Final report

PD109346

September 1, 2013-November 31, 2016

The goal of project numbered as OTKA PD-109346 is the study of correlation between the crystalline structure and optical or mechanical properties of the product. Our aim is to establish quantitative correlations between the structural parameters of crystalline structure and the mechanical or optical properties is possible. Our further aim was the synthesis of possible nucleating agents for isotactic polypropylene (iPP), which can be used for modification of crystalline structure and consequently the properties of the product. The efficiency of these nucleating agents was qualified also within this project. All results obtained in this OTKA project are summarized in the followings.

The main aim of the project is the exploration and quantitative characterization of those structural parameters, which influences the mechanical or optical properties of the product. Accordingly, the correlation between the structural parameters and properties were being studied intensively during the entire project. It was revealed that the molecular structure of the polymer chain correlates strongly to their inclination for crystallization, consequently it influences the crystalline structure formed during solidification and the mechanical an optical properties as well. Our results were presented at several international conferences (1-3) published in Journals qualified as Q1 mostly [1, 2]. The crystalline structure was modified using commercial nucleating agents, which are partially soluble in iPP melt. It was observed that the nucleation agents undergo an unknown transition during heating and a fibrillar structure develops during this transition, which possess much larger efficiency compared to the original particles of the nucleating agent. These novel findings were shown also at an international conference (4) and in a publication in 2014 [3]. As it was shown in the first year of our project the molecular structure of the polymer has also important role, thus the accurate and reliable determination of molecular structure is crucial. Successive self-nucleation and annealing calorimetric experiments (SSA-DSC) are used in the literature to study the molecular structure of crystalline polymers and we suggested a faster and more reliable experimental method for characterization of molecular structure by calorimetry [4].

It was pointed out that optical properties of the product depends strongly on the supermolecular structure of the polymer and a novel calculation method was developed, which is able to provide the number of the nuclei formed during the crystallization process from the crystallization curve recorded in a DSC apparatus [5, 6]. This model was presented at conferences as well (5, 6). The nucleus density values obtained by our new calculation method were used to build a structural model, which describes the light scattering in the polycrystalline polymer [7] and consequently the haze of the product becomes predictable. According to our best knowledge no similar model exists in the open literature. Although, the model is not usable for accurate prediction in its present form, because the refractometric index of crystalline and amorphous iPP should be measured and included in the model this research provided valuable and novel results which were presented at a conference in Germany (7).

The quantitative description of mechanical properties was also the targeted goal of this project. The stiffness of the crystalline polymer depends on its crystallinity and lamellar structure, which structural parameters can be easily obtained by calorimetric measurements. An empirical equation was suggested, which calculates the modulus based on crystallinity (X) and lamellar thickness (l_{av}).

$$E = E_{\min} + \left(E_{\max} - E_{\min}\right) e^{-\left(\left(\frac{1-X}{X}\right)^{\alpha} + \left(\frac{1}{\ell_{av}}\right)^{\beta}\right)^{\gamma}} \qquad 1.$$

E_{min} relates to the stiffness of the amorphous and E_{max} to the modulus of the crystalline phases. The modulus values calculated using equation 1 was compared to experimental data obtained on different iPP polymers [2]. The correlation is shown in Figure 1. Our calculation model was introduced at conferences as well (2, 5). The main advantage of our model is that the modulus of structures, which do not exist in practice, can also be calculated, thus the limitation of stiffness of a selected polymer can be predicted too. The validity and applicability of equation 1 to other crystalline polymers will be the topic during our future research. We hope that our empirical model can be applied successfully to polyamides and different polyesters like poly-(lactic acid) and poly-(ethylene terephthalate) for example. An interesting and unexpected effect was observed during the study of mechanical properties, because at few polymer and nucleating agent combinations the improvement of modulus was accompanied by considerable enhancement of impact resistance (Figure 2). Usually impact resistance decreases with increasing of stiffness. This novel observation is important from industrial point of view, thus all these results were collected and shown at conferences (3) published in last year of the project [8]. Our results hint that the efficient nucleating agent induces morphological changes at lamellar level in few ethylene-propylene random copolymers, thus the distribution of the elastomer phase changes

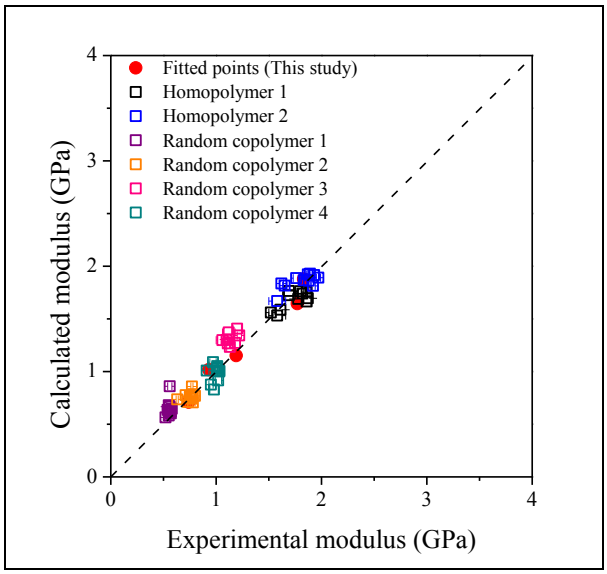


Figure 1 *Correlation between stiffness calculated using equation 1 and the experimentally obtained modulus*

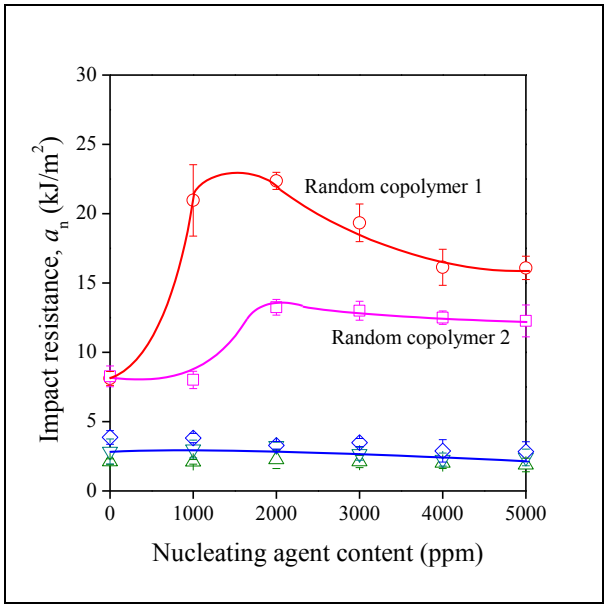
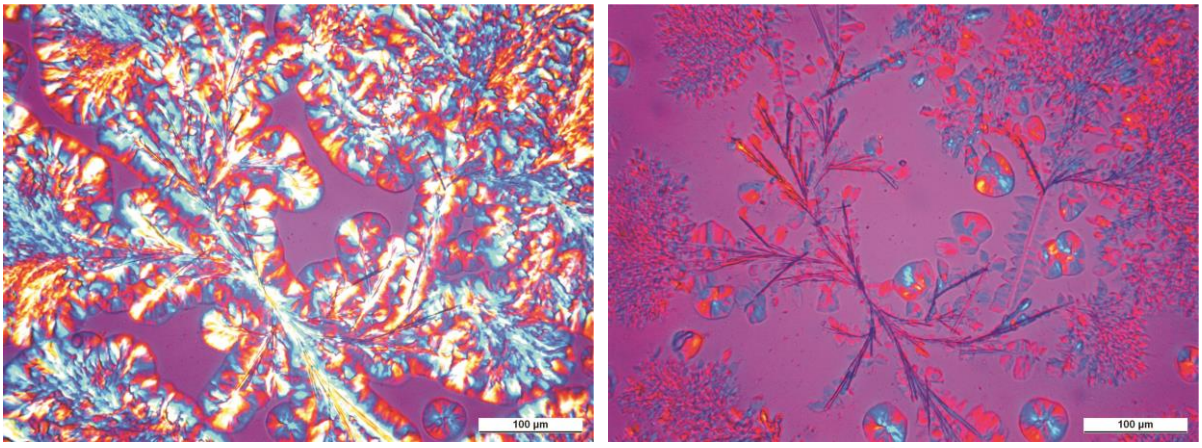


Figure 2 *Impact resistance as a fuction of nucleating agent content*

consequently the crack propagation becomes hindered. These morphological changes results in improved impact resistance.

The second aim of our project was the synthesis and characterization of novel compounds, which could be used as potential nucleating agent in iPP. The nucleating agents were designed to be partially soluble in iPP melt. According to our expectations, the new nucleating agents will induce both α- and β-modifications, thus the crystallization process is complex in the presence of these additives. Accordingly, the first step of this research was the development of experimental protocol, which allows the study of such complex crystallization processes. Furthermore, the novel experimental method can follow the development of both modifications and the crystallization kinetics of each modification can be evaluated separately based on calorimetric experiments. This experimental method was published [9] and demonstrated at an international conference as well (8). Meanwhile the characterization of nucleating agent, an interesting structure was observed. We found that a special structure, in which the finely dispersed α-iPP reinforces the tough β-matrix can be obtained if the thermal conditions of crystallization were adjusted properly (see in Figure 3).



a) b)

Figure 3 *Crystallization process of sample containing 10000 ppm DCHT. The melt was heated up to 250 °C and held there for 3 minutes. a) T = 135 °C and t = 15 min; d) reheating run T = 158 °C*

The rules of formation of this special reinforced structure were presented at a conference Ljubljana (9) and published in the last year of the project [10]. Several nucleating agent were synthesized, but only the first basic compound was published, because the new compounds might have industrial relevance and in that case they should be patented before publication. A standard and reliable experimental protocol was suggested for characterization of nucleating agents of iPP, which induce both modifications of iPP. The standard procedure is important because the number of papers dealing with novel nucleating agents is very large, but the results published in these papers usually cannot be used for comparison, because the experimental conditions are unknown. Dicyclohexyl-terephthalamide (DCHT) was synthesized and characterized and we found that it is partially soluble in the iPP melt, which harmonizes with our expectations. We found that if the nucleating agent dissolves in the melt and recrystallizes during crystallization a special structure formed in which the micro-sized α-

crystals are reinforce the β-matrix. The mechanical properties in the presence of DCHT are shown in Figure 4.

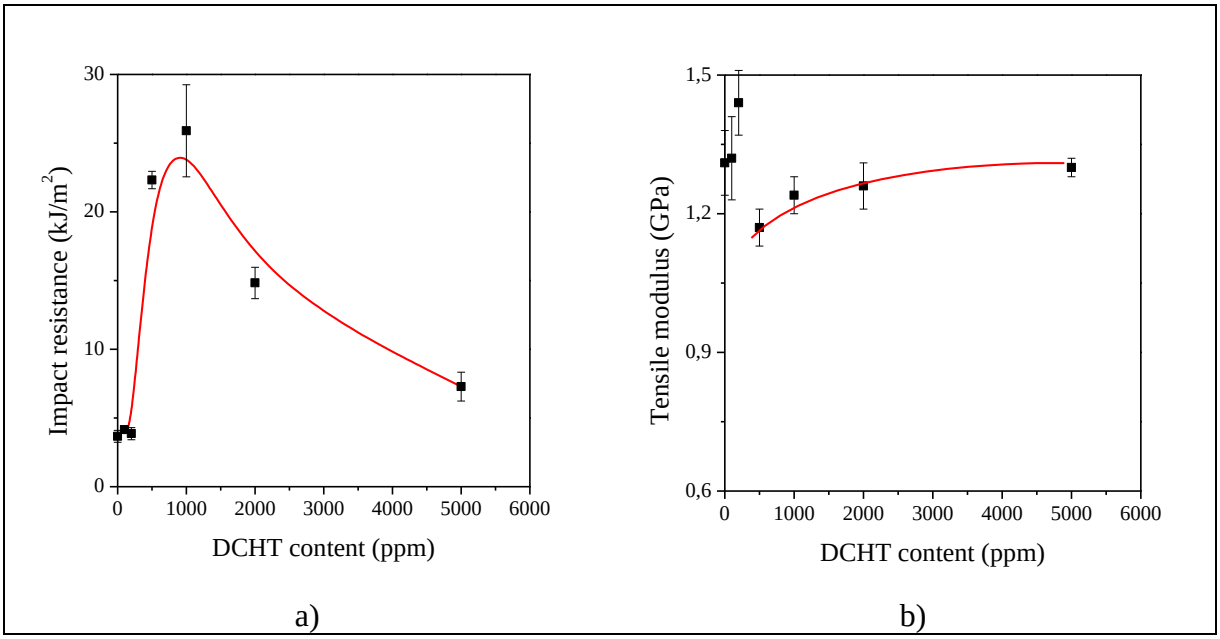


Figure 4 *Impact resistance (a) and tensile modulus (b) of samples nucleated by DCHT*

Summary

As a summary it can be established that the goals of our research were fulfilled. Novel empirical equation was presented which can be used for calculating modulus from crystallinity and lamella thickness data obtained by calorimetry. New calculation method was developed for determination of nucleus density from crystallization curve recorded in a calorimeter. A model was also proposed which describes the rules of light scattering in polycrystalline polymers. We hope that this model will be able to predict haze of the product after fine tuning. Valuable results were produced and 8 publications were presented in peer-reviewed Journals and 2 papers were published in Hungarian in Journal without impact factor. The results obtained in this research project were presented at 9 international conferences. We have to notice that we used several thermo-analytical methods in our studies, and we were asked to present a historical review about the thermal analysis in central Europe, which review was also published in a peer-reviewed Journal [11] during the project. Accordingly, the cumulative impact factor of our nine publications is 28,129. The importance of the topic is proved by the fact that these publications were cited more than 10 times, in spite of that most of them were published in the latest two years. There is intensive industrial interest for our research area, because the development of new nucleating agent is always a hot topic in polymer industry. In addition the modeling of mechanical or optical properties as well as the prediction of limitations of a polymer provides always valuable information for industrial development. This new way of targeted development is interesting for the industry, which is proved by they interest in cooperation with our research group.

Conference presentations (Oral)

1. Horváth, Zs., Menyhárd, A., Doshev, P., Gahleitner, M., Vörös, G., Varga, J., Pukánszky, B., Effect of the molecular structure of the polymer and nucleation on the optical properties of polypropylene homo- and copolymers APST3, September 9-10, 2013. Linz, Austria

2. Menyhárd, A., Suba, P., László, Z., Fekete, H. M., Mester, Á. O., Horváth, Z., Vörös, G., Varga, J., Móczó, J., Direct calculation way of elastic modulus from the parameters of crystalline structure estimated by calorimetry (1) IX Congresso Brasileiro de Análise Térmica e Calorimetrica, November 9-12, 2014. Serra Negra-Sao Paolo, Brasil (2) DVS Polymer meeting, May 11-13, 2015. Gmunden, Austria

3. Horváth, Zs., Menyhárd, A., Doshev, P., Gahleitner, M., Varga, J., Pukánszky, B., Improvement of the Impact Strength of Polypropylene Random Copolymers by Nucleation Workshop on Recent Advances and New Perspectives in Polymer Crystallization, September 29-30, 2014. Genova, Italy

4. Horváth, Zs., Gyarmati, B., Pénzes, G., Menyhárd, A., Doshev, P., Varga, J., Gahleitner, M., Pukánszky, B., The Role of Solubility and Critical Temperatures on the Efficiency of Sorbitol Clarifiers in PP APST3, September 9-10, 2013. Linz, Austria

5. Fleischer-Radu É., Molnár J., Maloveczky, A., Menyhárd, A., The use of calorimetry in modelling mechanical and optical properties of semicrystalline polymers ICTAC, August 14-19, 2016, Orlando, USA

6. Fleischer-Radu É., Molnár J., Menyhárd, A., Estimation of nucleus density during crystallization of semicrystalline polymers: possibilities, limitations and importance X Congresso Brasileiro de Análise Térmica e Calorimetrica, April 17-20, 2016, Sao Paulo, Brasil

7. Sepsi, Ö., Molnár, J., Lenk, S., Ujhelyi, F., Menyhárd, A., Relation between the supermolecular structure and light scattering behavior in birefringent semicrystalline polymers Electromagnetic and Light Scattering XV, June 21-26, 2015. Leipzig, Germany

8. Molnár, J., Dora, G., Horváth, Z., Varga, J., Menyhárd, A., Isothermal and non-isothermal crystallization kinetic of simultaneously developing polymorphic modifications in isotactic polypropylene, 5th Joint Czech-Hungarian-Polish-Slovakian Thermoanalytical Conference, September 6-10, 2015. Zakopane, Poland

9. Varga, J., Kovács, V., Gombár, T., Horváth, Z., Menyhárd, A., Rules of the formation of supermolecular structures in the presence of a non-selective β-nucleating agent in isotactic polypropylene 3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry, August 25-28, 2015. Ljubljana, Slovenia

Reference list

[1] Horváth, Z., Menyhárd, A., Doshev, P., Gahleitner, M., Vörös, G., Varga, J., Pukánszky, B., Effect of the Molecular Structure of the Polymer and Nucleation on the Optical Properties of Polypropylene Homo- and Copolymers, ACS Appl. Mater. Interfaces 6. 7456-7463 (2014)

[2] Menyhárd A., Vörös, G., Móczó, J., Horváth, Z., Suba, P., Orbánné Mester, Á., László, Z., Direct correlation between modulus and the crystalline structure in isotactic polypropylene Express Polym. Lett. 9. 308-320 (2015)

[3] Horváth, Z., Gyarmati, B., Menyhárd, A., Doshev, P., Gahleitner, M., Varga, J., Pukánszky, B., The Role of Solubility and Critical Temperatures for the Efficiency of Sorbitol Clarifiers in Polypropylene, RSC Adv. 4. 19737-19745 (2014)

[4] Horváth, Z., Menyhárd, A., Doshev, P., Gahleitner, M., Varga, J., Tranninger, C., Pukánszky, B., Chain Regularity of Isotactic Polypropylene Determined by Different Thermal Fractionation Methods, J. Therm. Anal. Calorim. 118. 235-245 (2014)

[5] Menyhárd, A., Bredács, M., Simon, G., Horváth, Z., Determination of nucleus density in semicrystalline polymers from non-isothermal crystallization curves Macromolecules 48. 2561-2569 (2015)

[6] Fleischer-Radu, É., Menyhárd, A., Szemikristályos polimerek gócsűrűségének számítása, Polimerek 3 (1) 2017 Elfogadott közlemény

[7] Molnár, J., Sepsi, Ö., Ujhelyi, F., Menyhárd, A., Az izotaktikus polipropilén optikai tulajdonságait befolyásoló szerkezeti tényezők meghatározása és modellezése, Polimerek, 2 (6) 177-181 (2016)

[8] Horváth, Z., Menyhárd, A., Doshev, P., Gahleitner, M., Friel, D., Varga, J., Pukánszky, B., Improvement of the Impact Strength of Ethylene-propylene Random Copolymers by Nucleation, J. Appl. Polym. Sci. 133. 43823 (2016)

[9] Molnár, J., Menyhárd, A., Separation of Simultaneously Developing Polymorphic Modifications by Stepwise Crystallization Technique in Non-isothermal Calorimetric Experiments, J. Therm. Anal. Calorim. 124. 1463-1469 (2016)

[10] Horváth, F., Gombár, T., Varga, J., Menyhárd, A., Crystallization, Melting, Supermolecular Structure and Properties of Isotactic Polypropylene Nucleated with Dicyclohexyl-terephthalamide, J. Therm. Anal. Calorim. Online First. 1-11 (2016)

[11] Sulcova, P., Sestak, J., Menyhárd, A., Liptay, G., Some Historical Aspects of Thermal Analysis on the Mid-European Territory, J. Therm. Anal. Calorim. 120. 239-254 (2015)