

# **Nucleating and clarifying agents for polymers**

Jitka Kučerová

---

Bakalářská práce  
2007/2008



Univerzita Tomáše Bati ve Zlíně  
Fakulta technologická

---

Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů

akademický rok: 2007/2008

## ZADÁNÍ BAKALÁŘSKÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Jitka KUČEROVÁ**

Studijní program: **B 2808 Chemie a technologie materiálů**

Studijní obor: **Chemie a technologie materiálů**

Téma práce: **Nucleating and clarifying agents for polymers**

Zásady pro vypracování:

The aim of this Bachelor thesis is to compile a view on the nucleating and clarifying agents used in polymeric materials. The application of the agents is common in the industry. The heterogeneous nuclei not only reduce the processing time but also influence crystallization kinetics, size of spherulites and, consequently, resulting properties. In particular, the formation of specific crystalline form in polymorphic polymers induced by addition of specific nucleating agent can influence the macroscopic behaviour quite dramatically. The Bachelor thesis should cover an overview of known nucleating and clarifying agents, their nucleating mechanisms and resulting properties of polymers.

Rozsah práce:

Rozsah příloh:

Forma zpracování bakalářské práce: **tištěná/elektronická**

Seznam odborné literatury:

1. Pritchard, G.: *Plastics additives - An A-Z reference*, Springer - Verlag, 1998, ISBN 0-412-72720-X
2. Zweifel, H.: *Plastics additives handbook*, Mnichov - Hanser, 2001, ISBN 1-56990295-X
3. Bart, J.C.J.: *Additives in polymers: Industrial analysis and applications*, Hoboken NJ: Wiley, ISBN 0470850620 and scientific articles

Vedoucí bakalářské práce:

**Ing. Jana Navrátilová**  
Ústav inženýrství polymerů

Datum zadání bakalářské práce:

**11. února 2008**

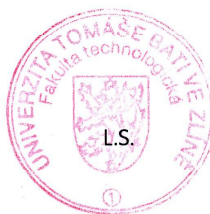
Termín odevzdání bakalářské práce:

**30. května 2008**

Ve Zlíně dne 11. února 2008



doc. Ing. Petr Hlaváček, CSc.  
*děkan*



Ing. Roman Čermák, Ph.D.  
*ředitel ústavu*

## **ABSTRAKT**

Tato práce se zabývá nukleačními/zjasňujícími činidly, jejich významem, aplikací a použitím v běžné praxi. Je také zaměřena na změny v chování nukleovaných/zjasněných polymerů. V práci jsou představeny také výhody použití těchto činidel jakožto i jejich přínos pro průmysl. Hlavní část práce je věnována polypropylenu. V případě tohoto materiálu se nukleační činidla používají velmi často, především kvůli zlepšení optických vlastností, zkrácování zpracovatelských časů či vyvolání krystalizace do požadované krystalické mřížky.

Klíčová slova: nukleační činidla, zjasňovací činidla, polypropylen, krystalizace, nukleace

## **ABSTRACT**

The Bachelor thesis deals with nucleating/clarifying agents, their purpose, applications and utilization in common practice. In addition, this work focuses on changes in behavior of nucleated/clarified polymers and presents the benefits of utilization of these agents and their contribution to the industry. The major part of the work is devoted to polypropylene. In this material nucleating agents are often used to improve optical properties, short processing times or induce the crystallization into preferred crystalline form.

Keywords: nucleating agents, clarifying agents, polypropylene, crystallization, nucleation

Thanks:

I would like to express my deepest gratitude and thanks to the supervisor of my bachelor thesis Jana Navrátilová for her guidance and support. My thanks go as well to the whole academic and pedagogic board of the Faculty of Technology on Tomas Bata University in Zlín for their education and teaching efforts which made this possible.

I declare I worked on this Bachelor Thesis by myself and I have mentioned all the used literature. In the case of publication of results I will as co-author.

In Zlín 28. 5. 2008

.....

Signature

## TABLE OF CONTENT

|  |           |
|--|-----------|
| <b>INTRODUCTION</b> .....                                    | <b>7</b>  |
| <b>1 POLYMER CRYSTALLIZATION</b> .....                       | <b>8</b>  |
| <b>2 NUCLEATING AGENTS</b> .....                             | <b>11</b> |
| 2.1 CONVENTIONAL NUCLEATING AGENTS .....                     | 11        |
| 2.2 ADVANCED NUCLEATING AGENTS .....                         | 11        |
| 2.3 HYPER NUCLEATING AGENTS .....                            | 12        |
| <b>3 NUCLEATING AGENTS FOR SPECIFIC POLYMERS</b> .....       | <b>13</b> |
| 3.1 POLYPROPYLENE.....                                       | 13        |
| 3.1.1 Polypropylene nucleating agents.....                   | 15        |
| $\alpha$ -nucleating agents.....                             | 16        |
| $\beta$ -nucleating agents.....                              | 18        |
| $\gamma$ -nucleating agents.....                             | 19        |
| 3.1.2 Features and benefits of nucleated polypropylene ..... | 19        |
| Properties of $\alpha$ -nucleated polypropylene .....        | 19        |
| Properties of $\beta$ -nucleated polypropylene .....         | 22        |
| 3.1.3 Application of nucleated polypropylene.....            | 23        |
| 3.2 POLYETHYLENE.....  | 24        |
| 3.2.1 Polyethylene nucleating agents .....                   | 25        |
| 3.3 POLYETHYLENE TEREPHTHALATE.....                          | 26        |
| 3.3.1 Polyethylene terephthalate nucleation.....             | 27        |
| <b>CONCLUSION</b> .....                                      | <b>28</b> |
| <b>LIST OF MENTIONED LITERATURE</b> .....                    | <b>29</b> |
| <b>LIST OF MENTIONED SYMBOLS AND ABBREVIATIONS</b> .....     | <b>32</b> |
| <b>LIST OF FIGURES</b> .....                                 | <b>34</b> |
| <b>LIST OF TABLES</b> .....                                  | <b>35</b> |

## INTRODUCTION

Physical properties and particularly mechanical properties of polymeric materials are the most important from their application point of view. Generally, behaviour of polymers within lifecycle is determined by their chemical nature. However, processability, applicability and durability of plastics can be essentially influenced by several smart ways. One of them is the modification of supermolecular structure of semi-crystalline polymers, particularly by addition of specific nucleating agent.

Homogeneous nucleation generally does not provide consistent properties, as nuclei appear throughout the crystallization, giving a broad distribution of sizes, and hence crystallization will be controlled too much by the processing conditions. Heterogeneous nucleation gives crystals of consistent size, as all nuclei are present at the start of crystallization and the nucleant controls crystallization [1]. Thus, the heterogeneous nuclei influence crystallization kinetics, size of crystallites and, consequently, properties of such materials. Moreover, in the case of polymorphic polymers the nucleating agent can induce the crystallization into preferred crystalline form.

Nucleating agents are often used in semi-crystalline polymers which crystallize slowly to increase the rate of crystallization. In this case the suitable representative is polyethylene terephthalate. The heterogeneous nucleation is also advantageously applied to improve clarity of the material. Such nucleating agents are called clarifying agents and they dramatically decrease the opacity of the polymer. For example, common clarifying agent used in polypropylene is commercial product Millad 3988, based on 1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol [2-6]. Further, the addition of nucleating agents can cause the improvement of mechanical properties, e.g. in polyethylene. Finally, as has been already mentioned, in polymorphic polymers the specific nucleating agent can induce the crystallization into specific crystalline phase. One of polymorphic polymer is isotactic polypropylene. Commonly, it crystallizes into monoclinic  $\alpha$ -phase [7]. By the addition of specific nucleating agent, it forms trigonal  $\beta$ -phase which possesses significantly higher toughness and lower sensitivity to photooxidation [8-11].

In this Bachelor Thesis, the types of nucleating agents and their influence on the processing and properties are discussed. For the most part the attention is paid to polyethylene as in this material the nucleating agents are often used.

## 1 POLYMER CRYSTALLIZATION

Crystallization is a process of formation of solid crystals from a uniform solution or melt. The crystallization process consists of two major events – nucleation and crystal growth. Requirements for polymer crystallization are [12]:

- To allow crystalline ordering the molecular structure of the polymer must be sufficient regular;
- The crystallization temperature of the polymer must be below the melting temperature, but still above glass transition temperature;
- Nucleation must occur prior to crystallization;
- Crystallization rate should be sufficiently high.

Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region), that becomes stable under the current operating conditions. These stable clusters constitute the nuclei. However when the clusters are not stable, they redissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such critical size is dictated by the operating conditions (temperature, supersaturation, etc.). It is at the stage of nucleation that the atoms arrange in a defined and periodic manner that defines the crystal structure [13].

The crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists. Supersaturation is the driving force of the crystallization; hence the rate of nucleation and growth is driven by the existing supersaturation in the solution. Depending upon the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained. Once the supersaturation is exhausted, the solid-liquid system reaches equilibrium and the crystallization is complete, unless the operating conditions are modified from equilibrium so as to supersaturate the solution again [13].

Many compounds have the ability to crystallize with different crystal structures, a phenomenon called polymorphism. Each polymorph is in fact a different thermodynamic solid state and crystal polymorphs of the same compound exhibit different physical



properties, such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. For this reason, polymorphism is of major importance in industrial manufacture of crystalline products [13].

Three types of nucleation can be distinguished. The first is spontaneous nucleation which refers to homogeneous nucleation under the influence of super-cooling. The second is orientation-induced nucleation, which is a result of alignment of crystals. The third type is heterogeneous nucleation. This involves the addition of a foreign phase which presents a new surface on which crystal growth can occur. This foreign phase takes the form of a nucleating agent which has been designed to have a good epitaxial match with the growing polymer crystal, see Fig. 1 [14].

When semi-crystalline polymers crystallize from the melt (typically during the cooling phase of a process), the lamellae organize from a primary nucleus to form complex micro-structures called spherulites. It is widely known that these spherulites continue to grow until they impinge on an adjacent spherulite at which point the growth ceases. The ultimate size of these spherulitic structures dictates a number of properties of the polymer, including optical and physical characteristics. The rate of crystal growth is strongly dependent on temperature.

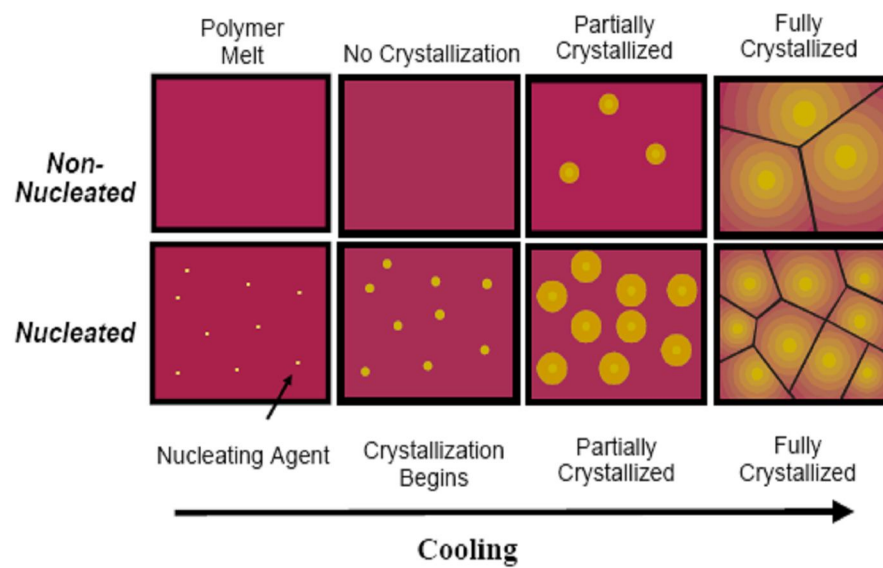


Fig. 1: Comparison of homogeneous and heterogeneous crystallization process [14]

Polypropylene is recognized as a relatively easy material to nucleate. This is because the rate of crystallization is low enough to allow the nucleating agent to have a direct impact on the nucleation density. Conversely, polyethylene has an extremely fast rate of crystallization, rendering most nucleating agents as ineffective.

## 2 NUCLEATING AGENTS

Nucleating agents are chemical substances which after incorporated in plastics form nuclei for the growth of crystals in the polymer melt. In PP, for example, a higher degree of crystallinity and more uniform crystalline structure is obtained by adding a nucleating agent as adipic and benzoic acid or certain of their metal salts.

Three classes of nucleating agents can be distinguished:

- conventional nucleating agents;
- advanced nucleating agents;
- hyper nucleating agents.

Nucleating agents that enhance the transparency of semi-crystalline polymers are referred to as clarifying agents. All clarifying agents are nucleating agents, but not all nucleating agents are clarifying agents [12].

The major application for clarifying agents is clarified polypropylene. The major class of clarifying agents (sorbitol acetals) dissolves in the PP melt during processing. Upon cooling from the melt, a fibrous network of clarifying agent is formed. This magnifies nucleation density yielding spherulites with reduced size (smaller than 1 micron) – in comparison to non-nucleated products [12].

### 2.1 Conventional nucleating agents

Conventional nucleating agents belong to the oldest nucleating agents. The most commonly used even until today are aromatic carboxylic acid salts, sodium benzoate, talc and certain pigment colorants [15]. Usage of talc brings about several modifications of polypropylene properties, which increase the industrial interest for this particular composite. Fillers such as talc usually induce the crystallization into  $\alpha$ -form in polypropylene. In some industrial applications talc is preferred for its lower cost [16].

### 2.2 Advanced nucleating agents

Beginning in the early 1980's, a newer advanced class of nucleating agents was introduced. These have since become widely used in copolymer resins that require additional modulus enhancement and faster crystallization. Most important among these

advanced nucleating agents are the phosphate ester salts. They are used predominantly for enhanced nucleation as compared to the conventional nucleating agents [15].

### **2.3 Hyper nucleating agents**

Hyper nucleating agents are known only about 5 years. They represent a significant technological advance over the previous nucleating technologies. Hyper nucleating agents allow for the fastest processing speed in molding and extrusion processes, while providing the same physical property improvements as traditional nucleating agents. In addition, this new class promotes more isotropic shrinkage, which reduces the potential for part warpage.

Certain pigments (such as blue and green phthalocyanines) are known to cause warpage issues due to anisotropic shrinkage properties. Hyper nucleating agents can be added to these pigment formulations to level out the effect of crystallization temperature and differential shrinkage [15].

Hyper nucleating agents are compatible with filled PP systems, including talc, calcium carbonate and glass filled polypropylene. While the filler provides the greatest contribution to the increase in flexural modulus with these systems, hyper nucleating agents still bring significant increase in other key performance areas such as polymer crystallization temperature, isothermal crystallization half-time and isotropic shrinkage. These attributes translate into benefits such as productivity gains in molding and extrusion processes and reduced potential for warpage in actual parts [15].

### 3 NUCLEATING AGENTS FOR SPECIFIC POLYMERS

Nucleating agents are usually used in polymers which have slow nucleation and crystallization rates. The examples are polyethylene terephthalate and mainly polypropylene.

Typical nucleating agents for polyethylene terephthalate are minerals such as chalk, clay, kaolin, talc and silicates, pigments such as cadmium red, cobalt yellow, then chromium oxide, titanium dioxide, magnesium oxide, carbonates, sulfates, carbon black, salts of carboxylic acids, benzophenone, several polymers, and many other organic liquids [17]. The organic liquids may increase the mobility of the polymer when present in small proportions.

Polyamides-66, -610 and -6, can be nucleated with 0.1 wt. % highly disperse silica. Polyamide-66 powder is used as a nucleant for lower melting polyamides. Other nucleants such as molybdenum disulfide, iron sulfide, titanium dioxide, talc and sodium phenylphosphate are used [18].

Polyethylene is a rapidly crystallizing polymer and is rarely used with nucleating agents. However, some nucleators are applied for properties modification. Potassium stearate is used with high density polyethylene. Some organic pigments can cause nucleation, giving high internal stresses and severe distortions in mouldings [18].

Polypropylene is polymorphic polymer and using a specific nucleating agent the crystallization into several crystalline phases can be induced. The application of nucleating agents is very common in this material, thus it is described in detail thereafter.

#### 3.1 Polypropylene

Professor Giulio Natta produced the first polypropylene resin in Spain in 1954. Natta utilized 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. The versatility of the polymer (the ability to adapt to a wide range of fabrication methods and applications) has sustained growth rates enabling polypropylene to challenge the market share of a host of alternative materials in plethora of applications [19].

Polypropylene is a linear structure based on the monomer  $C_nH_{2n}$ . It is manufactured from propylene gas in presence of a catalyst such as titanium chloride. The structure of polypropylene is shown in Fig. 2.

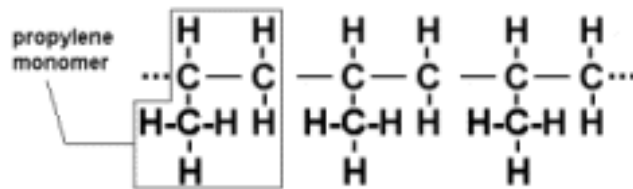


Fig. 2: Polypropylene structure [20]

Polypropylene is a stereoregular, thermoplastic polymer. It can be in syndiotactic, isotactic and atactic form (see Fig. 3).

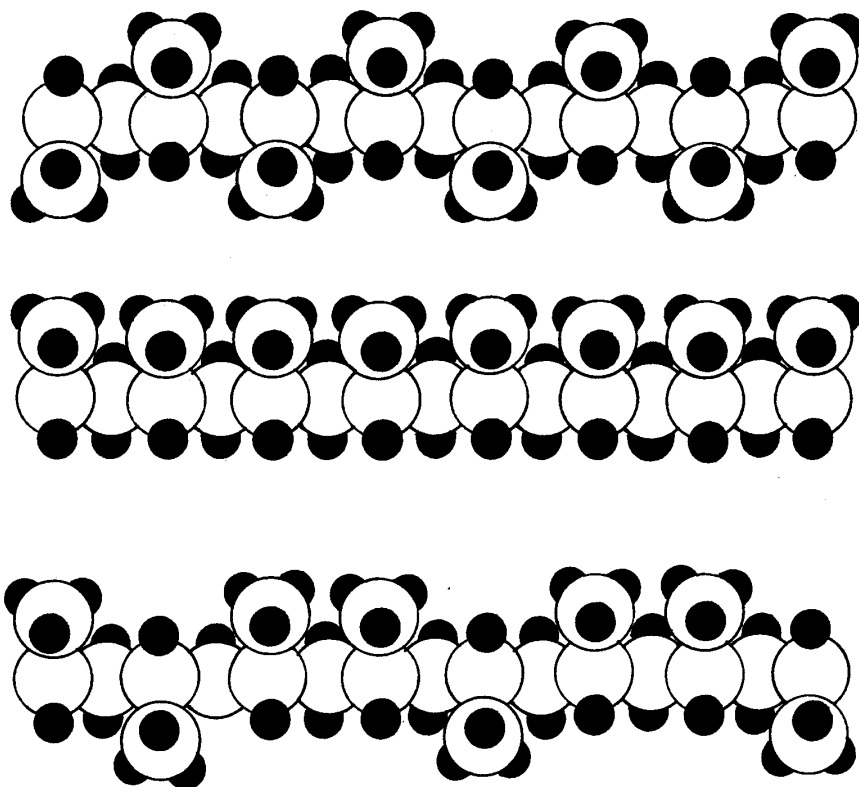


Fig. 3: Space-filling models of syndiotactic (top), isotactic (middle) and atactic (bottom) forms of polypropylene [21]

Polypropylene is a semi-crystalline material containing ordered crystalline regions that at room temperature typically make up about 60 % of the total matter; the remaining material is amorphous. As polypropylene is polymorphic polymer according to crystallization conditions it can crystallize into several crystalline forms. The most thermodynamically stable is monoclinic  $\alpha$ -phase. It always forms upon standard processing conditions [22]. The trigonal  $\beta$ -phase can be obtained via temperature gradient crystallization, crystallization in shear field or the most often using specific nucleating agents [23]. The orthorhombic  $\gamma$ -phase forms under high pressure or from low molecular-weight fractions or copolymers.

### 3.1.1 Polypropylene nucleating agents

Nucleating agents are found to have a significant effect on crystallization behavior of polypropylene. This material has a crystal grow rate some one hundred times lower than that of high density polyethylene for example. It therefore responds well to heterogeneous nucleation by well dispersed additives present in the crystallizing melt.

Application of nucleating agent in polypropylene is, together with shortening of processing time, traditionally used to improve physical properties and, in the case of some  $\alpha$ -nucleating agents called clarifying agents, dramatically improve aesthetics of PP [15].

Nucleating agents cause the crystalline regions to start forming earlier at a higher temperature. The result is a faster and more complete degree of crystallization in which the regions are smaller and more uniform. Nucleating agents for polypropylene are generally divided into two groups:  $\alpha$ -nucleating agent causing the crystallization into  $\alpha$ -phase and  $\beta$ -nucleating agent for inducing formation of trigonal  $\beta$ -phase. The typical  $\alpha$ -nucleating agents consist of sodium benzoate, kaolin or talc [24]. The  $\beta$ -nucleating agents are for example triphenodithiazine, pimelic acid with calcium stearate, quinacridone permanent red dye or N,N-dicyclohexylphthalene-2,6-dicarboxamide [22].

### $\alpha$ -nucleating agents

$\alpha$ -phase is the most common crystal form of polypropylene ( $\alpha$  = monoclinic), which melts at about 160 °C for Ziegler-Natta polymerized homopolymer. In an injection molded or extruded part over 95 % of the crystals are typically of the  $\alpha$ -type [25].

Some organogelators can act as nucleating/clarifying agents in polymer matrices. Organogelators are amphiphilic molecules exhibiting fibrillar structures in organic solvents. Their lipophilic moiety is solubilized in the organic solvent, and the polar one is capable of relatively strong bonding (by hydrogen or ionic bonds) which is essential for the formation of complex, stable, three-dimensional gel networks.

Sorbitol-based nucleators provide significant improvement over conventional nucleating agents in nucleating efficiency and clarity. The most common examples of this type are:

- 1,2,3,4-bis-dibenzylidene sorbitol (DBS)
- 1,2,3,4-bis-(*p*-methoxybenzylidene sorbitol) (DOS)
- 1,2,3,4-bis-(3,4-dimethylbenzylidene sorbitol) (MBDS)
- 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol (DMDBS)

The major drawback of DBS is its fast evaporation rate during processing. MBDS (see Fig. 4) have been developed to solve this problem and improve the nucleating efficiency. DMDBS is the most successful clarifying agent. When the PP cools, the nucleator first crystallizes in the form of a three-dimensional fibrillar network of nanometric dimensions. The nanoscale fibril network serves as nucleating sites for polypropylene, due to its large surface area, leading to enhanced nucleation of small polymer crystals. Investigation of the fibrillar structure by electron microscopy indicated a complex structure in which long and thin fibrils (less than 100 nm in cross-section) are composed of thinner nanofibrils (less than 10 nm in cross-section). Nucleators as DMDBS were found to be highly effective in reducing haze from 90 to 28 % in contrast to sodium benzoate, which didn't improve optical properties. These sorbitol-acetal-based clarifying agents also reduced cycle time (up to 30 %) during injection molding [19].



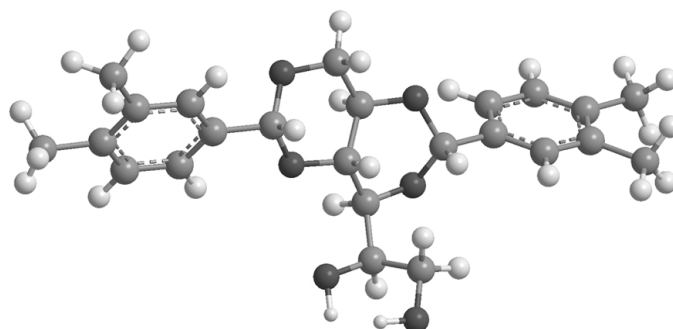


Fig. 4: Molecular structure of  $\alpha$ -nucleating agent Millad 3988; 1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol [19]

Metal salts of substituted aromatic heterocyclic phosphate were found to be very promising nucleators for polypropylene matrices. For example sodium 2,2'-methylene-bis-(4,6-di-*t*-butylphenylene)phosphate, known as NA-11, is a powerful nucleating agent widely used in the processing of iPP.

The effect of monovalent, bivalent and trivalent 2,2'-methylene-bis-(4,6-di-*tert*-butylphenyl)phosphate metal salts on crystallization of iPP was also investigated. It was found that monovalent metal salts of substituted aromatic heterocyclic phosphate such as sodium, lithium and potassium salts have good nucleating performance. With 0.2 wt.% of these salts incorporated into iPP, the crystallization peak temperature of iPP could be increased by 15 °C. The bivalent calcium salt (NA-20), magnesium salt (NA-12), zinc salt (NA-30) and trivalent aluminum salt (NA-13) of substituted aromatic heterocyclic phosphate had little effect on the properties of iPP. Such differences can be explained by the lattice matching between the crystal lattices of the matrix and the additives. Probably, the mismatching of crystal lattice between the nucleating agents and iPP is responsible for the low nucleation effect of the bivalent and trivalent salts [19].

### $\beta$ -nucleating agents

$\beta$ -phase is a less common form, known as trigonal crystal form, generally comprises less than 5 % of the crystals. The  $\beta$ -crystals have a melting point that is typically 12–14 °C below that of the  $\alpha$ -form. If a PP sample contains both crystal forms ( $\alpha$  and  $\beta$ ) a double melting peak will often be seen when a DSC analysis is performed [25].

A higher concentration of  $\beta$ -modification can be obtained via high crystallization temperatures, high temperature gradients, rapid cooling of the melt to 130–135 °C and from melts exposed to shear stress. However, the most common and favourable preparation way is the application of  $\beta$ -nucleating agent. There are several substances that can act as specific  $\beta$ -nucleators. The first effective  $\beta$ -nucleating agent was the  $\gamma$ -modification of linear *trans* quinacridone (LTQ). A series of calcium carboxylates, with different chemical structures and crystal forms, as nucleators for beta polypropylene were investigated too, and they were found to be effective nucleating agents. The Ca-salts of suberic (Ca-sub) and pimelic acid (Ca-pim) possess very high beta nucleating selectivity and efficiency. Another commercially available beta nucleator is N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide which is known under the trade name NJ Star NU-100 (NJS) and it is one of the most powerful nucleating agents. It was also observed that the higher the cooling rate, the larger the increase in level of the beta modification, indicating that increase in the cooling rate reduced the number of monoclinic  $\alpha$ -modifications [19].

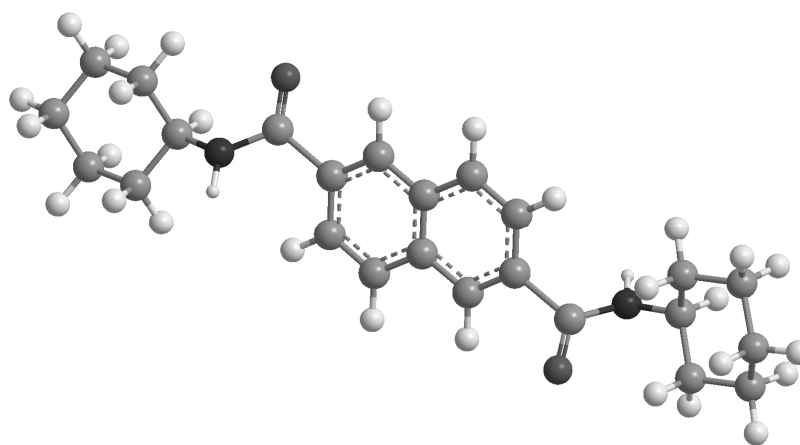


Fig. 5: Molecular structures of  $\beta$ -nucleating agent NJ Star NU 100; N,N'-dicyclohexylnaphthalene-2,6-dicarboxamide [19]

### **$\gamma$ -nucleating agents**

Gamma phase in iPP is formed under special conditions. There is only one nucleating agent that increases the formation of gamma modification in iPP/ethylene copolymer – it is a bicyclo[2.2.1]heptane dicarboxylate salt, commercially known as HPN-68, which is one of the most recent innovations in polypropylene nucleation technology. If properly dispersed, it supplies the fastest known PP crystallization rates at very low concentrations (200–600 ppm). [19]

In the first stage, the nucleating agent must be dispersed in a microemulsion to decrease its size from micro- to nanoscale. The second stage is the introduction of formulations containing the nucleator nanoparticles to a target molten thermoplastic resin, which is then cooled [19].

### **3.1.2 Features and benefits of nucleated polypropylene**

The application of nucleating agents gives some improvement of physical properties. In polypropylene, the type of the nucleating agent plays an important role in this modification.

#### **Properties of $\alpha$ -nucleated polypropylene**

$\alpha$ -nucleated polypropylene has better properties till standard polypropylene. For example crush resistance, extrudability or thermoform ability are better (see Table 1)

Table 1: Comparison of properties of  $\alpha$ -nucleated and standard polypropylenes [24]

|                             | <b>Standard PP</b> | <b>Nucleated PP</b> |
|-----------------------------|--------------------|---------------------|
| Crush resistance            | 0                  | **                  |
| Impact resistance           | 0                  | 0                   |
| Transparency of homopolymer | 0                  | **                  |
| Shrinkage, total            | *                  | 0                   |
| Mold ability                | 0                  | **                  |
| Extrudability               | 0                  | **                  |
| Thermoform ability          | 0                  | **                  |

0 Similar

\* Slightly better

\*\* Better

As has been already mentioned  $\alpha$ -nucleating agents can significantly improve the clarity of polypropylene. The use of clarifying agents has significantly increased potential applications in packaging. Polypropylene normally crystallizes slowly into relatively large spherulites. These are larger than the wavelength of visible light and reflect light. Table 2 shows the comparison of polypropylene clarified with Millad 3988 with other packaging materials like PET, PS or glass [26].

Table 2: Properties of clarified polypropylene comparison to other materials [26]

| Desired property                   | PET | PS | PVC | HDPE | PC | glass |
|------------------------------------|-----|----|-----|------|----|-------|
| See through transparency and gloss | 0   | 0  | 0   | ++   | 0  | 0     |
| Cost/unit volume                   | ++  | +  | +   | 0    | ++ | +     |
| Hot filling capability             | ++  | ++ | ++  | ++   | 0  | 0     |
| Moisture/vapour barrier            | +   | ++ | +   | 0    | ++ | -     |
| Lower density                      | ++  | +  | ++  | 0    | ++ | ++    |
| Taste and odor transfer properties | +   | 0  | +   | +    | 0  | -     |
| Drop impact strength               | +   | ++ | -   | -    | -  | ++    |
| Flexibility                        | 0   | ++ | 0   | 0    | 0  | ++    |
| Stiffness                          | -   | -  | -   | +    | -  | -     |
| Chemical resistance                | +   | +  | ++  | 0    | 0  | 0     |
| Oxygen barrier                     | -   | 0  | -   | -    | 0  | -     |

++ Much better

+ Better

0 Comparable

- Worse

Clarifying agents like DBS are odor-free and has no significant effect on the taste of contained food of liquids, so they are ideal for applications such as food containers, storage containers, bottles for food, juices, or other liquids and for film and sheet packaging [27].

### Properties of $\beta$ -nucleated polypropylene

In addition to the melting point differences the  $\beta$ -crystals produce other physical property changes, such as an improvement in impact strength, a lowering of the tensile yield strength and an increase in ductility (see Table 3). One very unique property of the  $\beta$ -crystalline phase is the fact that when a polypropylene part is deformed past its yield point, the  $\beta$ -crystals undergo a solid state transformation into  $\alpha$ -crystals. During this transformation microvoids develop in the deformed region, and the density of part goes down. If a sheet having a high level of  $\beta$ -crystallinity is stretched, it will generally turn an opaque white, since the microvoids scatter most of the light. The improved impact strength of a  $\beta$ -nucleated molded part is believed to be due to both the higher ductility of the beta crystal phase and the additional energy absorption that accompanies the formation of the microvoids [25].

Table 3: Static tensile characteristics of  $\alpha$ - and  $\beta$ -iPP [23]

| Property               | $\alpha$ -iPP | $\beta$ -iPP |
|------------------------|---------------|--------------|
| E-modulus [GPa]        | 2.0           | 1.8          |
| Yield stress [MPa]     | 36.5          | 29.5         |
| Yield strain [%]       | ~ 12          | ~ 7          |
| Necking stress [MPa]   | 27.5          | 28           |
| Necking strain [%]     | ~ 22          | -            |
| Tensile strength [MPa] | 39.5          | 44           |
| Tensile strain [%]     | ~ 420         | ~ 480        |

The  $\beta$ -phase has a higher inherent ductility than related material containing only  $\alpha$ -spherulites, and therefore an improvement of impact properties can be supposed. Table 4 show quantitative values of the notch impact strength as a function of NU100 concentration. Increasing concentration of the nucleant leads to slow growth of the notch impact strength. The impact strength of the specimens containing 0.02 wt. % of NU100 is slightly higher than that of the pure  $\alpha$ -phase. When the nucleant concentration reached to level of 0.03 wt.%, the impact strength rapidly increased up to 7,6 kJ/m<sup>2</sup>, which is a 246 % increase of notch impact strength as compared to non-nucleated samples.

Table 4: Notch impact strength  $A_k$  of the nucleated samples [28]

| wt. % NU100 | $A_k$ (kJ/m <sup>2</sup> ) |
|-------------|----------------------------|
| 0           | 2.19                       |
| 0.01        | 2.72                       |
| 0.02        | 3.84                       |
| 0.03        | 7.57                       |
| 0.04        | 7.05                       |
| 0.05        | 6.74                       |
| 0.07        | 6.20                       |
| 0.08        | 5.77                       |
| 0.10        | 5.72                       |
| 0.20        | 5.73                       |

Moreover, it has been found that  $\beta$ -nucleated polypropylene is less sensitive to photooxidative degradation as compared to common neat polypropylene [29, 30].

### 3.1.3 Application of nucleated polypropylene

$\alpha$ -nucleated polypropylene is usually used in many branches. For example garden furniture, door panels, pipe fittings, closures, battery cases etc. can be made from this material. Polypropylene containing  $\alpha$ -nucleating/clarifying agents is often used for packaging.

$\beta$ -nucleated polypropylene due to its high toughness is suitable for piping. Moreover, there is a possibility to use this material for micro-porous films with breathable feature [31]. The microvoiding is caused by  $\beta$ -to- $\alpha$ -phase transformation during drawing. It can also result in a significant density reduction of the final film and even in a production of films with high levels of vapour transmission or breathability. Another interesting film product based on  $\beta$ -nucleated polypropylene is biaxial-oriented film with a high degree of surface roughening which can be used in dielectric capacitors [32].

## 3.2 Polyethylene

Polyethylene is a thermoplastic polymer and it consists of long chains of the monomer – ethylene.

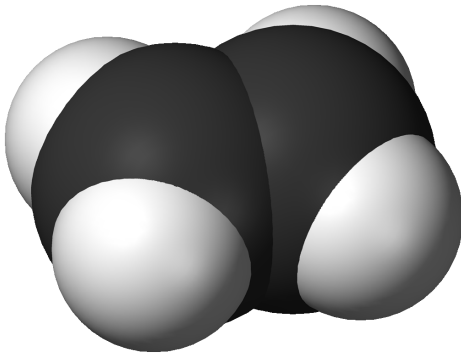


Fig. 6: Model of ethylene [33]

Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene. PE is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight [33].

Classification:

- |  |        |
|--|--------|
| • Ultra high molecular weight polyethylene | UHMWPE |
| • Ultra low molecular weight polyethylene  | ULMWPE |
| • High molecular weight polyethylene       | HMWPE  |
| • High density polyethylene                | HDPE   |
| • High density cross-linked polyethylene   | HDXLPE |
| • Cross-linked polyethylene                | PEX    |



### 3.2.1 Polyethylene nucleating agents

Nucleation of polyethylene has been studied over the years but there has never been commercial adoption of nucleation as a technique for modifying polyethylene properties. This is generally owing to insufficient performance enhancement achievable through nucleators typically designed for polypropylene. However, recently the Milliken Company has launched new nucleating agent for polyethylene with commercial name Hyperform HPN-20E that delivers optical improvements, an enhanced moisture barrier and improved mechanical properties [14].

The effect of nucleation in polyethylene can be seen in Fig. 7. This figure shows an image of a 40  $\mu\text{m}$  compression molded plaque taken under hot stage microscopy. The polyethylene is a 0,952  $\text{g}/\text{cm}^3$  HDPE which was heated to 200  $^{\circ}\text{C}$  and then cooled at the controlled rate of 10  $^{\circ}\text{C}/\text{min}$ .

Nucleated HDPE

Control HDPE

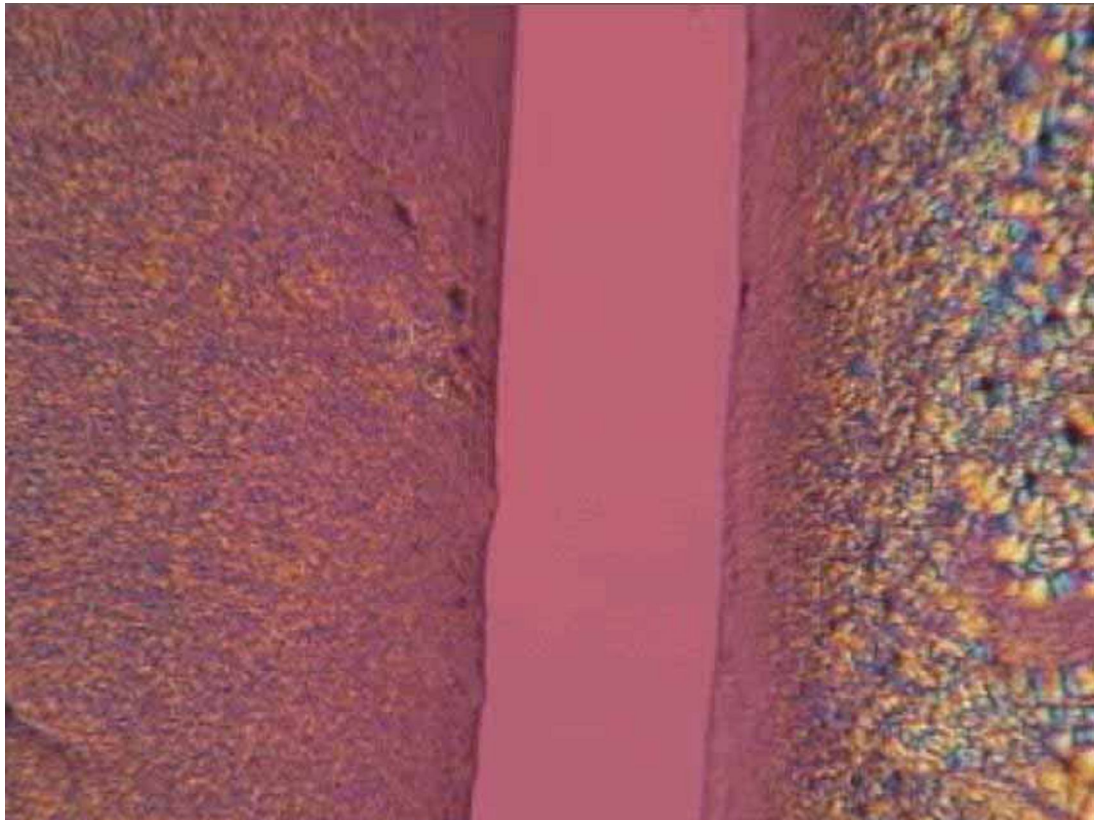


Fig. 7: Hot stage microscopy analysis of HDPE crystallization behavior [14]

### 3.3 Polyethylene terephthalate

Polyethylene terephthalate (PET) is linear thermoplastic, its monomer can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or the transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct [34].

Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with ethylene glycol as the byproduct (the ethylene glycol is recycled in production). PET has low water absorbability and good toughness [35]. Depending on its processing and thermal history, it may exist both as an amorphous (transparent) and as a semi-crystalline (opaque and white) material. Chemical structure of polyethylene terephthalate is shown in Fig. 8.

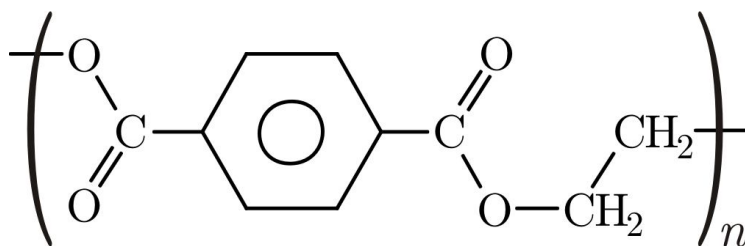


Fig. 8: Structure of polyethylene terephthalate [34]

### 3.3.1 Polyethylene terephthalate nucleation

Polyethylene terephthalate and polybutylene terephthalate (PBT) are the two most common commercial thermoplastic polyesters. Polyethylene terephthalate due to its slow rate of crystallization is mainly used for fiber applications while PBT due to its fast crystallization rate is mainly used in moulding applications [36].

DBS can melt along with polyethylene terephthalate and thus can be better distributed in the matrix than an inorganic nucleating agent. The spherulite size first decreased rapidly on addition of DBS and then decreased gradually with further addition of DBS. Correspondingly nucleation density increased rapidly at first and then increased gradually. The size of agglomeration increases when the level of DBS increased beyond 1 wt.%. This also leads to turbidity in the polymer. Crystallization rate of polyethylene terephthalate enhanced by an organic nucleating agent with 0.5 wt.% being an optimum level [36].

An industrially used nucleating agent is talc, which is also the benchmark for future improvements. Other nucleating agents that have been reported are ionomers, metal oxides and hybrids, many organic compounds, residual catalysts, polymers and fibers [37].

Hydroxyl group-containing triglyceride oils are effective nucleating agents for polyethylene terephthalate and provide improved crystallization properties. The hydroxyl group-containing triglyceride oil may be combined with a conventional organic acid metal salt nucleating agent. By covalently bonding the hydroxyl group-containing triglyceride oil with a metal carboxylates, improved crystallization properties are obtained [38].

## CONCLUSION

Recently the utilization of nucleating/clarifying agents is common in the industry all around the world. The addition of nucleating/clarifying agents into semi-crystalline polymer influences the crystallization kinetics and also the final properties of the material.

Nucleating agents should fulfill some attributes; for example they should be insoluble in the polymer, melting point of nucleating agent should be above the melting point of polymer etc. Nucleating agents have various structures depending on the material in which they are used. In polypropylene, substituted sorbitol acetals or organic salts are often applied, on the other hand, the common nucleating agents in polyethylene terephthalate are ionomer resins.

Every clarifying agent is nucleating agent too, but not every nucleating agent is clarifying agent. A good example is talc. It is efficient nucleating agent but it has not any better optical properties for polymer. On the other hand commercial Millad 3988 (based on sorbitol) is efficient nucleating agent and clarifying agent as well.

Nucleating/clarifying agents can significantly increase the range of utilizing for semi-crystalline polymers, because they are able to adjust properties of materials. For example, in packaging the clarity is desired property. However, polypropylene which is suitable for this application shows relatively high haze. By addition of clarifying agent the opacity can be dramatically decreased. Moreover, as nucleating/clarifying agents increase the rate of crystallization, the processing cycles are shorter. In the case of polymorphic polymers (e. g. isotactic polypropylene) specific nucleating agent can induce crystallization into preferred crystalline form.

**LIST OF MENTIONED LITERATURE**

- [1] Shanks, R.A., Tiganis, B.E. Nucleating agents for thermoplastics in: Pritchard, G., *Plastics additives - an A-Z references*, Springer-Verlag, 1998, ISBN 978-1-59124-134-8
- [2] Zweifel, H., *Plastics additives handbook*, Munich: Hanser, 2001, ISBN 1-56990-295-X
- [3] Marco, C., Ellis, G., Gomez, M. A., Arribas, J. M., (2002) *J Appl Polym Sci*, 84, 2440
- [4] Shepard, T.A., Delsorbo, C. R., Louth, R. M., Walborn, J.L., Norman, D. A., Harvey, N. G., Spontak, R. J., (1997) *J Polym Sci Pol Phys*, 35, 2617
- [5] Kristiansen, M., Werner, M., Tervooth, T., Smith, P., Blomenhofer, M., Schmidt, H. W., (2003) *Macromolecules*, 36, 5150
- [6] Marco, C., Gomez, M. A., Ellis, G., Arribas, J. M., (2002) *J Appl Polym Sci*, 84, 1669
- [7] Varga, J., *Crystallization, melting and supermolecular structure of isotactic polypropylene*. In: KARGER-KOCSIS, J., *Polypropylene: Structure, Blends and Composites*, London: Chapman & Hall, 1995, ISBN 0-412-58430-1
- [8] Varga, J., (2002) *J Macromol Sci Phys*, 41, 1121
- [9] Obadal, M., Čermák, R., Raab, M., Verney, V., Commereuc, S., Fraise, F., (2005) *Polym Degrad Stabil*, 88, 532
- [10] Shi, G., Zhang, X., Qui, Z., (1992) *Makromol Chem*, 193, 583
- [11] Raab, M., Kotek, J., Baldrian, J., Grellmann, W., (1998) *J Appl Polym Sci*, 69, 2255
- [12] Hoffmann, K., Huber, G., Mader, D. *Nucleating and clarifying agents for polyolefins*, *Macromol. Symp.* 2001, 176, 83-91
- [13] <http://en.wikipedia.org/wiki/Crystallization>
- [14] <http://www.hyperformnucleatingagents.com/PEHome/casest/Pages/case%20studies.aspx>
- [15] [http://www.hyperformnucleatingagents.com/PPHome/whynuc/Pages/pp\\_why\\_nucleation.aspx](http://www.hyperformnucleatingagents.com/PPHome/whynuc/Pages/pp_why_nucleation.aspx)
- [16] Ferrage, E., Martin, F., Boudet, A., Petit, S., Fourty, G., Jouffret, F., Micoud, P., De Parseval, P., Salvi, S., Fourtene, J.P., *Talc as nucleating agent of polypropylene: morphology induced by lamellar particles addition and interface mineral-matrix modelization*, *J. Mat. Sci.*, 2002, 37, 1561-1573

- [17] Petermann, J., Epitaxial growth on and with polypropylene, in Karger-Kocsis, J., Polypropylene structure, blends and composites, Vol.1 Structure and morphology, Chapman & Hall, London 1994, 119-139
- [18] Jansen, J., Nucleating agents for partly crystalline polymers, in Gachter, R. and Muller, H., Plastics additives Handbook, Hanser publishers, 1985, Munich, 674-683
- [19] Libster, D., Aserin, A., Garti, N., Advanced nucleating agents for polypropylene in: Polymers for advanced technologies, 2007, volume 18, page 685-695
- [20] <http://www.lenntech.com/polypropylene.htm>
- [21] <http://www.obrazky.cz/detail?id=eJyVjr1uwyAYRXcexCM/xo6dSihDILZDhg5dkqUCAkqU%2BA5TpPn3So1LXrPTpHd3cTEP0KKcLq%0AzdVUNsUgmpZVuRgQrK%2Bs88Uk8RwEGkuBF0KWZcF6NAEXGWZsLjPRXuZMgpxiyuQHNR01AJTjCYZ/%0Aah9//%2BCxBC%2B6lqHNtkec/rZckIPJGJzORiY9Yh0DcXmnt8f2OPDz1%2BcUz/ag2Nwm/q3U/uru3eF1%0A8bfTaut3nt8axOoeMdZbRTtWX%2BiGaqW5Ug9jTVxz%0A>
- [22] J. Varga, Crystallization, melting and supermolecular structure of isotactic polypropylene. In: J. Karger-Kocsis, Vol.1 Ed. Polypropylene: Structure, Blends and Composites, Chapman & Hall, London 1995
- [23] J. Varga, J. Macromol. Sci. Phys., 41 (2002) 1121
- [24] Maier, C., Calafut, T., Polypropylene: The definitive user's guide and databook, ISBN 1884207588, 1998, William Andrew Inc. Page 141
- [25] <http://www.mayzo.com/Paper/BetaNucleationPolypropylene.pdf>
- [26] Milliken Chemicals, Clarifying agents extend scope for polypropylene in packaging in: Plastics additives and compounding, volume 3, March 2001, page 30-34
- [27] <http://www.clearpp.com/eng/Why%20Clear/Taste%20and%20Odor/Pages/Tasteandodor.aspx>
- [28] Obadal, M., Čermák, R., Baran, N., Stoklasa, K., Impact strength of PP in: Int. Polym. Process., 2004, 19, 35
- [29] M. Obadal, R. Čermák, M. Raab, V. Verney, S. Commereuc, F. Fraïsse, Polym. grad. Stab. 2006, 91, 459

- [30] J. Výchopňová, R. Čermák, M. Obadal, M. Raab, V. Verney, S. Commereuc Polym. Degrad. Stab. 2007, 92, 1763
- [31] Jacoby, P., Lee, R.E., The Use of  $\beta$ -nucleation to Produce Microvoided Oriented Polypropylene Films, SPE ANTEC Proceedings, Boston, 2005
- [32] Fujiyama, M., J. Appl. Polym. Sci., 36, 985 (1988)
- [33] <http://en.wikipedia.org/wiki/Polyethylene>
- [34] [http://en.wikipedia.org/wiki/Polyethylene\\_terephthalate](http://en.wikipedia.org/wiki/Polyethylene_terephthalate)
- [35] <http://www.kenplast.com/project/pet/>
- [36] Misra, A., Structure-property relationships in crystalline polyesters and their blends in: ANTEC 1996, Plastic: Plastics-Racing into the future, Volume 2: Materials, ISBN 978-1-56676-443-8, 1996, Society of plastics engineers
- [37] Wit, G., Lemstra, P.J., A new solid-state process for chemici modification of PET for crystallization rate enhancement in: Polymer, volume 43, 2002, page 5709-5712
- [38] <http://www.patentstorm.us/patents/5356972/fulltext.html>

**LIST OF MENTIONED SYMBOLS AND ABBREVIATIONS**

|        |  |
|--------|--|
| Etc    | et cetera  |
| PP     | polypropylene  |
| iPP    | isotactic polypropylene                              |
| wt. %  | weight percentage                                    |
| Fig.   | figure   |
| DSC    | differential scanning calorimetry                    |
| PE     | polyethylene   |
| PET    | polyethylene terephthalate                           |
| PS     | polystyrene  |
| PVC    | polyvinyl chloride                                   |
| PC     | polycarbonate  |
| DBS    | 1,2,3,4-bis-dibenzylidene sorbitol                   |
| DOS    | 1,2,3,4-bis-( <i>p</i> -methoxybenzylidene sorbitol) |
| MBDS   | 1,2,3,4-bis-(3,4-dimethylbenzylidene sorbitol)       |
| DMDBS  | 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol         |
| UHMWPE | ultra high molecular weight polyethylene             |
| ULMWPE | ultra low molecular weight polyethylene              |
| HMWPE  | high molecular weight polyethylene                   |
| HDPE   | high density polyethylene                            |
| HDXLPE | high density cross-linked polyethylene               |
| PEX    | cross-linked polyethylene                            |
| MDPE   | medium density polyethylene                          |
| LDPE   | low density polyethylene                             |
| LLDPE  | linear low density polyethylene                      |



VLDPE      very low density polyethylene

$\alpha$             monoclinic phase

$\beta$             trigonal phase

$\gamma$             orthorhombic phase

**LIST OF FIGURES**

|  |    |
|--|----|
| Fig. 1: Comparison of homogeneous and heterogeneous crystallization process.....   | 10 |
| Fig. 2: Polypropylene structure.....   | 14 |
| Fig. 3: Space filling models of syndiotactic (top), isotactic (middle)<br>and atactic (bottom) forms of polypropylene.....       | 14 |
| Fig. 4: Molecular structure of $\alpha$ -nucleating agent Millad 3988;<br>1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol.....      | 17 |
| Fig. 5: Molecular structures of $\beta$ -nucleating agent NJ Star NU 100;<br>N,N'-dicyclohexylnaphthalene-2,6-dicarboxamide..... | 18 |
| Fig. 6: Model of ethylene.....   | 24 |
| Fig. 7: Hot stage microscopy analysis of HDPE crystallization behavior.....  | 26 |
| Fig. 8: Structure of polyethylene terephthalate.....   | 27 |

**LIST OF TABLES**

|   |    |
|---|----|
| Table 1: Comparison of properties of $\alpha$ -nucleated and standard polypropylenes..... | 20 |
| Table 2: Properties of clarified polypropylene comparison to other materials.....         | 21 |
| Table 3: Static tensile characteristics of $\alpha$ - and $\beta$ -iPP.....               | 22 |
| Table 4: Notch impact strength $A_k$ of the nucleated samples.....                        | 23 |

