.

Figure 4-6 shows the melting behavior of blends of PP with 5%PVOH 2019 and two different concentrations of g-PP. The melting point of PP in the blends considerably decreases with 5%g-PP, but at 10%g-PP, the melting temperature does not display further displacements. The melting peak of g-PP is located at lower temperatures compared with the PP/PV2(95/5) blend.

4.2. MECHANICAL PROPERTIES.

Table 11 shows the experimental results of modulus, tensile strength, and elongation to break for dry and wet samples of PP/PVOH blend systems and compatibilized systems. These results are the average values for four, quenched, fractured thin films of the studied blends systems and pure resins. From Table 11, higher values of the modulus and elongation to break for the wet samples compared to those of the dry samples in all the studied systems can be seen, while the dry samples

exhibit higher values of tensile strength than wet samples. This can be attributed to the fact that water may be acting as a plasticizer for the blend systems.

Figures 4-7 and 4-8 show the reduced modulus for blends of PP and PVOH as a function of composition for dry and wet samples, respectively. The prediction of the reduced modulus for the studied blends using Kerner's equation is also included in Figures 4-7 and 4-8. The reduced modulus is defined by the following expression:

$$\text{Reduced Modulus} = E_1 / E_{12} \quad (4-2-1)$$

where E_1 is the modulus of the polypropylene, and E_{12} is the modulus of the blends.

Figure 4-7 indicates that the experimental data for dry samples of both PVOH 1003 and PVOH 2019 fit the theoretical curve according to Kerner's prediction, except for the pure PVOH 1003. The reduced modulus increases with increasing PVOH content in both blend systems. At low concentrations of PVOH, both blended systems exhibit approximately the same values for the reduced modulus, while at 20%PVOH and higher concentrations, blends with PVOH 2019 show a higher reduced modulus values than those of blends with PVOH 1003. On the other hand, blends with g-PP exhibit higher values for the reduced modulus compared to the PP/PV2 (95/5) system. The reduced modulus of compatibilized blend systems increases slightly with increasing g-PP content.

Figure 4-8 shows a decrease in the reduced modulus as the PVOH content increases for wet samples of both PVOH 1003 and PVOH 2019 blend systems. The experimental data for both systems fit the predicted curve for the reduced modulus by

Table 11. Modulus, Tensile Strength, and Elongation to Break for samples of PP/PVOH and PP/g-PP/PVOH blend systems.

Sample	Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
DRY: PP3445	206.31 ± 33.48	26.47 ± 7.01	602.66 ± 61.44
PVOH 1003	771.52 ± 33.39	16.10 ± 5.91	1.02 ± 0.91
PP/PV1(95/5)	220.74 ± 39.25	24.85 ± 4.34	379.84 ± 60.58
PP/PV1(90/10)	243.93 ± 50.31	21.85 ± 2.79	320.24 ± 55.25
PP/PV1(80/20)	264.79 ± 0.01	17.67 ± 3.02	243.81 ± 50.60
PP/PV1(70/30)	307.24 ± 30.13	16.09 ± 2.39	193.15 ± 51.79
PVOH 2019	1694.19 ± 0.01	17.78 ± 3.74	1.67 ± 0.31
PP/PV2(95/5)	226.75 ± 10.63	23.71 ± 5.89	381.10 ± 70.24
PP/PV2(90/10)	247.26 ± 8.28	19.65 ± 3.65	312.60 ± 50.91
PP/PV2(80/20)	328.11 ± 25.29	18.60 ± 3.55	248.17 ± 52.86
PP/PV2(70/30)	508.41 ± 0.05	17.98 ± 2.00	193.63 ± 51.16
g-PP	1056.37 ± 26.74	183.18 ± 3.96	32.41 ± 1.02
PGV2(90/5/5)	280.21 ± 29.54	27.34 ± 1.01	504.09 ± 30.66
PGV2(85/10/5)	321.14 ± 49.48	36.34 ± 1.10	515.59 ± 31.15

Table 11. Cont'd.

WET: PP3445	238.64 ± 45.18	25.70 ± 5.82	655.91 ± 88.32
PVOH 1003	141.72 ± 23.82	13.25 ± 2.54	62.21 ± 13.50
PP/PV1(95/5)	237.89 ± 29.40	16.67 ± 0.68	423.54 ± 65.99
PP/PV1(90/10)	227.06 ± 21.33	15.33 ± 1.49	348.14 ± 62.53
PP/PV2(80/20)	218.68 ± 15.16	13.87 ± 0.46	274.20 ± 50.45
PP/PV1(70/30)	207.94 ± 16.70	13.87 ± 0.99	212.99 ± 50.35
PVOH 2019	97.77 ± 0.00	15.42 ± 1.89	62.07 ± 5.26
PP/PV2(95/5)	229.08 ± 15.20	20.41 ± 2.32	419.87 ± 68.13
PP/PV2(90/10)	224.60 ± 25.35	19.10 ± 0.64	348.03 ± 70.54
PP/PV2(80/20)	224.37 ± 21.94	18.82 ± 3.54	270.87 ± 71.11
PP/PV2(70/30)	160.61 ± 4.77	16.25 ± 4.32	214.92 ± 10.83
g-PP	1404.49 ± 45.84	152.117 ± 2.04	212.99 ± 50.35
PGV2(90/5/5)	273.66 ± 0.01	24.81 ± 2.45	688.72 ± 88.16
PGV2(85/10/5)	318.18 ± 0.12	27.46 ± 1.46	544.09 ± 68.92

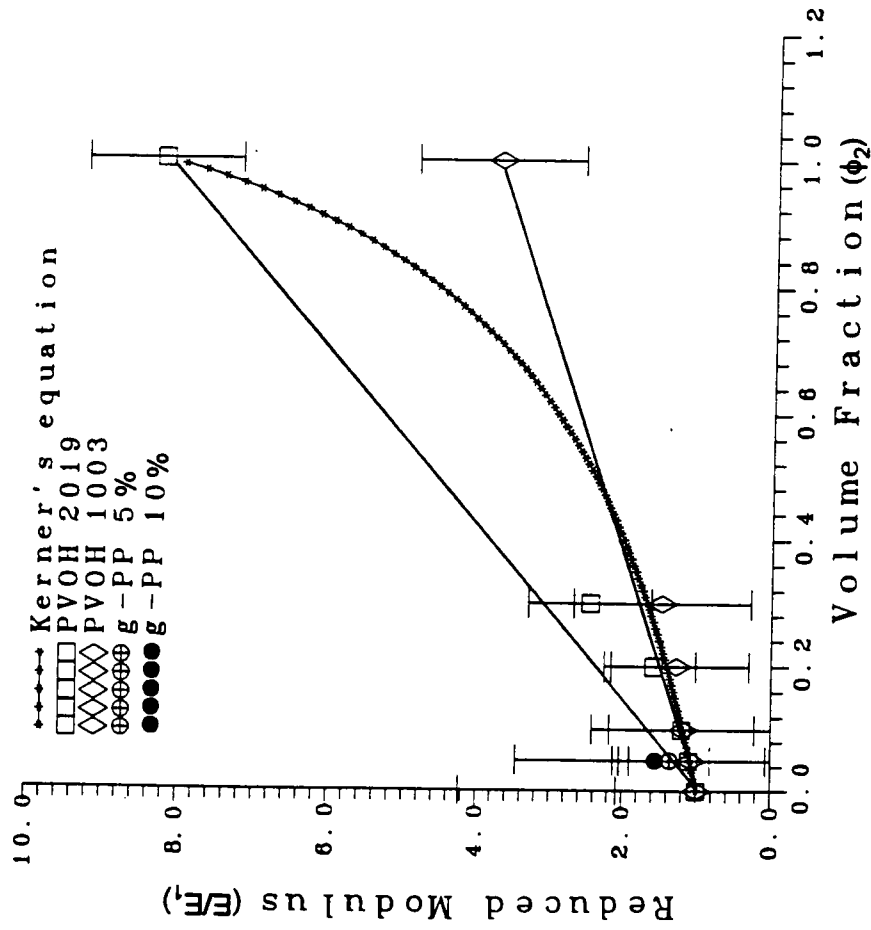


Figure 4-7. Reduced Modulus vs. Volume Fraction of Dry Samples.

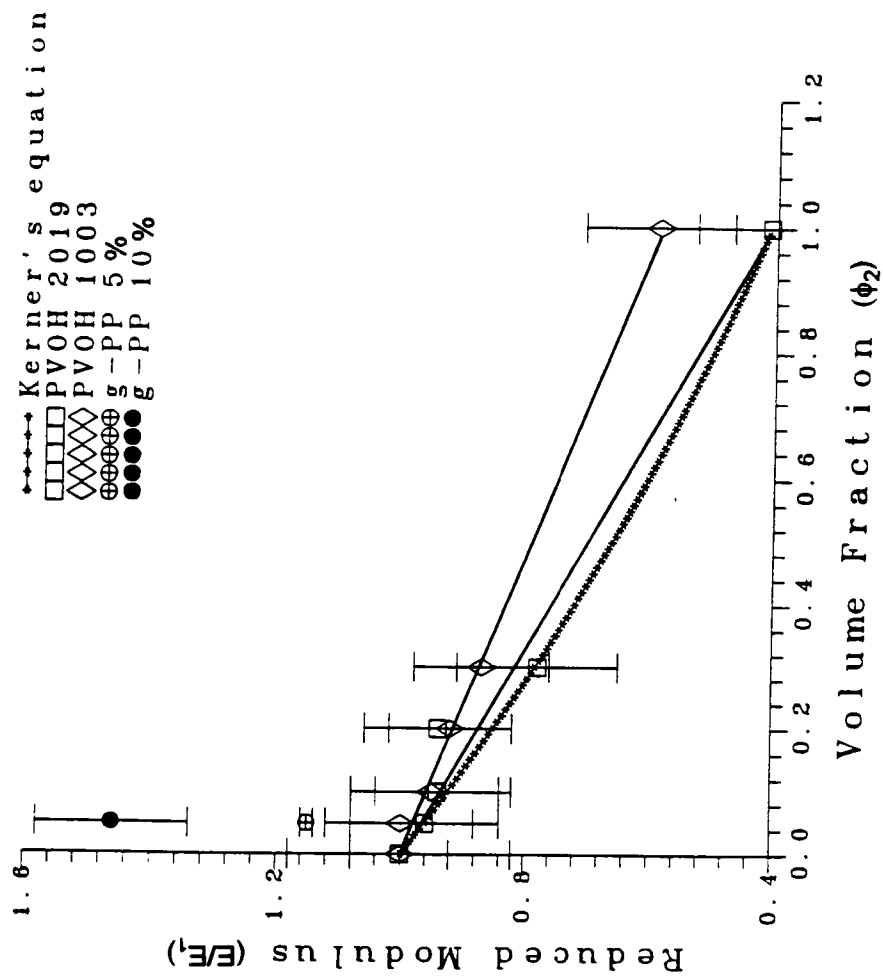


Figure 4-8. Reduced Modulus vs. Volume Fraction of wet samples.

Kerner, except for the pure PVOH resins. Blends of PP with PVOH 1003 exhibit higher values of reduced modulus compared to PP/PVOH 2019 blend systems. Blends with g-PP show higher reduced modulus values than blends that do not contain the compatibilizing agent (g-PP). Blends containing 10%g-PP exhibit higher reduced modulus values than blends with 5%g-PP and PP/PV2 (95/5).

Figure 4-9 shows the reduced modulus for dry and wet samples of the studied PP/PVOH blend systems. In Figure 4-9 lower values of the reduced modulus for wet samples can be observed compared to dry samples. This could be attributed to the effect that moisture has on the mechanical properties of polymer blends in which one of the components can absorb water.

Figures 4-10 and 4-11 show the experimental data and Nielsen's prediction for the tensile strength against the volume fraction of PVOH for dry and wet samples of PP/PVOH 1003, PP/PVOH 2019, and PP/g-PP/PVOH 2019 blend systems. From Figure 4-10 one can see that the experimental results of dry samples exhibit lower values of tensile strength than those obtained by Nielsen's equation for predicting tensile strength for filled systems. The tensile strength of the studied polymer blends decreases as the PVOH content in the blend systems increases. With respect to the compatibilized blends, an improvement in the tensile strength with g-PP content is observed. Figure 4-11 shows that for wet samples, the tensile strength of the studied samples also decreases with composition. The experimental values of tensile strength for the PP/PVOH blended systems are lower than those predicted by Nielsen's theory. In the same plot one can see that blends with PVOH 2019 possess higher tensile strength values than those containing PVOH 1003. An improvement in tensile strength as g-PP content increases is also observed.

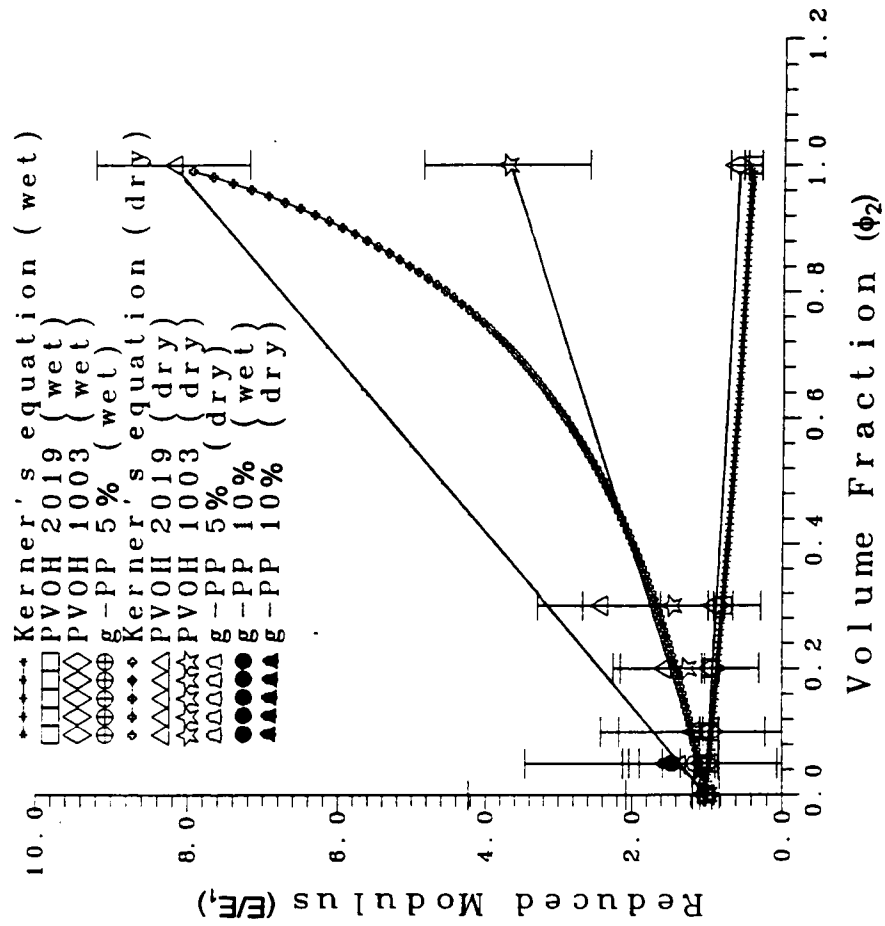


Figure 4-9. Reduced Modulus vs. Volume Fraction of wet and dry samples.

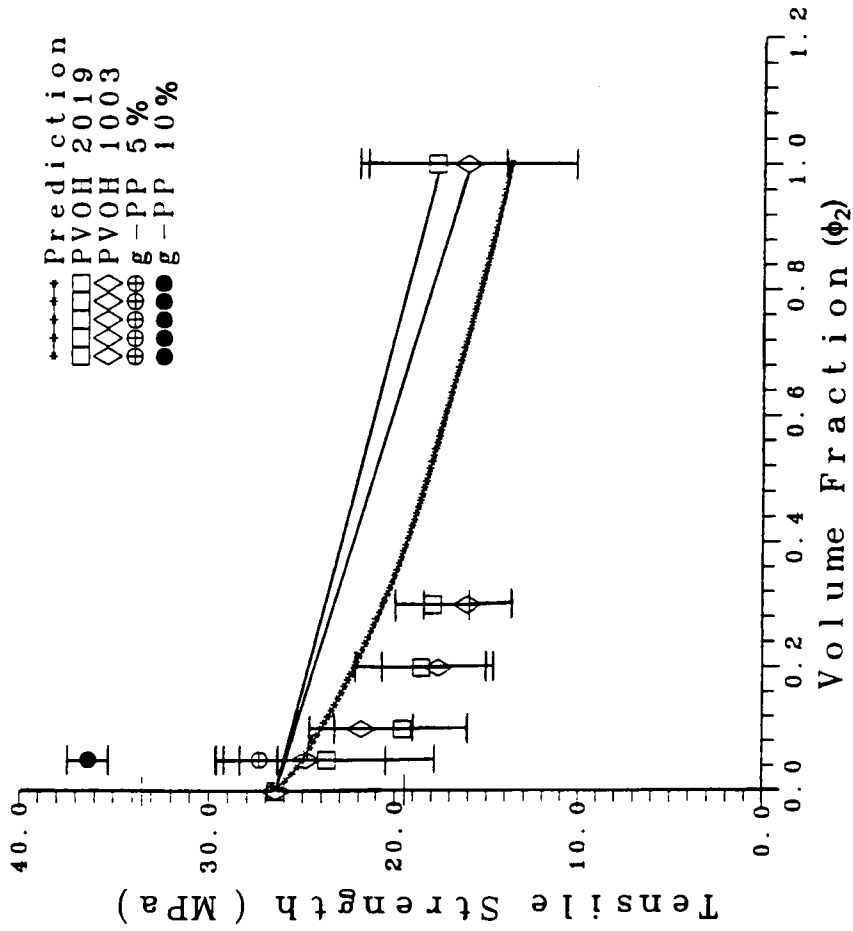


Figure 4-10. Tensile Strength vs. Volume Fraction of dry samples.

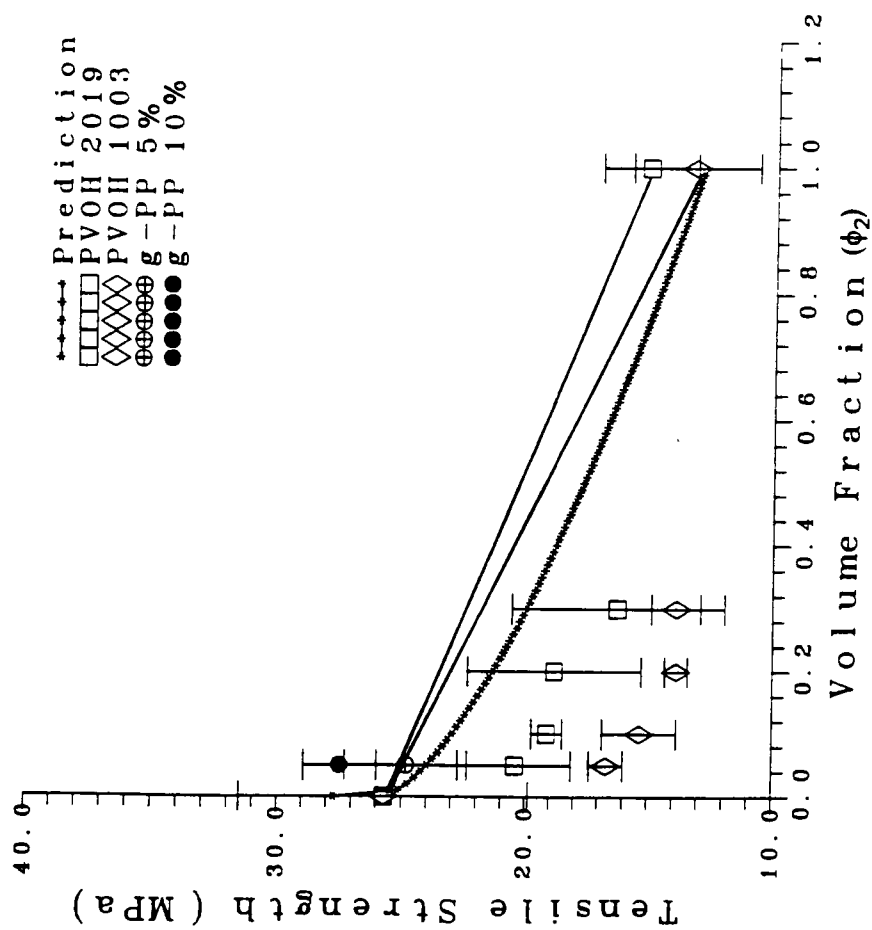


Figure 4-11. Tensile Strength vs. Volume Fraction of Wet Samples.

The elongation to break as a function of composition for dry and wet samples is shown in Figures 4-12 and 4-13. These figures show a very good fit between the experimental data and Nilesen's theory for predicting the elongation to break for filled systems. A decrease in the elongation to break as the PVOH content increases is observed. For both wet and dry samples, the blends with g-PP exhibit an improvement in elongation to break with increasing g-PP content.

4.3. DYNAMIC MECHANICAL ANALYSIS.

Dynamic Mechanical Analysis (DMA) was used in this work in order to study the relaxation processes in the pure resins and blended systems. The loss factor ($\tan \delta$) and storage modulus (E') were determined for all the studied samples, as well as the glass transition temperature of the blends.

Figures 4-14 to 4-16 show the loss factor ($\tan \delta$) vs. temperature spectra for PP/PVOH and PP/g-PP/PVOH blend systems. From Figure 4-14 one can see that the β -transition, which is associated with the glass transition of the amorphous regions of the PP, is between 10 ° to 13 °C. There is a slight temperature shift in the β -relaxation process for blended systems. With respect to the relaxation processes in PVOH 1003, one can see in Figure 4-14 that the β -relaxation is located at ca. 73 °C. The transition peak corresponding to the PVOH 1003 in the blended systems is not so evident, but it seems to be shifted to lower temperatures (50 ° to 60 °C). The α -relaxation process cannot be observed for any of the blend systems. Figure 4-15 shows that the β -relaxation for pure PP is at ca. 15 °C, while the β -transition for the blends is between -8 ° to 12 °C. The β -relaxation for pure PVOH 2019 is at ca. 80 °C, while in the blends of PP with PVOH 2019, the transition peak for the PVOH is not so evident, although it seems to be between 80 ° to 90 °C. Figure 4-16 shows that pure g-PP exhibits two transition peaks. These peaks are believed to be associated with the PP segments

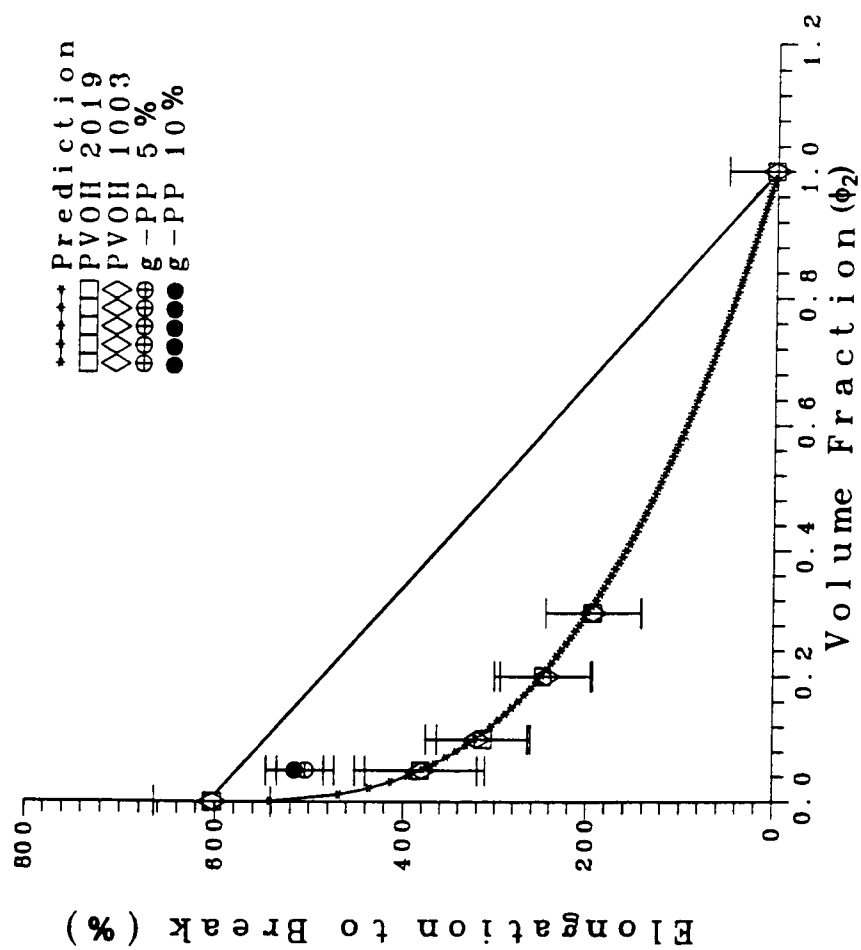


Figure 4-12. Elongation to Break vs. Volume Fraction of Dry Samples.

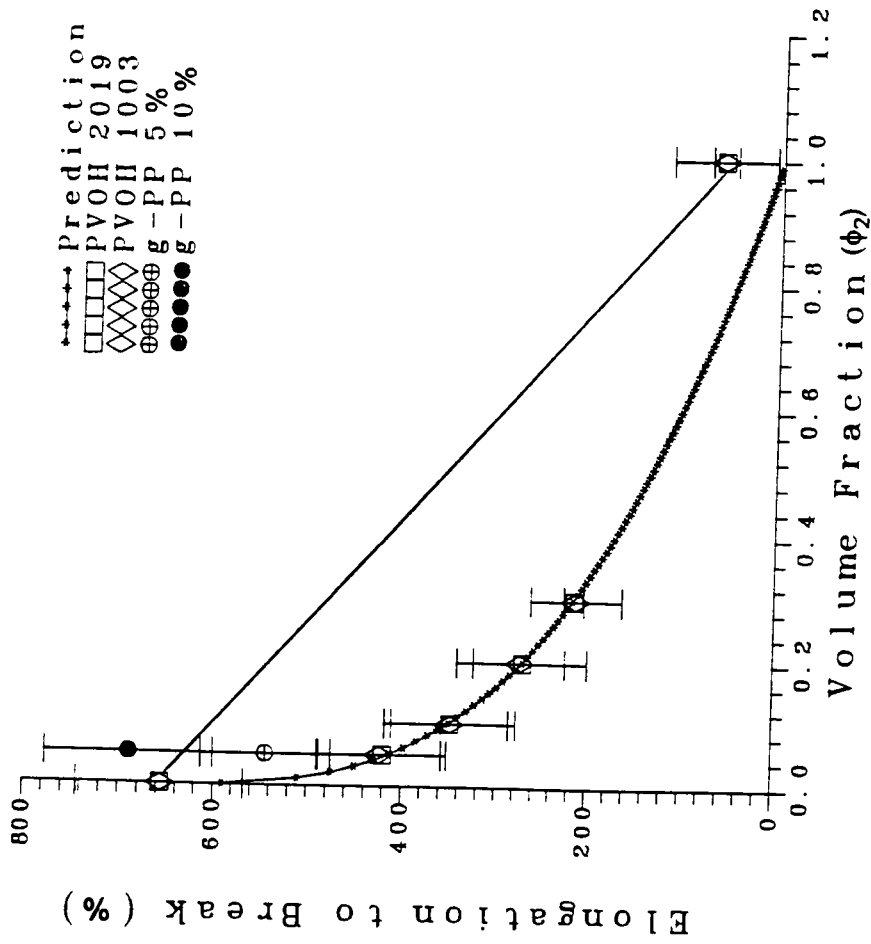


Figure 4-13. Elongation to Break vs. Volume Fraction of Wet Samples.

($\approx 8\text{ }^{\circ}\text{C}$) and the PP-g-MAH segments ($\approx 90\text{ }^{\circ}\text{C}$) conforming presence of the compatibilizing agent. The blends containing g-PP show a very slight temperature shift in the β -relaxation process.

Figures 4-17 to 4-19 give the storage modulus (E') of the blend systems. Figure 4-17 shows a noticeable transition region in the pure PP and blend systems between -10 ° to $50\text{ }^{\circ}\text{C}$. These transition regions are believed to be associated with the β -relaxation for the amorphous regions of PP. A transition region between 65 ° to $105\text{ }^{\circ}\text{C}$ for PVOH 1003 is observed in Figure 4-17, probably associated with the β -relaxation for the amorphous regions of PVOH 1003. At temperatures below the glass transition temperature, the storage modulus increases with increasing concentration of PVOH 1003. The PP/PV1 (90/10) blend exhibits a steep decrease in the modulus-temperature curve between 0 ° to $40\text{ }^{\circ}\text{C}$, followed by an increase at $60\text{ }^{\circ}\text{C}$. Figure 4-18 shows a steep decrease in modulus between 60 ° to $95\text{ }^{\circ}\text{C}$ for PVOH 2019. Pure PP and PP/PVOH 2019 blends exhibit a noticeable transition region between -12 ° to $25\text{ }^{\circ}\text{C}$ as shown in Figure 4-18. The storage modulus for PP/PVOH 2019 blend systems at temperatures below T_g increases with increasing concentration of PVOH, even though at 20% and 30%PVOH, there is not a significant change in the storage modulus of the blends. After T_g , the trend of modulus with increasing PVOH content is at random. Figure 4-19 shows the storage modulus for blends with g-PP. A steep decrease in modulus for pure g-PP can be observed. Figure 4-19 also shows that at temperatures below T_g , the storage modulus increases with increasing g-PP content, and the presence of a transition region between -10 ° to $12\text{ }^{\circ}\text{C}$.

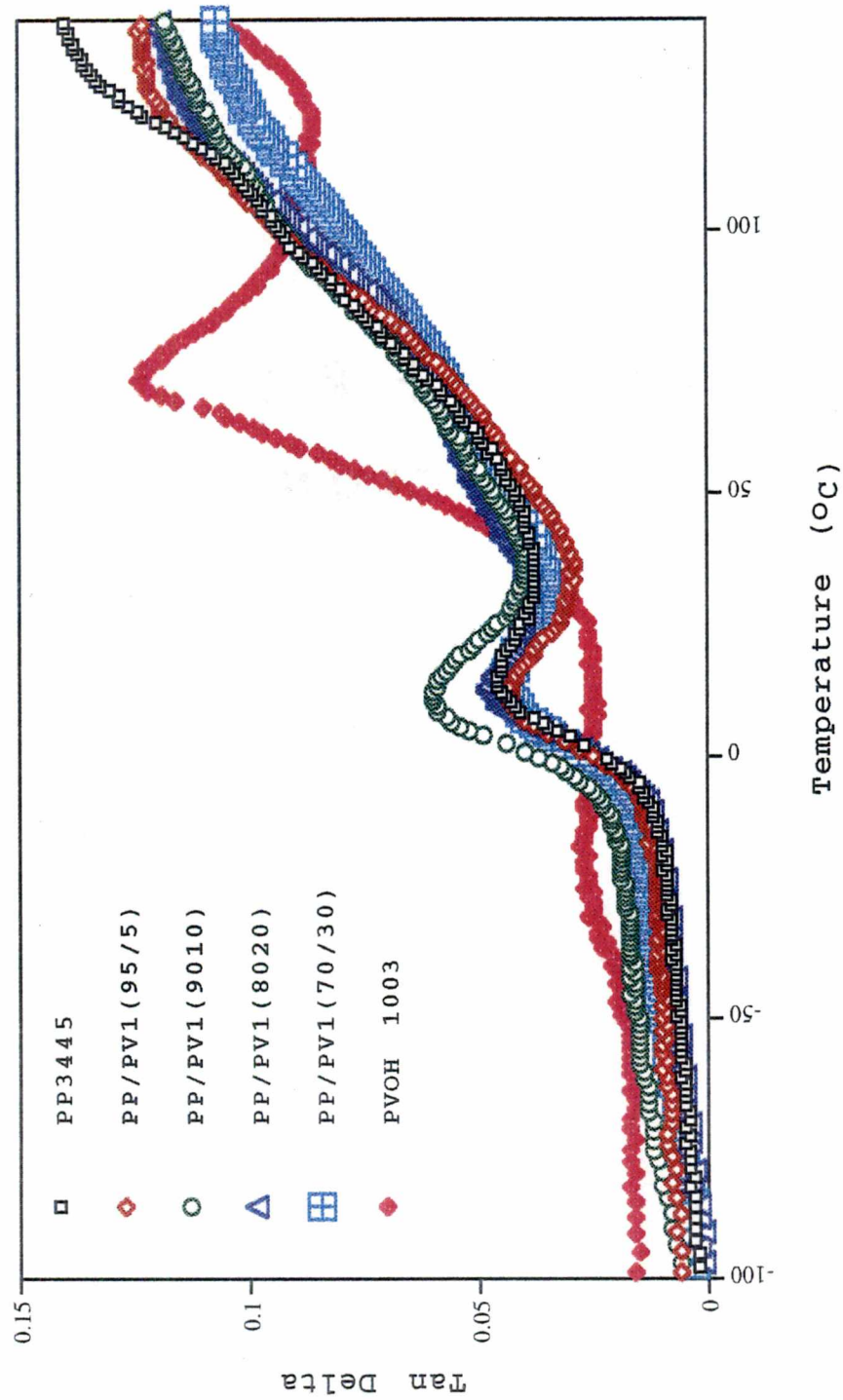


Figure 4-14. Tan Delta of PP/PVOH 1003 Blends.

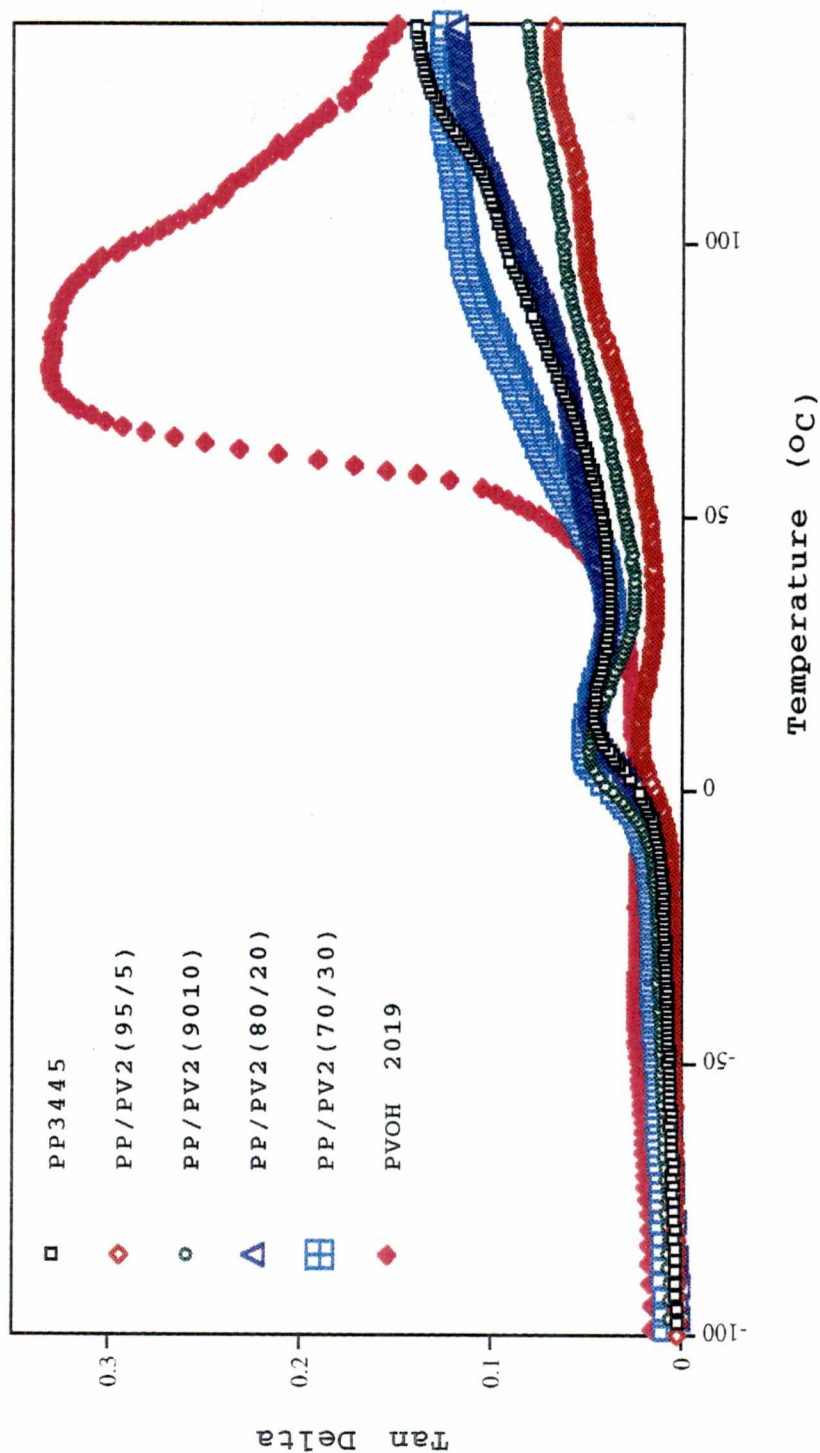


Figure 4-15. Tan Delta of PP/PVOH 2019 Blends.

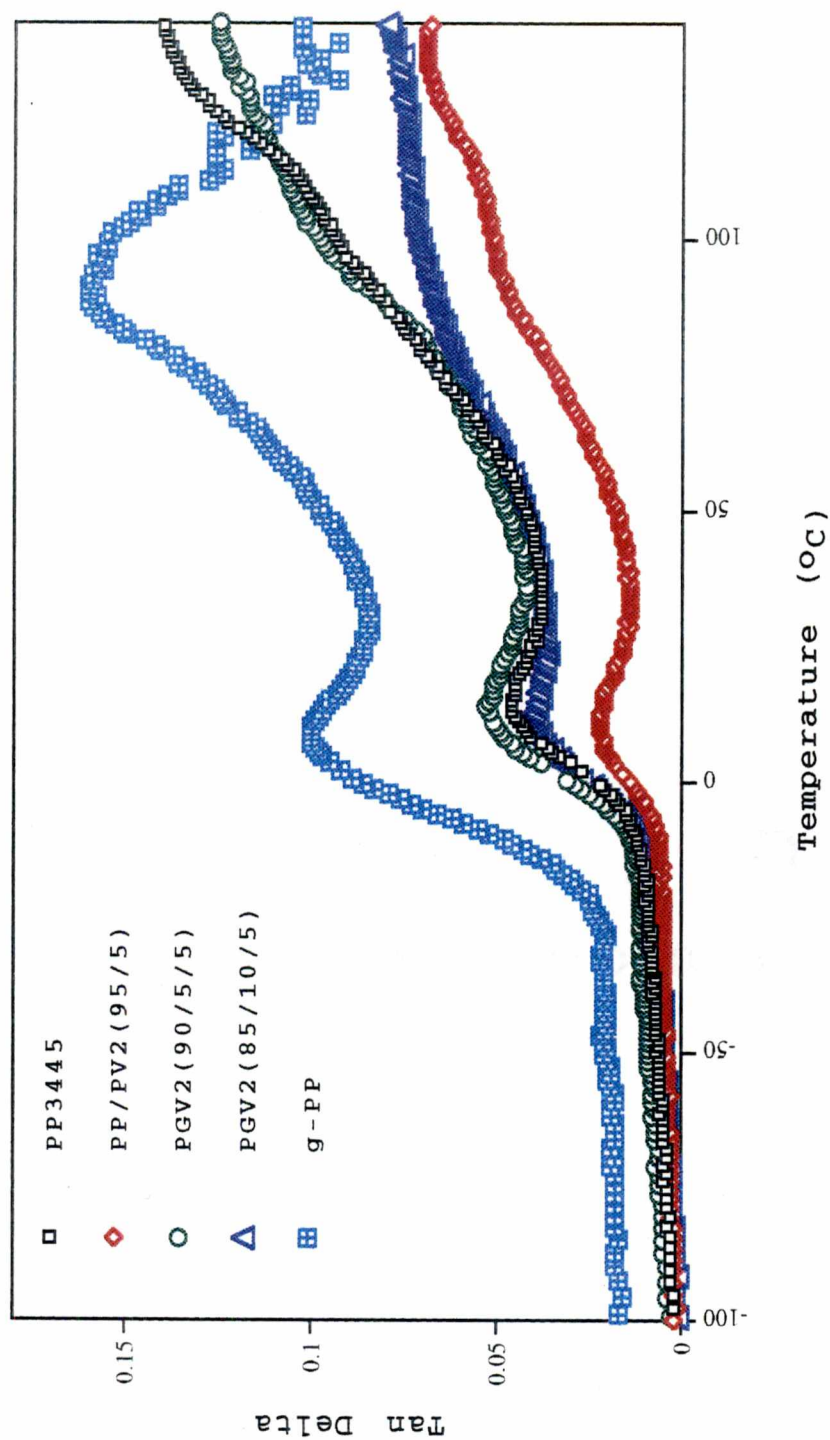


Figure 4-16. Tan Delta of PP/g-PP/PVOH 2019 Blends.

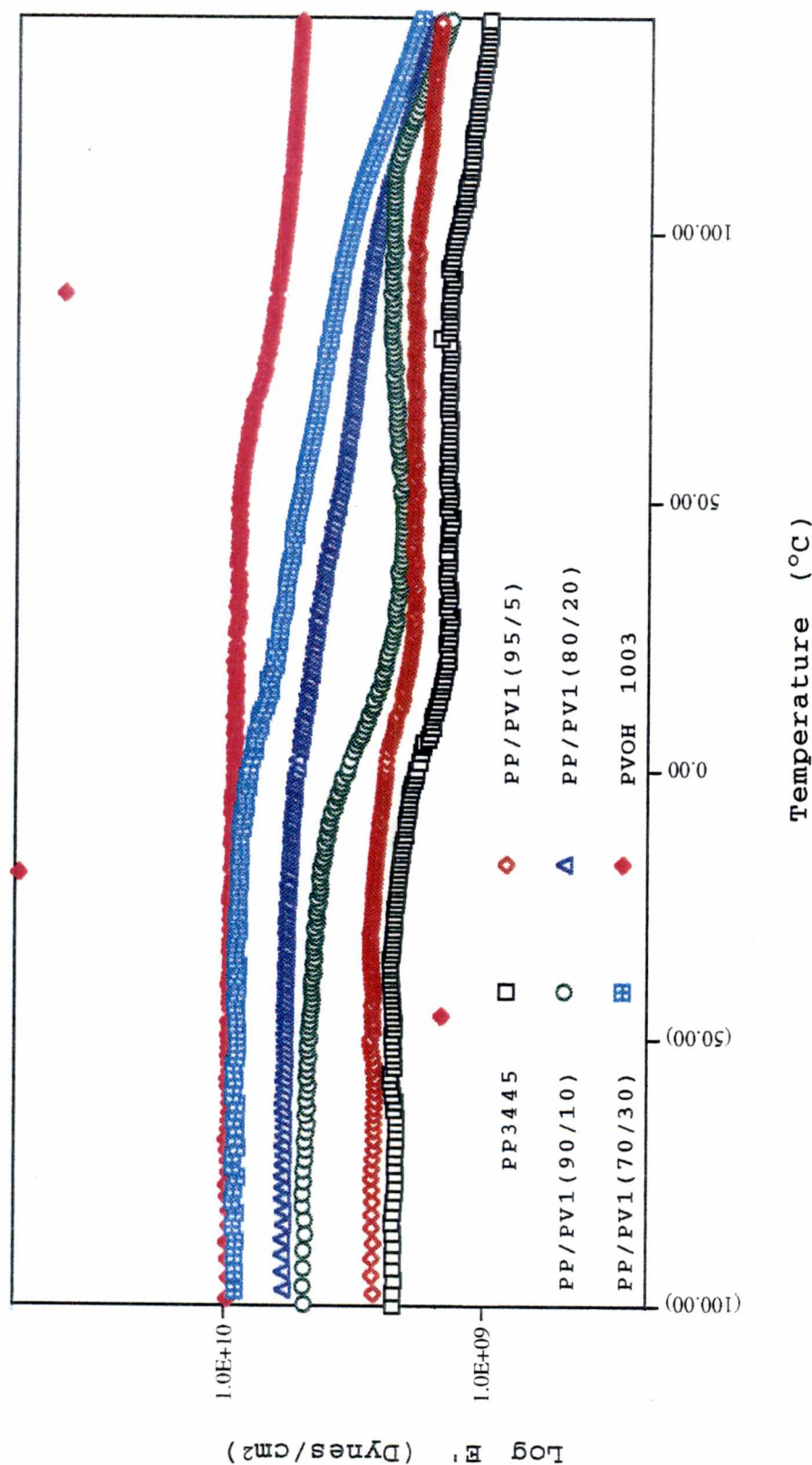


Figure 4-17. Storage Moduli of PP/PVOH 1003 Blends.

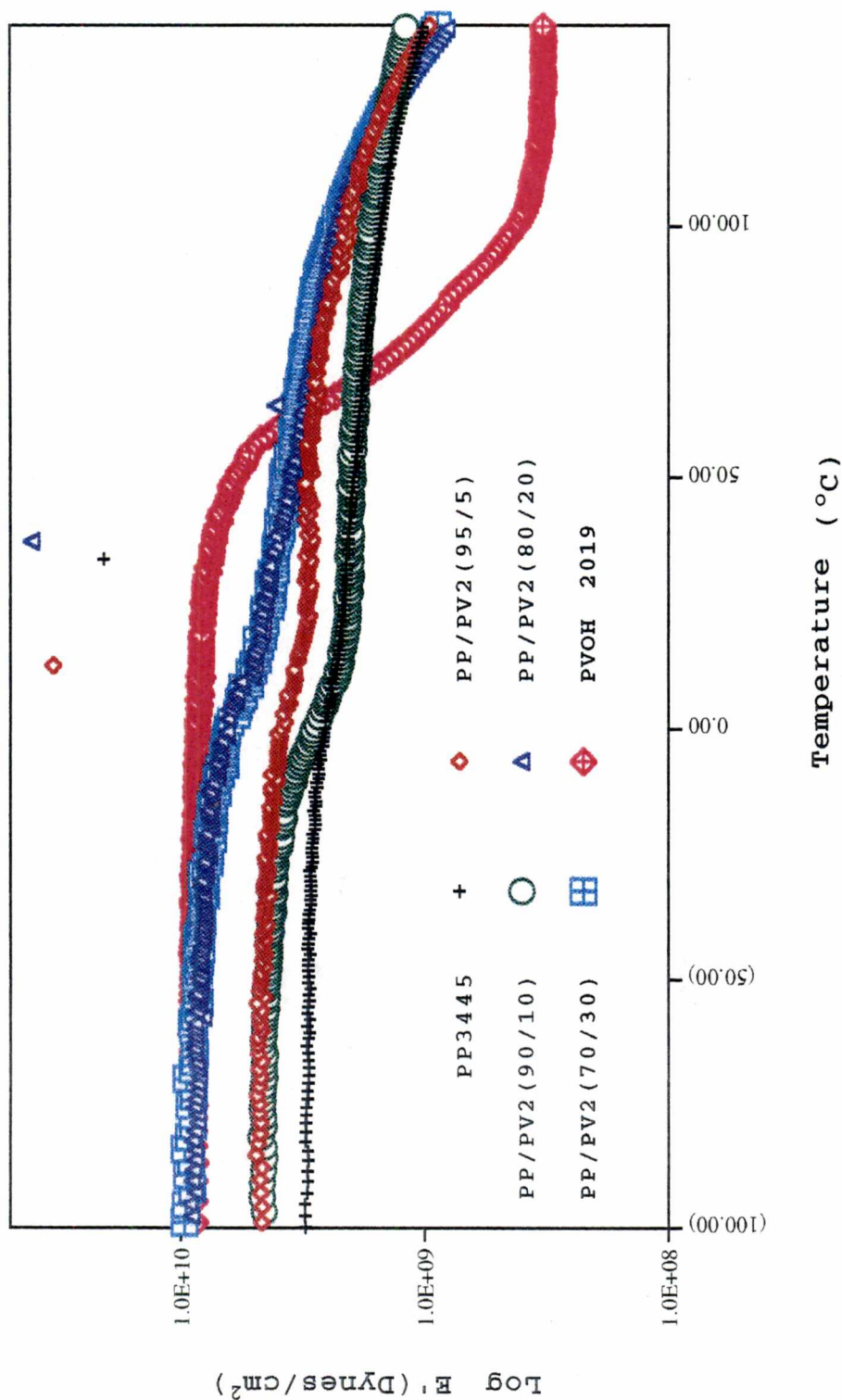


Figure 4-18. Storage Moduli of PP/PVOH 2019 Blends.

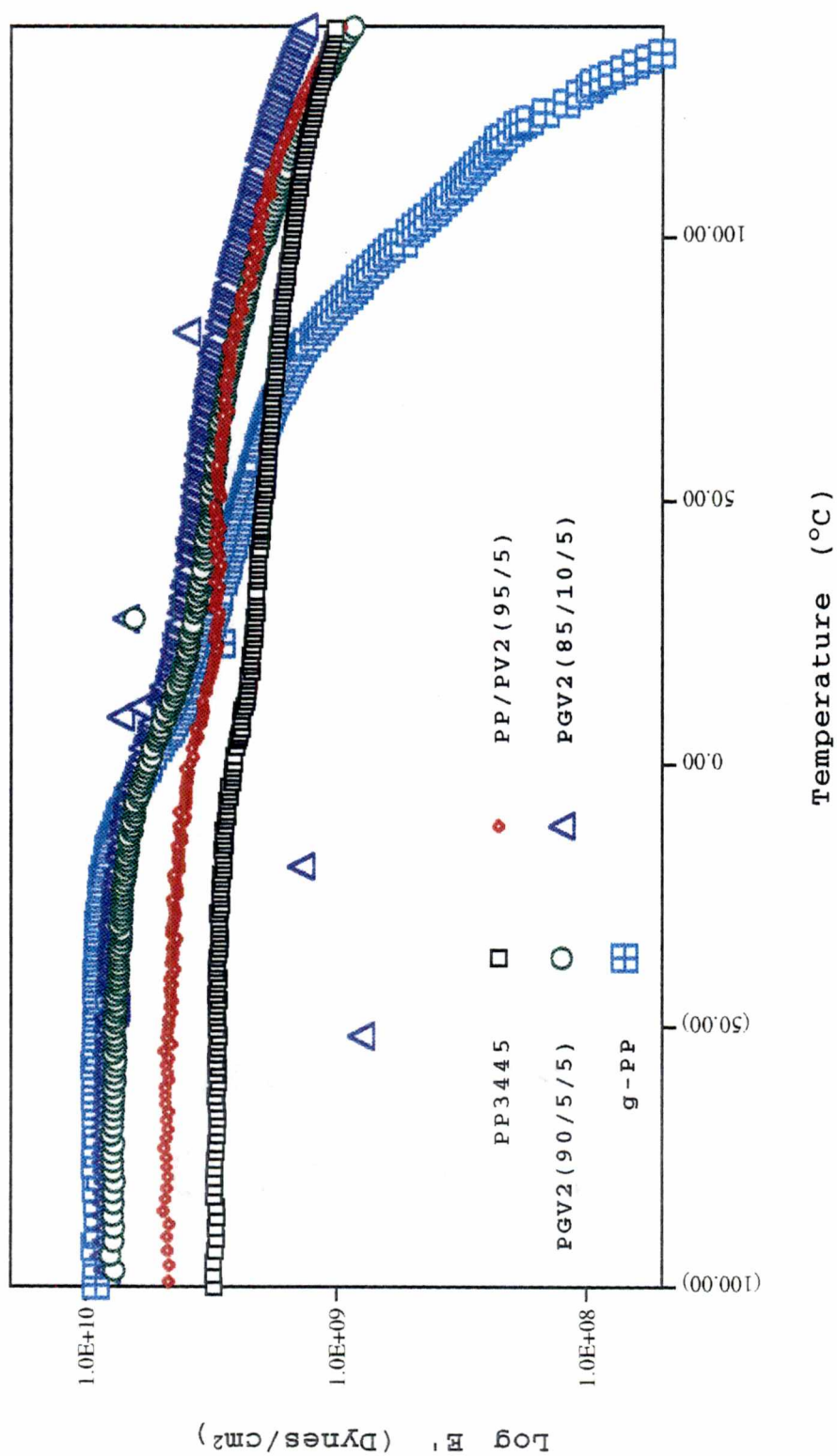


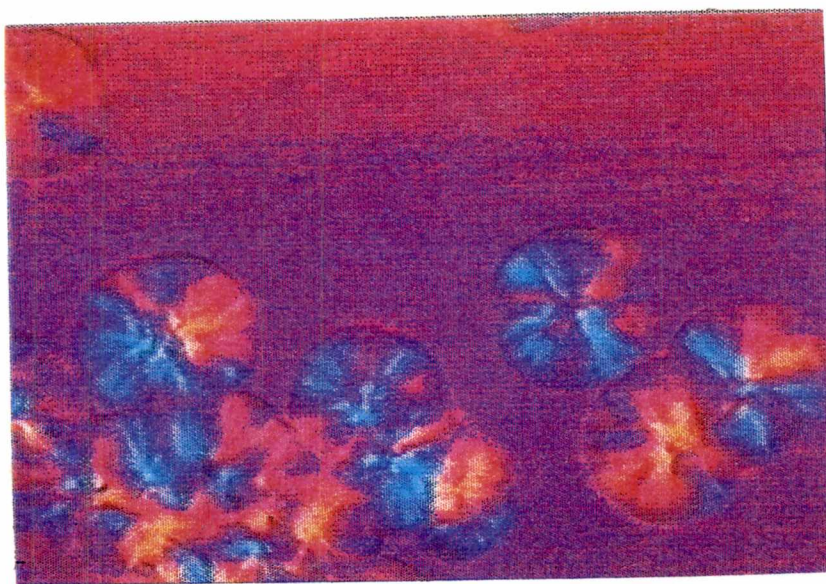
Figure 4-19. Storage Moduli of PP/g-PP/PVOH 2019.

4.4. MORPHOLOGY OF PURE MATERIALS AND BLENDED SYSTEMS.

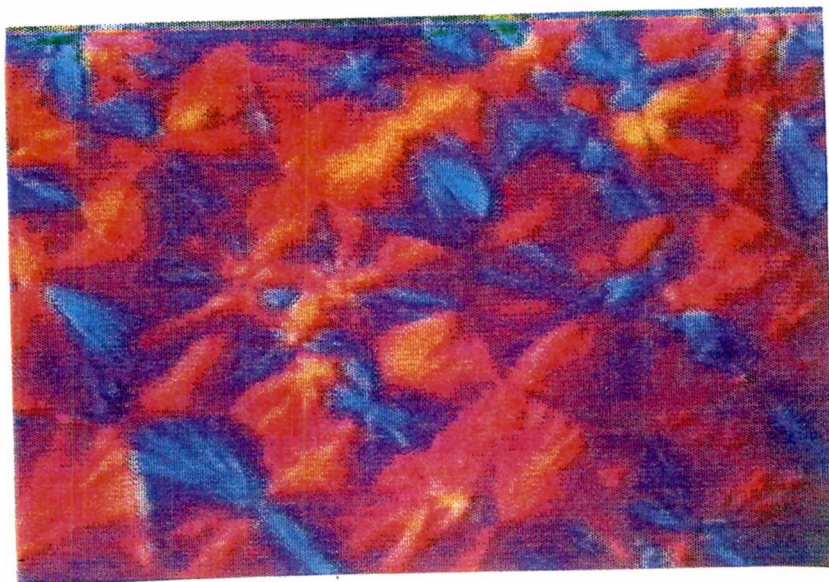
A Polarized Light Microscope was used to study the morphology of PP/PVOH blended systems and compatibilized blends, as well as pure resins. The observations were made using a magnification of 20X.

The morphology of PP3445 was studied upon cooling from 175 °C to room temperature, while both PVOH 1003 and PVOH 2019 were cooled from 230 °C to room temperature. Pure PP shows spherulitic growth under isothermal conditions at 120 °C (Figure 4-20). The diameter of the spherulites of PP3445 are larger than 150 microns. PVOH 1003 was studied under isothermal conditions at 205 °C. Because PVOH is sensitive to humidity, bubbles are observed under the light microscope. Growing of PVOH 1003 crystals is very fast, which makes it difficult to follow the crystallization of the sample. Slow crystallization rates (1 °C/minute) cannot be used because degradation of the resin is likely to occur. Figure 4-21 shows the final morphology of a PVOH 1003 sample. PVOH 1003 crystals are very small, and no spherulitic morphology is observed. The particle size ranges from 8 to 30 microns. In the case of PVOH 2019, the crystallization conditions were the same as those for PVOH 1003. The resulting morphology of PVOH 2019 is shown in Figure 4-22. Small dark particles are dispersed through the sample. These particles are not crystals because no birefringence can be seen under the polarizing microscope.

The blends of PP with PVOH 1003 exhibit relatively the same behavior for all compositions. In order to prevent degradation of the PVOH present in the blends, the samples were heated up to a temperature at which only the PP resin was melted away (180 °C). Afterwards, crystallization of PP under isothermal conditions at temperatures between 115 ° and 120 °C was carried out. Domains of PVOH dispersed through the sample are observed at (Figures 4-23 (a) and 4-24 (a) which correspond to time=0 minutes). The PVOH domains increase in size with composition. Blends with



(a)



(b)

Figure 4-20. Sequence of Crystallization of a PP3445 sample:

(a) Intermediate Morphology (time: 12:57 minutes)

(b) Final Morphology.

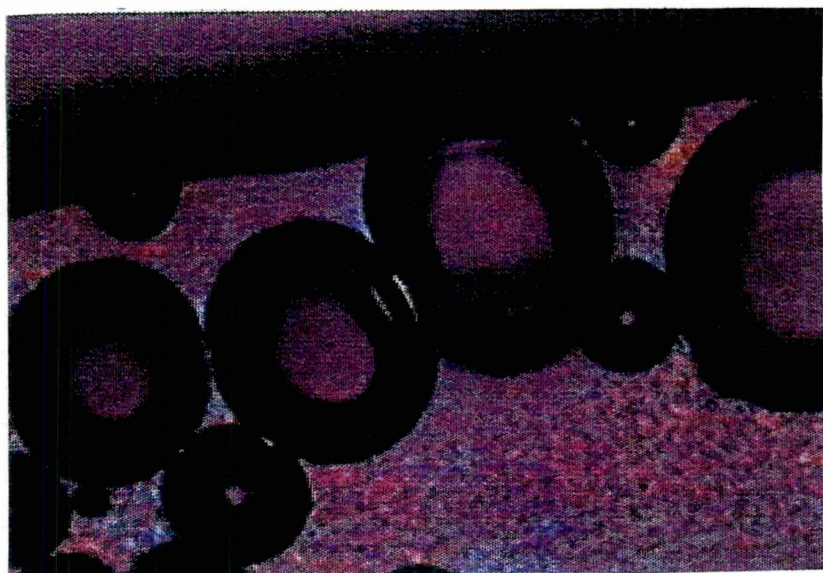


Figure 4-21. Final Morphology of a PVOH 1003 sample.

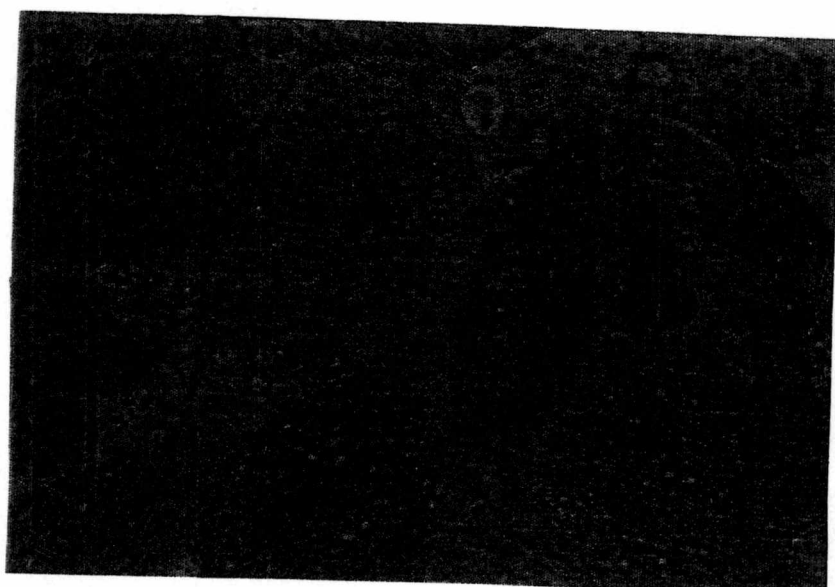
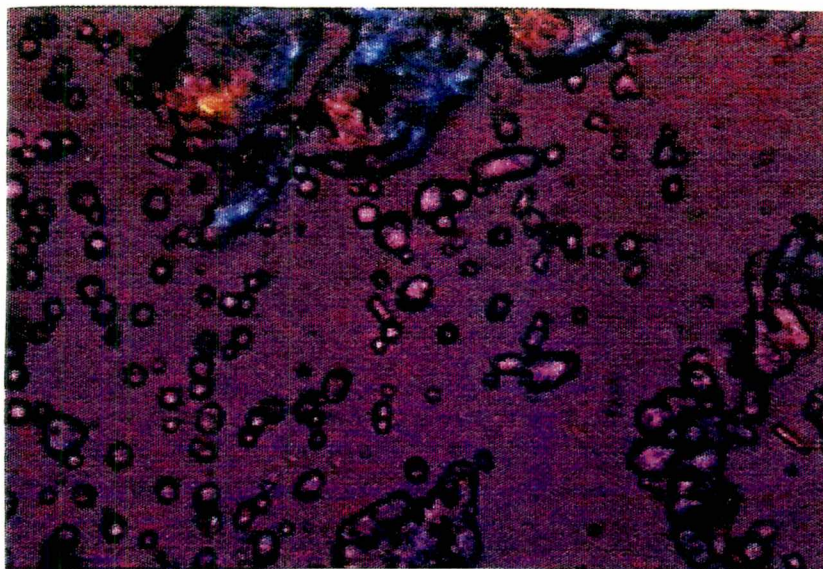
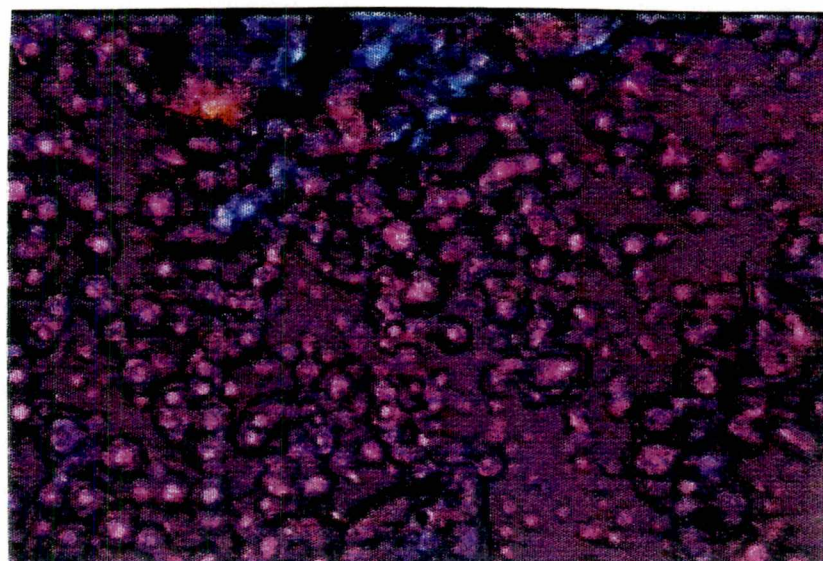


Figure 4-22 . Final Morphology of a PVOH 2019 sample.



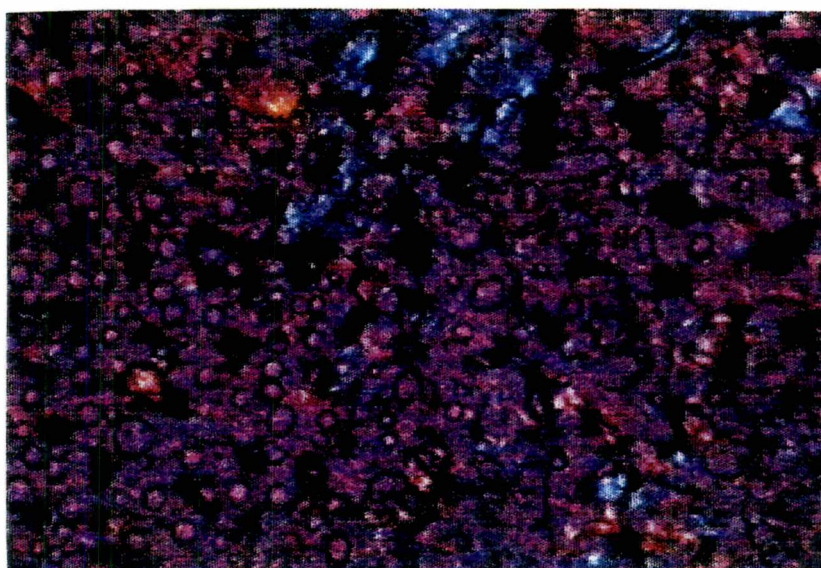
(a)



(b)

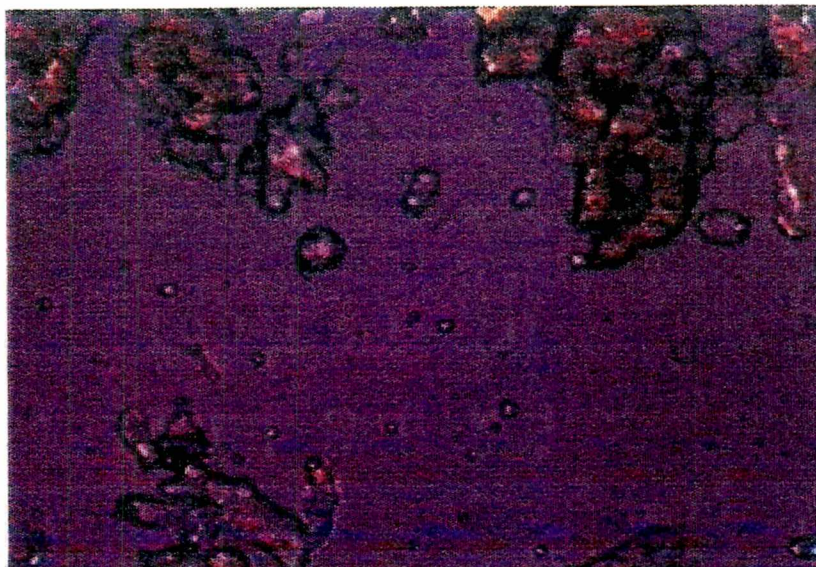
Figure 4-23. Sequence of Crystallization of a PP/PV1 (90/10) sample:

(a) Initial Morphology (molten PP), (b) Intermediate Morphology
(time: 8:20 minutes), (c) Final Morphology.

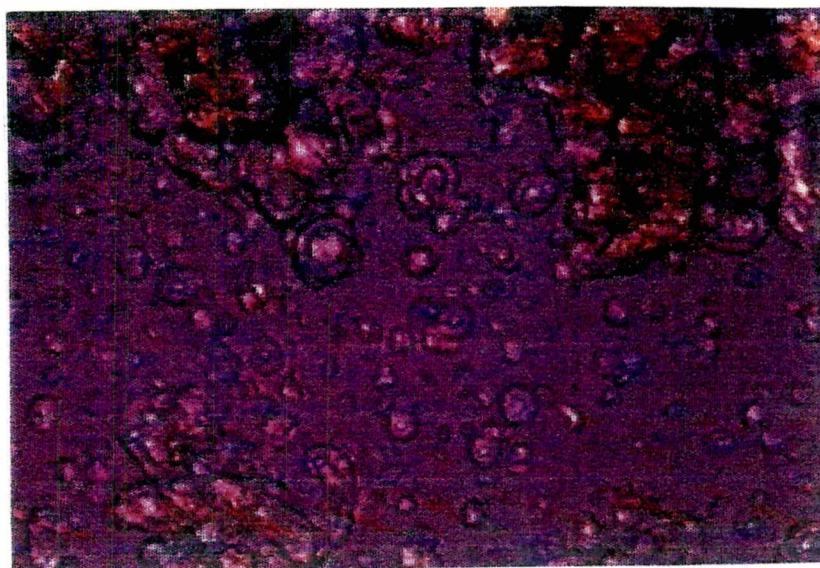


(c)

Figure 4-23. Cont'd.



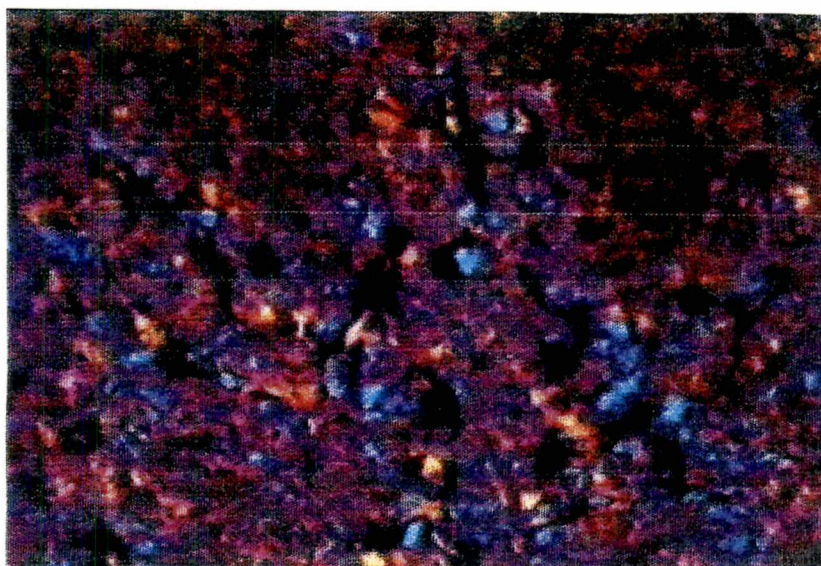
(a)



(b)

Figure 4-24. Sequence of Crystallization of a PP/PV1 (70/30) sample:

(a) Initial Morphology (molten PP), (b) Intermediate Morphology
(time: 11:11 minutes), (c) Final Morphology.

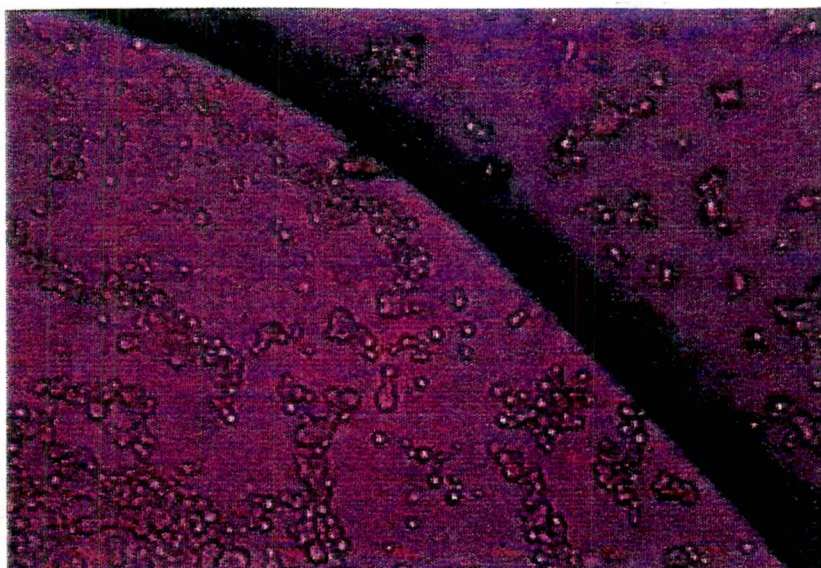


(c)

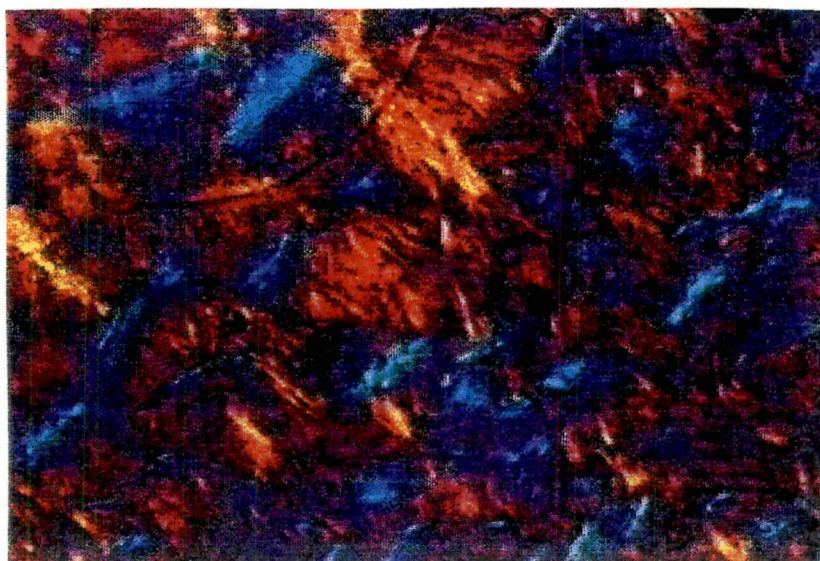
Figure 4-24. Cont'd.

10%PVOH and above, show PVOH domains of irregular shape (Figures 4-23 (a) and 4-24 (a)). On the other hand, PP crystals in PP/PVOH 1003 blend systems do not exhibit a maltese cross pattern at any composition, even though PP crystals grow radiating from the center, are circular in shape and their size varies from 60 to 100 microns. Growing of PP crystals in blends with a PVOH 1003 content of 10% and above is initiated around the PVOH domains. Figures 4-23 and 4-24 show a sequence of the crystallization of PP/PV1 (90/10) and PP/PV1 (70/30) blend systems. The PVOH 1003 domains in molten PP are shown in Figures 4-23 (a) and 4-24 (a). Part (b) of Figures 4-23 and 4-24 shows the growing of PP crystals, which is denoted as "intermediate morphology", because the crystallization of the samples is not completed, and part (c) of Figures 4-23 and 4-24 show the final morphology of the blends. In part (c) of both figures, dark areas can be observed through the samples.

Blends of PP with PVOH 2019 were heated up to 170 °C in order to melt PP crystals away. Samples of PP/PVOH 2019 blends were not heated up to 180 °C, because degradation of the PVOH was easily promoted. The temperature was held at 170 °C for a few minutes. Black particles, circular in shape are observed when PP is melted away (Figures 4-25 and 4-26, part (a)). The black particles tend to agglomerate at small compositions (5% and 10%PVOH). This might be due to the fact that they have a big surface tension and tend to form agglomerates in order to reduce it. At PVOH concentrations of 20% and above (Figure 4-26 (a)), the size of the black domains increases. These domains are elliptical to circular in shape. The sizes of the circular domains range from 60 to 100 microns. The major axis of the elliptical domains varies from 100 to 300 microns, while the minor axis ranges from 90 to 200 microns. The domains seem to be associated with the amorphous phase of PVOH 2019 because no birefringence can be observed under the polarizing microscope. PP/PVOH 2019 blend systems were studied under isothermal conditions at temperatures between



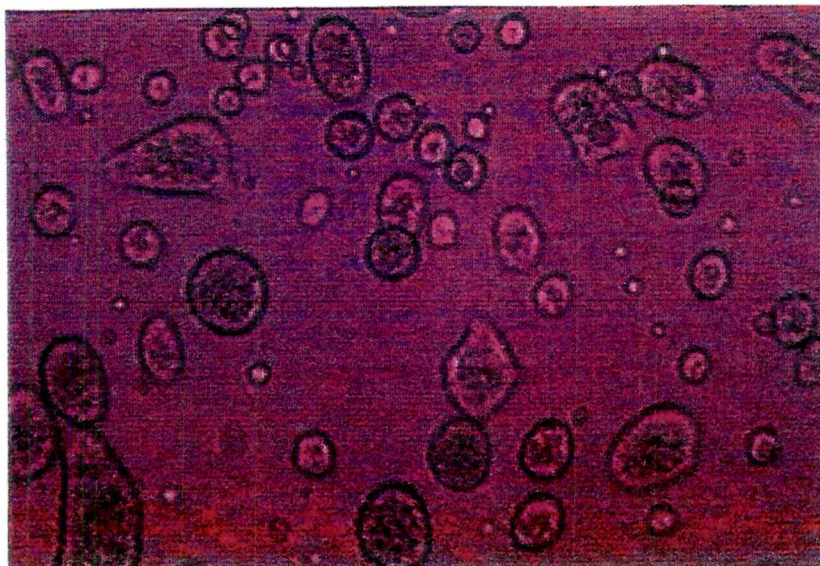
(a)



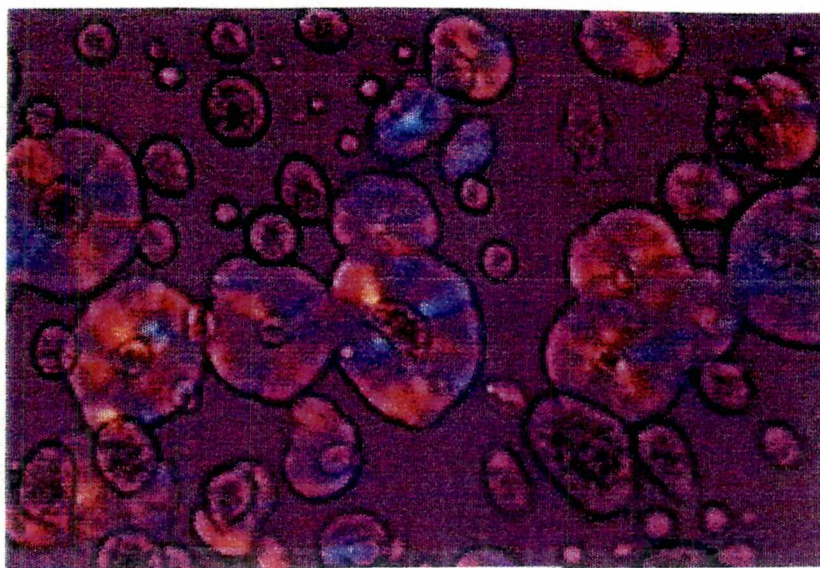
(b)

Figure 4-25. Sequence of Crystallization of a PP/PV2 (95/5) sample

(a) Initial Morphology, (b) Final Morphology.



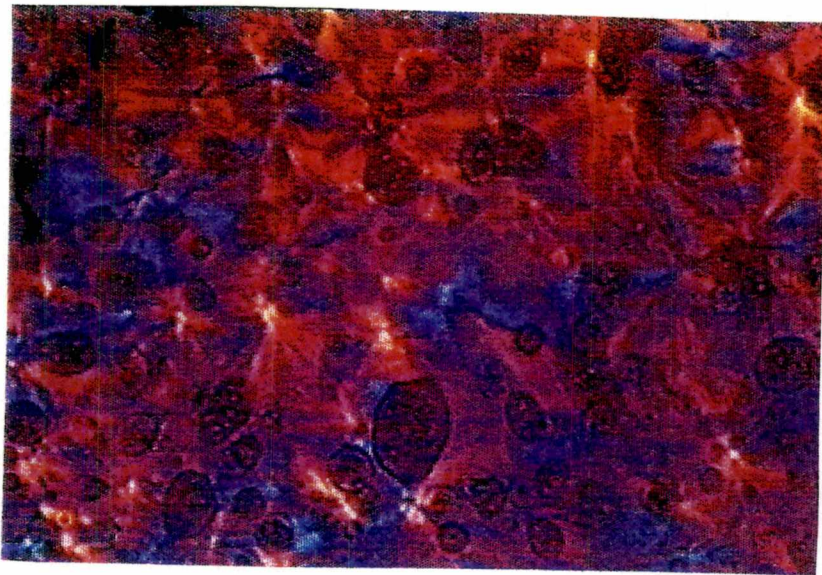
(a)



(b)

Figure 4-26. Sequence of Crystallization of a PP/PV2 (80/20) sample:

(a) Initial Morphology, (b) Intermediate Morphology (time: 6:29 minutes), (c) Final Morphology.



(c)

Figure 4-26. Cont'd.

118 ° and 124 °C. In all blend compositions, the PVOH domains apparently act as nucleating agents of PP (Figures 4-25 and 4-26, part (b)). This behavior is more evident at higher compositions (20% and 30%PVOH 2019). The final morphologies of PP/PV2 (95/5) and PP/PV2 (80/20) blend systems are shown in parts (b) and (c) of figures 4-25 and 4-26, respectively. PP exhibits a spherulitic morphology in blends of PP with PVOH 2019 at all compositions, the spherulites are greater than 100 microns, and the PVOH domains are not excluded by the PP spherulites.

The morphology of pure g-PP is shown in Figure 4-27. Crystals of g-PP look like grains and are circular in shape. The size of g-PP crystals varies from 5 to 8 microns. Blends of PP, 5%PVOH 2019, and g-PP were heated up to 170 °C in order to melt the PP and g-PP crystals away. Very small, dark grains remained dispersed through the sample. These grains were assumed to be PVOH 2019 particles. Figure 4-28 (a) shows the presence of PVOH 2019 grains dispersed in the sample. The importance of this observation is that PVOH domains in PP/PV2 (95/5) samples were larger than those observed in the g-PP blends. Additionally, the dispersion of those domains in the g-PP blend systems is much better. Crystallization of PP and g-PP crystals was carried out at isothermal conditions (120 °C). The g-PP crystals are not distinguishable, while PP exhibits a spherulitic growth. Figure 4-28 shows the morphology of PGV2(85/10/5). No phase separation is observed. Samples of PGV2(90/5/5) exhibited the same behavior as PGV2 (85/10/5).

4.5. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR).

In this study, FTIR was used to determine spectral differences between the two PVOH resins as well as the spectral change between the pure resins and their blends. The characteristic absorption bands of a generic PVOH resin and isotactic PP are listed in Tables 12 and 13.

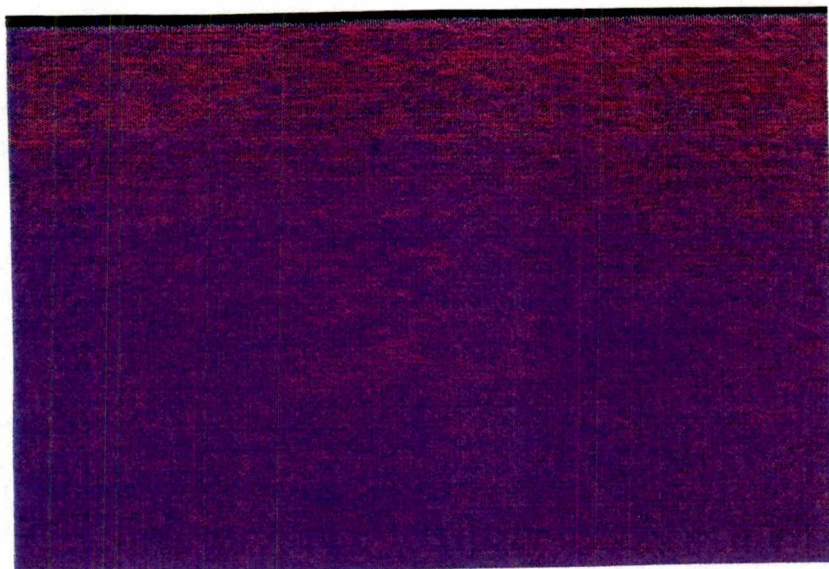
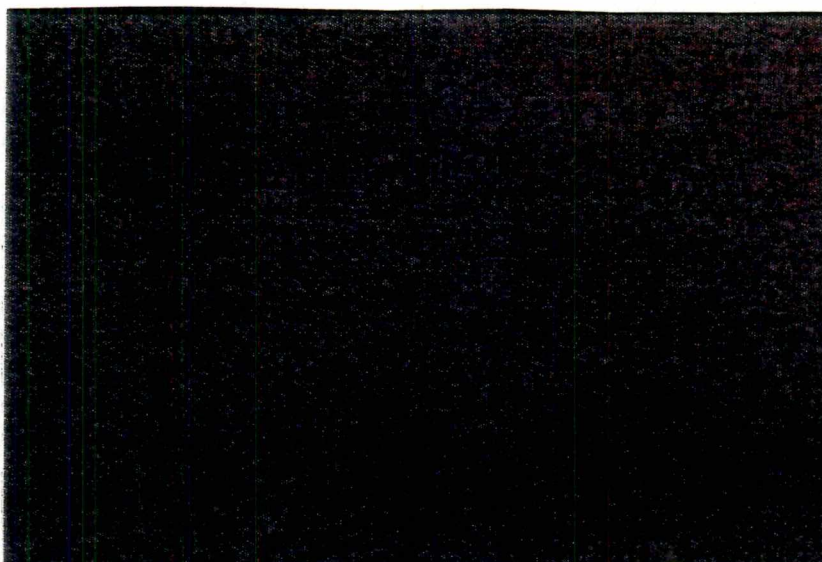
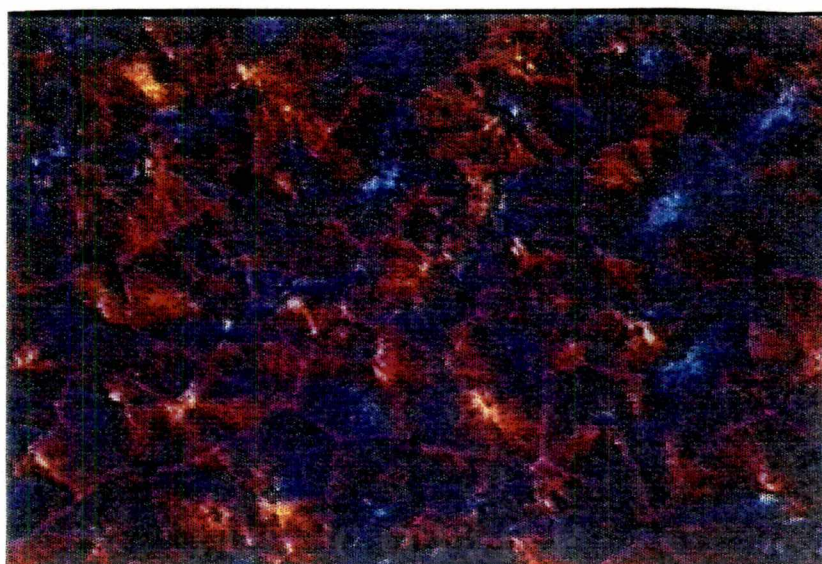


Figure 4-27. Final Morphology of a g-PP sample.



(a)



(b)

Figure 4-28. Morphology of a PGV2 (85/10/5) sample: (a) Initial Morphology (molten PP and g-PP), (b) Final Morphology.

Table 12. Main Characteristics of the FTIR Spectrum of PVOH (with probable assignments) (4).

Wavenumber (cm ⁻¹)	Relative Intensity	Assignment
3340	Very strong	O-H stretching
2942	Strong	C-H stretching
2910	Strong	C-H stretching
2840	Shoulder	C-H stretching
1850-1650	Strong	C=O stretching
1446	Strong	O-H and C-H bending
1430	Strong	CH ₂ bending
1376	Weak	CH ₂ wagging
1326	Medium	C-H and O-H bending
1320	Weak	C-H bending
1235	Weak	C-H wagging

Table 12. Cont'd.

Wavenumber (cm ⁻¹)	Intensity	Assignment
1215	Very Weak	-
1144	Medium	C-C and C-O stretching
1097	Strong	C-O stretch and O-H bending
1087	Shoulder	-
1040	Shoulder	-
916	Medium	Skeletal
890	Very weak	-
850	Medium	Skeletal
825	Shoulder	CH ₂ rocking
640	Medium, very broad	O-H twisting
610	Weak	-
480	Weak	-
410	Weak	-
360	Shoulder	-
185	Very weak	-
135	Very weak	-

Table 13. Infrared Band Assignment for Isotactic Polypropylene (7).

Wavenumber (cm ⁻¹)	Assignment
1365	CH ₂ wagging, C-H bending
1360	C-H bending, CH ₂ twisting
1326	C-H bending
1304	CH ₂ wagging, CH ₂ twisting
1254	CH ₂ twisting, C-H bending
1168	CH ₃ rocking
998	CH ₃ rocking, C-H bending
973	CH ₃ rocking
899	CH ₃ rocking, CH ₂ rocking
842	CH ₂ rocking
809	CH ₂ rocking

Figure 4-29 shows the spectra of pure PVOH 1003 (bottom) and pure PVOH 2019 (top). The main difference between the two PVOH resins used in this study is found in the intensity of the peak at 1740 cm⁻¹. This peak is an indication of stretching vibrations of carbonyl groups which in turn indicates the presence of poly(vinyl acetate). The spectrum of PVOH 2019 resin exhibits a stronger peak at 1740 cm⁻¹ than that of PVOH 1003. Therefore, The 1740 cm⁻¹ peak was chosen as a proof of the presence of carbonyl groups. The presence of carbonyl groups in the blends might favor molecular interactions between chains in the blended systems (i.e. hydrogen bonding).

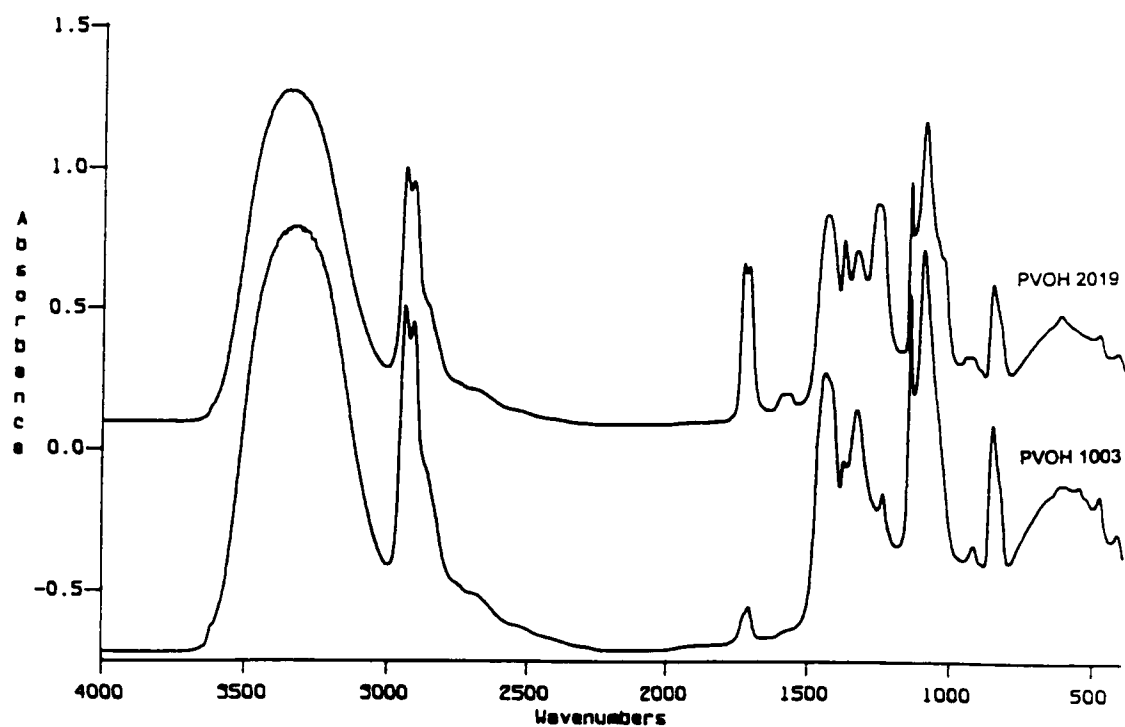


Figure 4-29. FTIR Spectra of PVOH 1003 and PVOH 2019.

Figure 4-30 shows the spectra of pure PP (bottom) pure PVOH 1003 (top), and the blends with different concentrations of PVOH (in between). The strongest and most typical peak of PVOH resins is located at 3340 cm^{-1} which corresponds to the O-H groups vibrations (Table 13). In the spectrum of PP there is no such peak. Therefore, the peak at 3340 cm^{-1} was chosen as an indication of the presence of PVOH in the blend systems. From Figure 4-30 one can see that the intensity of this peak increases as PVOH content increases.

Similar observations can be made for PP/PVOH 2019 systems. Figure 4-31 shows the spectra of pure PP (bottom), pure PVOH 2019 (top), and the blends with different amounts of PVOH (in between). The absorption band corresponding to the carbonyl groups vibrations is more noticeable as PVOH increases. At 5%PVOH the carbonyl absorption band is not distinguishable. No displacement of the 1740 cm^{-1} peak is observed. The intensity of the peak located at 3340 cm^{-1} increases with increasing PVOH content.

Figure 4-32 (a) shows the FTIR spectra of pure g-PP (top), PP/PV2 (95/5) (bottom), and blends with 5% and 10%g-PP (in between). The most significant difference between the spectra lies on the intensity of the peak at 1740 cm^{-1} . Figure 4-32 (b) clearly shows that the intensity of the 1740 cm^{-1} peak increases as the g-PP content in the blends increases. This Figure also shows that pure g-PP exhibits a double peak at 1850 cm^{-1} and 1794 cm^{-1} which probably are characteristic of anhydrides.

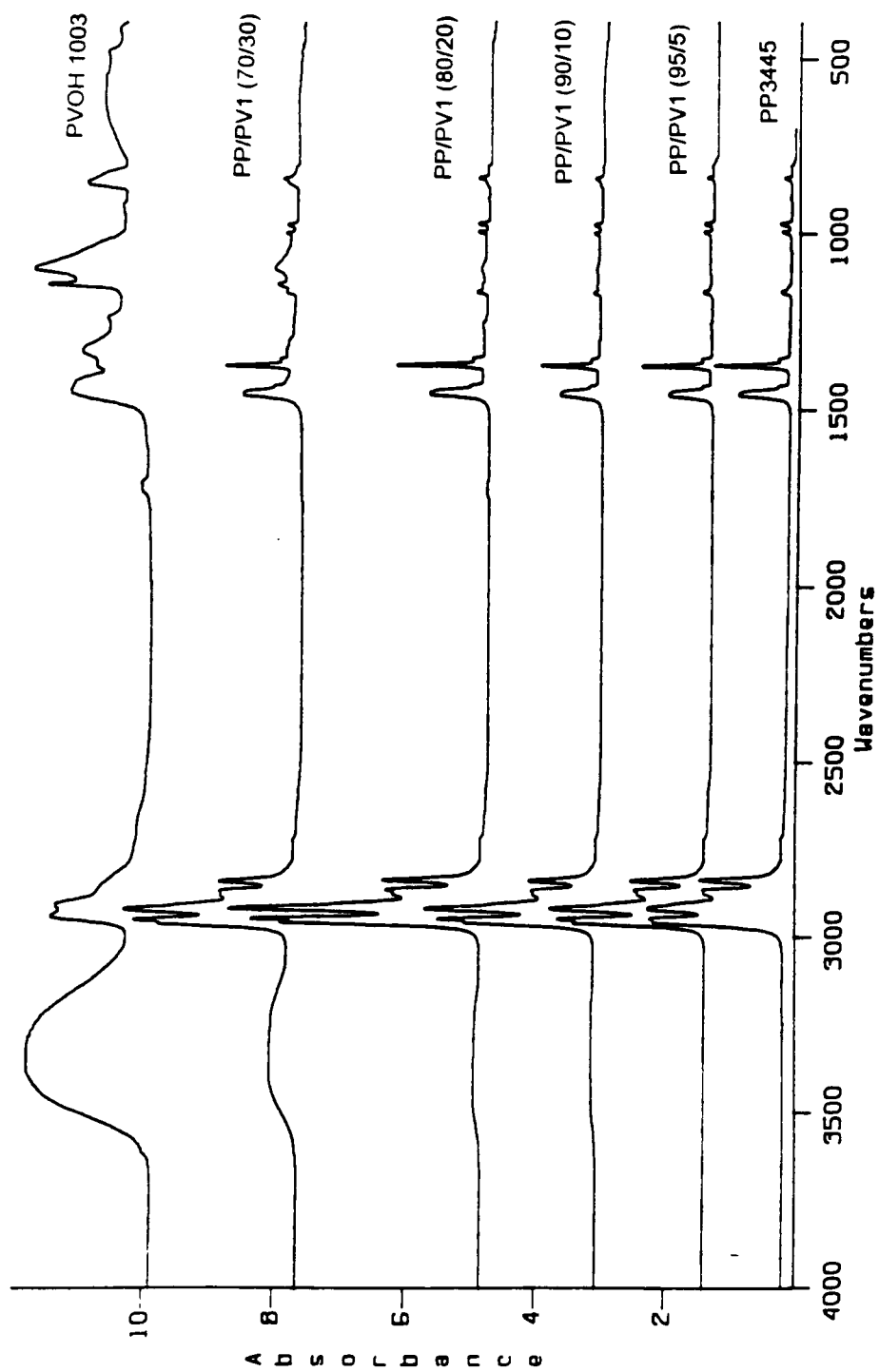


Figure 4-30 . FTIR Spectra of PP/PVOH 1003 Blends.

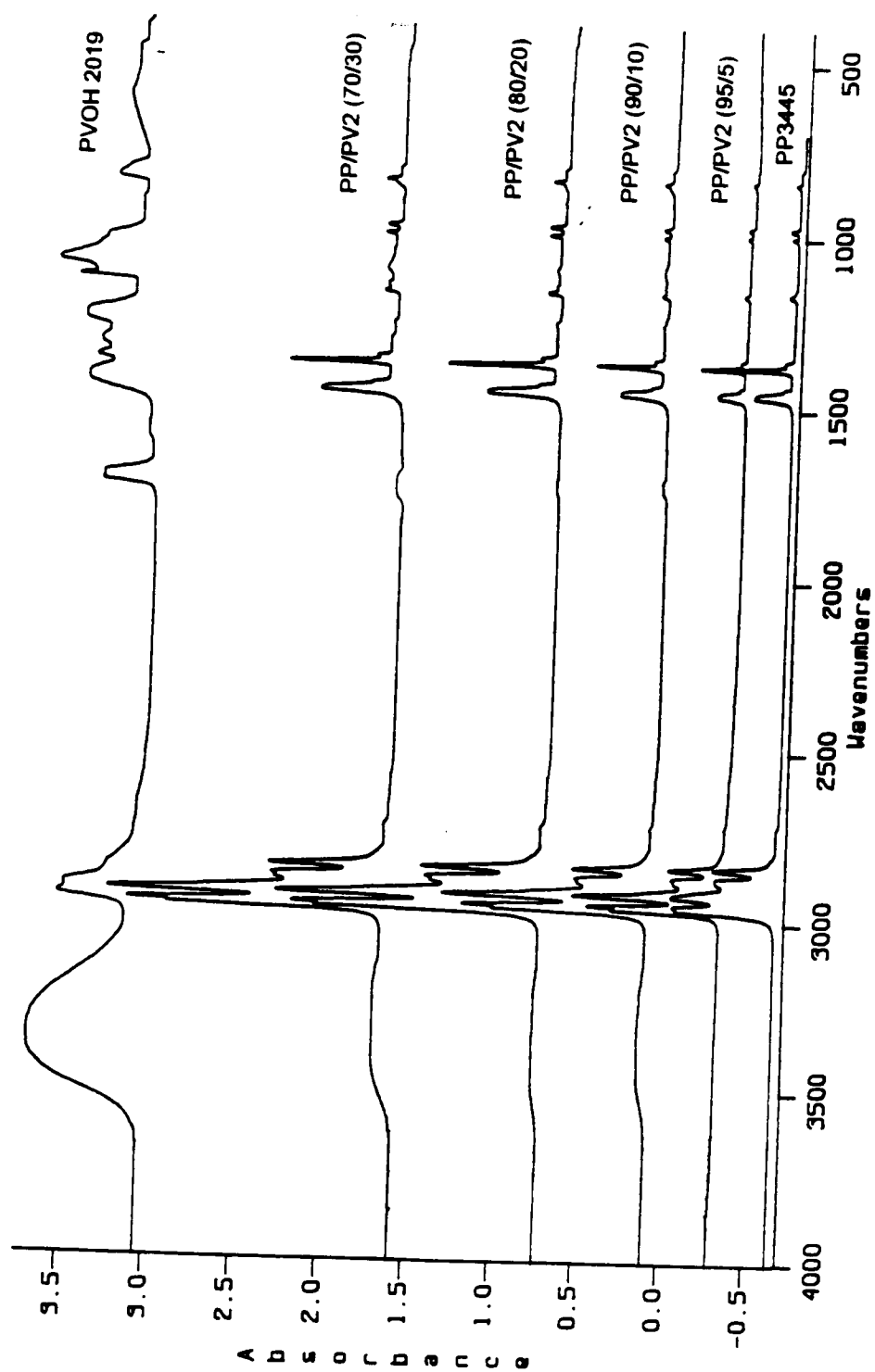
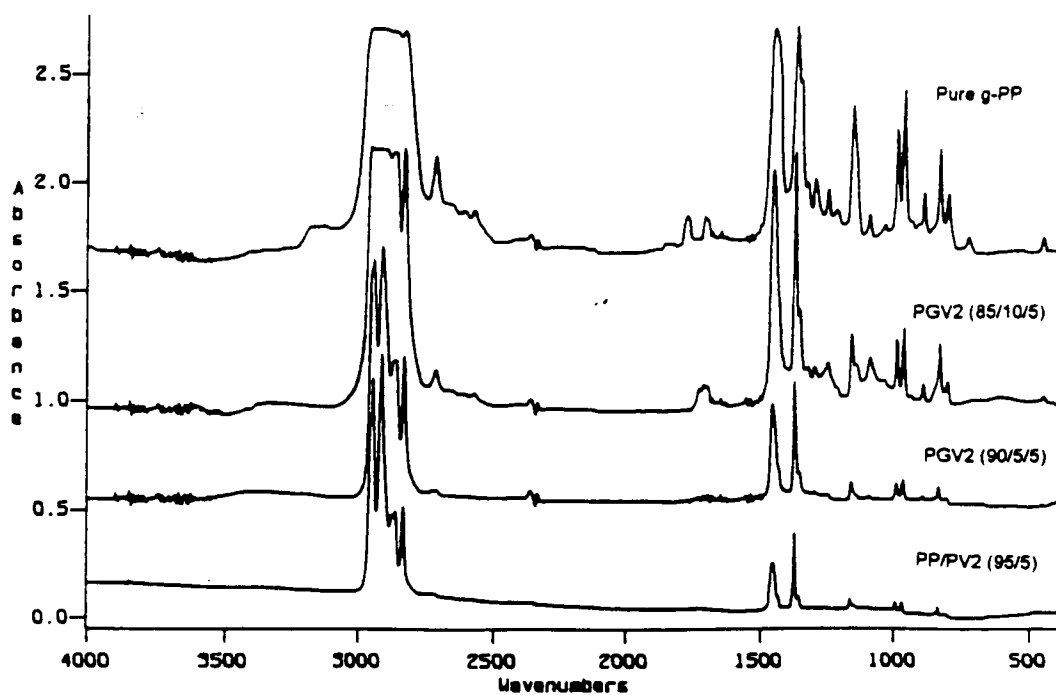
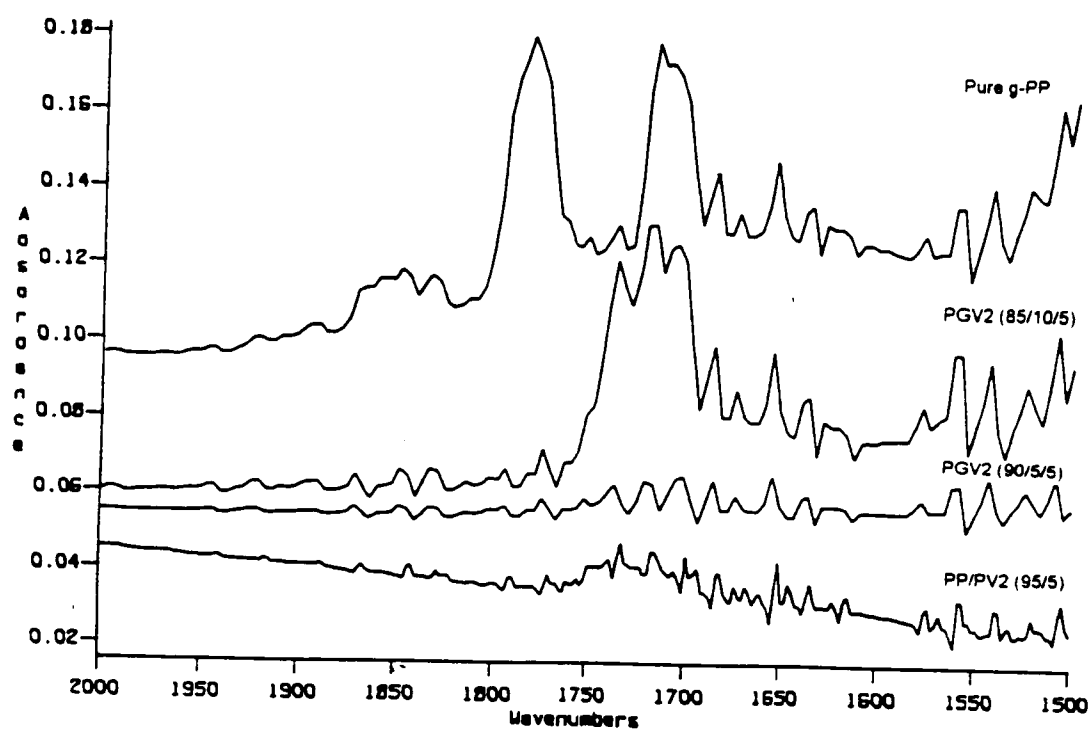


Figure 4-31 FTIR Spectra of PP/PVOH 2019 Blends.



(a)



(b)

Figure 4-32 . FTIR Spectra of PP/g-PP/PVOH 2019 Blends.

4.6. X-RAYS DIFFRACTION.

Table 14 shows the degree of crystallinity as a function of the blend composition for the studied blend systems.

Table 14. Percentage of crystallinity of PP/PVOH blends and PP/g-PP/PVOH 2019 blends determined by X-rays diffraction.

Sample	Crystallinity (%) (± 2)
PP3445	67
PVOH 1003	37
PP/PV1 (95/5)	48
PP/PV1 (90/10)	44
PP/PV1 (80/20)	42
PP/PV1 (70/30)	42
PVOH 2019	8
PP/PV2 (95/5)	58
PP/PV2 (90/10)	58
PP/PV2 (80/20)	53
PP/PV2 (70/30)	48
g-PP	43
PGV2 (90/5/5)	56
PGV2 (85/10/5)	54

Figure 4-33 shows a steep decrease in the degree of crystallinity of blends of PP with PVOH 2019 as the PVOH content in the blends increases. Figure 4-33 also shows that the percent crystallinity of PP/PVOH 1003 blend systems decreases with increasing PVOH content, but in blends with 20%PVOH and above, there is not a significant change. With respect to the blends containing 5% and 10%g-PP, a decrease in the degree of crystallinity as the g-PP content increases is observed. (Figure 4-34).

4.7. WATER ADSORPTION.

Water adsorption tests were conducted in order to study the change in weight of pre-weighed samples when immersed in water for certain periods of time. Tables 15 to 21 show the initial weight, immersion time, variation of weight (Delta Weight), and percentage of change of weight of the pure materials and the blend systems. The reported values are an average of four tested samples for each material.

Figure 4-35 shows the variation of weight against the immersion time of PP, PVOH 1003, and their blends. From Figure 4-35 (a) one can see that PP does not absorb water because there is no weight change. On the other hand, PVOH 1003 exhibits an increase in weight up to two hours of immersion in water after which, a decrease in weight is observed; at an immersion time of 14 hours, the sample weight is lower than the initial weight, indicating dissolution of the PVOH in water; after 22 hours, the weight remains stable. Figure 4-35 (b) shows an increase in weight for all the PP/PVOH samples up to five hours of immersion in water, after which, a drop of the weight is evident. The variation of weight stabilizes after an immersion time of 22 hours.

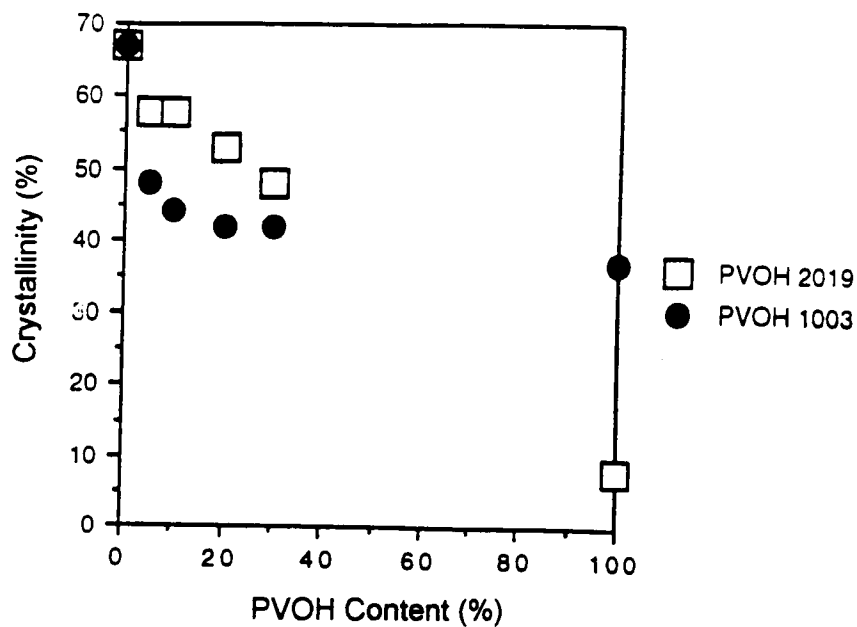


Figure 4-33. Percentage of Crystallinity of Blends of PP and PVOH as a function of PVOH content.

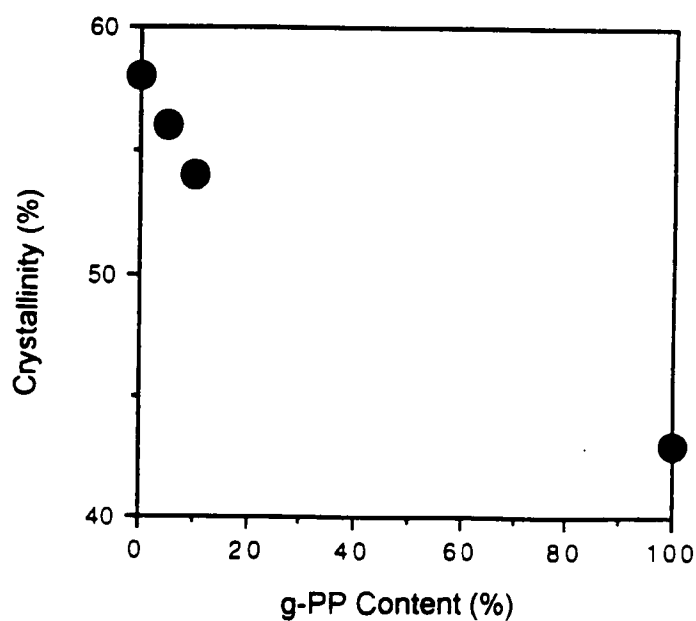
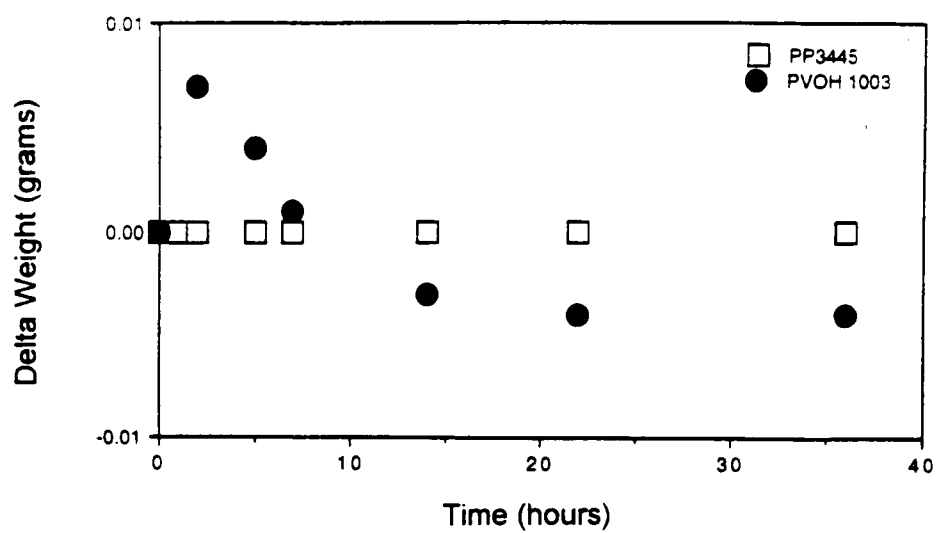
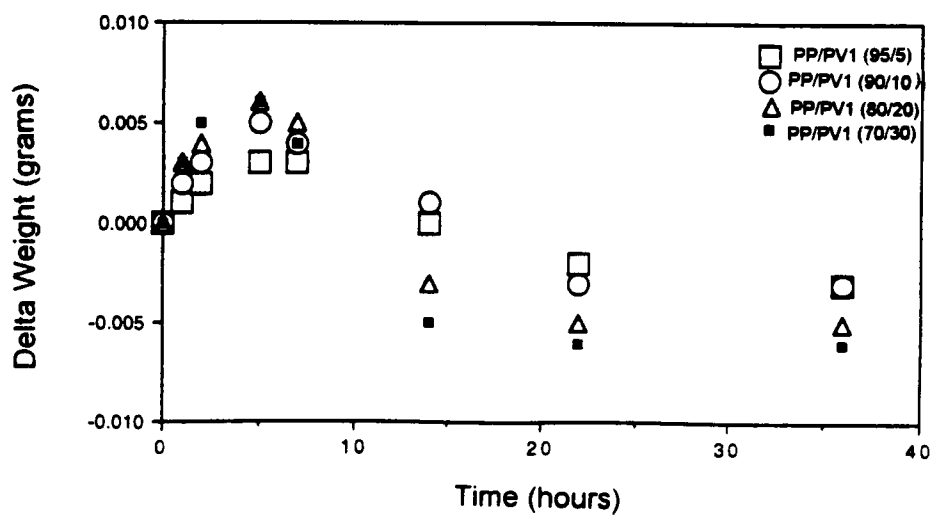


Figure 4-34. Percentage of Crystallinity of Blends of PP, g-PP, and 5% PVOH 2019 as a function of g-PP content.



(a)



(b)

Figure 4-35 . Variation of Weight (Delta Weight) vs. Immersion

Time: (a) PP3445 and PVOH 1003 samples,

(b) Blends of PP3445 and PVOH 1003.

Table 15. Initial Weights of Pure Resins, PP/PVOH Blend Systems, and PP/g-PP/PVOH 2019 Blends.

Material	Initial Weight (grams)(± 0.001)
PP3445	0.132
PVOH 1003	0.318
PP/PV1(95/5)	0.044
PP/PV1(90/10)	0.176
PP/PV1(80/20)	0.139
PP/PV1(70/30)	0.137
PVOH 2019	0.172
PP/PV2(95/5)	0.312
PP/PV2(90/10)	0.193
PP/PV2(80/20)	0.126
PP/PV2(70/30)	0.132
g-PP	0.108
PGV2(905/5)	0.056
PGV2(85/10/5)	0.099

Table 16. Variation of Weight (Delta Weight) and Immersion Time of PP/PVOH 1003 blends.

Immersion Time (hrs)	Delta Weight (grams) (± 0.001)					
	PP3445	PVOH1003	PP/PV1(95/5)	PP/PV1(90/10)	PP/PV1(80/20)	PP/PV1(70/30)
1	0.000	0.023	0.001	0.002	0.003	0.003
2	0.000	0.007	0.002	0.003	0.004	0.005
5	0.000	0.004	0.003	0.005	0.006	0.006
7	0.000	0.001	0.003	0.004	0.005	0.004
14	0.000	-0.003	0.000	0.001	-0.003	-0.005
22	0.000	-0.004	-0.002	-0.003	-0.005	-0.006
36	0.000	-0.004	-0.003	-0.003	-0.005	-0.006

Table 17. Variation of Weight (Delta Weight) and Immersion Time of PP/PVOH 2019 blends.

Immersion Time (hrs)	Delta Weight (grams) (± 0.001)					
	PP3445	PVOH2019	PP/PV2(95/5)	PP/PV2(90/10)	PP/PV2(80/20)	PP/PV2(70/30)
1	0.000	-0.152	0.004	0.004	0.004	0.004
2	0.000	-0.172	0.000	0.005	0.006	0.005
5	0.000	-	-0.002	0.000	0.005	-0.002
7	0.000	-	-0.005	-0.005	-0.005	-0.006
14	0.000	-	-0.007	-0.008	-0.008	-0.009
22	0.000	-	-0.009	-0.010	-0.010	-0.011
36	0.000	-	-0.009	-0.010	-0.011	-0.012

Table 18. Variation of Weight (Delta Weight) and Immersion Time of PP/g-PP/PVOH 2019 blends.

Immersion Time (hrs)	Delta Weight (grams) (± 0.001)		
	g-PP	PGV2(90/5/5)	PGV2(85/10/5)
1	0.000	0.002	0.002
2	0.001	0.004	0.007
5	0.004	0.007	0.006
7	0.004	0.006	0.005
14	0.007	-0.002	-0.006
22	0.009	-0.002	-0.008
36	0.009	-0.002	-0.008

Table 19. Percentage of Change of Weight of PP/PVOH 1003 Blend Systems.

Immersion		Percentage of Change of Weight (%) (± 0.1)				
Time (hrs)	PP3445	PVOH 1003	PP/PV1 (95/5)	PP/PV1 (90/10)	PP/PV1(80/20)	PP/PV1 (70/30)
1	0.0	8.0*	2.3*	1.1*	2.2*	2.2*
2	0.0	2.2*	4.5*	1.7*	2.9*	3.6*
5	0.0	1.3*	6.8*	2.8*	4.3*	4.4*
7	0.0	0.3*	6.8*	2.3*	3.6*	2.9*
14	0.0	0.9**	0.0	0.6*	2.2**	3.6**
22	0.0	1.3**	4.5**	1.7**	3.6**	4.4**
36	0.0	1.3**	6.8**	1.7**	3.6**	4.4**

* Gain in weight with respect to the initial weight of the sample.

**Reduction of weight with respect to the initial weight of the sample.

Table 20. Percentage of Change of Weight of PP/PVOH 2019 Blend Systems.

Immersion		Percentage of Change of Weight (%) (± 0.1)				
Time (hrs)	PP3445	PVOH 2019	PP/PV2 (95/5)	PP/PV2 (90/10)	PP/PV2(80/20)	PP/PV2 (70/30)
1	0.0	86.0**	1.3*	2.1*	3.2*	3.0*
2	0.0	100.0**	0.0	2.6*	4.8*	3.8*
5	0.0	-	0.6**	0.0	4.0*	1.5**
7	0.0	-	1.6**	2.6**	4.0**	4.5**
14	0.0	-	2.2**	4.1**	6.3**	6.8**
22	0.0	-	2.9**	5.2**	7.9**	8.3**
36	0.0	-	2.9**	5.2**	8.7**	9.1**

* Gain in weight with respect to the initial weight of the sample.

**Reduction of weight with respect to the initial weight of the sample.

Table 21. Percentage of Change of Weight of PP/g-PP/PVOH 2019 Blend Systems.

Immersion Time (hrs)	g-PP	Percentage of Change of Weight (%) (± 0.1)	
		PGV2(90/5/5)	PGV2(85/10/5)
1	0.0	3.6*	2.0*
2	0.9*	3.5*	7.1*
5	4.6*	12.5*	6.1*
7	4.6*	10.7*	5.1*
14	7.4*	3.6**	6.1**
22	9.3*	3.6**	8.1**
36	9.3*	3.6**	8.1**

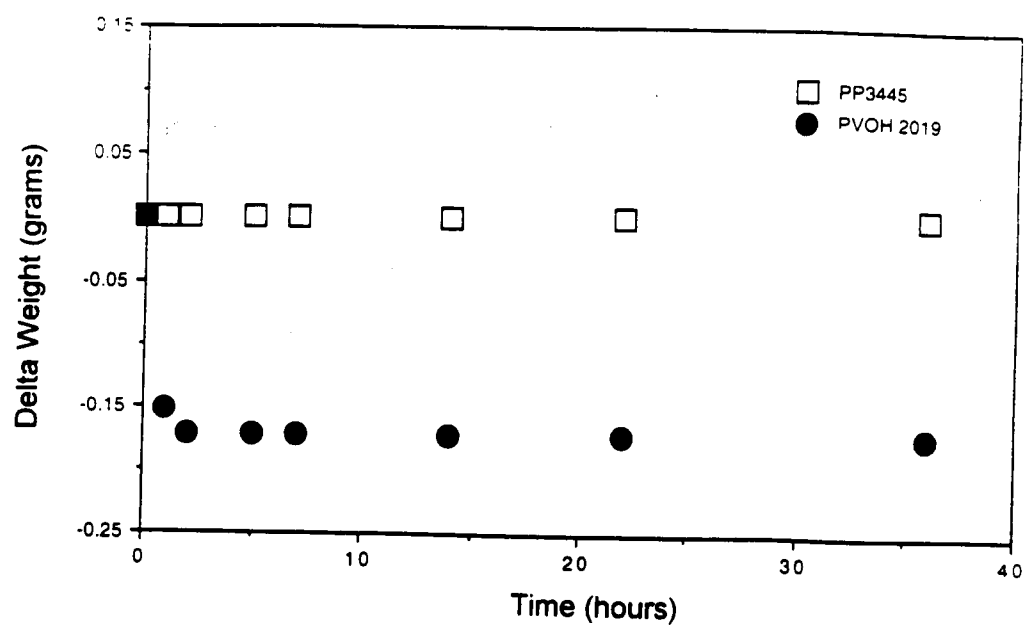
* Gain in weight with respect to the initial weight of the sample.

**Reduction of weight with respect to the initial weight of the sample.

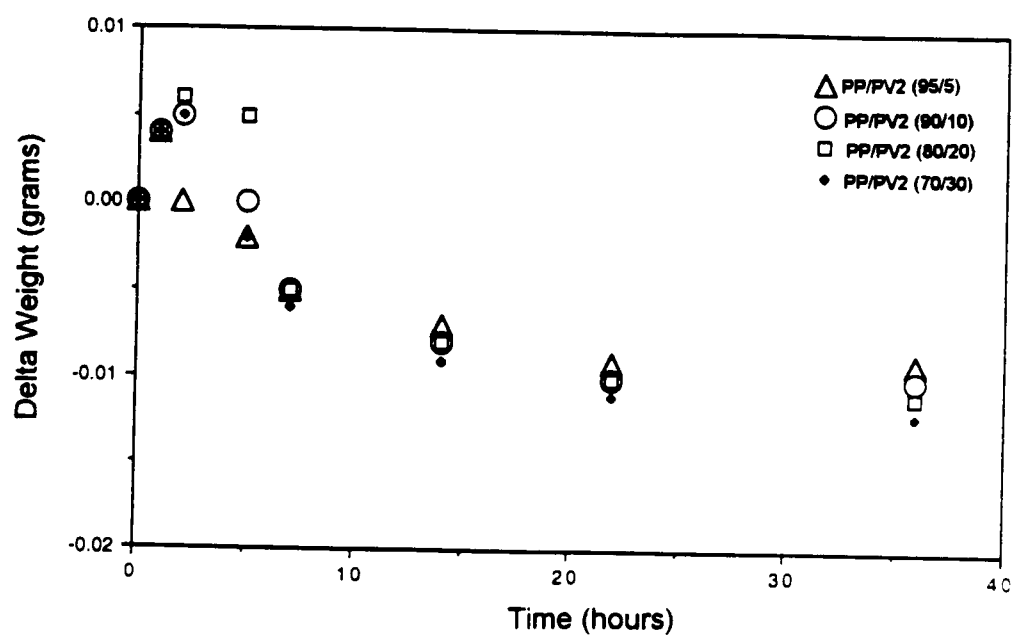
Figure 4-36 shows the change of weight as a function of the immersion time for the studied samples. No change in the weight of PP is shown in Figure 4-36 (a), while the PVOH 2019 completely dissolves after being immersed in water for one hour.

Blends of PP with PVOH 2019 (Figure 4-36 (b)) exhibit an increase in weight up to two hours of immersion of the samples in water. After an immersion time of five hours, the weight of the samples decreases, and finally, it stabilizes after 22 hours.

Figure 4-37 shows the variation of weight of blends of g-PP, PP, and 5%PVOH 2019. Samples with 5%g-PP exhibit an increase in weight up to an immersion time of two hours, after which the weight drops, and finally stabilizes at 22 hours. Samples with 10%g-PP exhibit an increase in weight up to five hours of immersion in water; after an immersion time of five hours, the samples weight decreases and finally stabilizes at 14 hours. Samples of pure g-PP show an increase in weight up to 22 hours. The samples containig g-PP exhibit a more pronounced increase in weight than samples without g-PP (i.e. PP/PV2 (95/5)); after an immersion time of five hours, samples of PP/PV2 (95/5) show a stronger decrease in weight than those containing g-PP.



(a)



(b)

Figure 4-36 . Variation of Weight (Delta Weight) vs. Immersion

Time: (a) PP3445 and PVOH 2019 samples,

(b) Blends of PP3445 and PVOH 2019.

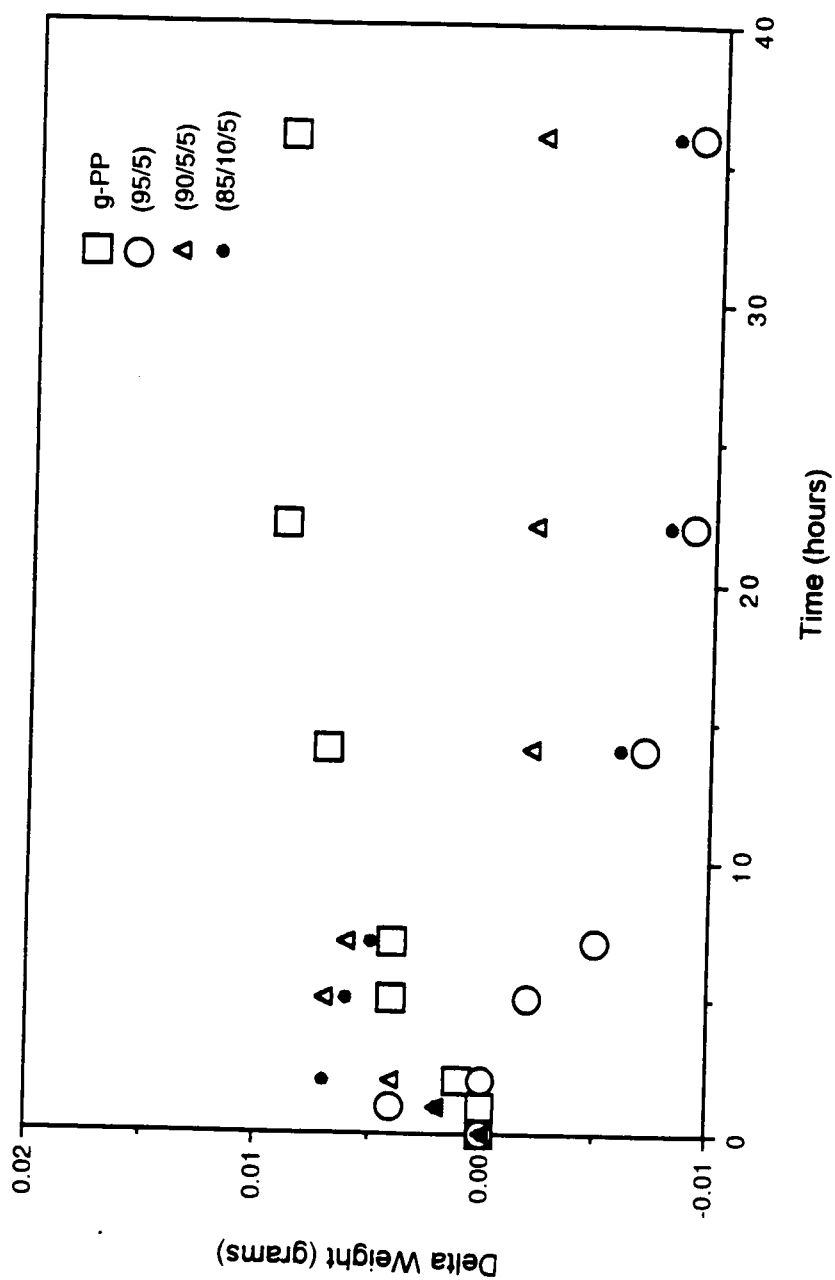


Figure 4-37 Variation of Weight (Delta Weight) vs. Immersion Time of Blends of PP3445, g-PP, and 5% PVOH 2019

V. DISCUSSION.

5.1. MORPHOLOGY OF STUDIED SAMPLES.

Binary blends can be made of pairs of polymers where neither one of the components, only one of them, or both resins are crystallizable. In the case of PP/PVOH 1003 blends, both components are capable of crystallizing, while PP/PVOH 2019 can be considered a semi-crystalline-amorphous blend system due to the low level of crystallinity in the PVOH 2019, as shown in Table 14, in which the percentages of crystallinity of the studied samples were reported. In any case, studies have shown that both components of the blend may influence each other giving rise to very interesting effects, some of which will be discussed in this work.

Polymer blends can be classified according to their morphologies. Many properties and, subsequently, uses of those polymer blends will critically depend on the arrangement and relative dimensions of the phases and on the degree of adhesion between them.

In the case of semi-crystalline blends, several types of morphologies can be encountered: type I morphology, in which crystals of both components are dispersed in an amorphous matrix; type II morphology in which one component exhibits spherulitic growth while the other crystallizes in a simpler structure; type III morphology, in which both components show a separate spherulitic structure, and type IV morphology, where the two constituents of the blend crystallize giving rise to the formation of mixed spherulites containing lamellae of both resins. Even though the spherulitic structure of PP is not clear, blends of PP with PVOH 1003 seem to exhibit a type II morphology (Figures 4-23 and 4-24). From Figures 4-23 and 4-24, dispersed domains of PVOH 1003 crystals are observed in the sample when PP is melted; the crystals of PP in the blends display an inconspicuous spherulitic structure considerably smaller than that of

the pure resin (Figure 4-20). Even though the maltese cross pattern in the PP crystals is not clear, the radial growth of the crystals is evident. Similar observations have been made by Martuscelli et al. (32). They studied blends of atactic polystyrene (aPS) with isotactic polystyrene (iPS) using a polarizing microscope; their observations led to the conclusion that aPS is incorporated within iPS spherulites, not in interlamellar regions but forming larger domains.

The most probable morphologies of blends in which one of the components can crystallize are (32): type I' morphology, in which the spherulites of the crystallizable component grow in a matrix consisting of the non crystallizable component; type II' morphology, in which the non-crystallizable component may be incorporated in the interlamellar regions of the spherulites of the crystallizable polymer, and type III' morphology, where the non-crystallizable component is included within the spherulites of the crystallizable resin, forming domains having dimensions larger than the interlamellar spacing. Figures 4-25 and 4-26 show the sequence of crystallization of some PP/PVOH 2019 blend systems. Figures 4-26 (b) and (c) clearly exhibit a type III' morphology; the PVOH 2019 is dispersed through the sample in the form of domains of amorphous material around which PP spherulites grow; in the final morphology one can see that the PVOH 2019 domains are not disturbed by the presence of PP crystals, they are located within the PP spherulites and are obviously larger than the interlamellar spacing. Similar observations have been made by Siegmann (76) regarding blends of isotactic PP (iPP) with isotactic polybutene-1 (iPB). Both iPP and iPB form spherulites when they crystallize from the melt. Blends with 25% of iPP result in a solid comprised of well developed spherulites resembling the iPP morphology, although less perfect with a coarser fine structure. In the 50/50 blends, a mixture of small crystalline aggregates of the two components is observed.

In blends of PP with PVOH the size of the PP crystals is considerably smaller and less perfect than those of the pure resin. This effect is clearly showed by the comparison of the optical micrographs of Figures 4-20 (b), 4-23 (c), 4-24 (c), 4-25 (b), and 4-26 (c). In Figure 4-20 (b) the spherulites of pure PP range from 150 to 350 microns; Figures 4-23 (c) and 4-24 (c), show the morphologies of (90/10) and (70/30) compositions of blends with PVOH 1003, in which the size of PP spherulites varies from 60 to 100 microns; in Figure 4-25 (b), corresponding to PP/PV2 (95/5) blends, PP spherulites range from 125 to 300 microns and, Figure 4-26 (c) shows PP spherulites ranging from 100 to 200 microns for PP/PV2 (70/30) blends. These observations suggest that the PVOH is acting as a nucleating agent which is very interesting from a practical point of view, as the superstructure strongly influences the thermal and ultimate properties of the blend systems. Krasnikova et al. (87) found analogous results by adding aPS to iPP.

In the case of PP/g-PP/PVOH 2019 blend systems, the g-PP also has an important effect on both PP and PVOH 2019. Figure 4-27 shows a very fine dispersion of PVOH 2019 particles through the sample when PP and g-PP are molten away. On the other hand, the final morphology of PGV2 (85/10/5) (Figure 4-28 (b)) exhibits PP spherulites which size ranges from 100 to 200 microns, and no phase separation seems to occur. The g-PP is a graft copolymer than can act as a emulsifier, namely interfacial agent in the system, reducing the surface tension of the PP and the PVOH 2019 and increasing their interfacial adhesion. The effect on the resulting morphology of the ternary polymeric system is to yield smaller size domains and better interfacial adhesion with improvement of the mechanical properties. The improvement in mechanical properties will be discussed later.

5.2. THERMAL BEHAVIOR.

As shown in Figures 4-1, and 4-2, a shift of crystallization temperature of PP in the blends towards higher temperatures is evident. In PP/PVOH 1003 blends, the crystallization temperature changes from 108 °C for pure PP to 124 °C for the (70/30) composition. In the case of PP/PVOH 2019 blend systems, the shift of the crystallization temperature of PP occurs from 108 °C for pure PP to 113 °C for blends containing 30 % PVOH 2019. This can mainly be attributed to the effect that PVOH particles have on the crystallization of PP. Because particles of PVOH crystallize earlier than PP, they would appear as heterogeneous nuclei for PP crystallization inducing formation of crystals of PP at higher temperatures. This observation infers that the PVOH is acting as a "nucleating agent". The nucleating agent character of PVOH was also evident in the study of the morphology of the PP/PVOH 2019 samples.

A material acts as a nucleating agent if certain requirements are fulfilled: the nucleating agent must be insoluble in the polymer that is being nucleated, it should be wetted or absorbed by the polymer, and its melting point should be higher than that of the polymer. The crystallization temperature of polymers usually increases with increasing nuclei density, i.e. with increasing activity of the nucleating agent. Figure 5-1 shows the DSC crystallization curves of PP with and without nucleating agent, while Figure 5-2 demonstrates the influence of a nucleating agent on the size of the PP spherulites. Notice that the size of the spherulites of PP decreases when a nucleating agent is added. The same observations are made for the PP/PVOH blend systems studied in this work which indicate the nucleating agent character of the PVOH particles in the systems.

Figure 4-1 and Table 8 also show an increase of the crystallization temperature of PVOH 1003 with composition from 184 °C for pure PVOH 1003, to 193 °C for

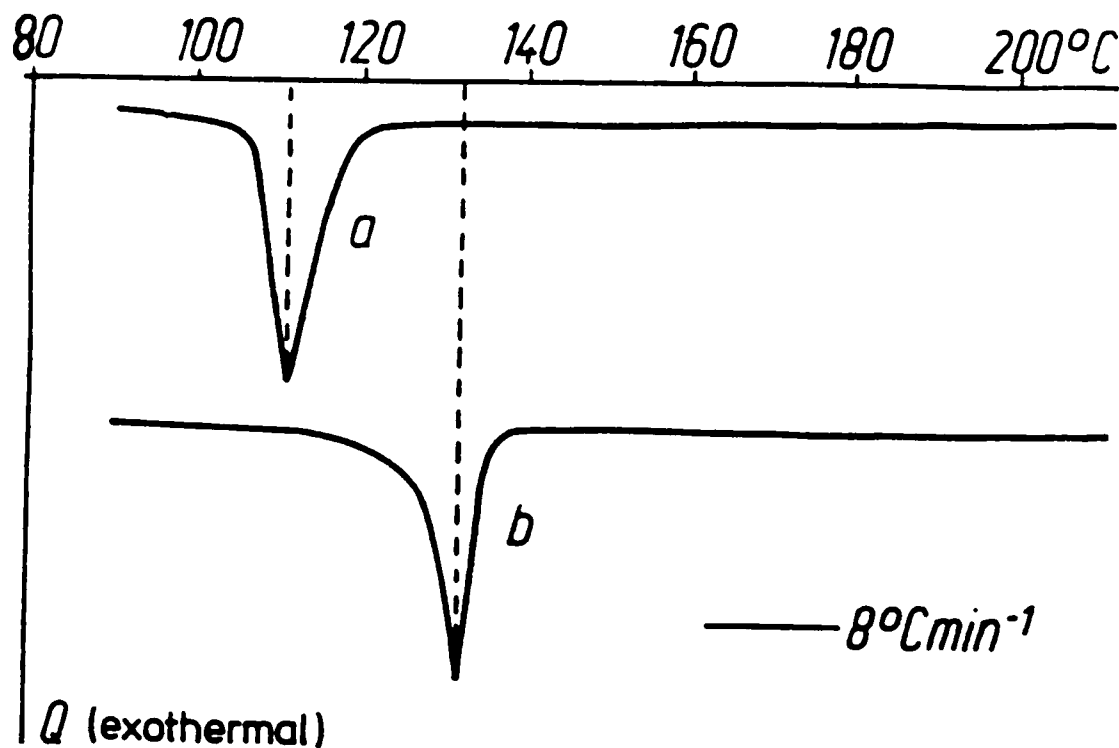


Figure 5-1 . DSC crystallization diagrams for polypropylene, cooling rate 8 °C/min. (a) without nucleating agent, (b) with 1 % sodium p-tert-butylbenzoate (88).

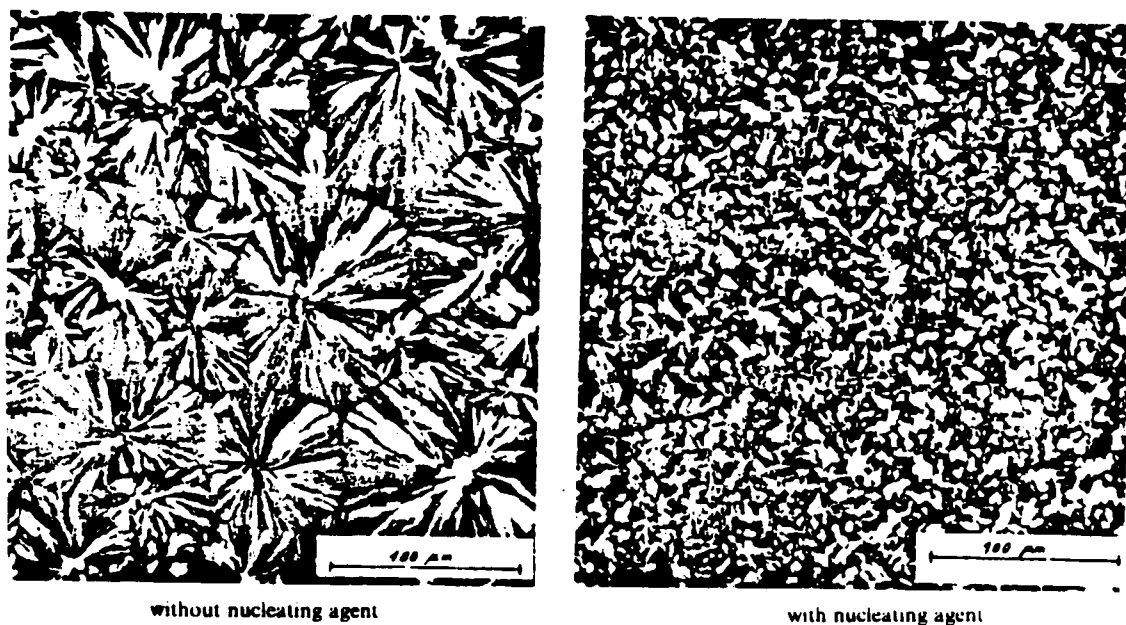


Figure 5-2 . Influence of a nucleating agent on spherulite size of polypropylene (88).

PP/PV1 (70/30) blends. A logical explanation for the increase of the crystallization temperature of PVOH 1003 in the blends cannot be provided.

Figure 4-3 shows that PP crystallization temperature is shifted to lower temperatures when g-PP is added to blends containing PP and 5% PVOH 2019. In blends with g-PP, the crystallization temperature of PP changes from 108 °C for pure PP to 113 °C for a PGV2 (90/5/5) sample. No further displacements of the crystallization temperature are observed with 10% g-PP. In the case of PP/g-PP/PVOH 2019 blend systems, the possible displacement of the crystallization peak as a result of the effect of the other constituents of the blend cannot be observed because the concentration of PVOH 2019 is very low. Observe that the crystallization curves for g-PP blends exhibit a single crystallization peak located between those of the pure g-PP and PP resins.

When samples containing crystalline polymers are cooled from the melt, an ordered structure is produced. The random tangled molecules in the melt tend to align and form small ordered regions called nuclei. The crystal nuclei grow by the addition of further chains. Crystallization is a time-dependent phenomenon with some polymers crystallizing much faster than others. In the case of blend systems containing g-PP, the formation of an ordered structure is not simple because the crystallization phenomenon involves the alignment of a polymer containing a PP segment with high mobility, and a PP-g-MAH (g-PP) segment more rigid and more difficult to accommodate in an ordered structure which retards the crystallization of the sample. The retardation of crystallization is evident when the PP/g-PP/PVOH are compared to PP/PV2 (95/5) blend (Table 10 and Figure 4-3).

The melting behavior of PP/PVOH blend systems was also studied in this work. In the case of PP/PVOH blends, a depression of the melting temperature of PP associated with the presence of PVOH can be seen (Figures 4-4 and 4-5). Such melting temperature depression has been reported for other blends, e.g., polypropylene with polybutene-1 (PB) (89), poly(ethylene terephthalate) (PET) with poly(butylene terephthalate) (PBT) (90), poly(2,6-dimethylphenylene oxide) (PPO) with isotactic polystyrene (iPS) (91), poly(vinyl chloride) (PVC) with poly-E-caprolactone (PCL) (92), and poly(vinyl alcohol) (PVOH) with poly(vinyl pyrrolidone) (PVP) (93).

The depression of melting temperature can be the result of several phenomena such as co-crystallization compatibility in the amorphous phase (94), smaller crystallite size, and decrease in the crystalline order. In PP/PVOH 1003 blend systems, the melting temperature of PP drops from 164 °C for pure PP to 159 °C for PP/PV1 (70/30) blends. In PP/PVOH 1003 systems, co-crystallization does not seem to be the cause of the depression of the melting temperature, because the DSC curves show the crystalline phase of both polymers in the studied compositions. Smaller crystallite size and decrease in crystalline order seem to be more likely to occur in PP/PVOH 1003 systems. With respect to PP/PVOH 2019 blend systems, the crystallization temperature of PP changes from 164 °C for pure PP to 161 °C for PP/PV2 (70/30). Because the crystallinity of PVOH 2019 is very low, blends of PP with PVOH 2019 can be considered to be of the type of blends where only one of the components is crystallizable. When there is compatibility of the components in the blend, the non-crystallizable component acts as a compatible diluent for the crystallizable polymer, while for systems in which compatibility in the melt state does not exist, the melting temperature depression has been attributed to kinetic and morphological effects of the non-crystallizable polymer producing a reduction in crystal size, lamellae thickness or crystal perfection. These causes of depression in melting temperature seem to be more

likely to occur in the PP/PVOH 20/19 blend systems studied in this work. The morphology studies of the three blend systems reveal a decrease in size of the PP crystals in the presence of the other constituents, as well as decreasing crystalline perfection.

Another important observation is that as PP is blended with PVOH, at 20% PVOH and above, the endothermic peak of PP slightly loses its prominence although the shape of the peak is retained. The reduction in magnitude of the endothermic peak area corresponds to a decrease of the degree of crystallinity. Studies of the three blended systems by x-rays diffraction corroborate a decrease in the degree of crystallinity as PVOH and g-PP content increase. The decrease in the degree of crystallinity will be discussed later.

In the case of blends with g-PP, a small endothermic peak corresponding to the g-PP can be observed. Blends with g-PP must have certain level of compatibility, because the melting temperatures of PGV2(90/5/5) and PGV2(85/10/5) are located between those of the pure g-PP and PP/PV2 (95/5). The same conclusion was reached from morphology studies of the compatibilized blends. No further displacements are observed with increasing g-PP content.

5.3. DEGREE OF CRYSTALLINITY.

The blends' total degree of crystallinity was determined by dividing the area under the peaks of the x-rays diffraction scans into amorphous and crystalline areas, with no further corrections. The ratio of the crystalline area to the total area was taken as the degree of crystallinity of the blends.

In Figure 4-33, the plot of crystallinity of PP/PVOH blends determined by x-rays diffraction versus composition of PVOH shows that crystallinity decreases with increasing PVOH concentration. Table 14 shows that for blends of PP with PVOH

1003, the total degree of crystallinity (including both phases) dropped gradually from 67% for pure PP to 37% for pure PVOH 1003. The total degree of crystallinity obtained for PP/PVOH 1003 blend systems, is lower than the linearly added contributions of the components indicating that the presence of the resins in the system, hinders to some extent the crystallization processes of both phases.

In the case of blends of PP with PVOH 2019, the decrease in the total degree of crystallinity of the blends is even more drastic than that observed for PP/PVOH 1003 blend systems: it drops from 67% for pure PP to 8% for pure PVOH 2019. The presence of 1,2-glycol structures and molecular branching in PVOH 2019 induces a disruption in its crystalline structure.

In the blends containing PP, g-PP, and PVOH 2019 (Figure 4-34), the total degree of crystallinity versus composition of g-PP decreases with increasing g-PP content. The percentage of crystallinity of the blend system drops from 58% for a PP/PV2 (95/5) blend to 43% for pure g-PP. The decrease in the total degree of crystallinity obtained for PP/g-PP/PVOH 2019 blend systems indicates that the presence of g-PP in the systems disrupts to some extent the crystallization process of the blend system.

5.4. FOURIER TRANSFORM INFRARED SPECTROSCOPY.

The DSC, tensile testing, and DMA data show incompatibility of the components of the PP/PVOH blends at all compositions. The theories concerning the adhesion between the polymeric components having a limited compatibility have shown that the adhesive strength is dependent on both the homogeneity of the system and superficial properties of the constituents (95). The adhesion between the thermodynamically incompatible polymers at the interface depends on their chemical nature (presence of polar groups, chain flexibility, etc.), the composition of the blend, the preparation mode

of the mixture, the presence of ingredients with compatibilizing effect, etc. (96). The study of blends of PP with PVOH by FTIR gives important information regarding the interactions taking place between the components of the blend system.)

The structural differences between PVOH 2019 and PVOH 1003 also promote different kinds of responses which makes important the development of a quantitative analysis of these resins by FTIR. Figure 4-29 shows the spectra for both PVOH 1003 and PVOH 2019. The intensity and frequencies of the characteristic bands of PVOH facilitate the differentiation of the resins. The following bands are of fundamental importance for this purpose: 3340 cm^{-1} , which corresponds to the O-H stretching, 1650 cm^{-1} , related to the C=O stretching, and 1144 cm^{-1} , which is the band whose intensity is related to the crystallinity of the PVOH sample.

In the case of PVOH 1003, one can see that the intensity of the band at 1144 cm^{-1} is significantly stronger than that observed for PVOH 2019, which is in complete agreement with the results of degree of crystallinity obtained by X-rays diffraction (Table 14). The presence of vinyl acetate groups in the main chain of PVOH 2019, has a marked effect on the ability of the resin to crystallize; the effective packing of the molecular chains is not possible, and consequently, the degree of crystallinity of PVOH 2019 is very low. On the other hand, resins with higher degrees of hydrolysis such as PVOH 1003, exhibit higher degrees of crystallinity, because the -OH groups are small enough to accommodate themselves in the crystals and additionally, the intermolecular hydrogen bonds promote a better packing of the chains.

The fact that PVOH 2019 has a lower -OH group content is the reason why the intensity of the band at 3340 cm^{-1} is weaker than that of PVOH 1003. With respect to the peak at 1650 cm^{-1} , one can see that its intensity is stronger for PVOH 2019 compared with the spectra of PVOH 1003. The presence of vinyl acetate groups in the

PVOH 2019 leads to a higher carbonyl group content in the resin is compared to that of PVOH 1003 which -CO content seems to be much lower.

Figures 4-30 and 4-31 show the spectra for blends of PP with PVOH 1003 and PVOH 2019, respectively. In both blend systems, the peak corresponding to the free hydroxyl stretching is located at 3365 cm^{-1} , which is in good agreement with the reported value of 3340 cm^{-1} in Table 12. The intensity of the peak of the hydroxyl groups increases as the PVOH content in the blends increases, as expected. The position of the characteristic bands of PVOH does not change with blend composition. This behavior suggests that the blending of the two components does not occur in the crystalline regions of PVOH. The change of intensity of the peak at 1740 cm^{-1} is also attributed to the variation of PVOH content in the blend systems.

The control of the morphology of polymer blends and the enhancement of interfacial interactions between the dispersed phase and the matrix are critical in order to improve the ultimate properties of the blend. The introduction of small quantities of block or graft copolymers, or reactive species, generally known as "compatibilizing agents" can be very helpful.

The addition of PP-g-MAH to PP/PVOH blends seems to stabilize the phase morphology and prevent the phase growth or coalesce according to results obtained by optical microscopy. Polymer blends having carboxyl and hydroxyl groups, such as PP/PP-g-MAH/PVOH blend systems, may have good adhesion between the phases due to the possible molecular association through hydrogen bonding. The addition of g-PP (PP-g-MAH-MAH) to PP/PVOH blends was with the intention to establish certain level of compatibility in order to improve the properties of the system.

In Figure 4-32 (a) one can see that the maximum of the peak of the OH stretching band, which is associated to hydrogen-bonded hydroxyls ($3000\text{--}3600\text{ cm}^{-1}$), shifts progressively towards higher frequencies upon blending with g-PP. The band

shift can be consistently interpreted by the hydroxyl-carbonyl hydrogen bonding between the PP/PP-g-MAH and the PVOH 2019 shown in Figure 5-3, reaction (B). The shift of this peak and the variation of its intensity are not related with the -OH groups of PVOH, because the PVOH content in the blend systems containing g-PP does not change. This indicates that some kind of interaction must be taking place between the PP, g-PP, and PVOH 2019. The possible reactions of compatibilization of PP/PVOH blend system are represented in Figure 5-3. The reaction (A) shown in Figure 5-3 can also be occurring in this blend system, because the peak corresponding to the vibrations of the COO groups conforming ester linkages can be observed in the spectra. Ester linkages are generally manifested as a strong band from 1300 to 1200 cm^{-1} which probably arises from the stretching of single bond carbon-oxygen where the carbon is an unsaturated atom. Spectra in Figure 4-32 do not exhibit such strong band in that region, but a small peak can be detected around 1200 cm^{-1} .

Figure 4-32 (b) shows an increase in the intensity of the peaks between 1850 and 1750 cm^{-1} with increasing g-PP content. These bands correspond to the carbonyl frequencies that usually fall between 1850 and 1650 cm^{-1} . Increase in the intensity of these peaks can also be an indication of carbonyl-hydroxyl hydrogen bonding. The spectrum corresponding to pure g-PP exhibits two peaks which are characteristic of the maleic anhydride: 1850 cm^{-1} and 1794 cm^{-1} (97). When the PP/g-PP reacts with the PVOH 2019, the distinction between those two peaks is not easy because opening of the ring takes place, and additionally, g-PP is present at very low concentrations in the blended systems (98).

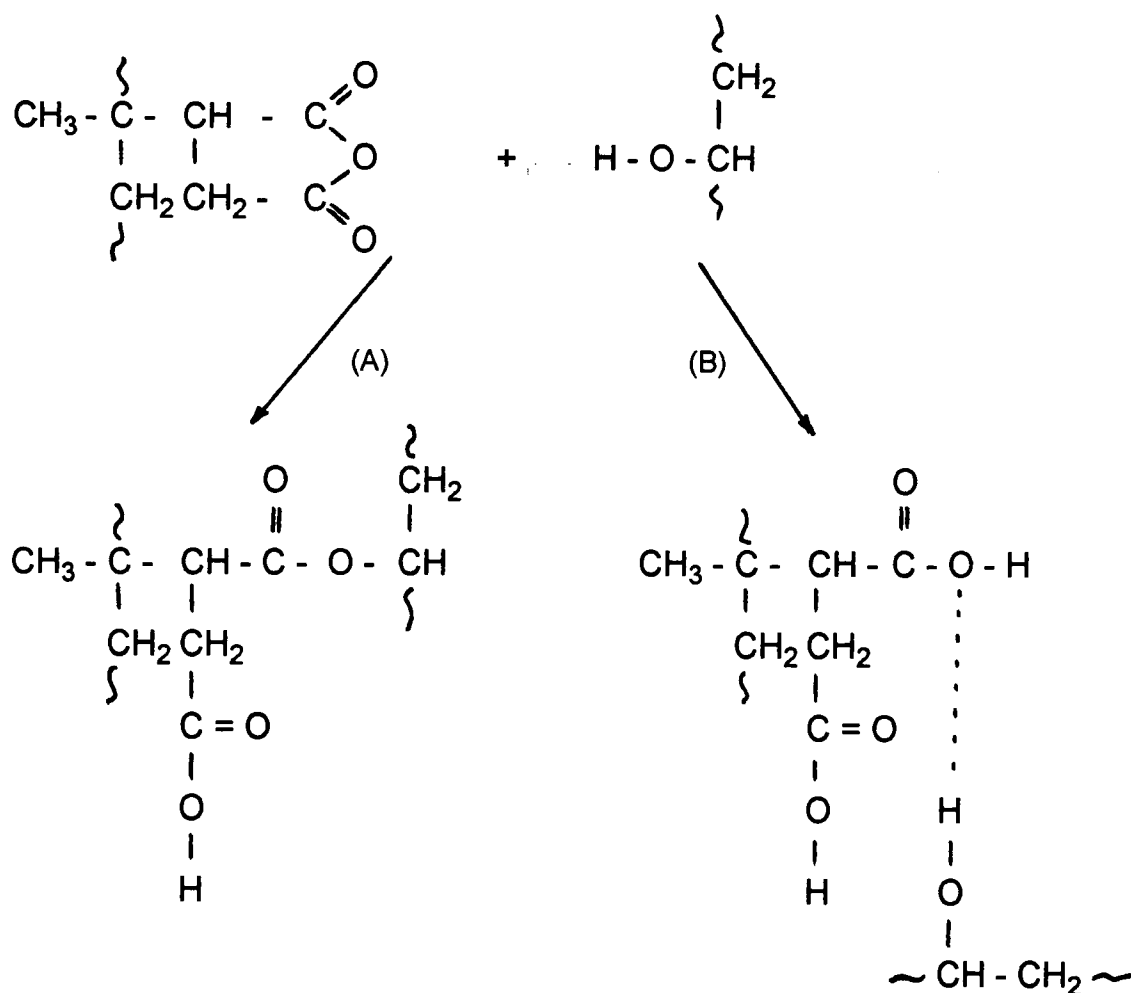


Figure 5-3 . Possible reactions of compatibilization of PP/PVOH blend systems.

5.5. MECHANICAL PROPERTIES.

The theories for predicting mechanical properties of filled systems generally assume perfect adhesion between the filler and the polymer matrix, as well as perfect dispersion of the individual filler particles. This requirements are not entirely fulfilled by PP/PVOH blends. Studies of the morphology of the studied blend systems reveal the formation of PVOH aggregates which size increases with increasing PVOH content.

In case of PP/PVOH 1003 blend systems, a very good fit between Kerner's prediction for the modulus and the experimental data is obtained (Figures 4-7 and 4-8), particularly at 5% and 10% PVOH for dry samples, and only at 5% PVOH for wet samples. This indicated that at low concentrations of the filler, the agglomerates' size does not cause significant deviations from the predicted results. By the same token, PP/PVOH 2019 blends exhibit a similar behavior at 5% and 10% PVOH content. The fit between Kerner's equation and the experimental data for blends containing PVOH 2019 can even be found at 20% PVOH. This could be due to the fact that the agglomerates of PVOH 2019 are much smaller than those for PVOH 1003, even at higher concentrations.

Kerner's equation is a mathematical theory capable of describing the reinforcing action of the filler particles. According to Kerner's equation, the modulus of a filled material should increase with the filler concentration (Figure 4-14). Kerner's equation is one of the most versatile equations used for predicting the modulus of filled systems, because it considers those cases in which the filler is more rigid than the matrix, which is certainly the case of systems where the matrix is conformed by PP and the filler is dry PVOH. Kerner's equation assumes that there is good adhesion between the filler and matrix phases. Actually, good adhesion is not important as long as the frictional forces between the phases are not exceeded by the applied external stresses (65). In most filled systems, there is a mismatch in the thermal coefficients of expansion so that cooling down from the fabrication temperature imposes a squeezing force on the filler by the matrix. In many cases, even if the adhesion is poor, the theoretical equations are valid because there may not be any relative motion across the filler-polymer interface.

In cases in which there is no adhesion between the filler and the matrix, the filler is not efficient as a reinforcing agent (66). When this happens, the modulus

decreases with the filler content. Figure 4-8 shows a decrease in modulus for wet samples, but this is not attributed to an extreme case of no adhesion between the phases, but to the effect of moisture on pure PVOH resins, which will be discussed later.

Morphological studies show that blends of PP with PVOH exhibit phase separation. This indicates that the adhesion between both phases is not strong enough, and consequently, the mechanical properties of the blends should not improve. Nevertheless, the tensile testing results suggest that some kinds of interactions must be occurring. The size and dispersion of the PVOH agglomerates must also influence the mechanical properties of the studied blend systems, but a precise explanation cannot be suggested, because an exact estimation of the distribution of the different phases cannot be specified.

When g-PP is added to the systems containing PP and 5% PVOH 2019, a better dispersion of the filler is observed, as well as a reduction in size of the PVOH domains. The size of PVOH domains in blends without g-PP ranges from 60 to 100 microns, while in blends containing g-PP, the PVOH does not form agglomerates but small grains (5 to 8 microns) which are dispersed through the sample. Because g-PP is acting as a nucleating agent, a higher degree of crystallinity with respect to (95/5) PP/PVOH blends is obtained (Table 14), which results in increased hardness, and consequently, higher modulus. Figures 4-7 and 4-8 exhibit an improvement in the modulus for compatibilized systems.

Figures 4-7 and 4-8 show the linearity predicted by the rule of mixtures for dry and wet samples of the studied blend systems. According to the rule of mixtures, the mechanical properties of two-component polymer mixtures are additive. Equation (2-3-29) and Figure 3-18 describe the basis of the rule of mixtures. Important considerations are not contemplated by this theory, such as the particle size of the filler

and the filler distribution into the matrix. Additionally, the interaction coefficient, I , included in equation (36), describes the level of synergism, or thermodynamic compatibility of the components in the blend (74). It has been reported that in blends where I has a positive value, the system exhibits a synergistic behavior indicating miscibility of the constituents of the blend (74). This response has been attributed to the contraction of free volume, or densification on mixing that is expected consequence of the energetic interactions responsible for miscibility (80). When I takes a negative value, a nonsynergistic blend results, in which the values of the property under study takes values below those predicted by the weighed arithmetic property averages of the components (74). For certain values of I , very close to the linear prediction, a "nearly additive" response for miscible blends with little densification, or for immiscible mixtures with good adhesion (65). The exact values of I in this region have not been specified.

Figure 4-7 shows that for dry samples of PP/PVOH 1003 and PP/PVOH 2019 blends, the experimental data for the modulus are slightly below the rule of mixtures' prediction (straight lines), which indicates that both blend systems exhibit a non-synergistic behavior. Figure 4-8 shows that wet samples of PP/PVOH 1003 and PP/PVOH 2019 blends practically fall on the straight line indicating a very good fit between the rule of mixtures and the experimental data. This reveals that both blend systems are additive. In the case of compatibilized systems, the values for modulus of the studied compositions are above the rule of mixtures' prediction, indicating a certain level of synergism. Interesting results could be obtained if samples containing different g-PP concentrations were tested in order to be able to determine if the compatibilized systems in fact exhibit a synergistic behavior.

Figures 4-10 and 4-11 show the experimental data for dry and wet samples, Nielsen's prediction, and the rule of mixtures' prediction for the tensile strength of blends of PP with PVOH. In general, fillers cause a dramatic decrease in the tensile

strength of polymer mixtures (66,71). In Figure 4-10, a decrease in the tensile strength for PP/PVOH systems is observed. A drastic decrease in the value of tensile strength of blends of PP/PVOH 2019 with small amounts of PVOH is evident: for dry samples, the tensile strength changes from 26.47 MPa (pure PP) to 17.67 MPa (for PP/PV1 (80/20); above a volume fraction of 20%, the tensile strength gradually decreases. For PP/PVOH 1003 blends, the decrease in tensile strength is gradual. In Figure 4-10, the curve corresponding to Nielsen's prediction is above those of the experimental data. The experimental data behave similar to the theoretical curve for tensile strength of filled polymer systems in which there is certain level of adhesion between the filler particles and the matrix (Figure 2-17). This indicates that some kind of interaction must be occurring in the PP/PVOH blends.

With respect to the rule of mixtures' approximation, the experimental data fall below the straight lines representing the linearity of the prediction, which indicates that both blend systems exhibit a non-synergistic behavior.

Figure 4-11 shows that tensile strength also decreases with PVOH concentration for wet samples. Similar behavior to that obtained for dry samples is observed in Figure 4-11, but the decrease of tensile strength of PP/PVOH 1003 blended systems is more drastic than that observed for the dry samples. The presence of imperfect crystallites at temperatures below T_g may be causing the drop in tensile strength. The tensile testing was performed at room temperature, which is below the theoretical value for the glass transition temperature, T_g , of PVOH (70-80 °C). When there are imperfect crystallites in the amorphous phase of PVOH, they can act as stress concentrations which will result in brittleness of the sample. The presence of voids produced during the crystallization process, can also induce brittleness. With respect to the rule of mixtures' prediction, the experimental data fall below the straight lines, indicating non-synergism.

When g-PP is added to the system, an increase in tensile strength is observed. As g-PP acts as a nucleating agent, it tends to reduce the size of PVOH domains, and a better dispersion of the filler particles is obtained. This results in increased tensile strength, compared with (95/5) PP/PVOH 2019 blend. Studies of the morphology of the compatibilized systems (Figures 4-25 and 4-27) show that the addition of the compatibilizing agent leads to the formation of a finer structure which favors a more uniform stress distribution on mechanical stress, leading to an improvement of the tensile strength.

Figures 4-12 and 4-13 show the elongation to break of PP/PVOH blend systems as a function of the PVOH content. Equation (31) represents Nielsen's prediction for the elongation to break. This equation was used for predicting the elongation to break for PP/PVOH blends. An excellent fit between the experimental data and the predicted values of elongation to break is observed in Figures 4-12 and 4-13. For both dry and wet samples, the elongation to break decreases with filler concentration. The decrease in elongation to break with rigid fillers, such as PVOH, arises from the fact that the actual elongation experienced by the polymer matrix is greater than the measured elongation of the specimen (80). This phenomenon is illustrated in Figure 5-4. Although the specimen is part filler and part matrix, all the elongation comes from the PP because the filler is rigid. The curves for elongation to break of PP/PVOH blend systems represented in Figures 4-12 and 4-13 show a very dramatic decrease in elongation even at small concentrations of filler, which is similar to the curve corresponding to a rough fracture surface shown in Figure 5-4. This type of fracture is characteristic of filled systems in which there are some kinds of interactions between the matrix and the filler. If there is no adhesion, the fracture surface is smooth, and the elongation to break decreases more gradually (65).

Figures 4-12 and 4-13 also show the rule of mixtures' prediction. The experimental values for elongation to break of PP/PVOH blends are below the straight line predicted by the rule of mixtures, indicating non-synergism of the blended systems. In Figure 4-12 even the dry compatibilized blends are below the rule of mixtures' prediction, while the wet PGV2 (85/10/5) blends is above the prediction (Figure 4-13). This could indicate synergism of the blends at 10% g-PP.

For compatibilized blend systems, an increase in the elongation to break with g-PP compared to the PP/PV2 (95/5) blend is observed. This could be attributed to the important interfacial role of g-PP.

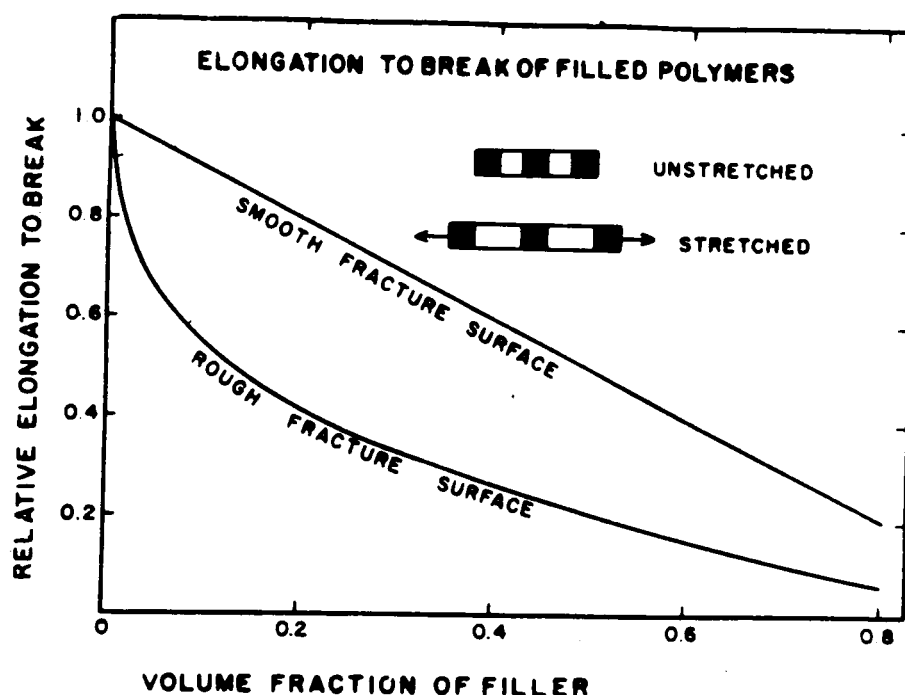


Figure 5-4 . Theoretical curves for the elongation to break of filled polymers as a function of filler concentration when there is good adhesion of the polymer conforming the matrix to the filler (65).

The strong effect of water on the mechanical properties of the three blend systems is very evident. The adsorption of moisture from air strongly affects the mechanical properties of the blends because of the ability of PVOH to absorb water. As shown in Figures 4-7 to 4-13, the modulus, tensile strength, and elongation to break of the blend systems considerably changes in the presence of moisture. For pure PVOH 1003 samples, the modulus drops from 771.52 to 141.72 MPa (Table 11), while for PVOH 2019, it drops from 1694.19 to 97.77 MPa. The drastic drop in modulus for PVOH 2019 compared with PVOH 1003 is due to the fact that PVOH 2019 is considerably more sensitive to humidity. In the case of the blends, a significant drop in the modulus can be observed (Figure 4-9). The water content transforms the PVOH from brittle and glassy, to rubbery and flexible.

With respect to the tensile strength, it also drops with moisture, while the elongation to break notably increases. For pure PVOH 1003, the elongation to break changes from 1.02 to 62.21 % and the tensile strength from 16.10 to 13.25 MPa; the elongation to break for PVOH 2019 changes from 1.67 to 62.07 %, while the tensile strength drops from 17.78 to 15.42. The studied PP/PVOH blend systems also exhibit higher values for elongation to break and lower tensile strength as water content increases.

In the case of blends with g-PP, which contain 5% PVOH 2019, the modulus decreases, as well as the tensile strength, while the elongation to break increases.

PVOH is a water-soluble polymer. For pure PVOH when it absorbs water, the resin changes from being a rigid to a soft material. PVOH 2019 samples even become sticky with moisture. In the studied blend systems, in which PVOH particles are dispersed into the PP matrix, when moisture is absorbed by those PVOH particles they become soft, acting as a plasticizer or internal lubricator in the PP matrix. This causes a decrease in the modulus and tensile strength, and an increase in elongation to break.

5.6. DYNAMIC MECHANICAL ANALYSIS.

In this study, DMA was employed to determine the glass transition temperature and storage moduli of pure materials and blend systems. For miscible blends, the properties of the blends are nearly the same as those for a random copolymer of the same composition. For immiscible polymer blends, the modulus temperature curves show two drops, and the damping curves show two peaks. The relative heights of the two damping peaks is determined by the concentration of the two components and the morphology of the system. Because PP/PVOH are immiscible systems, they should exhibit two main chain relaxation peaks corresponding to the molecular motion of the components of the blends.

Figures 4-14 to 4-16 show the loss factor ($\tan \delta$) versus temperature spectra for the three blended systems. Motions of long chain segments in the polymer structure have a profound effect on the loss factor of the dynamic mechanical properties. The largest loss peak is the β -peak, which is associated with the glass transition temperature. This transition occurs in the amorphous regions of the polymer with the initiation of the micro-Brownian motion of the molecular chains. The magnitude of β -peak in amorphous polymers, such as PVOH 2019, is much higher than that of semi-crystalline resins (PVOH 1003 and PP), because the chain segments in the amorphous regions have less restraints imposed by small crystalline regions.

In general, T_g depends on the chemical structure of the polymer. Flexibility, steric hindrance, and bulkiness of the side groups attached to the backbone chain affect the value of T_g . In vinyl polymers, of the type $-\text{CH}_2-\text{CHX}-$, the nature of the side group, X, has a profound effect on T_g . The presence of side groups on the main chain has the effect of increasing T_g through a restriction of bond rotation. The presence of polar groups, as it is the case for PVOH, tends to raise T_g more than non-polar groups of the same size. This is because the polar interactions restrict the

rotation around the backbone chain. As shown in Figures 4-14 and 4-15, PVOH 2019 exhibits a higher T_g than PVOH 1003, as expected (80° and 70° C, respectively), because the presence of vinyl acetate groups imparts rigidity to the main chain, which in turn, impedes rotation. The glass transition of PP is much lower than that of PVOH resins because of its non-polar character and higher flexibility of the molecular chains.

In the glassy region of PVOH 2019, thermal energy is insufficient to surmount the potential barriers for transitional and rotational motions of segments of the polymer molecules. The chain segments are frozen in fixed positions. Above the T_g , the amorphous polymer becomes softer and more flexible because the polymer chains are free to move, and a reduction of at least one order of magnitude in the modulus is observed. This reduction of modulus is due to the initiation of micro-Brownian motion of the molecular chains from the frozen state with increasing temperature (99,100).

Figures 4-14 and 4-15 show a slight displacement of the β -peak (corresponding to PP) to lower temperatures with PVOH content. For blends of PP with PVOH 1003, the T_g of PP changes from 14° to 10° C, while PP/PVOH 2019 blends' T_g changes from 14° to 6° C. As explained before for tensile testing results, water has a profound effect on the polymer properties, particularly if the resin is water-soluble, which is the case of PVOH. Jackson (101) has shown that water can be considered as a plasticizer for polar polymers. In the case of PVOH, only a few percent of water is enough to greatly reduce its glass transition temperature. This occurs because usually plasticizers tend to increase the free volume. The shift of T_g in blends containing PVOH 2019 is reasonable, provided that those blends contain PVOH in the form of domains dispersed into the PP matrix. The shift of T_g in blends with PVOH 2019 is higher than that found in blends with PVOH 1003, because the former is more sensitive to water.

The β -peaks corresponding to PVOH in the blends are not so evident because the magnitude of the β -peaks is dependent on the concentration of the components of

the blend. In the blend systems, the PVOH resins were used at relatively low concentrations, which makes the resolution of the peaks a difficult task.

Figures 4-14 and 4-15 also show that the $\tan \delta$ - temperature curves change randomly with PVOH content. If PVOH is considered to be a rigid filler, two possible trends in the damping can be observed: reduction or increase of damping with increasing filler content. The reduction of damping has not been clearly explained, while the increasing of damping by the addition of a filler, has been attributed to the introduction of new damping mechanisms. The new damping mechanisms taking place could be: particle-particle frictions, where particles touch one another as in weak agglomerates; particle-polymer frictions, where there is not good adhesion at the interface, and excess damping in the polymer near the interface because of induced thermal stresses or changes in polymer conformation or morphology.

Figure 4-16 shows a very slight reduction of the β -peak corresponding to PP in blends. The presence of PVOH in the blends promotes absorption of water, which lowers the T_g . The T_g for PGV2 (90/5/5) and PGV2 (85/10/5) are approximately the same, because even though a decrease of the glass transition temperature is caused by the plasticizing effect of water, an increase of the glass transition temperature is also promoted because of the introduction of bulky side groups that impede rotation. This indicates that a compromise is established, and for low concentrations of g-PP the T_g does not display significant changes.

The $\tan \delta$ - temperature curve of g-PP shows two β -peaks which correspond to the PP and the PP-g-MAH segments. The dynamic mechanical properties of copolymers are strongly influenced by the characteristics of the homopolymers and the composition of the copolymer (99). The composition of g-PP is unknown, but from the $\tan \delta$ - temperature curve of pure g-PP, one can see that the copolymer used in this study is heterogeneous, and the homopolymers tend to be insoluble in each other,

because both peaks corresponding to each of the components of the copolymer are detectable. The contribution of g-PP to the blends is not so clear in the $\tan \delta$ -temperature curves.

Figures 4-17 to 4-19 show the storage moduli (E') versus temperature for the studied blend systems. An increase of the modulus below T_g as PVOH and g-PP content increases is observed in Figures 4-17 and 4-18, and in Figure 4-19, respectively. The storage modulus below T_g in PP/PVOH 1003 blends changes from 4×10^9 dynes/cm² for pure PP, to 9×10^9 dynes/cm² for PP/PV1 (70/30) blends (Figure 4-17). In blends of PP with PVOH 2019, the storage modulus changes from 5×10^9 dynes/cm² for pure PP, to 9.5×10^9 dynes/cm² for blends containing 30% PVOH 2019 (Figure 4-18). In PP/g-PP/PVOH 2019 blends (Figure 4-19), the storage modulus changes from 5×10^9 dynes/cm² for pure PP, to 9.5×10^9 dynes/cm² for PGV2 (85/10/5), which is greater than that of PP/PV2 (95/5) (7×10^9 dynes/cm²). The storage modulus is a measure of the energy stored and recovered per cycle. It is usually presented as a measure of the strength of the polymer. In Figure 4-17, an increase of the modulus above T_g is also observed for PP/PVOH 1003 blends. Above T_g , the storage modulus changes from 9×10^8 dynes/cm² for pure PP, to 9.7×10^9 dynes/cm² for pure PVOH 1003. The modulus increases with PVOH 1003 content because PVOH 1003 is more rigid than PP, and consequently, when added to a PP matrix, it increases the modulus of the blend.

Figure 4-18 shows the storage modulus of blends of PP with PVOH 2019. A similar behavior to that of PP/PVOH 1003 blend systems is observed at temperatures below T_g . After T_g , the blends containing PVOH 2019 exhibit an increase in modulus over the pure PP, while the (90/10) composition shows a strong decrease of the modulus. For blends with 10% PVOH 2019, the dynamic modulus is below that of the (95/5) composition, but above that of the pure PP (the storage modulus of PP/PV2

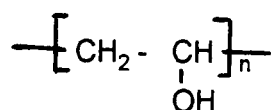
(90/10) is equal to 9.5×10^9 dynes/cm²). The PP/PV2 (90/10) blend clearly shows phase separation. The (80/20) and (70/30) PP/PVOH blends show the same kind of behavior in which the modulus-temperature curves do not change too much. This behavior can be attributed to the effect that the filler has on the modulus above T_g . It has been shown that rigid fillers have a larger effect in the modulus above T_g , because the modulus ratio E_2/E_1 of the components is larger in the rubbery state compared to the rigid glassy state (65).

Figure 4-18 also shows that the drop of modulus of the pure PVOH 2019 is steeper than that of pure PP and PP/PVOH 2019 blends. The drop of modulus begins around 40 °C and stabilizes at 110 °C which indicates a very broad range of temperature at which different molecular motions occur. This is because of the presence of bulky side groups, such as vinyl acetate groups, and other imperfections, such as 1,2-glycol structures in PVOH 2019.

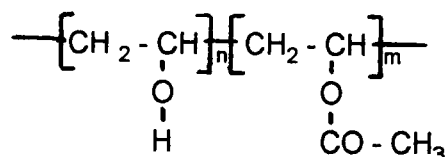
The modulus-temperature curves of blends containing g-PP are also shown in Figure 4-19. As the compatibilizing agent apparently improves adhesion by promoting the formation of hydrogen bonding, an increase of the dynamic modulus with g-PP is observed.

5.7. WATER ADSORPTION.

Poly(vinyl alcohol) is soluble in water. The solubility of PVOH in water is due to the presence of hydroxyl groups. The effect of the degree of hydrolysis is especially significant; the existence of many hydroxyl groups leads to have high affinity for water, with strong hydrogen bonding between the intra- and intermolecular hydroxyl groups, affecting the solubility of the resin in water. This is the case of PVOH 1003, whose degree of hydrolysis is greater than 98%. PVOH 1003 is a fully hydrolyzed poly(vinyl alcohol) resin which structure is:



The repeat unit of PVOH 2019 can be represented by:



this general representation does not indicate the features of non-random acetate-side-group distribution, and of the presence of side-chains, both of which are of significance in relation to the physical properties.

The principal structural variations in polymers are: chain length, chain length distribution, chain branching, chain branching distribution, and side-chain stereoregularity. More specific to PVOH resins, important structural variations include the degree of hydrolysis, or alternatively, the degree of acetylation.

There is a great deal of uncertainty regarding these structural features in PVOH resins. It is well known that the nature of several, if not all, of these features is related to the methods and conditions of polymerization of the poly(vinyl acetate) from which the poly(vinyl alcohol) is prepared. Since these conditions are rarely, if ever, published for commercial polymers, the structural characteristics and other important features such as, degree of polymerization, molecular weight, molecular weight distribution, etc., of the PVOH resins used in this work are unknown.

It should also be realized that commercial PVOH resins may be prepared to a particular specification by blending separate polymers of possibly different origins and properties, which will tend to broaden the range of the structural features previously mentioned.

The residual acetate groups in partially hydrolyzed PVOH 2019 weaken the intra- and intermolecular hydrogen bonding of adjoining hydroxyl groups. The presence of an adequate amount of these acetate groups increases the water solubility.

Sakurada (21) and Timasheff (102) have shown that with an increase in the number of acetate groups, the negative heat of dissolution (evolution of heat) increases, the critical temperature of the phase separation is lower, and the solubility at high temperatures decreases gradually. Since the presence of residual acetate groups weakens hydrogen bonding between the intra- and intermolecular hydroxyl groups, the solubility of partially hydrolyzed PVOH 2019 in water is higher than that of fully hydrolyzed PVOH 1003. Figures 4-35 (a) and 4-36 (a) clearly show this observation: PVOH 2019 completely dissolves in water after being immersed in the liquid for just one hour, while PVOH 1003 experiences swelling or uptake of water for up to 7 hours (8 to 0.3 % gain in weight) after which, a certain degree of dissolution occurs (1.3 % reduction of weight). PVOH 2019 blends require less time immersed in water for partial dissolution to occur (2 hours) causing a decrease in the sample weight (2.9 % for a (95/5) composition, to 9.1 % for PP/PV2 (70/30)), while blends with PVOH 1003 exhibit swelling (0.3 to 6.8 % gain in weight) followed by a certain degree of dissolution after an immersion time of 7 hours (1.7 to 4.4 % reduction of weight).

The solubility of PVOH films varies to certain extent with the heat treatment during which the film is dried (103). Heat treatment causes the crystallinity of fully hydrolyzed PVOH to increase, but if the heat treatment is kept below 100 °C, the solubility of fully hydrolyzed grades do not changes too much. Figure 5-5 shows the effect of heat treatment on crystallinity of PVOH. In the case of partially hydrolyzed PVOH resins, the water solubility remains almost constant unless the resins are subjected to severe treatment of 180 °C for periods of time longer than one hour (103). This indicates that the crystallinity of the films of the different samples used in this work

was not altered by heat treatment, because the samples were heated for 8 hours at 80 °C.

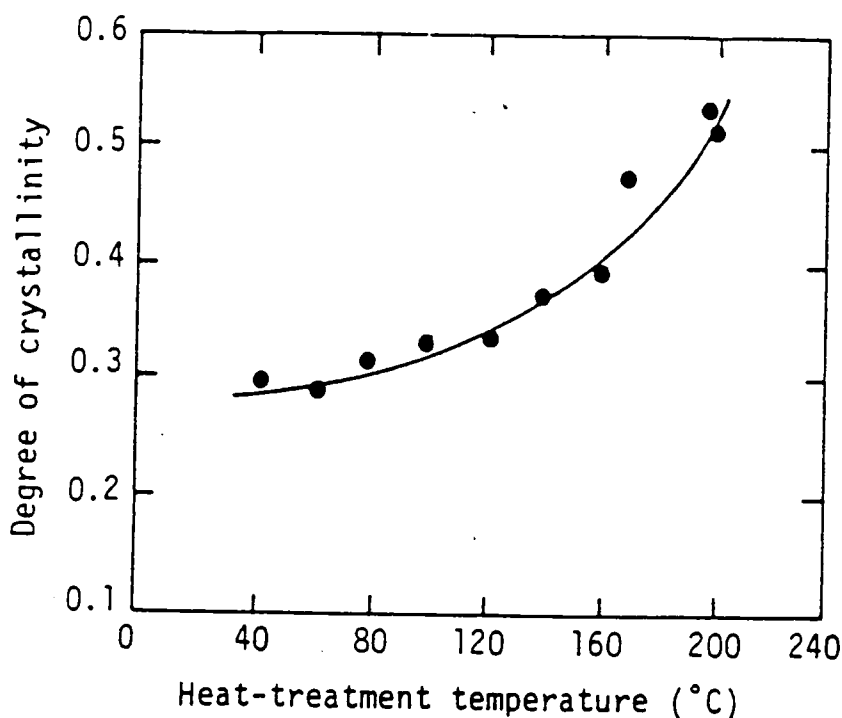


Figure 5-5. Effect of heat treatment on crystallinity of poly(vinyl alcohol) (103).

Many studies have been published on the modification of polypropylene in order to improve its adhesion with other materials that could broaden its practical usefulness (104-106). Other investigations involve modification of PP by the incorporation of mineral fillers such as talc, in order to improve its stiffness, strength, ability to adsorb water, and heat distortion (107). In this work, PVOH was added to PP in order to improve the wettability of the polyolefin. Figures 4-35 (a) and 4-36 (a) show that the weight of the PP samples is not altered at any immersion times. This is due to the fact that PP is a nonpolar polymer with outstanding chemical resistance. Polypropylene can

be slightly affected (swollen) by some nonpolar hydrocarbons. When PP is blended with PVOH, the PVOH domains, which definitely are affected by water, either swell or dissolve (or both), indicating that the addition of PVOH into the PP matrix does improve the wettability of the polyolefin.

Blends of PP with PVOH 2019 could be used for applications in which uptake of water for short periods of time is required. After 2 hours in contact with water, the PVOH domains will dissolve, and the adsorption of water will no longer be possible. In the case of PP/PVOH 1003 blends, the uptake of water could take place for longer periods of time (up to 7 hours), allowing these blends to be more effective in applications where adsorption of water is necessary.

In the case of blends with g-PP (Figure 4-37), the presence of the compatibilizing agent in the blends containing both PP and 5% PVOH 2019, differs from the behavior exhibited by PP/PV2 (95/5) samples, because in the latter, swelling occurs (1.3 % gain in weight) followed by dissolution of the PVOH 2019 after an immersion time of 2 hours, while samples containing g-PP exhibit swelling up to 7 hours of immersion in water (3.1 to 10.7 % gain in weight), after which, certain decrease in weight of the samples is observed (3.6 to 8.1 % reduction of weight), in a lower extent than that showed by PP/PV2 (95/5) blend systems. Dissolution of the samples is more difficult as g-PP content increases because the degree of crystallinity of the samples is increased (Table 14). This indicates that the addition of g-PP to blends containing 5% PVOH 2019 considerably increases the period of time at which the uptake of water takes place (from 2 hours for PP/PV2 (95/5) to 7 hours for compatibilized blends). For instance, blends containing g-PP and very small amounts of PVOH 2019 (5 %) could be effective in applications where adsorption of water is needed, for periods of time up to 7 hours.

VI. CONCLUSIONS.

In this study, new blends of polypropylene (PP) and water-soluble poly(vinyl alcohol) (PVOH) were developed and characterized. A graft-copolymer, PP-g-MAH, was blended at different compositions with PP and 5% PVOH 2019. The thermal properties, mechanical properties, dynamic mechanical properties, morphology, crystallinity, and water adsorption ability of the blends were studied. The conclusions obtained based on the results presented in this thesis can be summarized as follows:

1. PP/PVOH blends are immiscible at the studied compositions (5, 10, 20, and 30 % PVOH).
2. The PVOH content in PP/PVOH blend systems affects the mechanical properties of the blends. Results of tensile tests have shown that both tensile strength and elongation-to-break decrease with increasing PVOH content for dry and wet samples, while the modulus increases with composition for dry samples, and decreases as PVOH content increases for wet samples.
3. The results obtained from tensile tests imply that Kerner's prediction for the modulus of filled systems is a good fit for the experimental data of PP/PVOH blends, as well as Nielsen's prediction for tensile strength and elongation to break.
4. Blends containing g-PP exhibit an improvement of the mechanical properties. The results obtained from tensile tests, study of the morphology, and FTIR show that g-PP acts as a compatibilizing agent in the blends.

5. The morphology studies show that among the three different blend systems, the PP/g-PP/PVOH 2019 blends have the best mixing quality.
6. The moisture in the air strongly affects the mechanical properties of the blend systems.
7. Studies of the thermal properties of PP/PVOH blend systems have shown an increase in the crystallization temperature of PP with increasing PVOH content, which indicates that PVOH is acting as a nucleating agent.
8. Blends containing PVOH 2019 exhibit a tendency to absorb water up to 2 hours of immersion in the liquid, after which, dissolution of the PVOH starts to occur, while in blends with PVOH 1003, the uptake of water can take place up to 7 hours of immersion in water. When g-PP is added, the adsorption of water of the blends containing 5% PVOH 2019 can occur for 7 hours.

VII. RECOMMENDATIONS.

Based upon the results obtained in this thesis, further work should focus on:

1. Drawing of the phase diagrams of PP and PVOH, and PP/g-PP/PVOH 2019 systems in order to understand the thermodynamic behavior of these blend systems.
2. Blending of PP with higher concentrations of PVOH in order to study the properties of the resulting blends, and the phase inversion phenomenon.
3. Studies of the blended systems by Small Angle Neutron Scattering with regard to their compatibility and miscibility in the melt.
4. Study of the blended systems to examine their possible commercial importance in the nonwovens industry.

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