Structure and properties of β-polypropylene films

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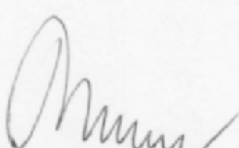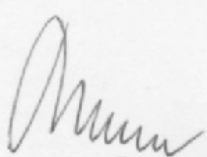
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ABSTRACT

In this master thesis the structure and properties of β-polypropylene films have been observed. Commercially available isotactic polypropylene Mosten 58412 and random copolymer Mosten GB 802 were modified by specific β-nucleation agent based on N,N´-dicyclohexyl-2,6-naphthalenedicarboxamide (NJ Star NU 100). From these materials the neat and nucleated films were cast using various chill roll temperatures (30, 60 and 90°C). Structure and properties of original materials and final cast films were studied with the help of differential scanning calorimetry, wide-angle X-ray scattering, scanning electron microscopy, polarized light microscopy, density measurement and mechanical properties.

ABSTRAKT

V této diplomové práci byla zkoumána struktura a vlastnosti fólií z β-polypropylenu. Komerčně dostupné polypropylény - izotaktický polypropylen Mosten 58412 a statistický kopolymer Mosten GB 802 - byly modifikovány přídavkem specifického β-nukleačního činidla chemicky založeného na N,N´-dicyklohexyl-2,6-naftalendikarboxamidu (NJ Star NU 100). Z těchto materiálů byly vytlačeny čisté a nukleované fólie při různých teplotách chladícího válce (30, 60, 90°C). Struktura a vlastnosti jak vstupních materiálů, tak i finálních fólií byly zjišťovány pomocí diferenciální snímací kalorimetrie, rentgenografie, snímací elektronové mikroskopie, polarizační mikroskopie, měření hustoty a mechanických vlastností.

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I would like to thank my supervisor, Martin Obadal, for the master-thesis leadership, help with experiments, incentive discussions, valuable advice and suggestions and for language corrrections. My sincere gratitude belongs to Jiřina Dohnalová for help with X-ray measurement.

I declare I worked on this Master Thesis by myself and I have mentioned all the used literature.

Zlín, 12. May 2006   ………………………..

                                                                              Dana Hnidáková

CONTENTS

INTRODUCTION

In today's period, conventional materials, such as metals, wood, glass and natural fibers are replaced by polymeric materials. Since the beginning of 20th century, they have found their way from the research lab to virtually any industrial application, ranging from medical to automotive, and from building industry to production of children toys.

Similarly, isotactic polypropylene has become one of the most commonly used thermoplastics. This fact rises from its versatility. The polymer exhibits excellent chemical resistance, low density, high tensile strength, relatively high melting point. One of the most often method of polypropylene processing is extrusion. Polypropylene film unambiguously belongs to versatile packaging materials. Almost 90% of plastic packaging is used in food applications. Other applications include film packaging for stationery products, cigarettes, and textiles.

Recently, there have appeared interesting film applications based on the use of β-nucleated polypropylene. This approach allows manufacturing sheets with enhanced thermoforming ability (with extended processing window) or using specific drawing condition to produce microporous film with breathable features. In this context, the aim of this work is to produce cast films from β-polypropylene at different processing conditions and to evaluate their structure with a particular interest directed towards an optimisation of β-phase content in cast films. Indeed, an integral part of the work is a basic assessment of their thermal and mechanical properties and drawability. For these purposes, cast films are prepared from commercially available isotactic polypropylenes Mosten 58412 homopolymer and from Mosten GB 802 random copolymer modified by a β-nucleating agent NJ Star NU 100 in the concentration of 0.03 wt. % of the nucleator. As known, the application of this amount leads to rapid increase of β-phase content and to the achievement of the maximum impact strength. An investigation of prepared films is carried out using several experimental techniques, namely wide-angle X-ray scattering, differential scanning calorimetry, polarized light microscopy, scanning electron microscopy, density measurement and tensile testing.

I. THEORETICAL BACKGROUND

1   POLYPROPYLENE

Professor Giulio Natta produced the first polypropylene resin in Spain in 1954. Natta utilised catalysts developed for the polyethylene industry and applied the technology to propylene gas. Commercial production began in 1957 and polypropylene usage has displayed strong growth from this date. Its versatility (the ability to adapt to a wide range of fabrication methods and applications) has sustained growth rates enabling polypropylene (PP) [1].

Polypropylene is an economical material that offers a combination of outstanding physical, chemical, mechanical, thermal and electrical properties not found in any other thermoplastic. Compared to low or high density polyethylene, it has a lower impact strength, but superior working temperature and tensile strength [2].

Polypropylene (PP) is a linear hydrocarbon polymer, schematically expressed as

$$-\!\left[CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}\right]_n$$
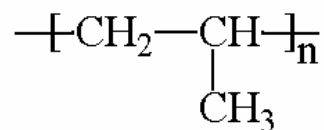
Fig.I.1 Polypropylene

1.1   Structure

Structurally, it is a vinyl polymer, and is similar to polyethylene, only that on every other carbon atom in the backbone chain it has an attached methyl group. Polypropylene can be made from the monomer propylene by Ziegler-Natta polymerization and by metallocene catalysis polymerization.
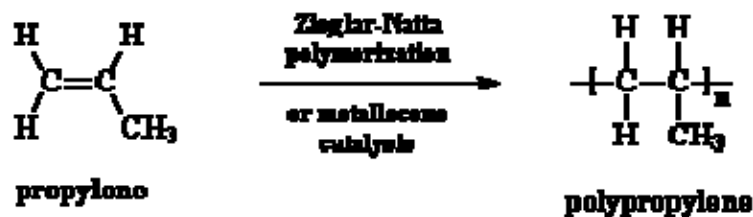
Fig. I.2 Polymerization of propylene

Consequently, polypropylene can be made with different tacticities. Most polypropylene we use is *isotactic* [3].

This means that all the methyl groups are on the same side of the chain, as follows:
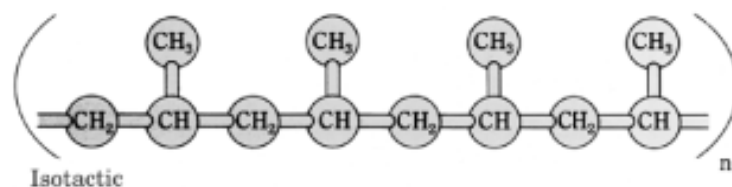
Fig. I.3 Isotactic polypropylene

In syndiotactic polypropylene, middle, consecutive pendant methyl groups are on opposite sides of the polymer backbone chain.

Fig. I.4 Syndiotactic polypropylene

But sometimes we use *atactic* polypropylene. *Atactic* means that the methyl groups are placed randomly on both sides of the chain, as follows:

Fig. I.5 Atactic polypropylene

However, using special metallocene catalysts, it is believed that we can make polymers that contain blocks of isotactic polypropylene and blocks of atactic polypropylene in the same polymer chain.

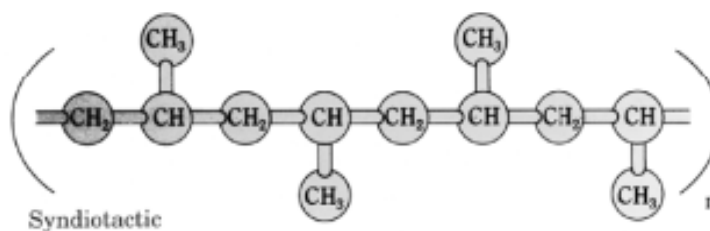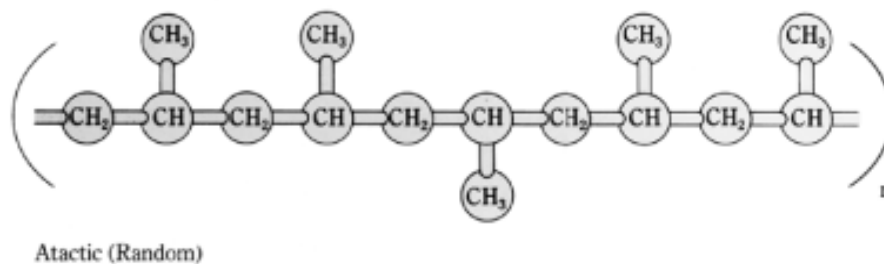This polymer is rubbery, and makes a good elastomer. This is because the isotactic blocks will form crystals by themselves. But because the isotactic blocks are joined to the atactic blocks, the little hard clumps of crystalline isotactic polypropylene are tied together by soft rubbery tethers of atactic polypropylene [3].

1.2   Properties of Isotactic Polypropylene

Mechanical properties of isotactic PP (iPP) strongly depend on its crystallinity. Increasing crystallinity enhances stiffness, yield stress, and flexural strength, however, decreases toughness and impact strength.

IPP does not present stress-cracking problems and offers excellent electrical and chemical resistance at higher temperatures. While the properties of iPP are similar to those of polyethylene, there are specific differences. These include a lower density, higher softening point and higher rigidity and hardness. Additives are applied to all commercially produce polypropylene resins to protect the polymer during processing and to enhance end-use performance [1].

1.3   Polymorphism of Isotactic Polypropylene

Each application of isotactic polypropylene needs macroscopic properties which are essentially based on the final supermolecular structure of polymer. Properties of isotactic polypropylene, because of its polymorphism, strongly depend on the supermolecular arrangement and phase composition of material [4].

Crystalline Structures in Isotactic Polypropylene

α-form   β -form   γ -form
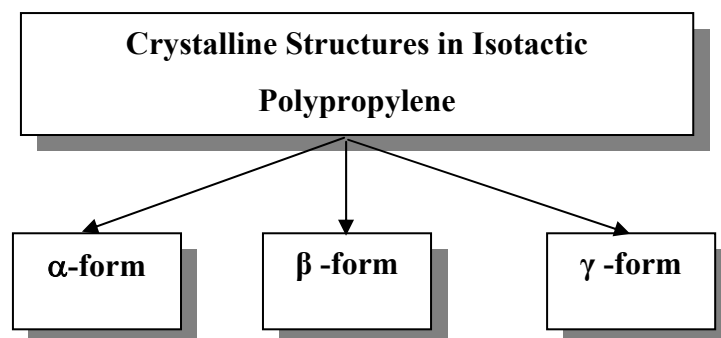
1.3.1 α-form of isotactic polypropylene

Polymer chains in the α-form of isotactic polypropylene form a helical structure in a monoclinic unit cell, with dimensions of 20.8 Å x 6.6 Å x 6.5 Å and fold into lamellae with thicknesses of 50–200 Å [5, 6].

Radial growth of lamellae is dominant; however, lamellae can also associate tangentially, with the tangential lamella branching off approximately orthogonally from the plane of the radial lamellae. This forms a cross-hatched structure in the lamellae, which aggregate to form spherulites [5, 7].

The lamellar structure produces positive, negative, and mixed birefringence. Negative birefringence results from spherulites in which radial lamella are dominant, while positive birefringence is due to spherulites with predominantly tangential lamellae. Both negatively and positively birefringent spherulites form a Maltese cross pattern under crossed polarizers. In spherulites with mixed birefringence, neither tangential nor radial lamellae are predominant, and a distinct Maltese cross is not formed. The birefringence changes from positive to negative with increasing crystallization temperature, as the tangential lamella undergo premelting [5, 8].

The α-form of isotactic polypropylene is the primary form of polypropylene obtained under normal processing conditions [6].

1.3.2 β-form of isotactic polypropylene

The β-form of isotactic polypropylene has a trigonal unit cell structure, with more disorder than the α-form. The parallel, stacked lamellae do not show cross-hatching. Lamella have been observed to form sheaf-like spherulitic structures with interconnected boundaries, different from the distinct boundaries of α-form spherulites; in experiments with high purity β-form polypropylene, this structure resulted in lower elastic moduli and yield strength at a given strain rate and higher impact strength and breaking strain values than α-form polypropylene.

The β-phase is observed only occasionally during crystallization from the melt, and its higher amounts can only be achieved by using special crystallization conditions or selective β-nucleating agents. The addition of selective β-nucleators is the most reliable

method to prepare β phase [9]. In general, the arrangement of macromolecules in the β-phase is less tight than that in the α-phase. This results in lower density and approx. 20°C lower melting temperature of the material with dominanting β-phase (β-PP), as compared to PP containing solely the α-phase (α-PP).

The content of the β-phase significantly influences the mechanical and optical properties of the material. Consequently, isotactic polypropylene containing the β-phase is currently classified among common polymeric materials and rated as a suitable alternative to conventional α polypropylene for specific applications. The application of β-iPP is favored in some fields which is based on its high-impact resistance and toughness. Other application fields are exploiting the micro-void formation and strain-hardening characteristics as well as the βα-recrystalization tendecy during partial melting of β-iPP.

From the scientific and patent literature, it is known that β-iPP is used for:

❑   industrial pipeline construction

❑   dielectric capacitors with roughened surface

❑   paper-like films

❑   uniaxially and biaxially stretched microporous film for gas exchange membranes

❑   porous fibers with improved moisture adsorption [9].

1.3.3   γ-form of isotactic polypropylene

The γ-form of isotactic polypropylene was initially considered to have a triclinic unit cell with dimensions similar to the α-form, but the crystal structure was recently reassigned as an orthorhombic unit cell with nonparallel, crossed lamellae.

In experiments with polypropylene crystallized at high pressures and different crystallization temperatures, the crossed lamellae formed a feather-like structure (*Figure I.6*) that was shown from microscopy to result from self-epitaxial (tangential) growth [5, 8].

γ-form polypropylene does not usually form under typical processing conditions. It can occur in low molecular weight materials (Mn ≅ 6000), during crystallization at ele-

vated pressures, or in chains with regular defects, produced using metallocene catalysts. The α-form is present at atmospheric pressure; as the pressure is increased, the γ-form begins to coexist with the α-form until it becomes dominant at a pressure of 200 MPa [7, 8, 10].

Figure I.6 Reflection optical micrograph of lamellae in isotactic

polypropylene arranged in feather-like structures. [8]

1.3.4 Smectic form

The mesomorphic or smectic form of polypropylene is a noncrystalline phase, intermediate in order between crystalline and amorphous forms. Early experiments indicated that this form might be a paracrystalline phase resulting from deformed or distorted lattice structures. Examples of lattice defects include atoms forced out of normal lattice or unit cell positions due to surrounding amorphous material, changes in polymer chain folding, the presence of atoms of foreign material in the lattice, and screw dislocations that disrupt the spherulite structure by initiating lamellar growth in an irregular location. Polymer chains have been shown to form helical structures, but the unit cell and lamellar structures have not yet been well resolved. Experiments indicate a lack of lamellar order in addition

to a low density and small size of ordered structures. These characteristics result in high clarity, useful in quenched film applications [11].

1.4 Commercial Forms of Isotactic Polypropylene

Polypropylene is produced commercially in different forms depending on the properties desired. Polypropylene homopolymer contains only propylene monomer in the polymer chain. Homopolymer provides stiffness and toughness but exhibits low impact strength at low temperatures, and clarity is too low for some applications.

Propylene copolymers contain one or more different types of monomers in the polymer chain. Random copolymers are used in applications requiring higher clarity or a lower melting point, and impact copolymers are used in automotive and other applications that require high impact resistance at low temperatures.

1.4.1 Homopolymers

The primary application of homopolymers is in the extrusion of fibers and filaments for cordage, webs, carpet backing and face yarns, upholstery fabrics, apparel, filters, geotextiles, disposable diapers, medical fabrics, fabric for automobile interiors, bags, and strapping tape.

Oriented and unoriented films are also extruded for pressure-sensitive tapes, electrical applications, shrink film, and packaging for retortable pouches. Sheets greater than 250 μm in thickness are used for counter tops and tank liners; thinner sheets are thermoformed into packaging containers.

Injection molded homopolymers are used in automobile parts, appliances, housewares, packaging containers, trigger sprayers, furniture, and toys [12, 13].

1.4.2   Random copolymers

Random copolymers are produced by adding the comonomer, ethylene or, less commonly, 1-butene or 1-hexene, to the reactor during the polymerization reaction [14]:

$$CH_2 = CH_2 \; CH_2 = CHCH_2CH_3$$

ethylene 1-butene

$$CH_2 = CHCH_2CH_2CH_2CH_3$$
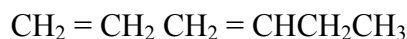
1-hexene

The comonomer substitutes for propylene in the growing polymer chain. Insertions are randomly or statistically distributed along the chain and can consist of single monomers, as shown for ethylene in *Figure I.7*, or multiple monomers (two or more sequential ethylene molecules along the polymer chain).

Random copolymers generally contain 1–7 wt. % ethylene, with 75% single and 25% multiple insertions. In practice, depending on the catalyst, polymerization conditions, and the reactivity of the comonomer compared to propylene, random copolymers can become somewhat blocky, with some regions of the polymer chain containing only polypropylene units and other regions containing only comonomer [12-15].

The structure of random copolymers is similar to isotactic polypropylene, but the regular, repeating arrangement of atoms is randomly disrupted by the presence of comonomer units. The effect is similar to that of increasing atacticity. Crystallinity is reduced, and mobility of the polymer chain is increased due to less steric interaction of the pendant methyl groups of polypropylene [15].
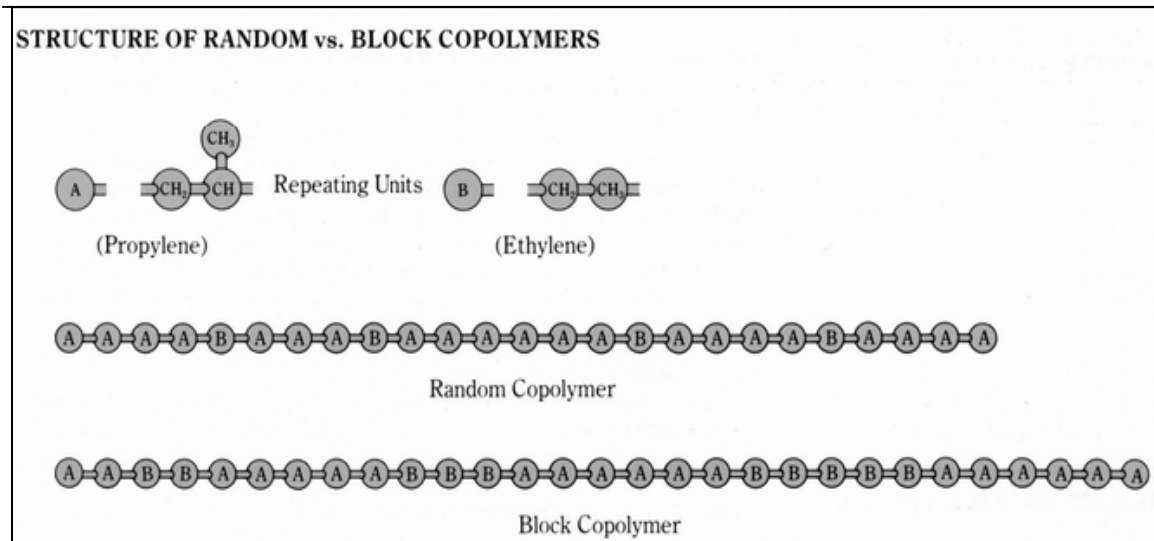
Figure I.7 Random and impact copolymers, shown using ethylene

as the copolymer [16]

1.4.3 Impact copolymers

Impact copolymers are formed by the addition of ethylene-propylene rubber (EPR), ethylenepropylene-diene monomer (EPDM), polyethylene, or plastomers to homopolymers or random copolymers. Copolymer levels in impact copolymers range from 5–25%. Plastomers are very low density (<0.880 g/cc) copolymers of ethylene and an olefin (such as ethylene-butene) produced using metallocene catalysts. Due to the single polymerization site on metallocene catalysts, comomomer can be inserted uniformly, producing a homogeneous compolymer with both elastomeric and plastic characteristics. They have a narrow molecular weight distribution and more long-chain branching than EPDM or EP rubbers [17-19].

1.5   Nucleating agents

Nucleating agents are added to polypropylene to improve processing characteristics and clarity and alter its mechanical properties. The addition of nucleating agents provides a

large number of sites for the initiation of crystallization, so that spherulites formed are smaller and more numerous than in unnucleated polypropylene. The effect of nucleation on spherulite size is shown in *Fig. I.8*. [15, 20].

Nucleation increases the crystallization temperature and the rate of crystallization; as a result, parts can be removed from the mold at higher temperatures, and molding cycle times are reduced. Crystallization is more complete in nucleated resins than in unnucleated resins producing high levels of crystallinity.

Nucleated materials have higher tensile strength, stiffness, flexural moduli and heat deflection temperatures than unnucleated materials, but impact strength can be lower. The high levels of crystallinity can result in reduced tolerance to radiation sterilization compared to unnucleated polypropylene, and the effectiveness of hindered amine light stabilizers and other stabilizing additives can be reduced. Because nucleated polypropylene shrinks more rapidly in the mold, shrinkage of the resin onto mold cores can occur if parts are not ejected fast enough [15, 21].

Clarity is enhanced due to the increased cooling rate and the decreased spherulite size, which reduces the scattering of light as it passes through the material. Smaller spherulites can reduce warpage in some applications and can provide a harder, more stainresistant surface [15, 21].

Nucleating agents used in polypropylene include carboxylic acid salts, benzyl sorbitols, and salts of organic phosphates. Carboxylic acid salts provide limited clarity enhancement but do enhance the mechanical properties by an increase in the crystallization rate. Dibenzylidene sorbitols reduce crystal size dramatically, resulting in greatly improved clarity. Benzyl sorbitols can result in odor generation during processing which produces odor in the finished part. Pigments, such as phthaloxyanine blue and green and phthalyl blue, and mineral fillers such as talc can also act as nucleating agents, although talc is not as effective [15, 20, 22]. Another important characteristics of some nucleator is their specific nucleating ability associated with iPP polymorphism.
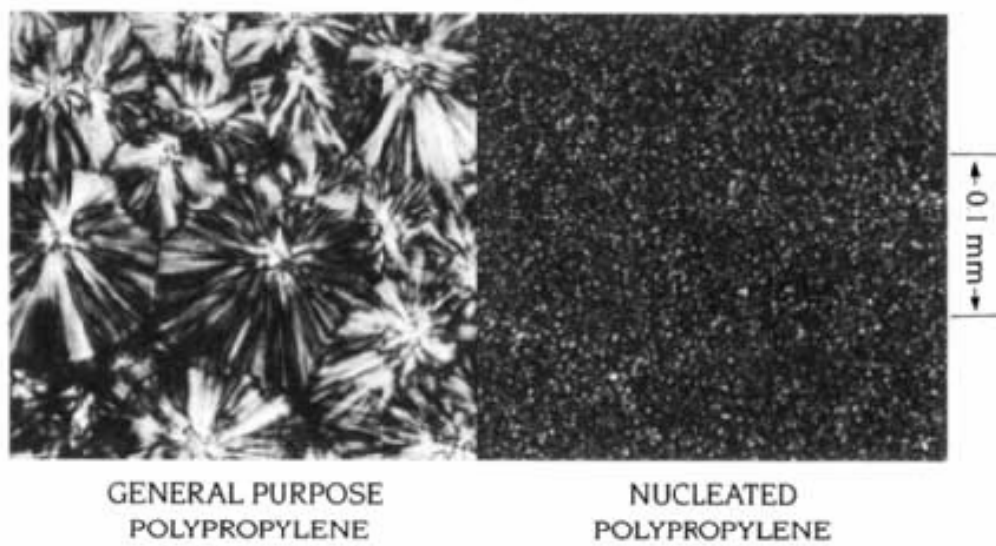
GENERAL PURPOSE
POLYPROPYLENE

NUCLEATED
POLYPROPYLENE

Figure I.8 An optical micrograph showing the effect of
a   nucleating agent on spherulite size.

2   FILMS

Polypropylene film is one of the most versatile packaging materials. It is economical due to its low density and is replacing other materials, such as polyethylene, polyvinyl chloride, polyester, and cellophane, in packaging applications. Almost 90% of plastic packaging is used in food applications; other applications include film packaging for stationery products, cigarettes, and textiles [23-25].

Both random copolymers and homopolymers are used in film production. Films can be unoriented, uniaxially oriented or biaxially oriented and are defined as sheet materials that are less than 0.254 mm (10 mils) in thickness; thicker films are referred to as sheets. Resins with melt flow indexes of ~2–8 g/10 minutes are generally used in films, although higher melt flow rate resins are also used. Higher melt flow resins are used in cast film processes [13, 16].

2.1   Unoriented film

Unoriented polypropylene films can be produced by casting or blown film processes. Chill roll casting and tubular water quenching are commonly used. Conventional air quenching, widely used for polyethylene, produces brittle films with poor clarity in polypropylene; however, newer polypropylene resins and copolymers developed for air quenched processes can provide economical alternatives to polyethylene. The tubular water quench process is commonly used to produce monolayer film [12, 14, 27].

Unoriented films have a very soft hand and are easily heat sealed. They exhibit good heat stability, low flexural moduli, excellent puncture resistance, excellent impact strength, and low moisture permeability but provide only poor barriers to gases, such as oxygen and carbon dioxide, some perfumes, and oil such as peppermint oil. Clarity of unoriented random copolymer film is moderate and is affected by processing conditions. Because its physical properties are balanced, unoriented film is easier to process on bag making equipment than cast oriented film, and slitting and sealing is easier in the transverse direction.

Applications include packaging for shirts, hosiery, bread, and produce, use as a strength and barrier layer in disposable diapers, and use in electrical capacitors [14, 27].

2.2   Cast film

Cast processes are usually used to produce uniaxially oriented film, oriented in the machine direction. Physical properties of the film depend on the degree of orientation, and a film is produced with different surface properties on each side.

Oriented cast polypropylene film is clear and glossy, with high tensile strength. It is about three times stiffer and stronger than low-density polyethylene film. Cast film provides good moisture barrier properties and scuff resistance at low cost. Low temperature brittleness is a problem with homopolymer polypropylene film; this can be overcome by the use of a copolymer resin [16, 23].

A water bath is sometimes used instead of a chill or casting roll; the water bath process quenches the melt on both sides at the same time, producing a film with the same surface properties on each side. The machine direction orientation in the water bath process is somewhat different than that obtained using the casting roll, and the very rapid quenching lowers the crystallinity, producing a tougher film [16].

Tear initiation, by impact, puncture, or ripping, is difficult in oriented polypropylene films (OPP); once initiated, however, the resistance to tear propagation is low. Tear strength depends on grade and process conditions and on whether the tear propagates in the machine or transverse direction. A tear strip is usually incorporated in OPP film packs to facilitate opening [16, 26].

2.3   Biaxially oriented film

Biaxially oriented polypropylene film (BOPP) is film stretched in both the machine and transverse directions, producing molecular chain orientation in two directions. BOPP film is produced by the tubular process, in which a tubular bubble is inflated, or a tenter frame process, in which a thick extruded sheet is heated to the softening point (not to the melting point) and is mechanically stretched by 300–400%. Stretching in the tenter frame

process is usually 4.5:1 in the machine direction and 8.0:1 in the transverse direction, although ratios are fully adjustable. It is a widely used process, more common than the tubular process, and a glossy, transparent film is produced.

Biaxial orientation results in increased toughness, increased stiffness, enhanced clarity, improved oil and grease resistance, and enhanced barrier properties to water vapor and oxygen. Impact resistance, low temperature impact resistance, and flexcrack resistance are substantially modified. BOPP films are used in food packaging and are replacing cellophane in applications such as snack and tobacco packaging due to favorable properties and low cost [16, 25].

Oriented films can be used as heat shrinkable films in shrink wrap applications or can be heat set to provide dimensional stability. Heat sealing is difficult in BOPP films but can be made easier by either coating the film after processing with a heatsealable material (such as polyvinylidene chloride) or by coextrusion with one or more copolymers before processing, to produce layers of film.

Copolymers used in sealing layers must have high gloss and clarity and should have low sealing temperatures to prevent distortion of the oriented polymer during sealing. Random copolymers containing 3–7% ethylene are often used as sealing layers; the lower melting point (<132°C) results in a 30% increase in line speeds, and they can be recycled with no significant loss of strength or clarity. Coating or coextrusion increases the barrier properties of BOPP film, decreasing its permeability to gases. Common barrier polymers are ethylene vinyl alcohol, polyvinylidene chloride, and polyamide; five or more layers may be coextruded or laminated, or the barrier polymer can be dispersed in the matrix polymer [16, 25, 28].

Recently it has been reported that biaxially oriented film with high levels of microvoiding can be produced using material containing higher amounts of β-phase. The microvoiding is caused by β-to-α phase transformation during drawing. It can also results in a significant density reduction of the final film and even in a production of films with high levels of vapor transmission or breathability [29, 30]. Another interesting film product based on β-phase polypropylene application is biaxially oriented film with a high degree of surface roughening which is important when the film is used as a capacitor dielectric. The roughened surface after drawing improves the impregnation properties of insulating oils [31].

3   METHODS OF ANALYSIS

3.1   Differential scanning calorimetry (DSC)

It is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment.

Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. DSC may also be used to observe the 2th order phase changes, such as glass transitions. DSC is widely DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing [32-34].

3.1.1   Power Compensated DSC
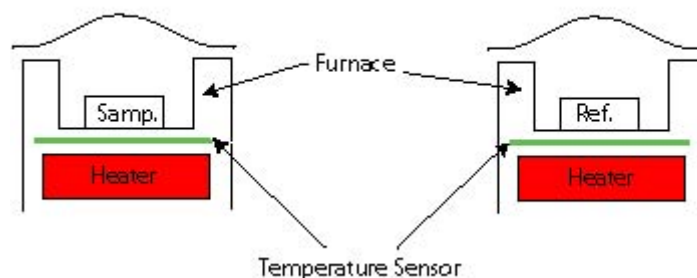
Fig. I.9 Diagram of a power compensated

differential scanning calorimeter

In power compensated calorimeters, separate heaters are used for the sample and reference. This is the classic DSC design pioneered by the Perkin-Elmer company. Both the sample and reference are maintained at the same temperature while monitoring the electrical power used by their heaters. The heating elements are kept very small (weighing about 1 gram) in order to ensure that heating, cooling, and thermal equilibration can occur as quickly as possible. The sample and reference are located above their respective heaters, and the temperatures are monitored using electronic temperature sensors located just beneath the samples. Generally platinum resistance thermometers are used due to the high melting point of platinum.

Electronically, the instruments consist of two temperature control circuits. An average temperature control circuit is used to monitor the progress of the temperature control program. This circuit is designed to assure that the temperature scanning program set by the operator is the average temperature of the sample and reference. A differential temperature control circuit is used to determine the relative temperatures of the sample and reference, and adjust the power going to the respective heaters in such a way as to maintain both at the same temperature. The output of the differential temperature control circuit is used to generate the DSC curve [32, 34].

3.1.2 DSC Curves

The result of a DSC experiment is a heating, cooling or isothermal curve. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:
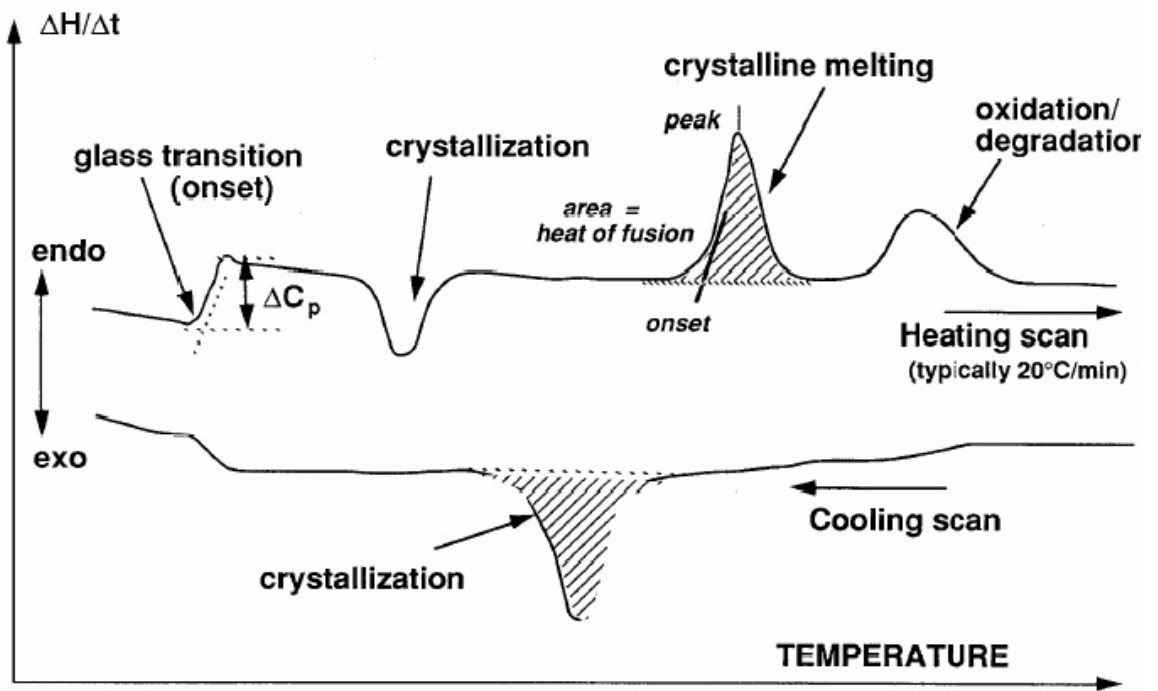
$$\Delta H = KA, \qquad (1)$$

where ΔH… the enthalpy of transition,
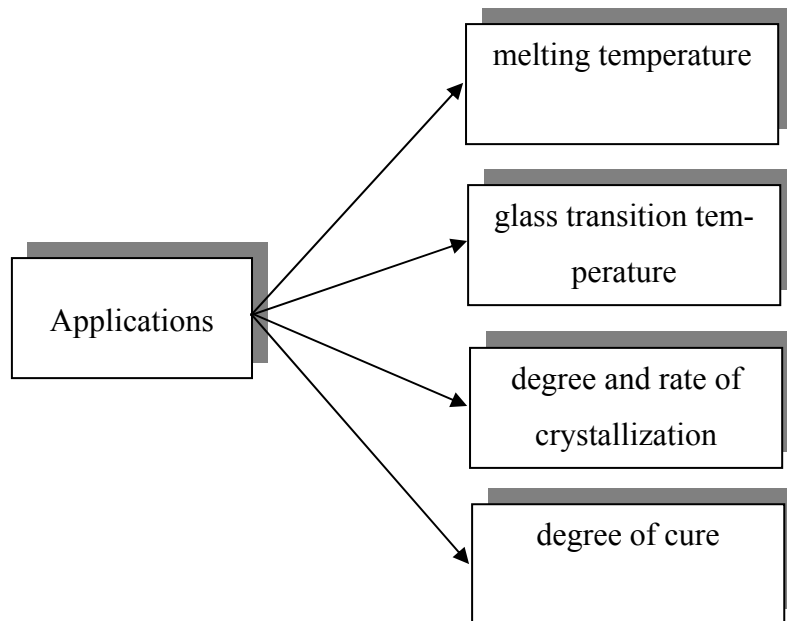
$\quad$ K … the calorimetric constant,

$\quad$ A … the area under the curve.

The calometric constant will vary instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition [33].

Fig.I.10 Typical polymer DSC thermogram [35]

3.2   Polarized light microscopy

Polarized light microscopy is a contrast-enhancing technique that may be utilized for both quantitative and qualitative analysis of optically anisotropic specimens. In order to reveal details that are poorly observed using traditional microscopy techniques, light microscopes must be equipped with a polarizer positioned in the light path before the specimen and an analyzer in the optical pathway between the observation tubes or camera port and the objective rear aperture. It is then the interaction of plane-polarized light with a birefringent specimen that results in image contrast. More specifically, this interaction produces two individual wave components with different velocities that fluctuate with the propagation direction through the specimen and that are each polarized in mutually perpendicular planes. When the light components pass through the specimen, they undergo phase alterations, but are eventually recombined with constructive and destructive interference when they pass through the analyzer [36].

The thickness of samples for polarized microscopy is largely dependend on the nature of polymer being analyzed. For instance, in case of polypropylene or poly(butylenes terephthalate) the spherulitic structures are quite fine and therefore sections with thickness of several microns are required.

Samples can be viewed between cross polars, using a polarized optical microscope to determine if the polymer is crystalline or has in-built orientation. If there is no specimen between the cross polar, then the field of view should be completely dark. By inserting a crystalline or oriented sample between the polars, the plane of polarized light is rotated and the sample appears bright. In white light, some colors are transmitted and others are not, and because of this birefringence, the sample appears brightly colored.

Useful information can also be obtained by interpreting the birefringence observed when a crystalline or oriented sample is viewed between cross polars. Polymer melts or stress-free glassy polymers show no optical anisotropy, and therefore the field of view is black. The main use of polarized microscopy has been to study the spherulitic morphology of semicrystalline polymers.

Under polarized light, semicrystalline polymers generally show banded polyhedral spherulites that impinge upon one another. The spherulites have sharp boundaries and a dark Maltese-cross (or isogyral extinction pattern) which is characteristic of spherulitic structures. The twisting nature of the radiating spherulitic fibrils produces regions in which the molecular axis is parallel to the direction of the polarized illumination. These areas of zero birefringence are seen as concentric extinction rings.

The degree of orientation at different regions of the image can be estimated by using a tint plate (or lambda plate), which is a compensator inserted at a 45° angle between the polarized filters. This causes blue or yellow interference colors to be observed [37].
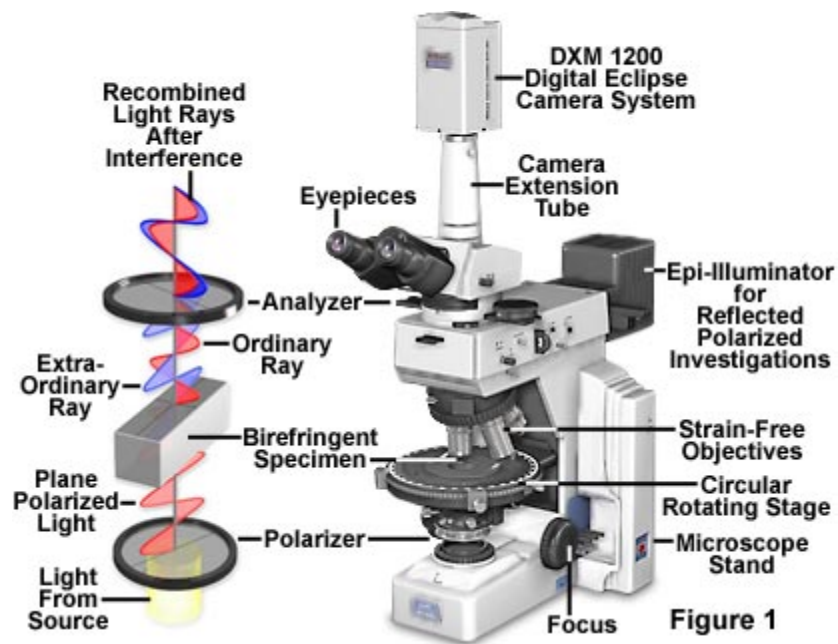
Fig.I.11 Polarized light Microscope configuration [36]

3.3 Scanning electron microscopy

Scanning electron microscope (SEM) is a microscope that uses electron rather than light to form an image. There are many advantages to using SEM instead of a light microscope.

SEM has a large depth of field, which allows a large amount of sample to be in focus at one time. SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes SEM one of the most common used instruments in research areas today.

SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. Th electron beam follows a vertical path through the columm of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image [38]. In *Figure I.12* is schematically shown how SEM works [38].
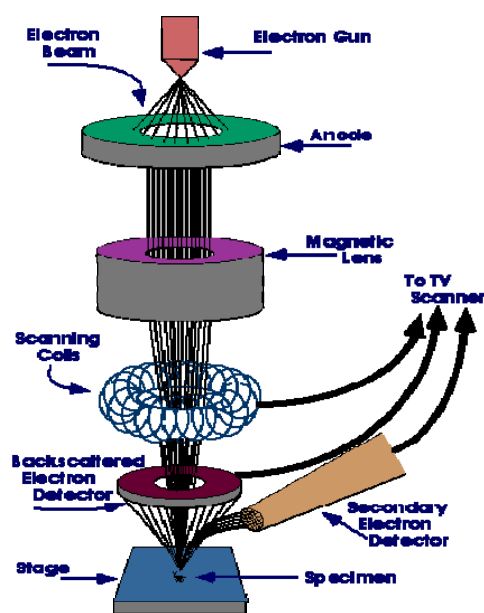
Fig.I.12 Scheme of SEM

3.4   X-Ray Methods

X-ray crystallography is a technique in crystallography in which the pattern produced by the diffraction of x-rays through the closely spaced lattice of atoms in a crystal is recorded and then analyzed to reveal the nature of that lattice. This generally leads to an understanding of the material and molecular structure of a substance. The spacings in the crystal lattice can be determined using Bragg's law. The electrons that surround the atoms, rather than the atomic nuclei themselves, are the entities which physically interact with the incoming X-ray photons. This technique is widely used in chemistry and biochemistry to determine the structures of an immense variety of molecules, including inorganic compounds, DNA and proteins [39].

By considering crystals as reflecting gratings for X-rays, Bragg derived his now famous equation for the distance d between successive identical planes of atoms in the crystal:

$$d = \frac{n \cdot \lambda}{2 \cdot \sin \theta} \qquad\qquad (2)$$

where λ is the X-ray wavelength, θ is the angle between the X-ray beam and these atomic planes, and n represents the order of diffraction, a whole number. It turns out that both the X-ray wavelength and the distance between crystals produces a series of spots.

See *Fig.I.13*
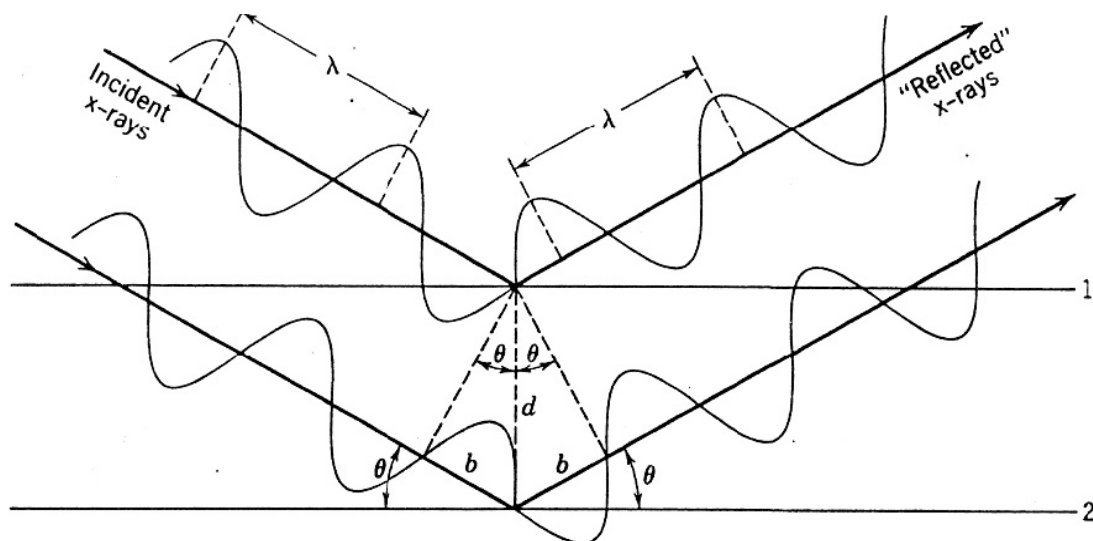
Fig.I.13 Geometry of the Bragg reflection analogy [40]

However, not every crystalline substance can be obtained in the form of macroscopic crystals. This led to the Debay-Scherrer method of analysis for powdered crystalline solids or polycrystalline specimens. The crystals are oriented at random so the spots become cones of diffracted beams that can be recorded either as circles on a flat photographic plate or as arcs on a strip of film encircling the specimen. The latter method permits the study of back reflections as well as forward reflections.

Basically, the intensity of the diffraction spot or line depends on the scattering power of the individual atoms, which in turn depends on the number of the atoms with regard to the crystal planes, the angle of reflection, the number of crystallographically equivalent sets of planes contributing, and the amplitude of the thermal vibrations of the atoms. Both the intensities of the spots or arcs and their positions are required to calculate the crystal lattice [37].

3.4.1   Percent Crystallinity in Polymers

Most polymers are semicrystalline; that is, a certain fraction of the material is amorphous, while the remaining part is crystalline. The reason why polymers fail to attain 100% crystallinity is kinetic, resulting from the inability of the polymer chains to completely disentangle and line up properly in a finite period of cooling or annealing. There are several methods for determining the percent crystallinity in such polymers. The first involves the determination of the heat of fusion of whole sample by calorimetric methods such as DSC.

A second method involves the determination of the density portion via X-ray analysis of the crystal structure, and determining the theoretical density of a 100% crystalline material. The density of the amorphous material can be determined from an extrapolation of the density from the melt to the temperature of interest.

A third method stems from the fact that the intensity of X-ray diffraction depends on the number of electrons involved and is thus proportional to the density. Besides Bragg diffraction lines for the crystalline portion, there is an amorphous halo caused by the amorphous portion of the polymer. This last occurs at a slightly smaller angle than the corresponding crystalline peak, because the atomic spacings are larger. The amorphous halo is broader than the corresponding crystalline peak, because of the molecular disorder.

This third method, sometimes called wide-angle X-ray scattering (WAXS), can be quantified by the crystallinity index, *CI*,

$$CI = \frac{A_c}{A_a + A_c} \qquad\qquad (3)$$

where *Ac* and *Aa* represent the area under the Bragg diffraction line and corresponding amorphous halo, respectively.

Naturally, these methods will not yield the same answer a given sample, but surprisingly good agreement is obtained. For many semicrystalline polymers, the crystallinity is

in the range of 40% to 75%. Of course, annealing usually increase crystallinity, as does orientation the polymer in fiber or film formation [37].

3.5   Tensile testing

Tensile tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. The data is often used to specify a material, to design parts to withstand application force and as a quality control check of materials. Since the physical properties of many materials (especially thermoplastics) can vary depending on ambient temperature, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment [41].

Tensile test is probably the simplest and most widely used test to characterize the mechanical properties of a material. Tests under conditions of constant rate of straining or stressing have been widely used for the mechanical evaluation of many classes of material long before they were adopted by the plastics community. When applied to plastics, ramp excitation is primarily used to measure strength, for which it is eminently satisfactory. However, during the initial stages of the ramp, it imposes an approximately constant straining rate on the specimen and with appropriate instrumentation short-term secant moduli and tangent moduli can be derived from the force-deformation curve. For plastics materials those moduli are multivalued because the force-deformation and stress-strain relationships vary with the deformation rate and the ambient conditions and additionally are not linear [42].

Tensile measurements of strength are simple to conduct and the results so generated are reliable, though not necessarily easy to interpret and not even meaningful if failure occurs far beyond the yield point. Tensile tests intended to measure modulus are more troublesome in that they should entail the use of an extensometer because actuator movement does not translate accurately into specimen strain. [42].

3.5.1 Tensile characteristics

During tensile test experiment, when a uniaxial loading is applied, the cross-sectional area of the specimen is changing appreciably toward the end of the loading. Clearly, the bar stretches along its axis and contracts in the radial direction. The effect of this lateral contraction, and the associated decrease in cross-sectional area, gives rise to a difference between true stress and engineering stress [43, 44].

Engineering stress and strain measures incorporate fixed reference quantities. In this case, undeformed cross-sectional area is used. True stress and strain measures account for changes in cross-sectional area by using the instantaneous values for area, giving more accurate measurements for events such as the tensile test (*Figure I.14*) [43, 44].
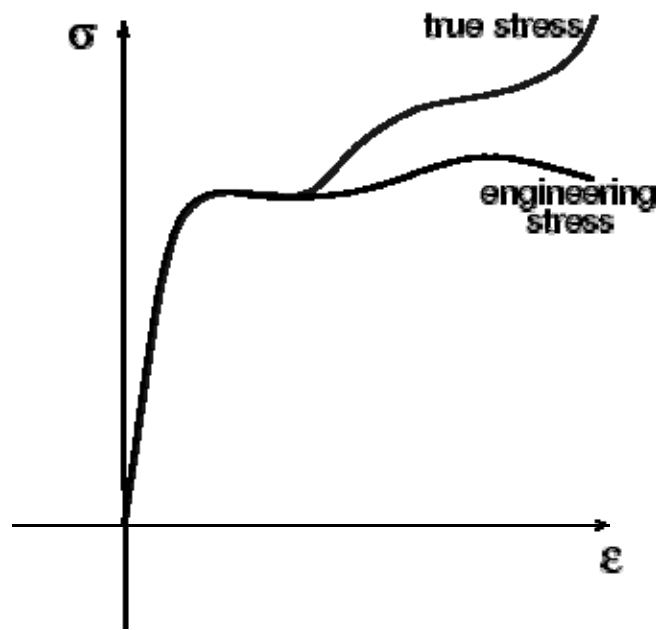
*Fig. I.14 Engineering stress-strain curve
vs. true stress-strain curve [43]*

Stress is an applied force or system of forces that tends to strain or deform a body. For a tensile test the stress is given by:

$$\sigma = \frac{F}{A_0} \quad \text{[MPa]} \tag{4}$$

Where σ is an evaluated value of a tensile stress, **F** is a measured force and A_0 is an original cross-sectional area of the specimen [43].

Strain and deformation produced by stress. Strain is defined as the fractional change in length of the specimen. For a tensile test specimen the strain is given by:

$$\varepsilon = \frac{(l - l_0)}{l_0} = \frac{\Delta l}{l_0} \cdot 100 \quad \text{[\%]} \tag{5}$$

Where ε is an evaluated value of a strain, l_0 is an original length of a specimen, **l** is a final length of the specimen and Δl is an elongation [43].

The stress-strain (*Figure 1.15*) curve shows the relationship between the stress and strain of the test specimen. It shows that the curve linear within the elastic range of the material. Any strain within the elastic range is reversible if the stress is removed. When the stress exceeds the elastic limit the material starts to deform plastically. This phenomenon is known as yielding of the material and the point at which it starts yielding is called yield point. Eventually the load reaches a maximum value, which is known as the ultimate tensile strength of the material. The specimen then starts necking (a reduction in area) before

it fails by fracture. Actually the history of the stress-strain curve showed in *Figure 1.15* is universal, the real history of the stress-strain curve is different and its history depends on tested kind of plastics and straining rate [45, 46].
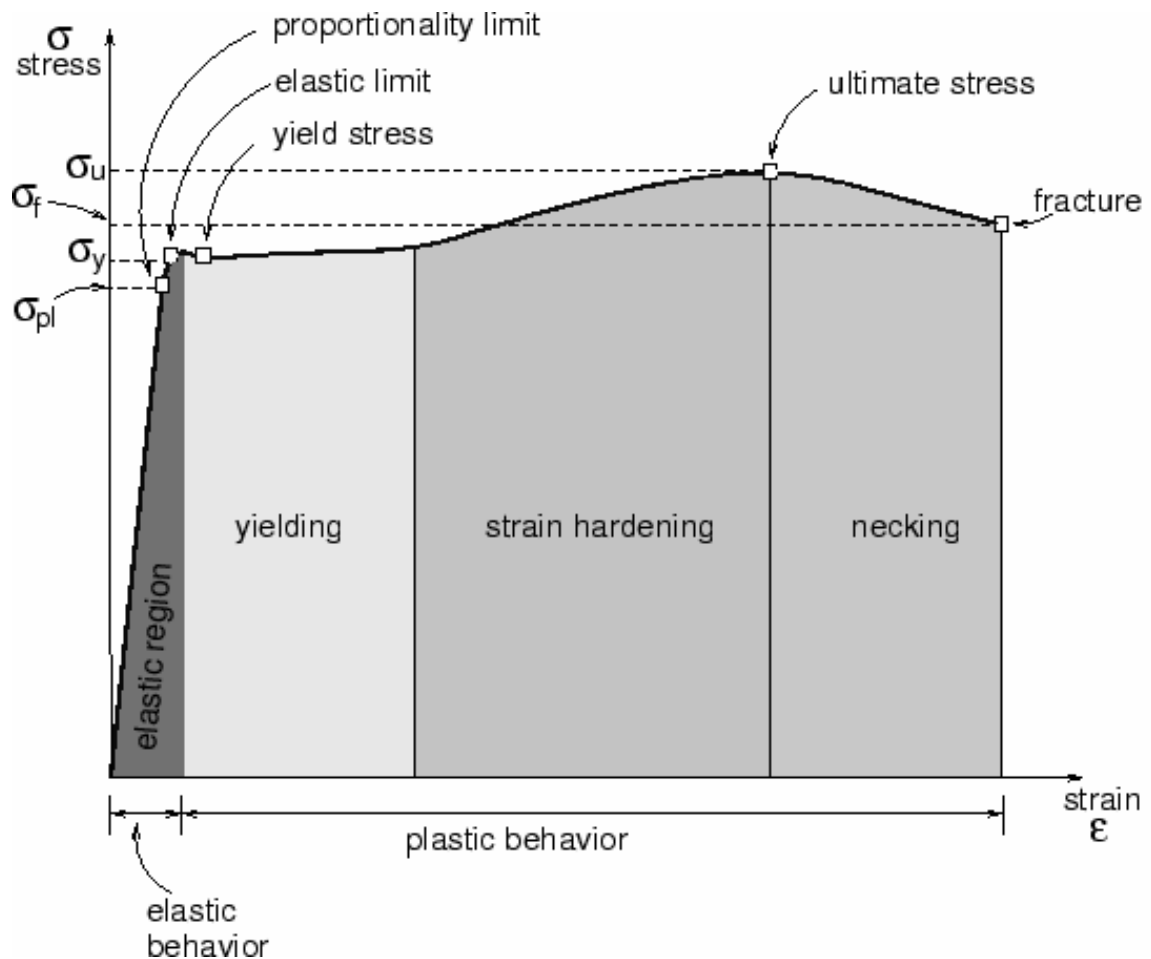
Fig. I.15 Stress-strain curve: σ_{pl} = proportionality limit, σ_y = yield stress, σ_f = fracture stress and σ_u = ultimate stress [43].

The yield stress, ultimate tensile stress, and elastic or Young's modulus of a material can all be determined from the stress-strain curve for that material. It is most often plotted using engineering stress and strain measures, because the reference length and cross-sectional area are easily measured [43, 44].

Most of the elastic region corresponds to linear-elastic response. Linear elasticity refers to the notion that stress is linearly proportional to strain. In the elastic region, the slope of the stress-strain curve is the Young's modulus. For a tensile test the Young modulus is given by:

$$\sigma = E \cdot \varepsilon \quad [MPa] \tag{6}$$

Where σ is an evaluated value of a tensile stress, E is a constant - Young's modulus and ε is a strain [43].

II. EXPERIMENTAL

4 SAMPLE PREPARATION

4.1 Materials

4.1.1 Polypropylene MOSTEN 58412

Commercially available isotactic polypropylene Mosten 58412, produced by Chemopetrol Litvinov a.s., Czech Republic, is homopolymer, with middle distribution of molecular weight *Mw* about 170000. It is multipurpose material, suitable for injection moulding, production of belts, ropes and cords, as well as sheets intended for subsequent thermoforming. Some characteristics of this material featured by producer are shown in *Tab.II.1*.

Tab.II. 1 Characteristics of PP MOSTEN 58412

Property	Unit	Typical merit	Test method
Melt flow index (230°C/2.16 kg)	g/10 min	3.3	ISO 1133
Density	kg/m^3	914	ISO 1183
Yield stress	MPa	34	ISO 527
Ultimate strength	MPa	22.5	ISO 527
Elongation at yield	%	7.6	ISO 527
Elongation at break	%	280	ISO 527
Flexural E-modulus	MPa	1450	ISO 178
Tension E-modulus	MPa	1600	ISO 527
Melting temperature	°C	155-168	ISO 11357
Isotacticity index	%	98.5-99	ISO 9113

4.1.2   Polypropylene GB 802

Polypropylene Mosten GB 802 is a random copolymer with a basic additivation, intended for production of preforms by injection blow moulding, for subsequent blow moulding of bottles. Typical application is production of bottles for non-carbonized beverages, fruit juices, oils, etc. Mosten GB 802 can also be used for standard blow moulding applications and for production of co-extruded thermoforming films, as well as for injection moulding. Some typical properties of this material are shown in *Tab. II.2*

Tab.II.2 Characteristics of PP GB 802

Property	Unit	Typical merit	Test method
Melt flow index (230°C/2.16kg)	g/10 min	2	ISO 1133
Density	kg/m^3	910	ISO 1183
Yield stress	MPa	27	ISO 527
Elongation at break	%	250	ISO 527
Flexural E-modulus	MPa	1000	ISO 178
Charpy notched impact strenght 23°C	kJ/m^2	21	ISO 179
Charpy notched impact strenght -20°C	kJ/m^2	1.8	ISO 179
Vicat softening temperature	°C	133	ISO 306

4.1.3 NJ Star NU100

Generally, the content of β-modification in iPP articles processed under common conditions is insignificant; therefore, to enhance the content of β-modification, NJ Star NU100 nucleating agent was used. Previous studies have confirmed its high nucleating activity; the addition of 0.03 wt. % nucleating agent led to β-modification content rise to 90 %. The chemical formula is N,N'-dicyclohexyl-2,6-naphtalenedicarboxoamide (*Figure II.1*) and it is produced by Rika Inc., United Kingdom.
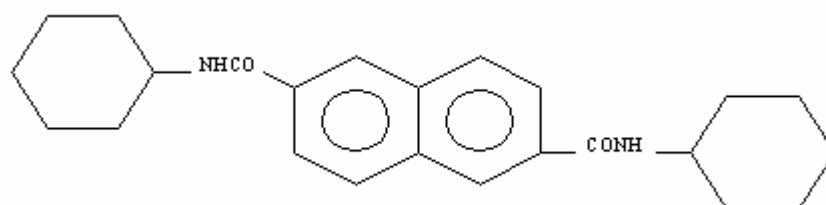
Fig. II.1 Nucleating agent NJ Star NU100

4.2   Blends

A Brabender DSK 42/6D twin screw extruder was used for preparation and homogenization of blends containing PP Mosten 58412 (or PP GB 802), NU100 nucleating agent and 0.3 wt.% of paraffin oil for better dispergation of the nucleating agent.

Firstly, the dried nucleating agent was dispersed by the help of paraffine oil (0.3 wt. %) among iPP pellets (or rPP pellets) in a container with a compounding element. Subsequently, the blend was rehomogeneized and repelleted by a Brabender DSK 42/6D twin-screw extruder.

4.3 Processing methods

4.3.1 Compression moulding

From prepared blends sheets were compression moulded using hand-press and appropriate frames with following dimensions: 125 x 60 x 0.50 mm and 125 x 125 x 2 mm. Processing conditions are mentioned in *Tab.II.3.*

Tab.II.3 Compression-moulding conditions

Temperature of press	Preheating time	Time of compression moulding	Cooling-hydraulic press	
210°C	3 min	4 min	60°C	130°C

4.3.2 Film Casting

Films with 100μm thickness were cast with an extruder equipped with a slit die from the pellets at extrusion temperature of 220°C and chill roll temperatures of 30°C, 60°C and 90°C. Screen speed was 35 rpm and barrel temperatures: 220°C, 200°C, 180°C, and 160°C, feed zone was cooled by cold water.

4.4 Specimens

4.4.1 Specimens for WAXS

Specimens for wide angle X-ray scattering (WAXS) were cut out from the central part of the samples prepared by compression moulding. The specimen dimension was 2 mm thickness, 10 mm width and 30 mm length. Specimens from casting films were prepared by the same way. The specimen dimension was 100μm thickness, 10 mm width and 30 mm length.

4.4.2 Specimens for DSC analysis

From the central part of compression moulded sheets, 6 mm diameter discs were cut out. The discs with weight approx. 9 mg were put into aluminous pan and covered with aluminous cover. The pan and the cover were crimped with a special tool supplied by Perkin-Elmer Co. The same process was carried out with the cast films. In this case, a weight of discs was about 2 mg.

4.4.3 Specimens for Polarized Light Microscopy

Compression moulded specimens for polarized light microscopy were cut out using a FOK GYEM OE-908 microtome. The prepared slices of thickness approx. 40 μm were placed on the slide, dripped by paraffin oil and covered by a mount.

4.4.4 Specimens for Scanning Electron Microscopy

Samples for SEM were prepared from central part of the drawing films. Samples were cut out using scissors and placed on the plastic corpuscle with help adhesive tape. Then they were coated with a very thin layer of gold by a machine called a sputter coater. Samples were placed inside the microscope vacuum column through an air-tight door.

4.4.5 Specimens for density measurement

Specimens for density measurement were prepared from central part of the cast films. They were cut out using scissors. Specimens were 100μm thickness, 15 mm width and 50 mm length.

4.4.6 Specimens for tensile test

Tensile dumbbell test bars with a gauge length of 115 mm, width 6 mm and thickness of 100μm cut out from the cast films according to ČSN EN ISO 527 (Tensile test).

5 ANALYZING METHODS AND DEVICES

5.1 Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) assessment of the cast films was performed in reflection mode with an URD 6 diffractometer equipped with CuKα. Radial scans of intensity vs. Diffraction angle *2θ* were recorded in the range of 10° to 30° by steps of 0.03° and length of step scan 5 s. The compression-moulded sheets were evaluated using the same diffractometer working in transmission mode. In this case, the measurement range was 10° to 30° with 0.04 step and 5 s scan.

5.2 DSC Analysis

For the purpose of this study, a power-compensated differential scanning calorimetr (DSC Pyris1, The Perkin-Elmer Co., USA) was employed. Nitrogen as a purge gas was used and constantly passed (20 ml/s) through the heat sink and over the cells. Temperature calibration was performed using indium as a standard. The compression-moulded samples were heated to 210°C at 10°C/min, hold at 210°C for 5 minutes to erase previous thermal history, the cooled down at 10°C/min and then finally heated to 190°C at 10°C/min. The cast films were heated to 190°C at various rates (10, 40°C/min) to observe their melting behaviour.

5.3 Polarized light microscopy

In order to study morphology of the crystallized samples, a Zeiss NU microscope was used. The samples were placed on the microscope stage and observed in the thorough polarized light. Micrographs of the observed structure were taken using a SONY F-717 digital camera. Common graphic software was used for editing of final images.

5.4   Scanning electron microscopy

Photographs of specimens were made with help of scanning electron microscope Jeol JSM-35.

5.5   Density measurement

Density measurement corresponded with the Standard ČSN 64 0111. It was applied hydrostatic method. As an immersion liquid, denatured ethanol was used. The density of the alcohol was measured using pycnometr method.

5.6   Tensile testing

Tensile properties of the cast films were determined by a Zwick tensile tester. The arrangement, realization and condition of each test corresponded with ČSN EN ISO 527 (Tensile test). Five specimens were tested under three constant straining rates - namely 100 mm.min^{-1}, 200 mm.min^{-1} and 10 mm.min^{-1}. Tensile characteristics were evaluated by tester internal software. Tensile test was measured without extensometer.

III. RESULTS AND DISCUSSION

6 ASSESSMENT OF BASE MATERIALS

6.1 X-Ray analysis

Relevant WAXS spectra of compression moulded samples are shown in *Figs III.1* and *III.2*. Namely, *Fig. III.1* illustrates the spectra of the compression moulded samples solidified at 130°C; it is evident that the strong diffraction maxima reflect regular crystalline structure. These diffraction peaks can be assigned to all known polypropylene polymorphism, see α_1, α_2, α_3, β and γ diffraction peaks. The most significant β-diffraction peak is visible in the compression moulded sample made from Beta-PP material solidified at 130°C. Small β-diffraction peak can also be observed in PP 58412 cooled at 130°C. This peak is not surprisingly visible in any compression moulded sample prepared from random PP even in the material containing nucleating agent. However, in this case, the polymorphic part within the crystalline phase consists of α and γ- phases. What is particularly interesting is the fact that nucleated random PP contains more γ-phase (the γ-peak is more significant) as compared to this material without nucleating agent.

Fig III.2 shows quite similar results as compared with *Fig.III.1*. Compression moulded samples, WAXS spectra of which are mentioned in this figure, were solidified at 60°C. It is clear that the most significant β-diffraction peak is visible in the sample prepared from Beta-PP material cooled at 60°C. This peak (in this case rather small) is also visible in the sample produced from random PP with nucleating agent at 60°C, the γ-diffraction peak is also visible – a rare three phase crystalline system in polypropylene is created.
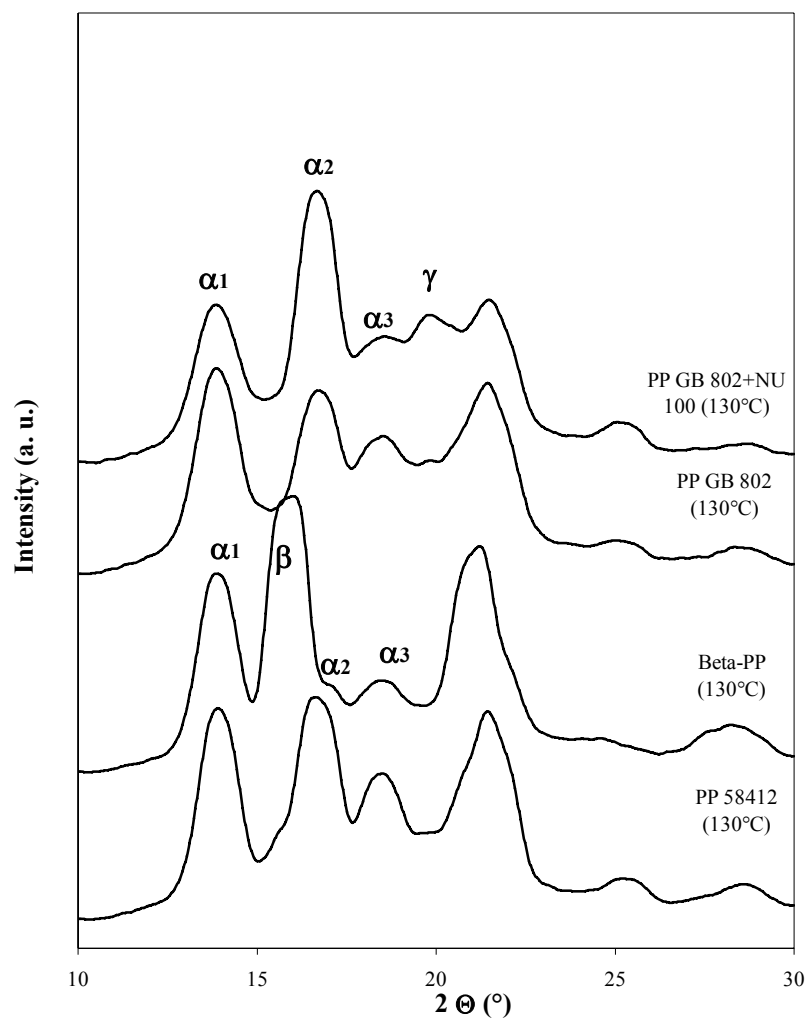
Fig. III.1 WAXS spectra of compression-moulded
samples solidified at 130°C
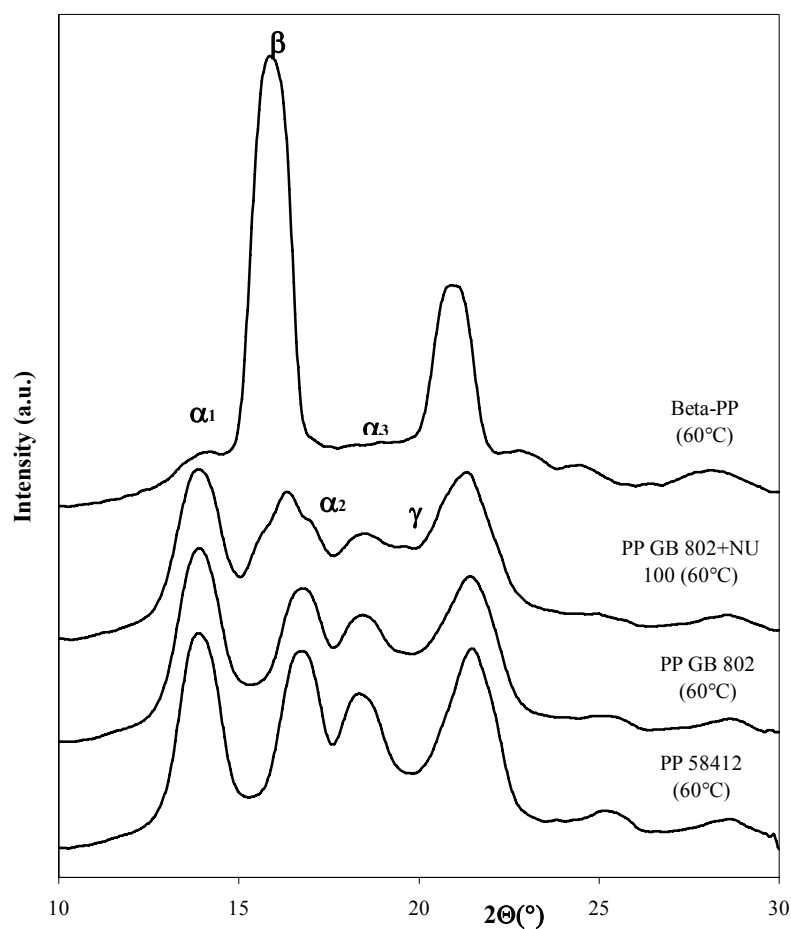
F*ig. III.2 WAXS spectra of compression-moulded*
samples solidified at 60°C

Figs III.3 and *III.4* show the percent of crystallinity of compression moulded samples. The highest crystallinity is observed for Beta-polypropylene cooled at temperature 130°C. This value is, however, very similar to neat homopolymer. It is interesting that neat random PP has a higher value of crystallinity than random PP with nucleating agent. As expected the overall crystallinity of random PPs is lower as compared to homopolymer because of the higher molecular irregularity in random PP. Similar situation can be observed in the samples solidified at 60°C.
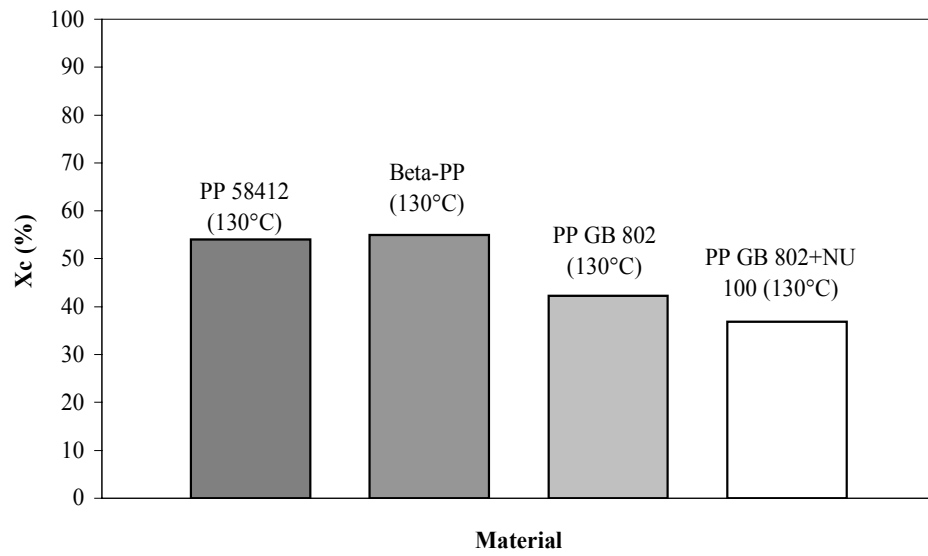
Fig. III.3 Relative crystallinity of compression-moulded samples solidified at 130°C
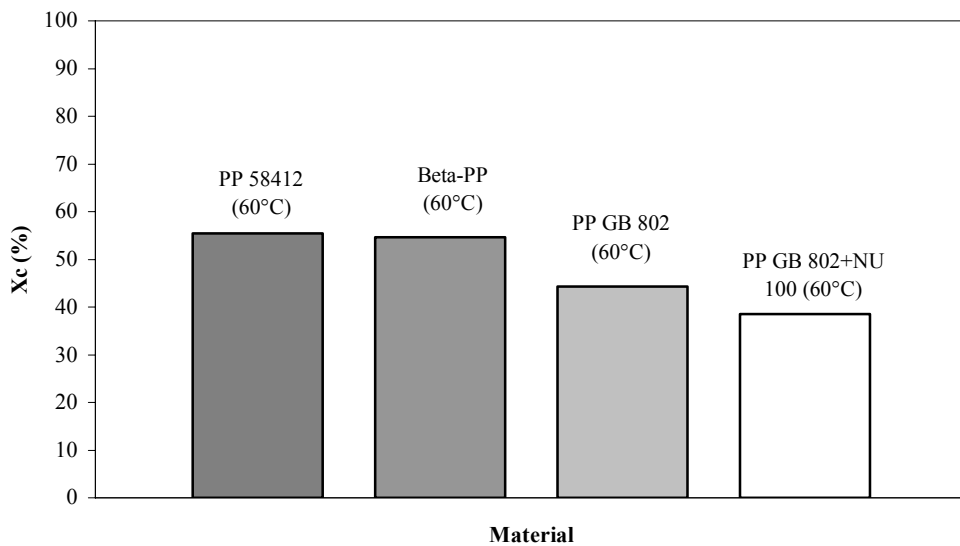
Fig.III.4 Relative crystallinity of compression-moulded samples solidified at 60°C

The variation of β-phase content (k value) is mentioned in *Fig. III.5*. As already drawn, the highest content of β-phase is observed at Beta-PP cooled at 60°C. The β-phase content is visible also in samples prepared from Beta-PP at 130°C, neat PP 58412 at 130°C and random PP with nucleating agent cooled at 60°C. In other samples the β-phase content was not detected. It can be stated out that a very high crystallization temperature does not support the β-phase formation in nucleated samples – both homopolymer and copolymer, as well.
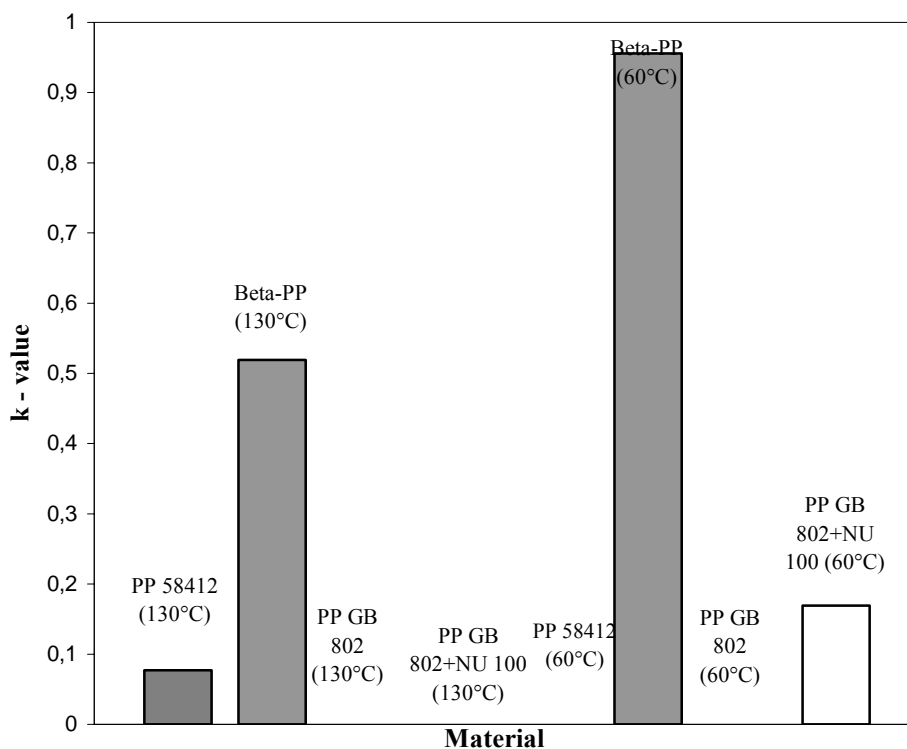
Fig.III.5 K-value (β-phase content) of compression-moulded samples solidified at different temperatures

6.2   DSC analysis

The compression moulded samples were analysed using DSC according to the method described in chapter 5.2.

Fig.III.6 shows crystallization exotherms of compression moulded samples cooled at a cooling rate of 10°C/min. From this figure it is evident that nucleated samples, namely Beta-PP and random PP GB 802+NU 100 crystallize earlier than the non-nucleated materials. The highest crystallization temperature represented maximum of exothermic peak is visible in Beta-PP. Generally, it can be said that the crystallizability of random PP is lower as compared to the homopolymer - although nucleated random PP contains a number of heterogeneous nuclei, the maximum of its crystallization peak is lower than that of neat homopolymer. The heat of crystallization is higher in nonnucleated samples than in nucleatedsamples (see *Tab.III.1*).
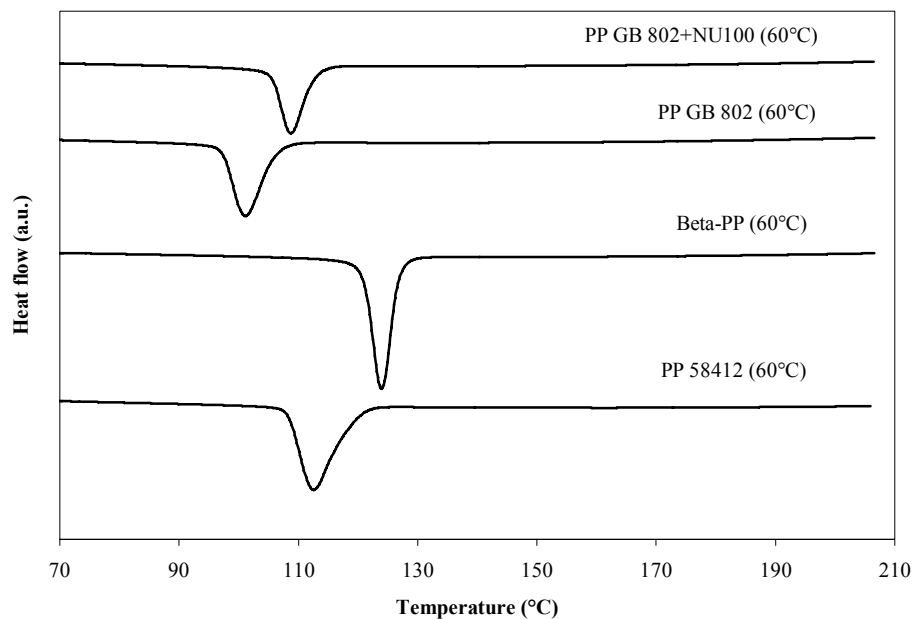
Fig. III.6 Crystallization exotherms of compression-moulded samples measured at cooling rate of 10°C/min

Fig. III.7 illustrates the melting thermograms of the samples, which were heated at a 10°C/min rate. From this figure, it is evident virtually the only one endothermic α-phase

melting peak in non-nucleated samples, namely in homopolymer PP 58412 and random PP GB 802. Two endothermic melting peaks, the β-phase and α-phase, can be observed in nucleated compression samples. This is particularly evident in Beta-PP. In this case, the melting peak of α-phase shows the doubling which generally connected with β to α recrystallization during heating. Samples prepared from homopolymer - both neat and nucleated - have higher melting temperature than samples from prepared random PPs. The melting temperature of both α- and β-phases is approx. 20°C shifted to lower values in the case of random PPs.
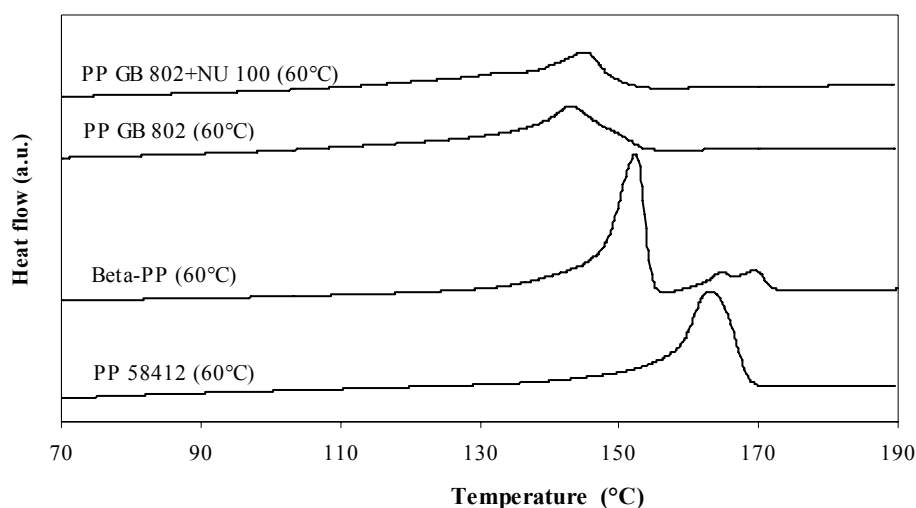
Fig. III.7 Melting endotherms of compression-moulded samples measured at heating rate of 10°C/min

Tab.III.1Melting and crystallization heat of compression-moulded samples

Material	ΔH_m (J/g)	ΔH_c (J/g)
PP 58412 (60°C)	90.274	123.037
Beta-PP (60°C)	98.101	94.043
PP GB 802 (60°C)	48.865	70.241
PP GB 802+NU 100 (60°C)	55.461	67.712

6.3 Microscopy

Polarized light microscopy provides information about the morphology of compression moulded specimens. Following figures show structure of neat and β-nucleated polypropylenes.
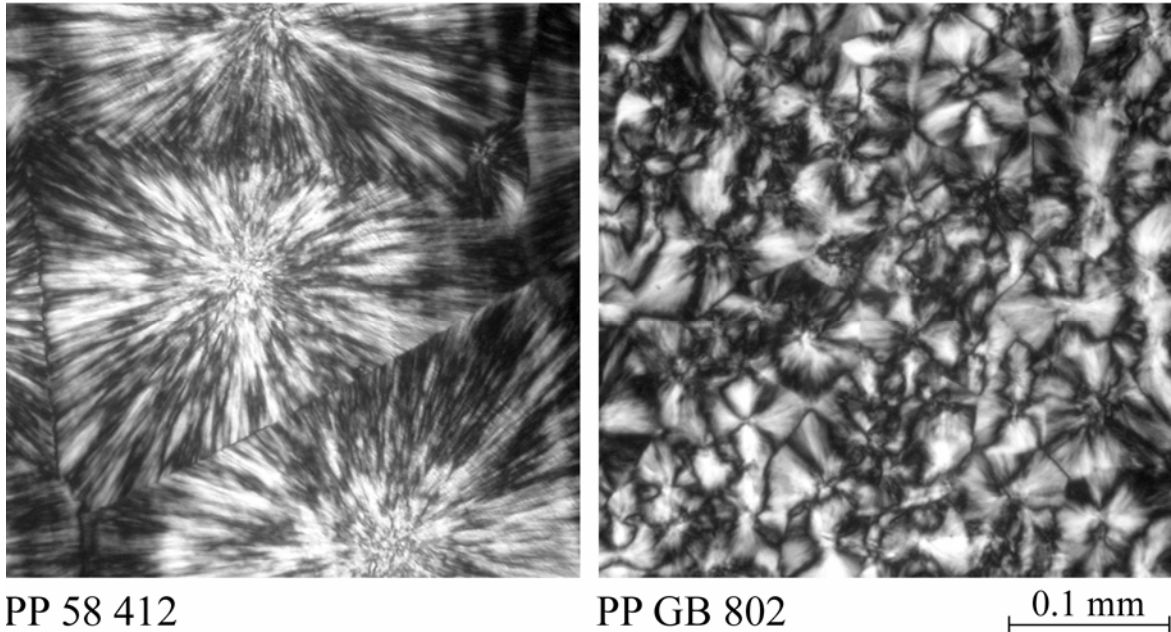
Fig.III.8 Morphology of neat polypropylenes solidified at 130°C
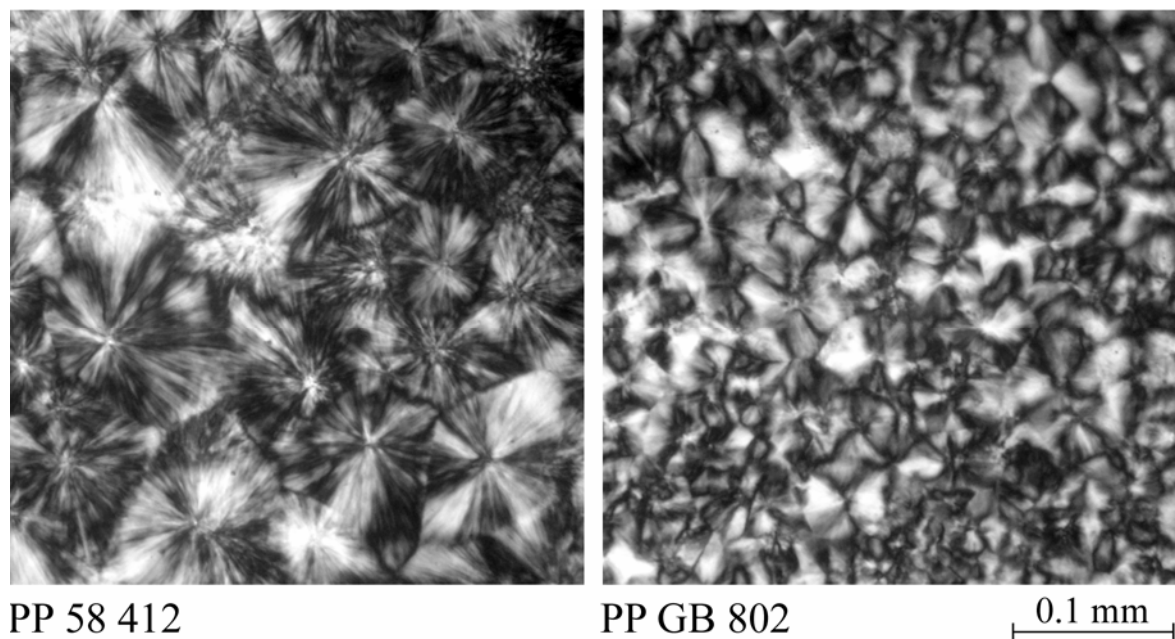
Fig.III.9 Morphology of neat polypropylenes solidified at 60°C
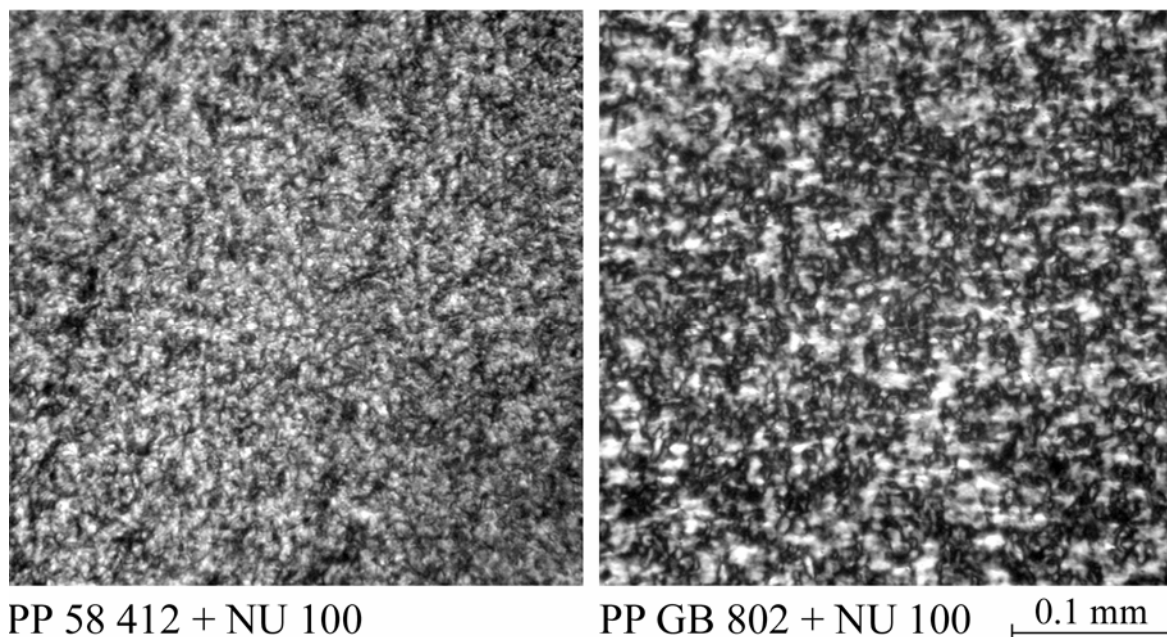
Fig.III.10 Morphology of β-nucleated polypropylenes solidified at 130°C
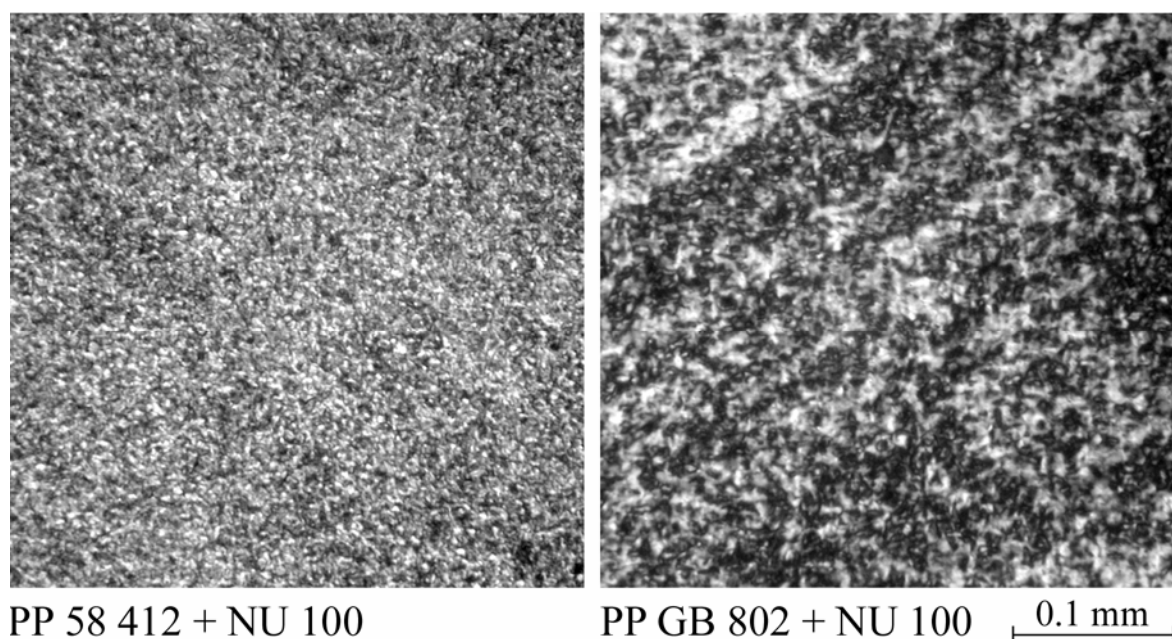
Fig.III.11 Morphology of β-nucleated polypropylenes solidified at 60°C

Figures III.8-III.11 show that the size of spherulites increases with increasing crystallization (solidification) temperature. From *Fig.III.8* and *III.9* it is visible that the size of spherulites in homopolymer PP 58412 is higher than the size of spherulites in random PP GB 802. Moreover, the effect of crystallization temperature on final morphology

is more significant in homopolymer. An opposite tendency is evident in the samples, which are nucleated as show figures *III.10* and *III.11*. It is interesting that the size of spherulites in Beta-PP is lower than the size of spherulites in random PP GB 802 with nucleating agent.

7 ASSESSMENT OF CAST FILMS

7.1 X-Ray analysis

First of all, the structure of cast films was evaluated. Relevant WAXS spectra are shown in *Figs III.12* and *III.13*. From a comparison of both figures it is evident that solidification at 90°C (setting of chill-roll) led to rather higher crystallinity of the films (indicaded by sharp diffraction maxima) while the spectra of the films cooled at 30°C show high amorphous halo and their structure can be assigned to smectic arrangement.

Fig. III.13 illustrates also the spectra of the films solidified at 60°C and it is evident that their structure does not show smectic arrangement and consists of regular crystalline structure. In the case of polymorphic composition, it is clear that the most significant β-diffraction peak is visible in the film made from Beta-PP material and cooled at 90°C. This peak is also visible in the film produced from random PP with nucleating agent at 90°C. In the film solidified at 30°C, the content of β-phase is virtually insignificant in all films. What is also particularly interesting is that although the films cooled at 60°C possess significant crystalline amounts, the β-diffraction peak even in β-PP is not important.
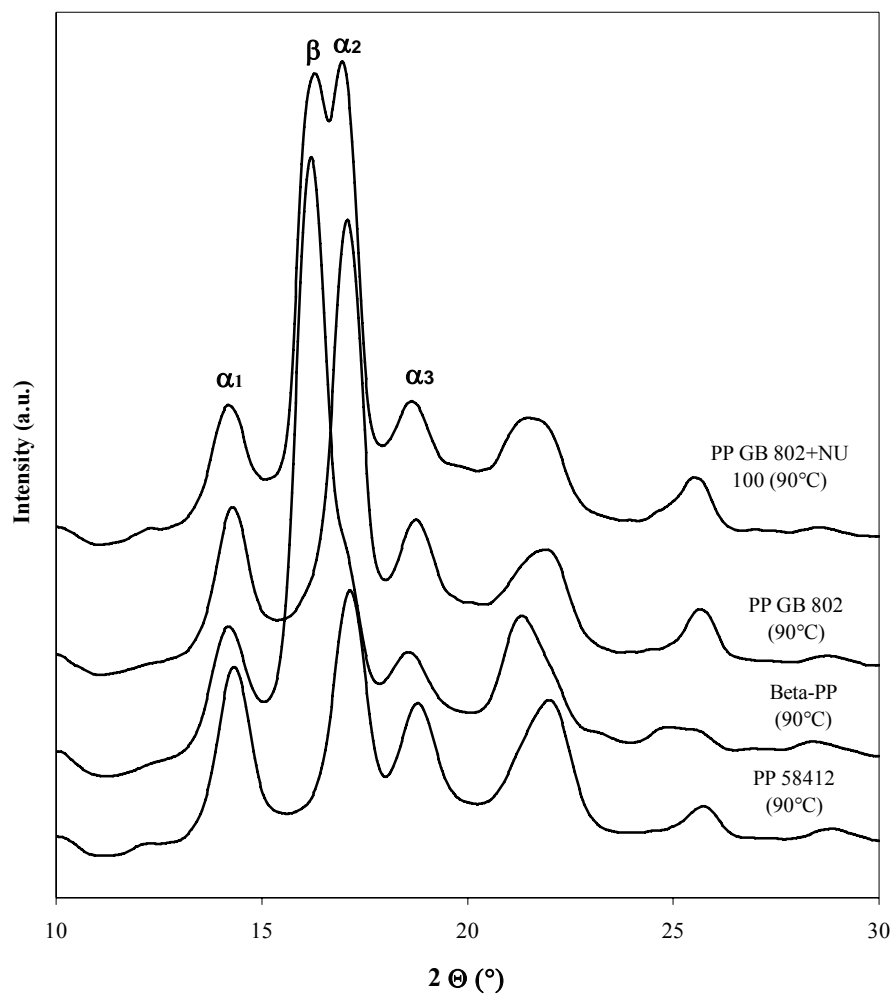
Fig.III.12 WAXS spectra of cast films solidified at 90°C

chill roll temperature
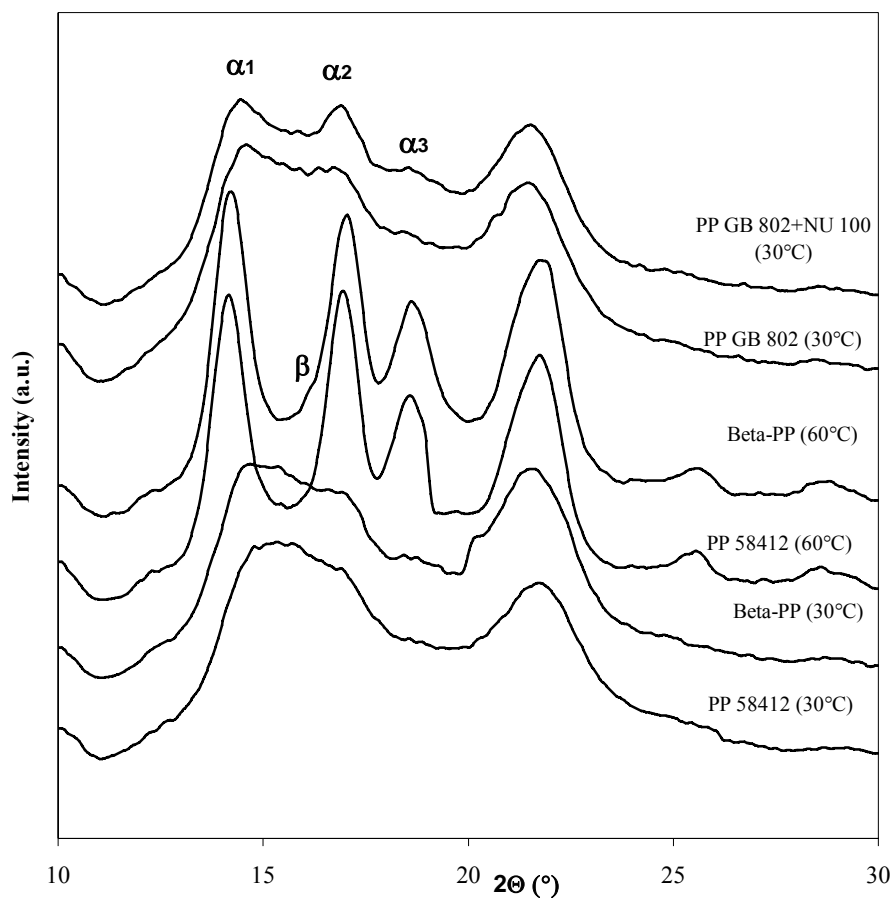
Fig.III.13 WAXS spectra of cast films solidified
at 30 and 60°C chill roll temperatures
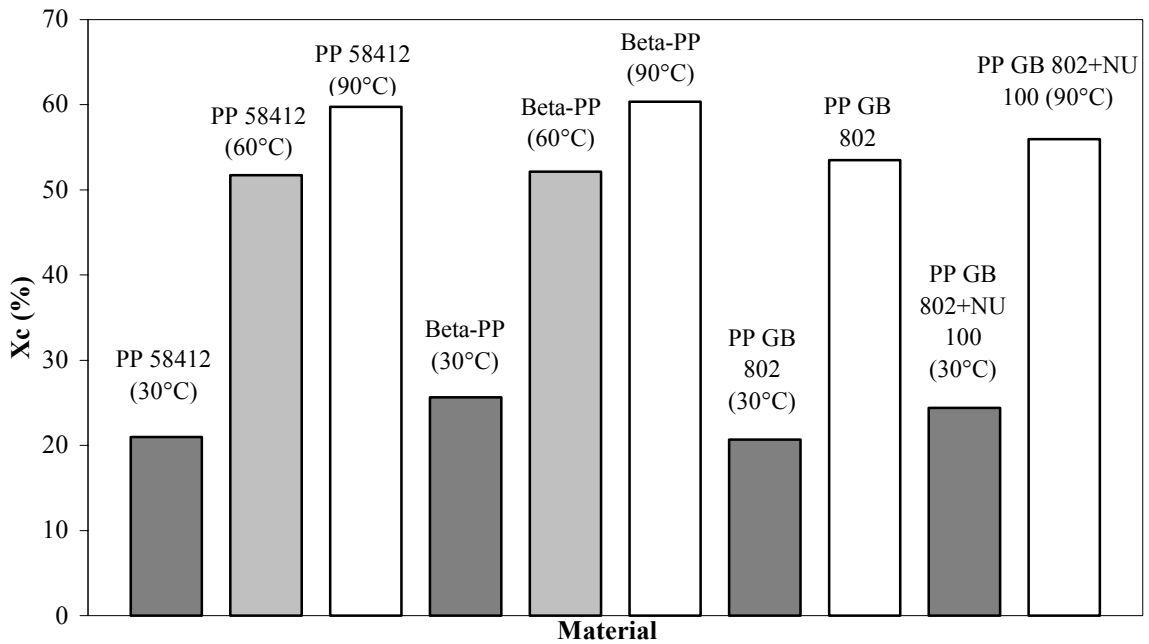
Fig.III.14 Relative crystallinity of cast films from different materials
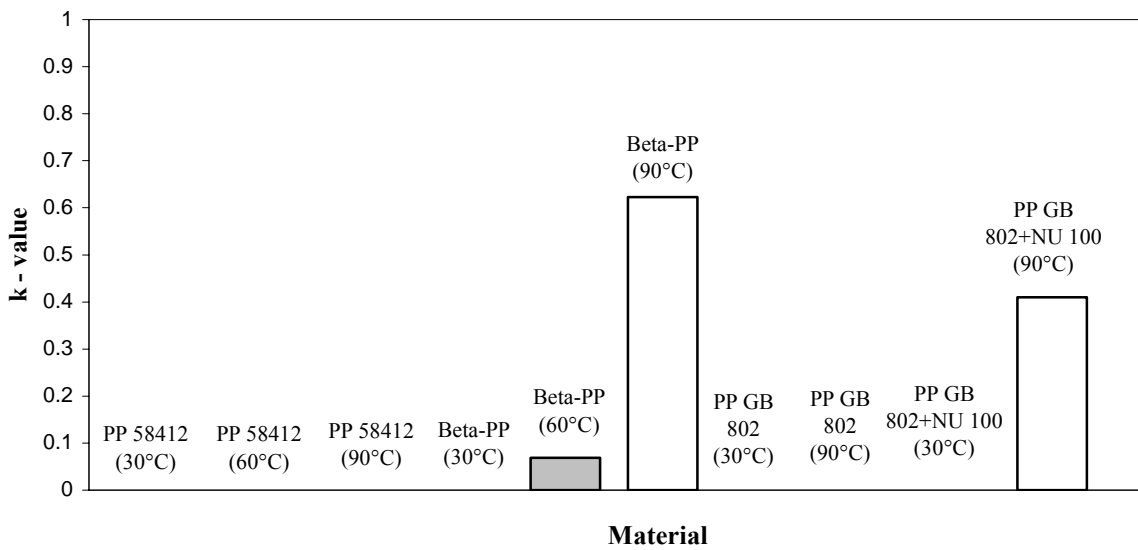
Fig.III.15 K-value of cast films solidified at various chill-roll temperatures

Figure III.14 shows crystallinity values of the cast films produced from different materials at various chill roll temperatures. It is evident that with increasing chill roll temperature the percent of crystallinity increases. The highest crystallinity possesses the film produced from Beta-PP at a 90°C chill-roll temperature. The films cooled using 30°C chill-

roll temperatures have particularly low crystallinity, approx. 20 %. Also in this case, the values of crystallinity are slightly enhanced by the nucleator additon.

The variations of β-phase content (k-value) are mentioned in *Fig. III.15*. Only three β-nucleated cast films contain β-phase within their crystalline phase. The highest k-value was detected in Beta-PP (approx. 60 %) solidified at 90°C; when the chill-roll temperature was lowered to 60°C, the cast films made from this material contained less than 10 % of β-phase (k-value < 0.1). The film manufactured from Random PP with nucleating agent a 90°C chill-roll temperature had approx. 40 % of β-phase. It can be stated out that the k-value favourably increases with increasing chill-roll temperature.

7.2 DSC analysis

The cast films were heated to 190°C at various rates (10, 40°C/min) to observe their melting behaviour.
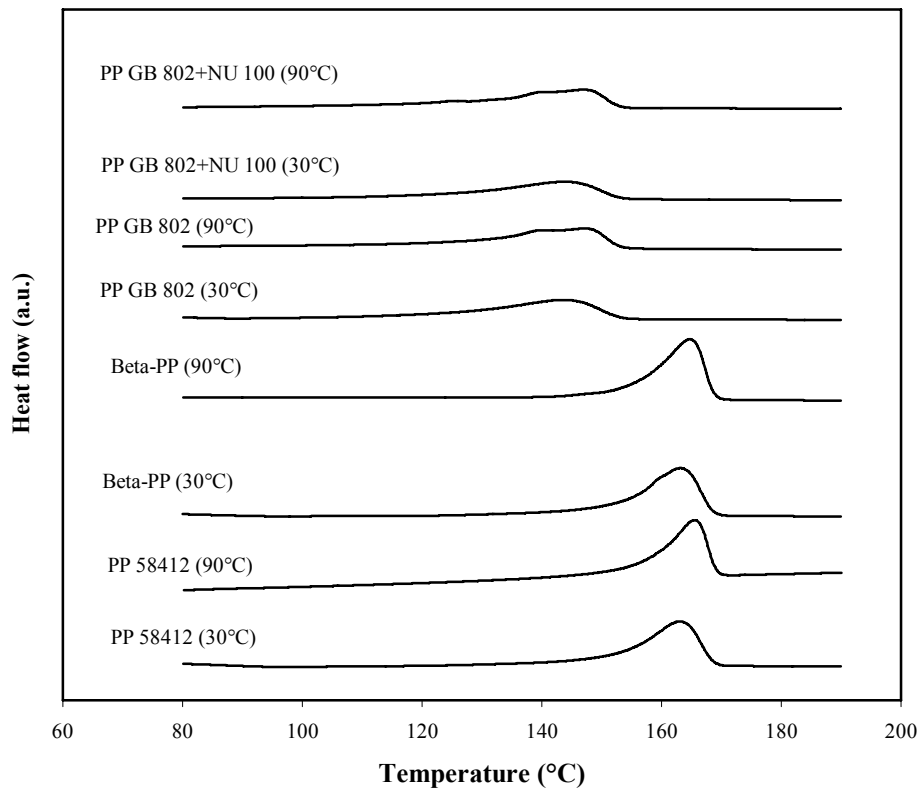
Fig.III.16 Melting endotherms of cast films heated at 10°C/min rate

Fig. III.16 shows the melting thermograms of the cast films heated to 190°C at a rate of 10°C/min. In this figure it can be observed only one endothermic α-phase melting peak. This is even evident in Beta-PP (90°C). It can be said that at rate 10°C/min β-phase could recrystallize to α-phase. Again, it is visible that the melting temperatures of films prepared from homopolymer are higher than the melting temperatures of cast films produced from random PPs.

To eliminate a possible β-to-α recrystallization, melting endotherms were taken at higher scanning rate. Following *Fig. III.17* illustrates the melting thermograms of cast films heated to 190°C at 40°C/min. There are visible two endothermic melting peaks in nucleated cast films, namely Beta-PP (90°C) and random PP GB 802+NU 100 (90°C). The β-peak could be detected because of the rate of heating 40°C/min led to the reduction of β/α recrystallization. However, also in this case the β-melting peak is rather small.
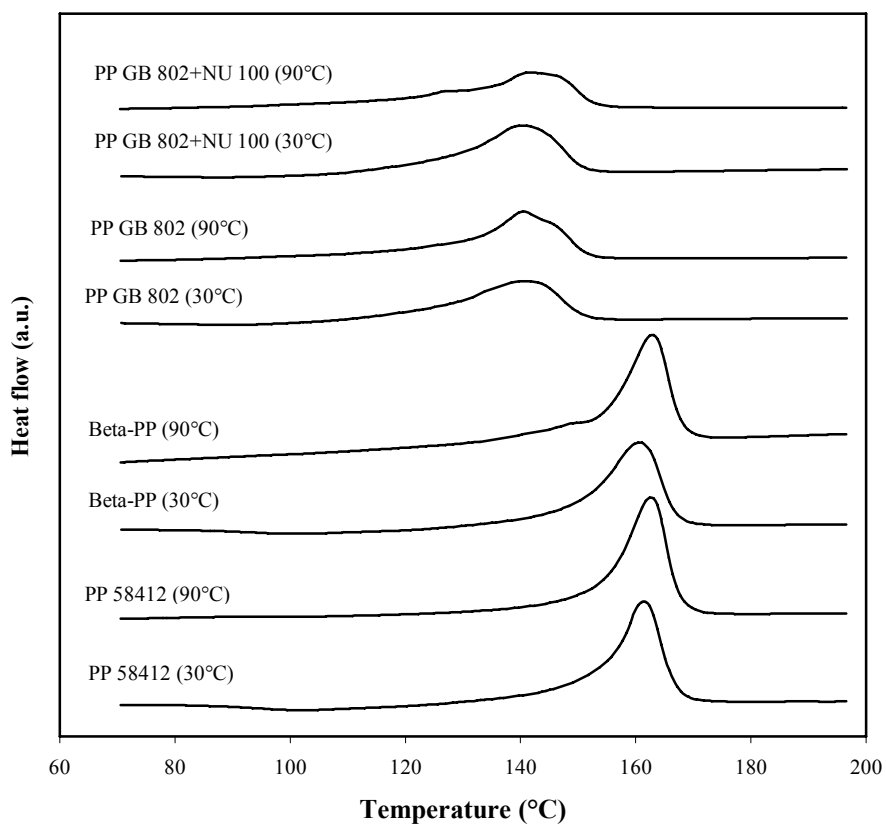
Fig.III.17 Melting endotherms of cast films

heated at 40°C/min rate

7.3 Density measurement
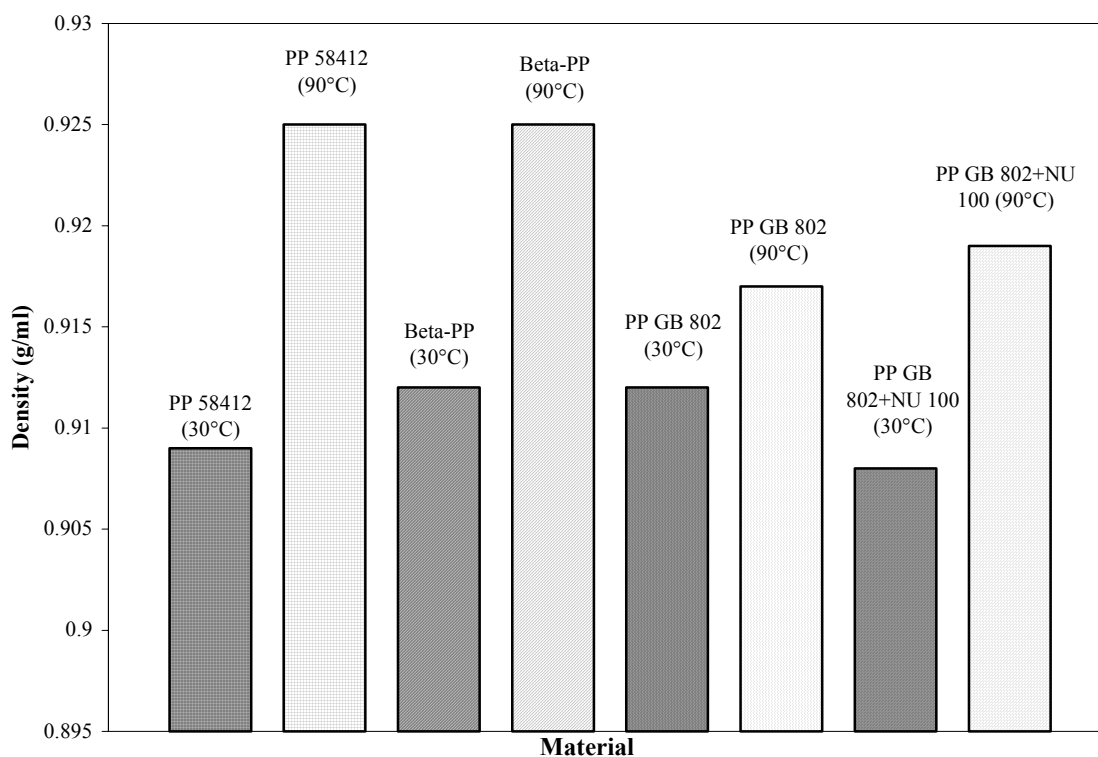
Fig.III.18 Density of cast films from different materials

Figure III.18 illustrates the data obtained from density measurement. Density of the cast films increases with increasing chill roll temperature and follows the trend of increasing crystallinity. From this graph it is evident that the highest density is achieved in the cast film produced from homopolymers – both neat and nucleated - at chill-roll temperature of 90°C. It is visible that in other cases except of random PPs solidified at 30°C, the nucleated films possess higher values of density than neat cast films.

7.4   Tensile testing

The analysis of tensile behaviour was realized under three constant-elongation rates (100, 200 and 10 mm/min) in order to compare the effect of prepared structures on mechanical characteristics. It is worth noting that the mechanical properties are not the most important characteristics rising from the use of cast films manufactured from β-polypropylenes. Following figures *III.19-III.27* show various tensile characteristics.
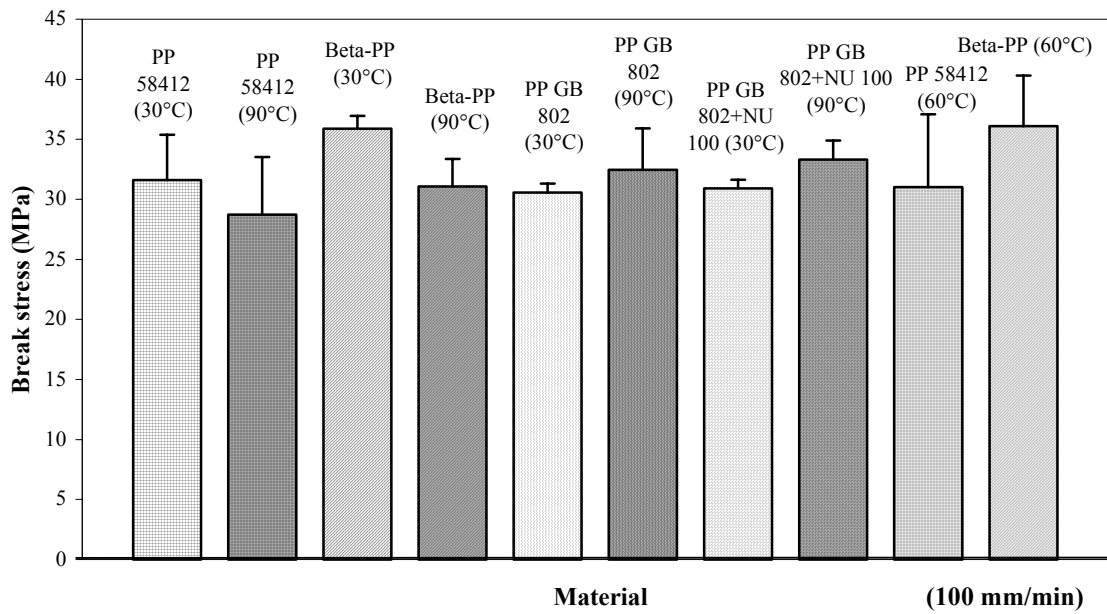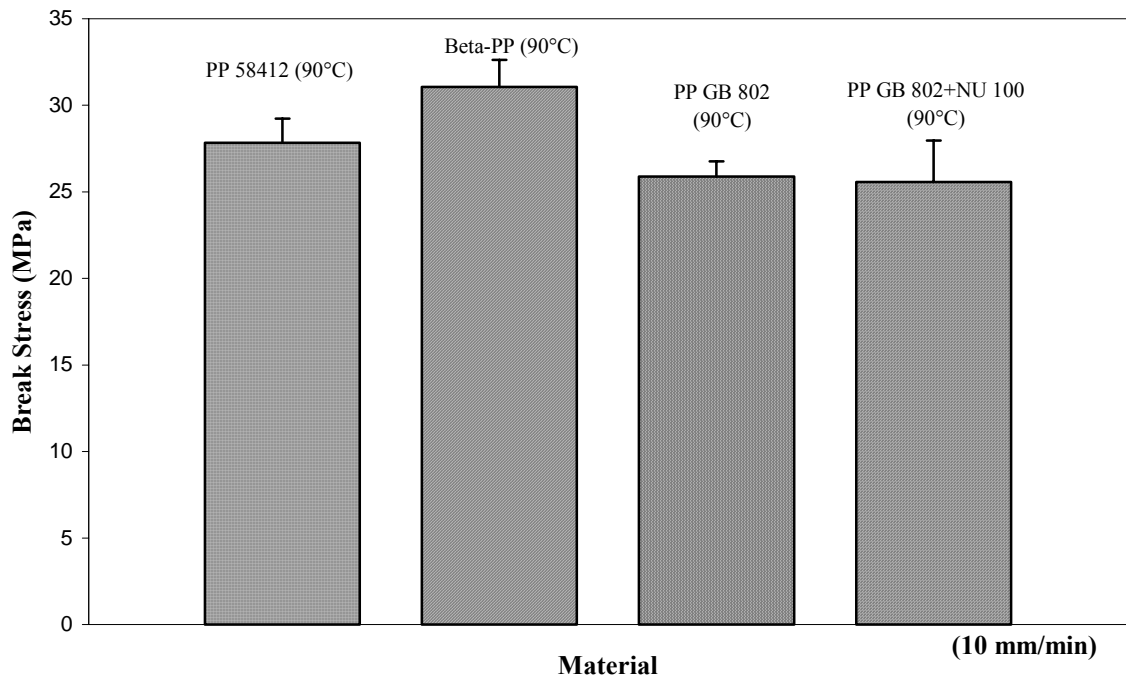

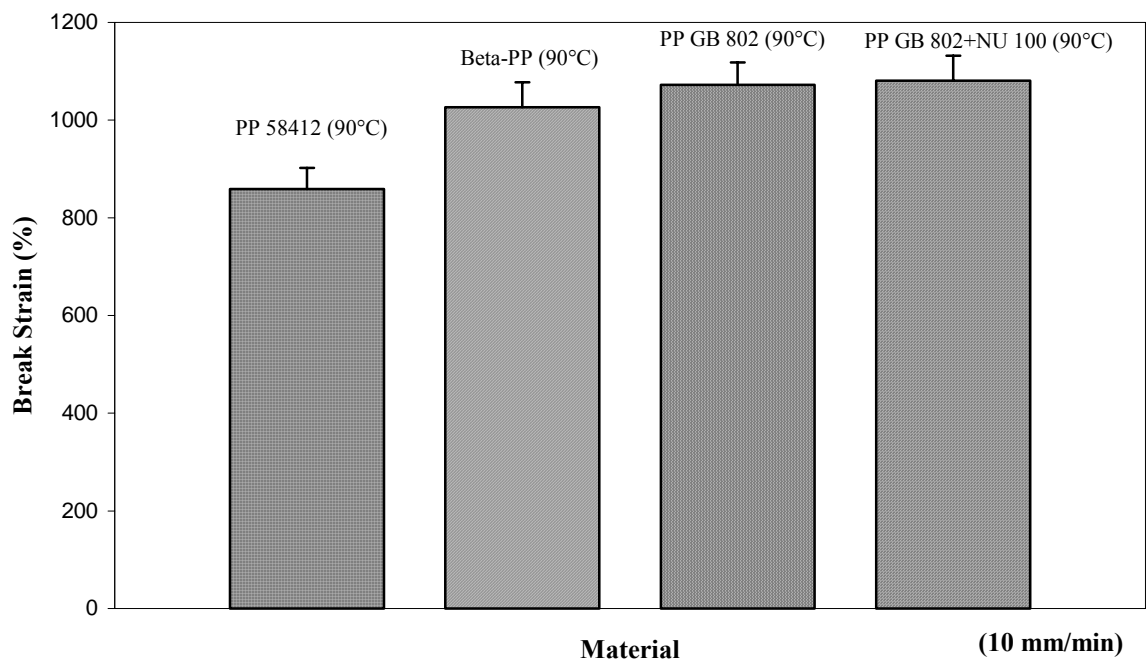*Fig.III.19 Break stress of cast films elongated at 100 mm/min*
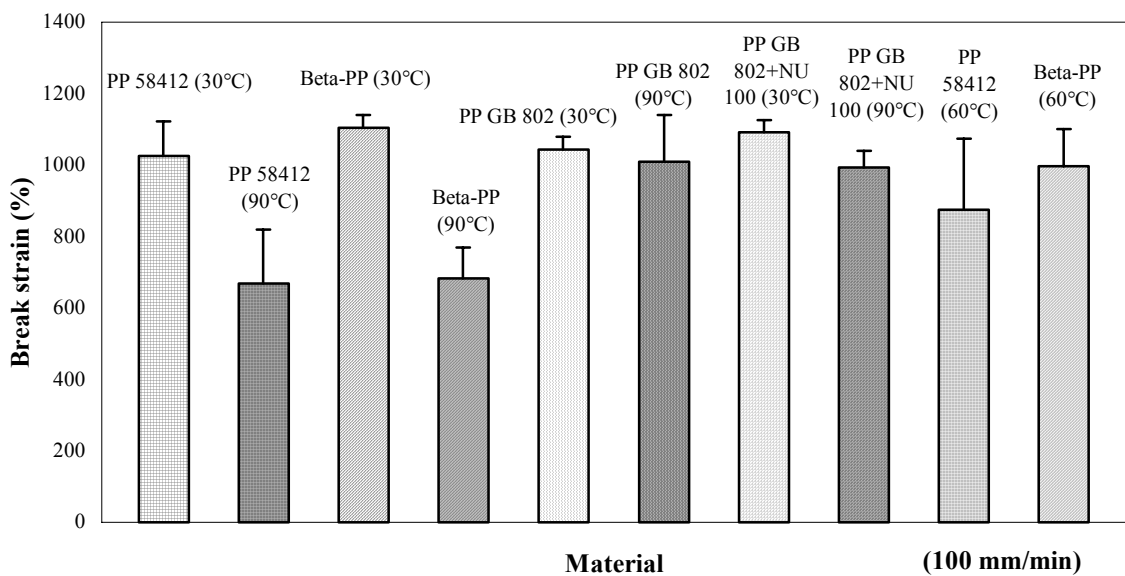
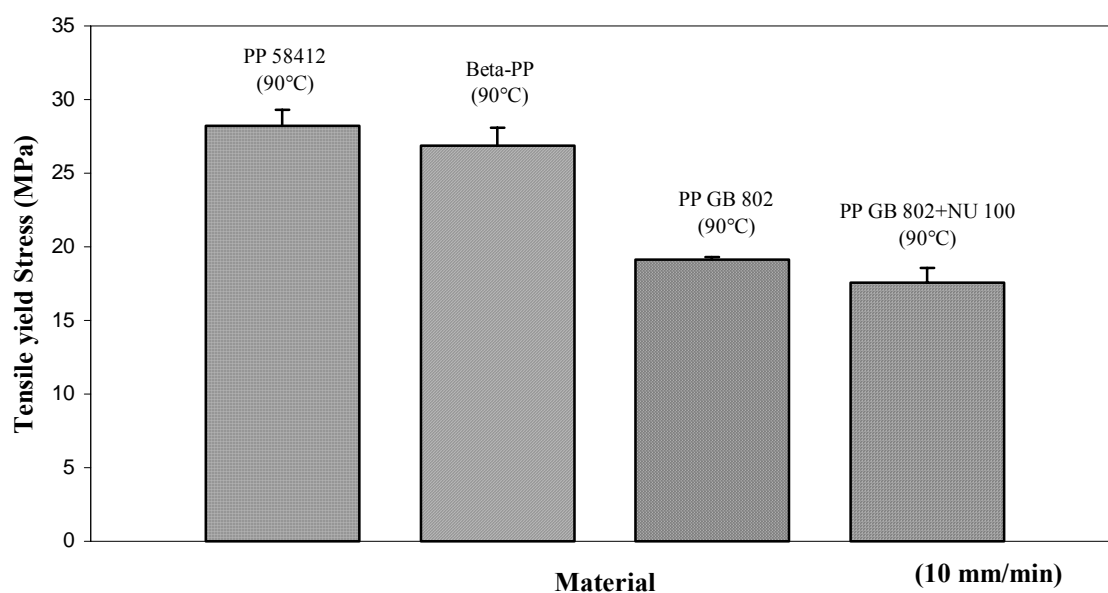*Fig.III.20 Break strain of cast films elongated at 100 mm/min*
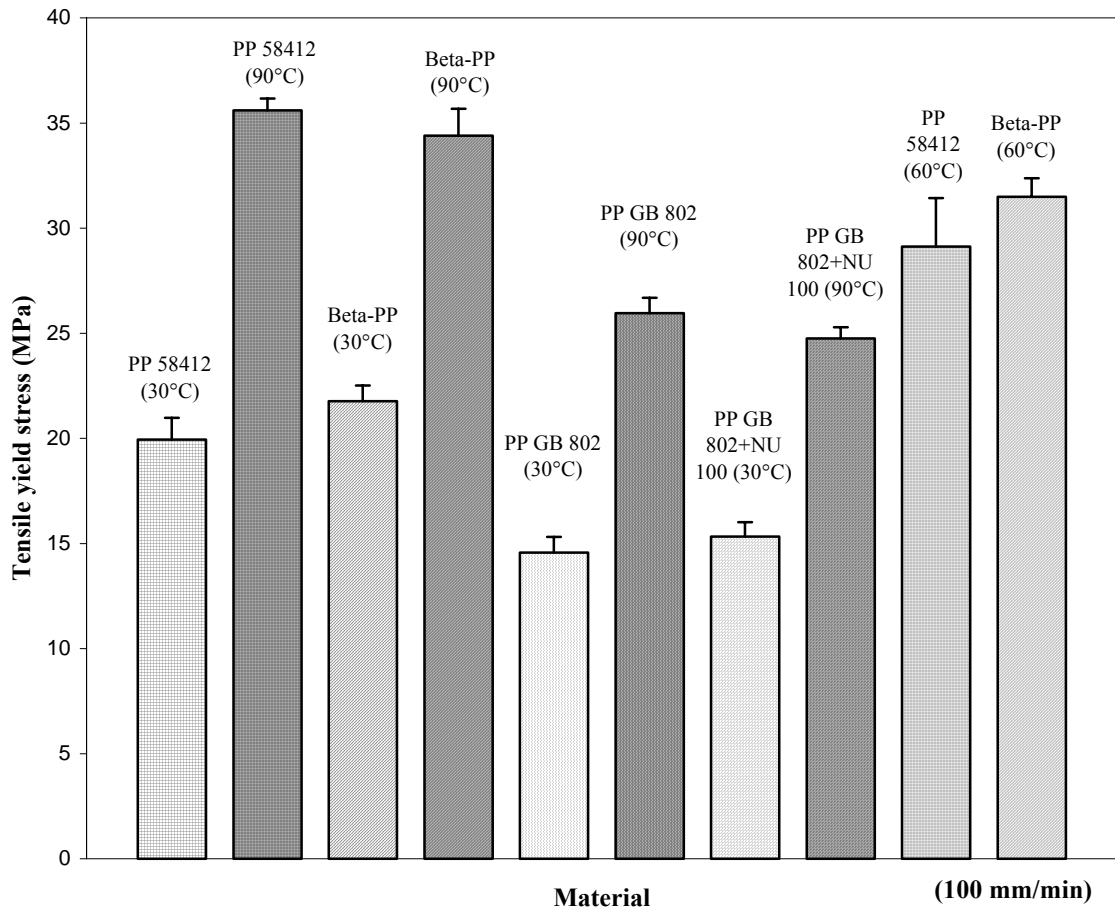
Fig.III.21 Tensile yield stress of cast films elongated at 100 mm/min

Figure III.19 illustrates values of break stress of different types of cast films. There can be observed that the break stress of the cast films does not show significant trend; it slightly decreases with increasing chill roll temperature in the case of homopolymers – both neat and nucleated. Opposite situation is evident in random PPs.

Fig.III.20 illustrates the break strain of cast films. It is visible that the break strain decreases at all cast films with increasing chill roll temperature. From a comparison of nucleated and neat material it is evident that the effect of the nucleation is not particularly intensive. The impact of solidification temperature is thus dominant again.

The values of yield stress are recorded in *Fig. III.21*. Similar to the strain at break values, it is evident that tensile yield stress increases with increasing chill roll temperature. Again, the yield stress of neat and nucleated materials values are comparable. It should be

pointed out that the films produced from random PPs have significantly lower yield stress (tensile strength) as compared to hopomopolymers.

Following figures *III.22-III.24* show the tensile behavior of cast films, which were elongated at a rate of 200 mm/min.
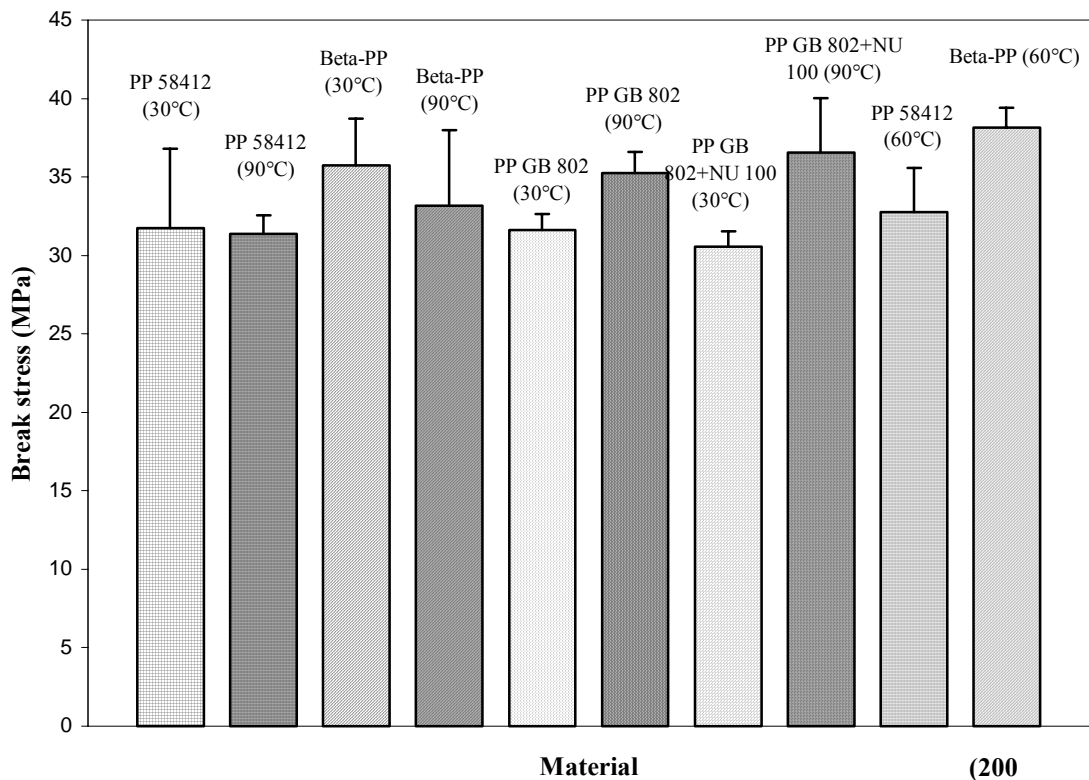
Fig.III.22 Break stress of cast films elongated at 200 mm/min
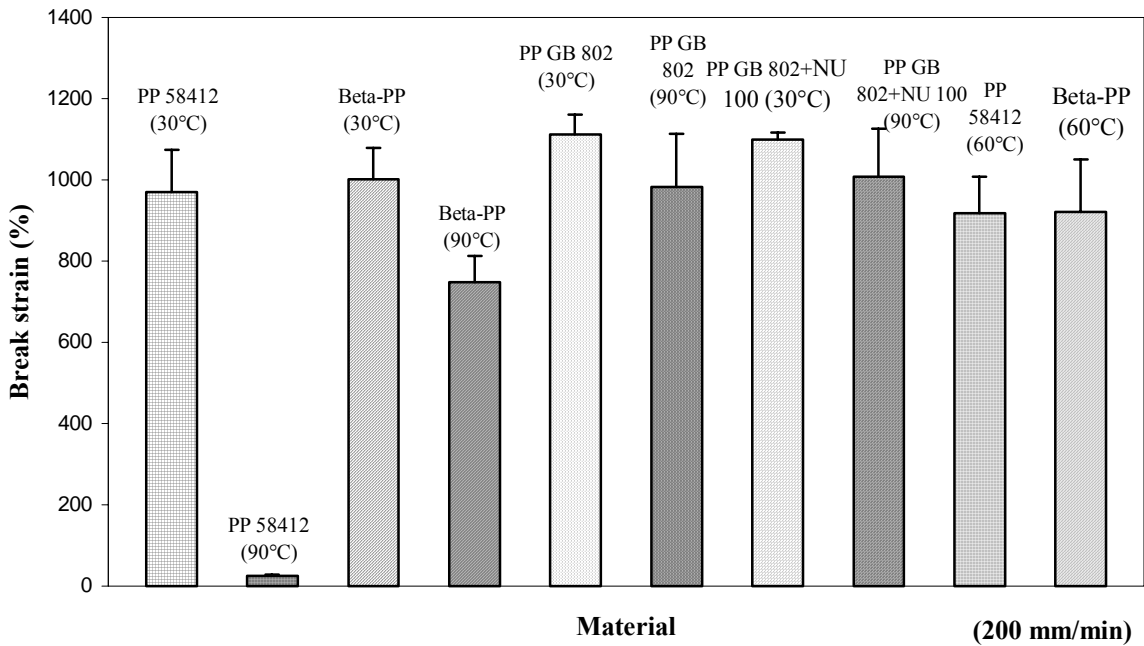
Fig.III.23 Break strain of cast films elongated at 200 mm/min
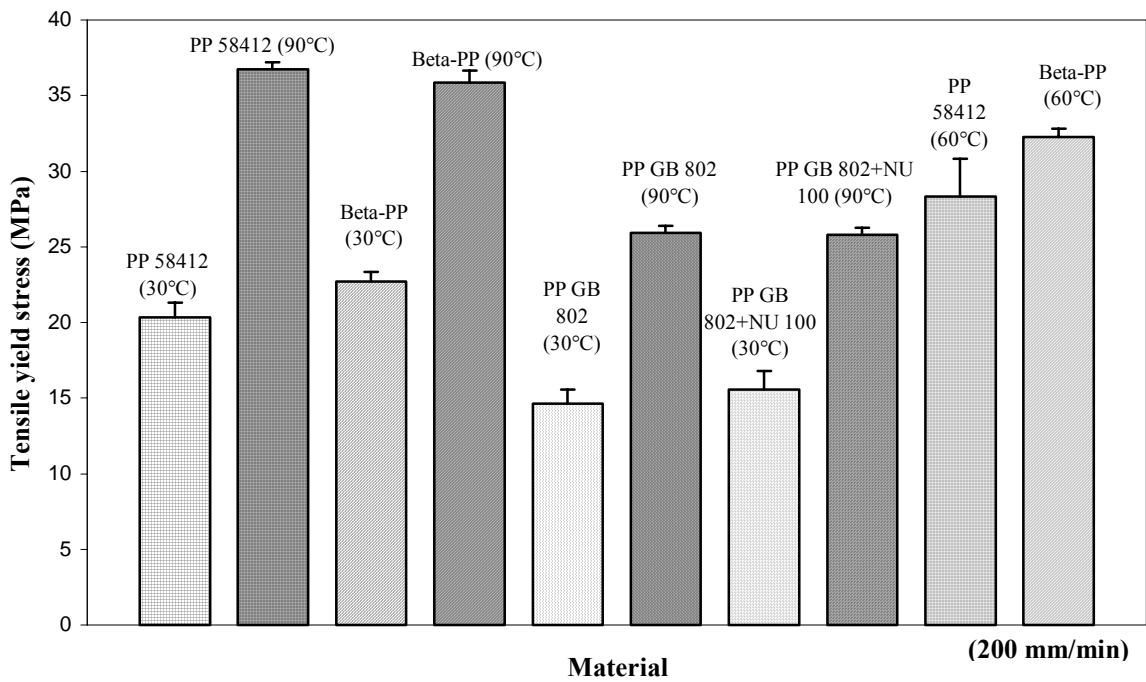
Fig.III.24 Tensile yield stress of elongated at 200 mm/min

Figure III.22 shows break stress values of cast films prepared from different materials. In this case, break stress decreases with increasing chill roll temperature. Similar re-

sults are evident for the cast films, which were elongated at 200 mm/min. Only for random PPs the break stress rises with increasing chill roll temperature.

Fig.III.23 shows break strain of cast films and brings interesting results. There we can see enormous differences between neat PP 58412 (90°C) and nucleated Beta-PP (90°C). The value of break strain is about 26% for neat PP 58412 (90°C) and about 750% at nucleated Beta-PP (90°C). This confirms significantly higher drawability of Beta-PP as compared to neat PP 58412. Generally, the break strain decreases at all cast films with increasing chill roll temperature. Random PPs show slightly higher elongation at break as compared to homopolymers.

Tensile yield stress values are described in *Fig.III.24*. Generally, we can say that tensile yield stress increases with increasing chill roll temperature. It is evident that the highest tensile yield stress has neat PP 58412 (90°C). For the cast films, which were prepared at chill roll temperature of 60°C, the effect of nucleations the most visible, and as a result nucleated cast films have higher tensile yield stress than cast films made from non-nucleated material. The films from random PPs possess significantly lower tensile strength as compared to homopolymers.

Fig.III.25 Break stress of cast films elongated at 10 mm/min

Fig.III.26 Break strain of cast films elongated at 10 mm/min

Fig.III.27 Tensile yield stress of cast films elongated at 10 mm/min

Finally, the films most differing in polymorphic composition (solidified at 90°C) were strained using 10 mm/min rate (see *Figs III.25 –III.27*). It is known that a rather slow drawing of β-nucleated PP leads to the increase of stress at break values. This was confirmed in the case of β-nucleated homopolymer on the contrary to random PPs, the mechanical properties of which are not significantly affected by nucleation. As for the elongation at break, Beta-PP film shows similar elongation as films manufactured from both neat and nucleated copolymers. However, at the same time Beta-PP film possesses significantly higher yield stress than both random PP films and similar values as compared to the film made from homopolymer PP 58412.

8 ASSESSMENT OF DRAWING FILMS

8.1 X-Ray analysis

First of all, the structure of drawing films was evaluated. Relevant WAXS spectra are shown in *Figs III.28* and *III.29*. *Fig. III.29* illustrates the spectra of the β-nucleated cast films, which were manually elongated by a special tool. The elongation was approx. 300 %, elongation speed of 20 mm/min and following drawing temperatures: 25, 110 and 130°C. The spectra of these films show virtually only diffraction peaks relevant to α-phase. As evident from figure *Fig. III.12*, the film manufactured from Beta-PP at a 90°C chill-roll remperature showed intensive β-diffraction peak, which disappeared after elongation. Clearly, we can talk about β-to-α trasnsformation caused by drawing. This effect is evident at all elongation temperatures observed. The film made from Beta-PP at a 30°C chill-roll temperature retained the smectic structure even after elongation.

Fig. III.29 shows the spectra of the drawing films solidified at 30°C and 90°C and elongated at 200 mm/min. The spectra of the films, except the film manufactured from neat homopolymer, show high amorphous halo. From the point of view of desired β-to-α phase transformation, it can be thus stated out that the high elongation speed at low temperature does not allow this recrystallization, on the contrary to drawing at high temperature or at a low elongation speed. It should be noted that even at high elongation temperature and rather low elongation speed, the films showed necking which is not favourable to obtain microporous film. These observations are only preliminary insight into wide theme concerning the drawing of β-phase cast films and can be included into necessary points before drawing under real processing conditions.
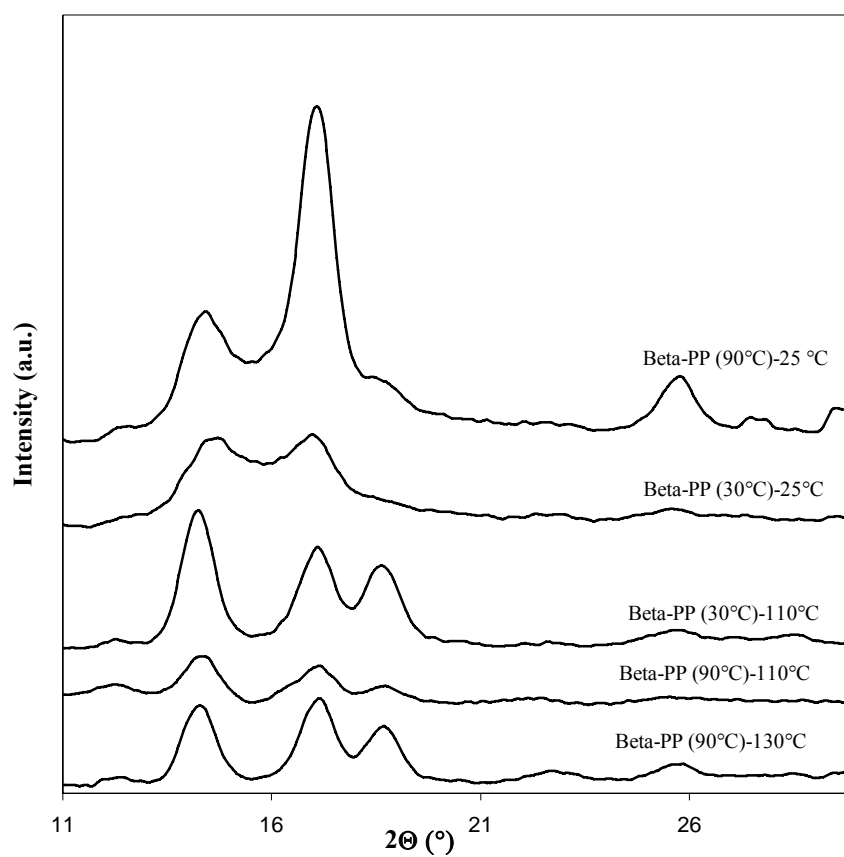
Fig. III.28 WAXS spectra of drawing films manually elongated
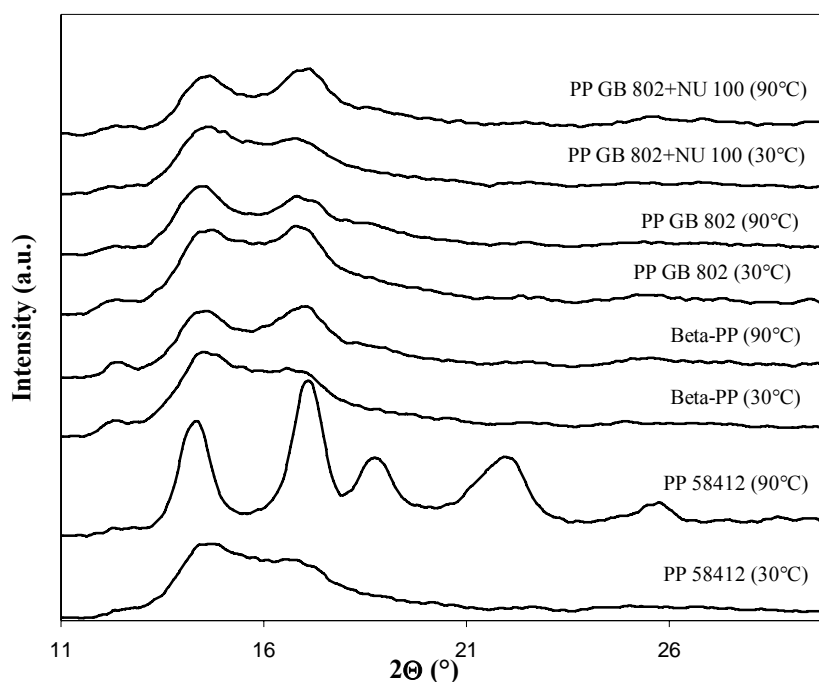
Fig. III.29 WAXS spectra of drawing films
elongated at 200 mm/min

8.2   Scanning electron microscopy

Surfaces of the cast film after drawing are shown in *Figures III.30-III.34*. It is evident that the surface consists of observable cracks possessing a random orientation. In the case of Beta-PP, the visibility of cracks decreases with increasing chill-roll temperature, on the contrary to neat PP indicating opposite tendency. What is also evident from the visual inspections of micrograph in *Fig.III.33* is that the surface of Beta-PP film solidified at 90°C shows certain roughening as observed by Fujiyama [31]. A round void, to which microporosity was described in the work of Kim [30], was observed only in the drawing film manufactured from nucleated random copolymer (see *Fig.III.34*). However, it should be noted that the round cracks are typical for biaxially oriented films, in particular.

Figs.III.35 and *III.36* show surfaces of neat and nucleated films which were manually elongated at 130°C. While the film made from neat material show clearly evident cracks, on the surface of Beta-PP cracks are not visible. Again, significant surface roughening is in this case evident.
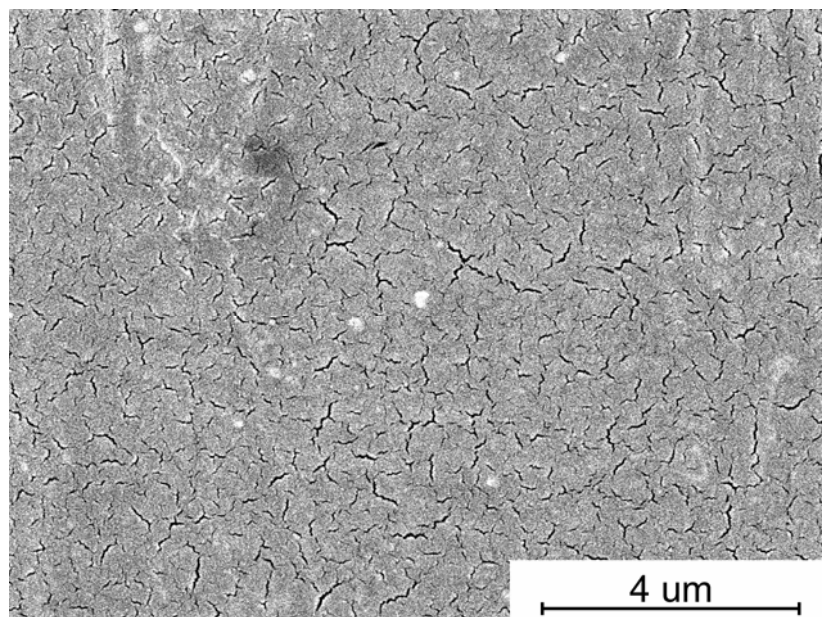
Fig. III.30 Surface of film manufactured from neat homopolymer using 30°C chill-roll temperature (drawing at 200 mm/min, room temperature)
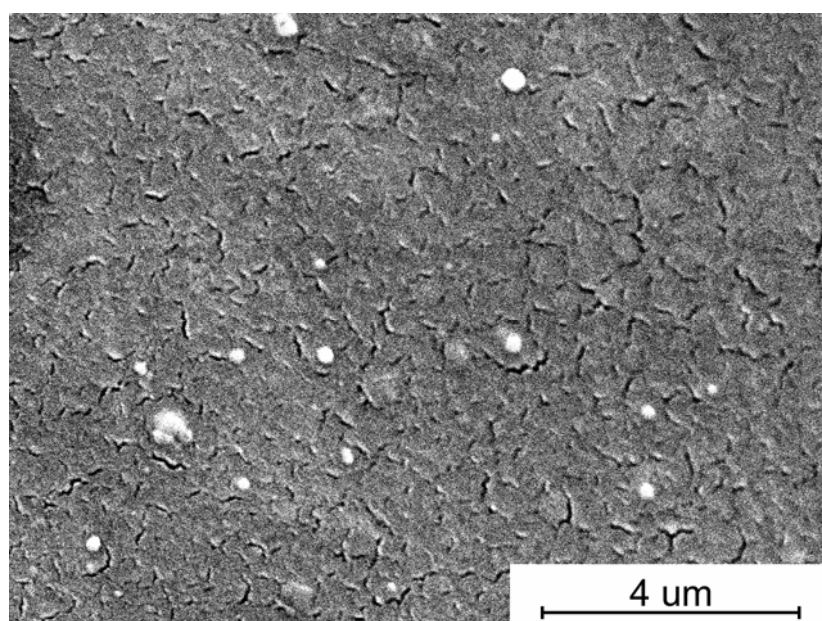
Fig. III.31 Surface of film manufactured from neat homopolymer using 90°C chill-roll temperature (drawing at 200 mm/min, room temperature)
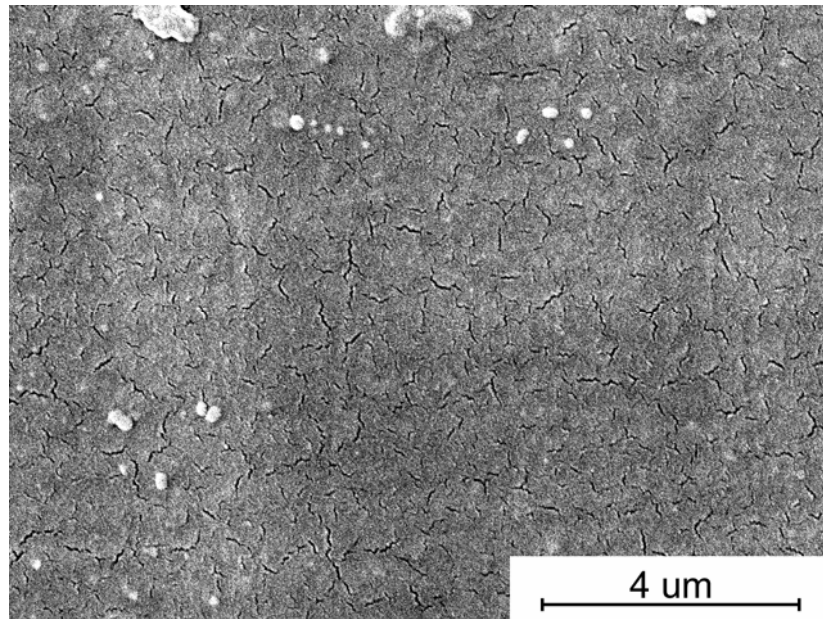
Fig. III.32 Surface of film manufactured from Beta-PP using 30°C chill-roll temperature
(drawing at 200 mm/min, room temperature)
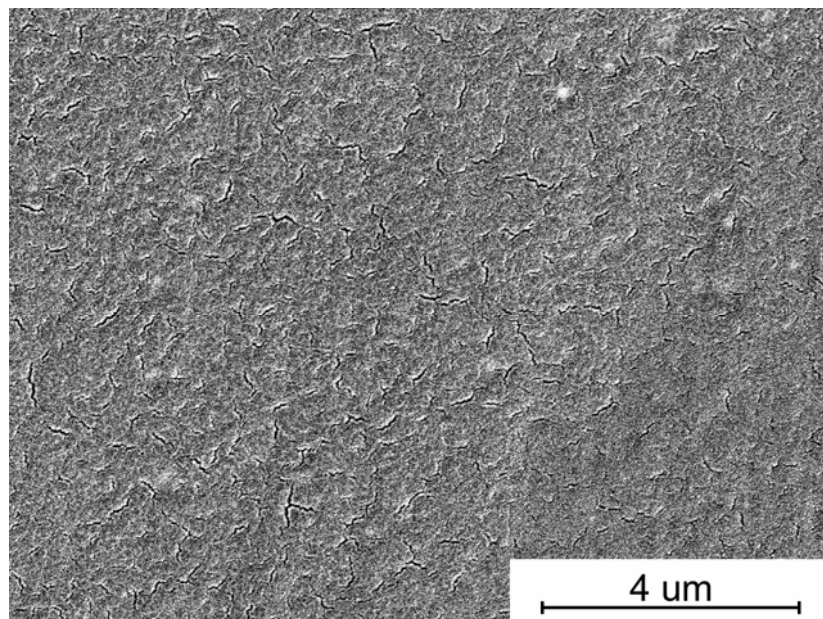
Fig. III.33 Surface of film manufactured from Beta-PP using 90°C chill-roll temperature
(drawing at 200 mm/min, room temperature)
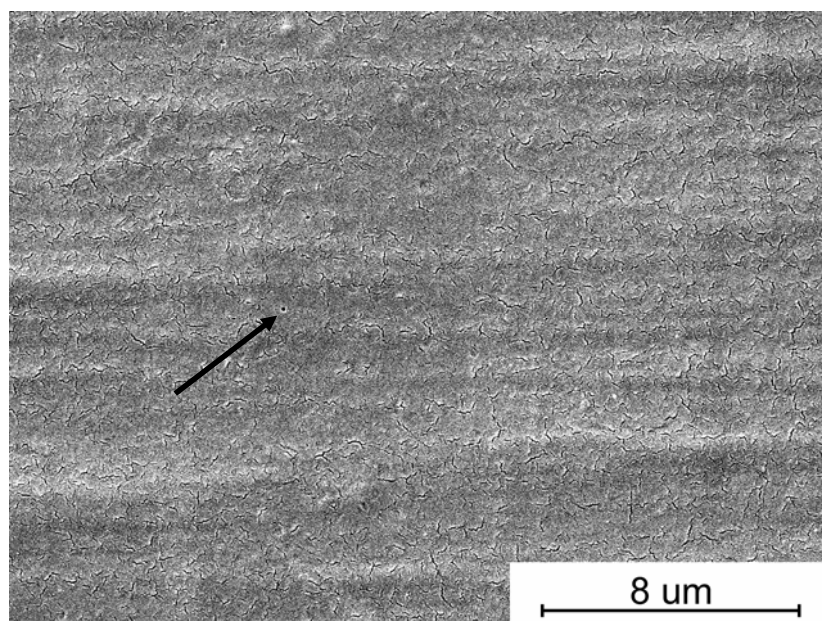
Fig. III.34 Surface of film manufactured from nucleated random PP using 30°C chill-roll temperature (drawing at 200 mm/min, room temperature)
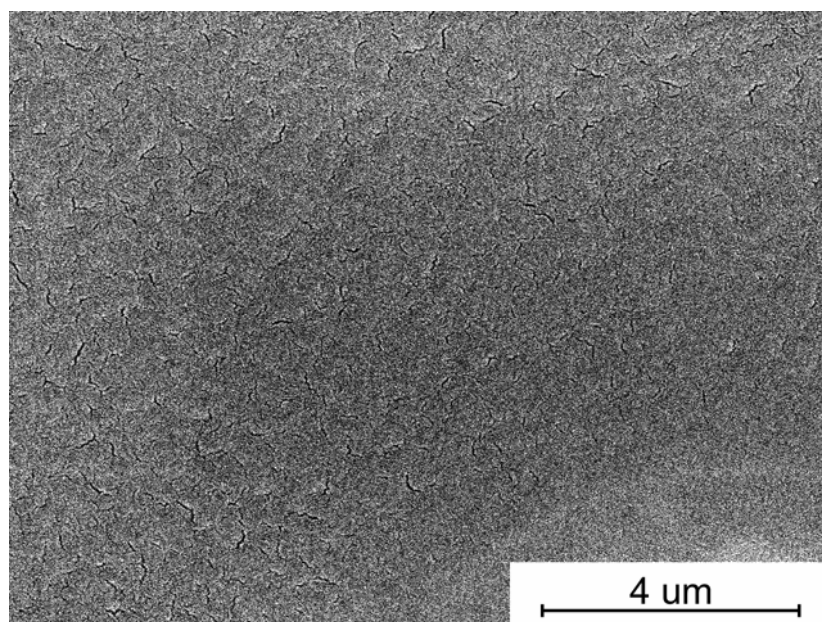
Fig. III.35 Surface of film manufactured from neat homopolymer using 90°C chill-roll temperature (manual drawing at 130°C)
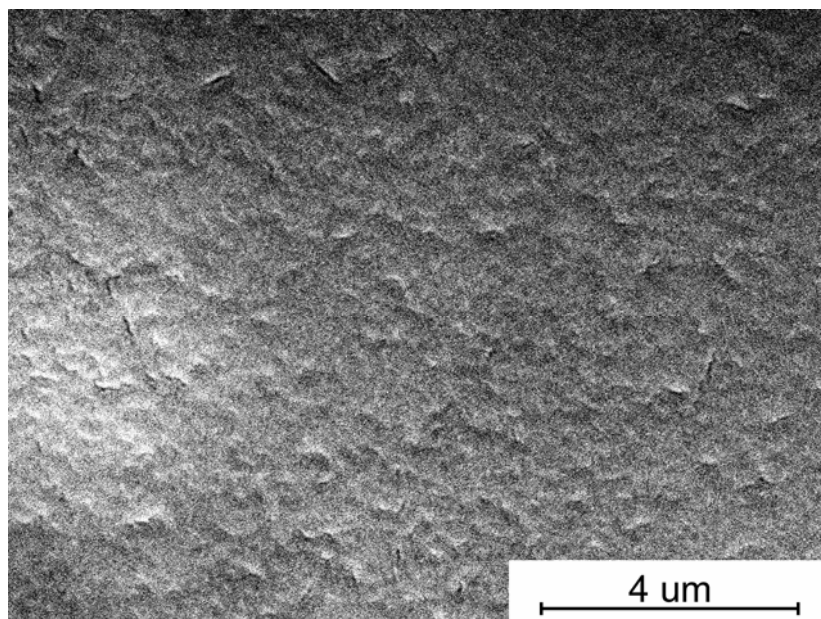
Fig. III.36 Surface of film manufactured from Beta-PP using 90°C chill-roll temperature

(manual drawing at 130°C)

CONCLUSIONS

This thesis deals with study of structure and properties of Beta-polypropylene films. For the preparation of cast films, commercially available isotactic polypropylene Mosten 58412 and random copolymer Mosten GB 802 were modified by a 0.03 wt. % specific β-nucleation agent (NJ Star NU 100).

First part of this thesis describes general crystallizability and structural characteristics of starting materials. From both neat and nucleated materials, plates with 2 mm thickness were compression moulded. The morphology and supermolecular arrangement were examined with the help of wide-angle X-ray scattering, differential scanning calorimetry and polarized light microscopy.

From wide-angle X-ray scattering and differential scanning calorimetry it was ascertained that the structure of compression moulded samples showed regular crystalline arrangement. The most evident β-diffraction peak was visible in the sample manufactured from Beta-PP, which was cooled in hydraulic press at 60°C. The highest percent of crystallinity was observed at Beta-PP cooled at 130°C. Polarized light microscopy brought information about compression-moulded specimen morphology. It was detected that the size of spherulites increases with increasing crystallization temperature and that the size of spherulites in the films made from neat isotactic polypropylene (PP 58412) is higher than that of spherulites from random PP GB 802. Opposite results were discovered in nucleated samples. The size of spherulites in Beta-PP film was smaller than in nucleated random PP GB 802.

The second and essentiall part of the work examined the effect of processing conditions on supermolecular arrangement in cast film. Indeed, the preliminary insight to mechanical properties and drawability was carried out.

From wide-angle X-ray scattering it is evident that the solidification at 90°C led to rather higher crystallinity of the films while the spectra of the films solidified at 30°C show high amorphous halo. In this case, the structure appeared to be smectic. The films solidified at 60°C consist regular crystalline structure. The highest content of β-phase and density was revealed in the film made from Beta-PP material and solidified at 90°C. It was also detected that the density increases with increasing chill roll temperature and with increasing content of β-phase.

The analysis of tensile behaviour was realized under three constant-elongation rates (100, 200, 10 mm/min). Generally, it can be said that with increasing chill roll temperature the break stress slightly decreases in the case of both homopolymers. It is interesting that opposite situation was indicated for neat and nucleated random PPs. Tensile yield stress increases with increasing chill roll temperature. It was also detected that with increasing β-phase content the break stress increases at low elongation rate.

The last chapter brings results from the assessment of drawing films. From wide-angle X-ray scattering is clear that the spectra of films elongated by hand at various temperatures show high crystallinity while the spectra of films elongated at 200 mm/min, except film made from neat PP 58412 (90°C), show significant amorphous halo. Scanning electron microscopy brings information about surfaces of the drawing films. It was observed that the visibility of cracks decreases with increasing chill-roll temperature in the case of Beta-PP. Neat PP 58412 indicated opposite tendency. The surface of Beta-PP solidified at chill roll 90°C showed a certain roughening. Round cracks, which are typical for biaxially oriented films, were observed in nucleated random copolymer only.

REFERENCES

[1] www.bpf.co.uk/bpfindustry/plastics materials polypropylene PP.cfm

[2] www.sdplastics.com/polypro.html

[3] www.huntsman.com/polymers/index.cfm

[4] OBADAL, M.; ČERMÁK, R.; HABROVÁ, V.; STOLKASA, K.; ŠIMONÍK, J.: International Polymer processing, Vol 19, Issue 3, Hanser Publisher, Munich (2004)

[5] PHILLIPS, R. A.; WOLKOWICY, M. D.: Structure and Morphology, Polypropylene Handbook, reference book (ISBN 3-446-18176-8)-Carl Hanser Verlag, 1996

[6] CHEUNG, F.; TJONG, S., C.; LI, R. K. Y.: Mechanical Behaviour of Kalcium Carbonate Filled Beta-Crystalline Form Polypropylene Composite, ANTEC 1996, conference proceeding-Society of Plastics Engineers, 1996

[7] PHILLIPS, P. J.; CAMPBELL, R. A.: The Crystallization Behavior of Polypropylene at Elevated Pressures, ANTEC 1991, conference proceeding-Society of Plastics Engineers, 1991

[8] MEZGHANI, K.; PHILLIPS, P. J.: The Morphology of Gamma Form of Isotactic Polypropylene at 200 MPa, ANTEC 1996, conference proceeding-Society of Plastics Engineers, 1996

[9] VARGA, J.: Journal of Macromolecular Science, Part B-Physics, Vol.41, Nos. 4-6, p. 1160, 2002

[10] KRESSLER, J., THOMANN, R., MULHAUPT, R.: Engineering of New Supermolecular Structures Defined by the Chain Architecture of Polypropylenes and Their Blends, ANTEC 1996, conference proceeding, Society of Plastics Engineers, 1996

[11] MAIER, C.-CALAFUT, T.: Polypropylene, the definitive user's guide and databook, Plastics Design Library in 1998, ISBN 1-884207-58-8

[12] MILLER, R. C.; BLAIR, R. H.; VERNON, W. D.; WALSH, T. S.: Polypropylene, Modern Plastics Encyclopedia 1992, reference book (M603.1.2), McGraw-Hill, 1991

[13] CAPSHEW, C.: Polypropylene: A Commodity Plastic Reaches Record Highs in 1995 Production, Modern Plastics Encyclopedia 1997, reference book, Vol. 73, No. 12, McGraw-Hill, 1997

[14] THOMSON, W., R.; BORTOLINI, W.; YOUNG, D. R.; DAVIES, J. K.: Polypropylene, Modern Plastics Encyclopedia1988, reference book (M603.1), McGraw-Hill, 1987

[15] PORTNOY, R.C.: Polypropylene for Medical Device Applications, Medical Plastics and Biomaterials, trade journal, vol. 1, no. 1 – Canon Communications, 1994

[16] Fortilene Polypropylene Properties, Processing, and Design Manual, supplier design guide Soltex, 1981

[17] CHENG, C.Y., ERDERLY, T.C., YU, T.C.: Plastomer and Polypropylene Blends for Fiber and Nonwoven Applications, ANTEC 1995, conference proceedings – Society of Plastics Engineers, 1995

[18] LANGHAUSER, F.: Metallocenes as Catalysts in Industrial Olefin Polymerization Processes, ANTEC 1995, conference proceedings – Society of Plastics Engineers, 1995

[19] Topics In Chemistry – BASF Plastics Research And Development, supplier technical report–BASF Aktiengesellschaft, 1992

[20] HARUNA, T., TOBITA, E: A New Organophosphorous Type Nucleating/Clarifying agent for Polypropylene, ANTEC 1992, conference proceedings-Society of Plastics Engineers, 1992

[21] Shell Polypropylene Injection Molding Guide, supplier design guide (SC: 797-89)-Shell Chemical Company, 1989

[22] LIN, Y.; ZHOU, J.; SPRUIELL, J. E.; STAHL, G. A.: The Effect of Pigments on Development of Structure and Properties of Polypropylene Filaments, ANTEC 1991, conference proceedings - Society of Plastics Engineers, 1992

[23] GRAVES, V.: Polypropylene: A Commodity Plastic Reaches Record Highs in 1994 Production, Modern Plastics Encyclopedia 1996, reference book (M603.1.6)-McGraw-Hill, 1995

[24] Shell Polypropylene Film Grade Resins Guide, Supplier technical report (SC: 1209-93)-Shell Chemical Company, 1992

[25] GODDARD, R.: Packaging Materials, reference book (ISBN 0 902799 34 7)-Pira-The Research Association for the P, 1993

[26] BARNETSON, A.: Plastic Materials for Packaging, monograph (ISBN 1-85957-068-2)-Rapra Technology Limited Ltd., 1996

[27] Himont-Seize the Oportunity to Open New Markets and Reduce Costs, supplier marketing literature (PL-007)-Himont, 1992

[28] Polymers in Contact with Food, conference proceeding (ISBN 0 90 2348 66 3)-Rapra Technology Ltd., 1991

[29] JACOBY, P.; LEE, R. E.: The use of beta nucleation to produce microvoided oriented polypropylene films, ANTEC 2005, p.3310-3313

[30] KIM, S.: β-crystalline polypropylene and oriented film applications, Polypropylene Product development

[31] FUJIYAMA, M.; KAWAMURA, Y.; WAKINO, T.: Study on Rough-Surface Biaxially Oriented Polypropylene Film, Journal of Applied Polymer Science, Vol.36, p. 985-993, 1988

[32] DEAN, J. A.: The Analytical Chemistry Handbook, New York, Mc.Graw Hill, Inc. 1995, p. 15.1-15.5

[33] PUNGOR, E.: Practical Guide to Instrumental Analysis, Boca Raton, Florida, 1995, p.181-191

[34] SKOOG, D. A.; HOLLER, F., A.; NIEMAN, T.: Principles of Instrumental Analysis, Fith Edition, New York, 1998, p.905-908

[35] CHEREMISINOFF, N. P.: Polymer Characterization- Laboratory Techniques and Analysis, Note Publications in 1996, ISBN 0-8155-1403-4

[36] www.microscopyu.com/articles/polarized/polarizedintro.html

[37] SCHEIRS, J.: Compositional and Failure Analysis of Polymers- A practical Approach, Ltd. 2000, p.766, ISBN 0-471-62572-8

[38]   http://mse.iaste.edu/microscopy/home.html

[39] GLUSKER, J. P.; LEWIS, M.; ROSSI, M.: Crystal Structure Analysis for Chemists and Biologist, VCH Publisher, NY 1994, ISBN 047 1185 434

[40] LEROY, E. A.: X-Ray diffraction in Polymer Science, Wiley Interscience, New York, 1996

[41] www. astm.org: Tensile testing of Plastics

[42] WOODWARD, A. E.: Understanding the Polymer Morphology, Munich, Carl Hanser Verlag, 1995

[43] DU, J.; KLAMECKI, B.: Tensile Test Exercise, Twin Cities (USA): The University of Minnesota, 1997

[44] www.instron.com/applications/test/types/tension/index.asp

[45] TURNER-JONES, A.; AIZLENWOOD, J. M.; BECKETT, D. R.: Crystalline form of Polypropylene, Makromolekular Chemistry, 1964, No.75

[46] MOORE, D. R.; TURNER, S.: Mechanical evaluation strategie for plastics, Cambridge, CRC publishing, 2001

LIST OF SYMBOLS

PP   polypropylene

iPP   isotactic polypropylene

β-PP   β-nucleated polypropylene

α   monoclinic crystallic phase of polypropylene

β   trigonal crystallic phase of polypropylene

γ   orthorhombic crystallic phase of polypropylene

DSC   differential scanning calorimetry

WAXS   wide-angle X-ray scattering

SEM   scanning electron microscopy

2θ [deg] angle of diffraction

wt. %   [%]   weight percent

X_c [%]   percentage of crystallinity

MPa   MegaPascal

ΔH_m [J/g]   melting heat

ΔH_c [J/g]   crystallization heat

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Experimental

Results and discussion