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**Crystallization and Melting Characteristics and  
Supermolecular Structure of the  $\beta$ -Modification of  
Isotactic Polypropylene and its Multi-Component  
Systems**

PhD Thesis

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11. Menyhárd A., Varga J., Pozsgay T.,  *$\beta$ -gócképző parciális oldódásának hatása a polipropilén kristályosodására* Kutatóközponti Tudományos Napok MTA KK, 2006 Május 18-19
12. A. Menyhárd, J. Varga: *New Aspects of  $\beta$ -Nucleating Agents for Isotactic Polypropylene: Solubility, Selectivity and Efficiency.* 8<sup>th</sup> Austrian Polymer Meeting, Sept. 20-22, 2006. Linz
13. Faludi G., Menyhárd A., Varga J., *Maleinsavval ojtott polipropilén  $\beta$ -nukleált változatának olvadási és kristályosodási jellegzetességei* MTA Termoanalitikai Munkabizottság ülése. 2007. február 20.
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## 1. Introduction

Isotactic polypropylene (iPP) is one of the most commonly used polymers. Semicrystalline iPP is a polymorphic material, with several crystalline modifications including the monoclinic ( $\alpha$ ), trigonal ( $\beta$ ), and orthorhombic ( $\gamma$ ) forms. The commercial grades of iPP crystallize essentially into the  $\alpha$ -form, which is its thermodynamically stable form. Crystallization in temperature gradient or in sheared or strained melt encourages the development of the  $\beta$ -iPP in commercial polypropylene. In practice, the most reliable method for preparation of  $\beta$ -iPP is the introduction of selective  $\beta$ -nucleating agents. The toughness (ductility) and impact resistance of  $\beta$ -iPP are superior to those of the traditional  $\alpha$ -iPP. These characteristics of  $\beta$ -iPP, which are very advantageous in several applications, justify the extensive basic and applied research related to this material.

### 1.1. Preparation of $\beta$ -iPP

The most reliable method of preparation of  $\beta$ -iPP is the introduction of efficient, selective  $\beta$ -nucleating agents. The first efficient  $\beta$ -nucleating agent was the  $\gamma$ -form of linear trans- $\gamma$ -quinacridone (LTQ) introduced by Leugering. The efficiency of a two-component  $\beta$ -nucleating agent consisting of pimelic acid and calcium stearate was demonstrated by Shi *et al.* Similarly efficient compounds, which have more defined composition and structure, are the calcium salts of pimelic and suberic acid produced in our laboratory. N,N'-dicyclohexil-2,6-naphthalene-dicarboxamide (NJS) is also an efficient  $\beta$ -nucleating agent, which was developed and marketed in the last few years. These nucleating agents have different nucleating efficiency and selectivity. The formation of pure  $\beta$ -iPP has an upper ( $T(\beta\alpha) = 140 - 141$  °C) and a lower ( $T(\alpha\beta) \approx 105$  °C) temperature limit.

### 1.2. Supermolecular structure of $\beta$ -iPP

Within the characteristic temperature interval of the formation of pure  $\beta$ -iPP different types of supermolecular structures are formed during crystallization in isotropic melt. Depending on the crystallization temperature negative radial ( $\beta_{III}$ ), or negative banded  $\beta$ -spherulites ( $\beta_{IV}$ ) can be formed. Hedritic structure can be observed in the early stage of crystallization of  $\beta$ -iPP. The hedrites might be transformed into  $\beta$ -spherulites during the later stages. Fully developed hedrites can only be observed during crystallization at high temperature (near to  $T(\beta\alpha)$ ).

The supermolecular structure of iPP nucleated with selective  $\beta$ -nucleating agent can be studied mostly by PLM during crystallization from isotropic melt, or on sections cut from processed samples. The structure depends basically on the concentration of the nucleating agent and the thermal conditions like cooling rate and crystallization temperature.

### 1.3. Melting behavior of $\beta$ -iPP

The melting behavior of  $\beta$ -iPP depends strongly on the thermal posthistory of the sample. This unique melting behavior was designated as “melting memory effect”. During the heating of  $\beta$ -iPP sample previously cooled under the critical  $T_R^* = 100$  °C temperature recrystallizes into the  $\alpha$ -modification during the partial melting of the  $\beta$ -phase ( $\beta\alpha$ -recrystallization), which leads to an enhanced apparent  $\alpha$ -content determined from the melting curves. On the contrary, no  $\beta\alpha$ -recrystallization occurs during heating, and a separate  $\beta$ -melting peak appears on the DSC trace, if  $\beta$ -iPP is not cooled down below  $T_R^*$  after crystallization. In this case, the polymorphic composition of  $\beta$ -nucleated samples having mixed polymorphic content can be determined from the calorimetric melting curves. Attention should be paid to the fact that  $\beta\alpha$ -recrystallization, which seriously complicates the proper determination of polymorphic composition, usually has not been eliminated during the calorimetric studies of iPP samples nucleated with  $\beta$ -nucleating agents.

### 1.4. Processing of $\beta$ -iPP

For the manufacturing of products containing predominantly  $\beta$ -iPP, some prerequisites should be fulfilled in respect to the processing conditions:

- applying of  $\beta$ -nucleating agents with high activity and selectivity and with sufficient thermal stability,
- appropriate selection of the processing parameters for crystallization in temperature range between  $T(\alpha\beta)$  and  $T(\beta\alpha)$ ,
- optimization of the flow and relaxation condition of the melt in order to avoid or to minimize the formation of row-nucleated  $\alpha$ -phase,
- avoidance of the use of additives (filler, pigments, stabilizers, etc.) with  $\alpha$ -nucleating ability in  $\beta$ -iPP compounds.

The  $\beta$ -iPP can be produced by all of the traditional techniques (compression and injection molding, or extrusion, etc.) if the abovementioned prerequisites are fulfilled.

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- [4] Menyhárd A., *Műanyag- és Gumiipari Tanszék, Műanyag- és Gumiipari Évkönyv*, **1**. 22-24 (2003)
- [5] Menyhárd A., Pukánszky B., Varga J., Nagy G., Mester A., *The influence of transparency by different types of highly active nucleating agents in polypropylene systems*, Periodica Polytechnica: Chemical Engineering, **47**, 76-77 (2003)
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- [7] Móczó J., Menyhárd A., Pukánszky B., *A BME Műanyag- és Gumiipari Laboratóriumának szakmai tevékenysége*, Műanyag és Gumi, **44**. (2) 48-51 (2007)

### 4.3. Conference Presentations

1. Varga J., Menyhárd A., *Polipropilén-poli(vinilidén-fluorid) alapú polimerkeverékek* MKE Műanyag Kollokvium. Szeged. 2001. május 10-11.
2. Varga J., Menyhárd A., *Gócképző hatású adalékanyagok polimerekben* MKE Műanyag Kollokvium. Balatonföldvár. 2003. jún. 12-13.
3. Menyhárd A., Pukánszky B., Varga J., Nagy G., Orbánné M. Á., *Különböző gócképzők átlátszóságra gyakorolt hatása iPP rendszerekben* MKE Műanyag Kollokvium. Balatonföldvár. 2003. jún. 12-13.
4. A. Menyhárd, Á. Liber, G. Belina, J. Varga, *Polymer Blends Based on the  $\beta$ -Modification of Polypropylene* PC2003 Polymer Crystallization and Structure Formation in Processing, September 19-20. 2003-Linz
5. J. Varga, A. Menyhárd, *Interfacial Morphology in Polypropylene Blends and Composites* International Conference on Interfaces and Interphases in Multicomponent Materials (IIMM) October 5-8, 2003, Balatonfüred
6. A. Menyhárd, Á. Liber, G. Belina, J. Varga, *Polymer Blends Based on the  $\beta$ -Modification of Polypropylene* International Conference on Interfaces and Interphases in Multicomponent Materials (IIMM) October 5-8, 2003 Balatonfüred.

of the phases. If the majority of the  $\beta$ -nucleating agent is located in the polar component, the iPP matrix crystallizes in the  $\alpha$ -form. [5].

6. We proved that the use of a compatibilizing agent modifies the distribution of the nucleating agent among the phases and under appropriate conditions a blend can be produced, in which the PP matrix crystallizes mainly in the  $\beta$ -form.

## 4. Publications

### 4.1. The thesis is based on following papers

- [1] Menyhárd, A., Varga, J., Molnár, G., *Comparison of Different  $\beta$ -Nucleators for Isotactic Polypropylene, Characterisation by DSC and Temperature-Modulated DSC (TMDSC) Measurements*, J. Therm. Anal. Calorim. **83**. 625-630 (2006)
- [2] Varga, J., Menyhárd, A., *The Effect of Solubility and Nucleating Duality of N,N'-Dicyclohexyl-2,6-Naphthalene-Dicarboxamide on the Supramolecular Structure of Isotactic Polypropylene*, Macromolecules **40**. 2422-2431 (2007)
- [3] Menyhárd, A., Varga, J., Liber, A., Belina, G., *Polymer Blends Based on the  $\beta$ -Modification of Polypropylene*, Eur. Polym. J. **41**. 669-677 (2005)
- [4] Varga, J., Menyhárd, A., *Crystallization, Melting and Structure of Polypropylene/Poly(Vinylidene-Fluoride) Blends*, J. Therm. Anal. Calorim. **73**. 735-743 (2003)
- [5] Menyhárd, A., Varga, J., *The Effect of Compatibilizers on the Crystallisation, Melting and Polymorphic Composition of  $\beta$ -Nucleated Isotactic Polypropylene and Polyamide 6 Blends*, Eur. Polym. J. **42**. 3257-3268 (2006)

### 4.2. Other publications

- [1] Belina G., Menyhárd A., Juhász P., Belina K., *Heterogén gócképzők hatékonysága PET hulladékban*, Műanyag és Gumi, **38**. 441-446 (2001)
- [2] Belina G., Menyhárd A., Juhász P., Belina K., *Gócképzők hatékonysága különböző szerkezetű polipropilénekben*, Műanyag és Gumi, **38**. 255-259 (2001)

## 1.5. Properties and application of $\beta$ -iPP

The crystal density, the melting point, and enthalpy of fusion and crystallization of the  $\beta$ -form is lower. The most important feature of  $\beta$ -iPP is its high impact resistance. The application of  $\beta$ -iPP is favored in some fields which are based on its high impact resistance and toughness. Other applications are exploiting its micro-void formation and strain hardening characteristic.  $\beta$ -iPP is used for the following, in the industrial practice: pipeline constructions, dielectric capacitors with roughened surface, paper-like films, stretched microporous membranes.

## 1.6. Blends based on $\beta$ -iPP

The primary goal of the preparation of polymer blends is to achieve properties, which are more advantageous than those of their components. The improvement of the impact strength of iPP by the introduction of elastomers is one of the most important examples for blending in industrial practice. As a consequence of the advantageous properties of  $\beta$ -iPP, systematic study was made since decades to prepare blends from iPP, which possess only the  $\beta$ -form as matrix. Most of the polymer blends are heterogeneous systems. The structure of the blend depends strongly on the characteristics of the additive polymers.

## 1.7. Goals

One scope of this thesis was a comparative study of various  $\beta$ -nucleating agents using the same polymer and experimental conditions, because such kind of comparative study was not performed yet. The selectivity of them was characterized by the polymorphic composition, which was determined by DSC measurements. A temperature program with limited recoiling step was applied in order to avoid the  $\beta\alpha$ -recrystallization. The polymorphic composition of the sample can be determined by this technique very accurately.

The other goal of this work was to continue the systematic study of iPP based blends and clear the basic conditions of the preparation  $\beta$ -iPP based blends. According to the results of the previous studies iPP blends with  $\beta$ -iPP matrix could be prepared easily, when the polymers added were amorphous, i. e. elastomers or semicrystalline polymers being in melt state during the crystallization of iPP. When semicrystalline polymers are added to iPP, the most important factor for the influencing the polymorphic composition of the iPP matrix is the  $\alpha$ -nucleation ability of the second polymer. The

other important factor is the crystallization temperature interval of a semicrystalline additive polymer. On the basis of these former results several semicrystalline polymers with different crystallization temperature interval and  $\alpha$ -nucleating ability were studied in this work, like syndiotactic polypropylene (sPP), poly(vinylidene-fluoride) (PVDF), and polyamide 6 (PA6).

## 2. Experimental

Tipplén H-890 grade iPP homopolymer (MFR = 0.35 g/10 min at 230 °C/2.16 kg) supplied by Tisza Chemical Works (TVK, Hungary) was used during the comparative studies of  $\beta$ -nucleating agents. The studied  $\beta$ -nucleating agents were LTQ, Ca-salt of pimelic and suberic acids (Ca-suberate and Ca-pimelate), N,N'-dicyclohexil-2,6-naphthalene-dicarboxamide (NJS) and an experimental product from Ciba designed as CG.

Tipplén H-781 homopolymer (MFR=0.7 g/10min at 230 °C/2.16 kg) produced by Tisza Chemical Works (TVK, Hungary) and its  $\beta$ -nucleated form were used as iPP component in the iPP/PVDF and iPP/sPP blends. The other blends (iPP/rPP, iPP/PA6, iPP/MAPP and iPP/MAPP/PA6) contain Tipplén H-890 supplied by TVK as matrix component. The additive polymers were sPP (WG 17 syndiotactic PP; MFI=3.2 g/10 min at 230 °C/5 kg;  $M_w$ = 230000 g/mol) supplied by Hoechst AG, rPP (Tipplén R-806; MFI=0.25 g/10 min at 230 °C; ethylene content = 3.5–4.5 wt %) by TVK, PVDF (SOLEF 6010; MFI = 2 g/10 min at 230 °C/2.16 kg) by Solvay, PA6 (DANAMID E;  $\eta_{rel}$  = 2.7 determined in 1 % solution of H<sub>2</sub>SO<sub>4</sub> (96%)) by Zoltek, and three types of maleic anhydride grafted iPP (Polybond 3150: MFR=50 g/10 min at 230 °C and 2.16 kg; AL = 0.5 wt%, Exxelor PO1015: MFR = 150 g/10min at 230 °C and 2.16 kg; AL = 1 wt%, Licomont AR 503:  $\eta$  = 500 – 800 mPas at 170 °C, AL=3 wt%) as compatibilizer for iPP/PA6 blends. Ca-suberate was the  $\beta$ -nucleating agent in all blends.

The calorimetric (DSC) traces were recorded using a Perkin Elmer DSC-7 at heating and cooling rate  $V_h=V_c=10$  °C/min. The mass of the samples were 3 – 5 mg. Polarized light microscopy (PLM) studies were performed in polarized light using a Leitz Dialux 20 or a Zeiss Axioscop 20 microscope equipped with a Mettler FP82 hot stage. SEM micrographs were taken from selected samples using JEOL ISM 5600 LV equipment. The wide angle X-ray scattering (WAXS) patterns were recorded using Philips PW 1830/PW type equipment with CuK $\alpha$  radiation at 40 kV and 35 mA.

## 3. New scientific results

1. We proved that the efficiency of various additives used as  $\beta$  nucleating agents, as well as their selectivity in the initiation of the  $\beta$ -form of PP differ considerably from each other. The higher is the selectivity, the lower is the efficiency of the  $\beta$ -nucleating agents studied. Both selectivity and efficiency must be considered in practical applications. [1]
2. We established that heterogeneous  $\beta$ -nucleating agents may dissolve partially or completely in the iPP melt, which modifies their effect. The solubility of the nucleating agent depends on its concentration and on the final temperature of heating. Depending on concentration, the final temperature of heating and on the conditions of cooling the formation of the following supermolecular structures can be observed in the presence of soluble non-selective  $\beta$  nucleating agents:
  - a. transcrystalline structure forming on the lateral surface of the nucleating agent,
  - b. dendritic structure,
  - c. microcrystalline aggregates,
  - d. flower-like formations.
3. We proposed a model for the interpretation of the supermolecular structure with mixed polymorphic composition, which forms in the presence of a non-selective nucleating agent dissolving partially or completely in the PP melt. The model takes into account the  $\alpha$ -nucleating effect of the lateral surface of the nucleating agent. [2].
4. We proved that the basic condition for the preparation of polymer blends with  $\beta$ -iPP matrix is the absence of any  $\alpha$ -nucleating effect of the additive polymer. If the second polymer nucleates the  $\alpha$ -modification of iPP, the polymorphic composition of the matrix depends on the conditions of crystallization. If the crystallization temperature of the second polymer is below that of the  $\beta$ -nucleated iPP matrix, the latter crystallizes in the  $\beta$ -form. [3-5].
5. We showed that if the polarity of the components of iPP based blends differs considerably, the heterogeneous nucleating agent is partitioned between them, and its quantity might dominate in one