Influence of Nucleants on the Formation of Shear-Induced Structures in Polypropylene

Markus Gahleitner, Johannes Wolfschwenger, Joachim Fiebig, Wolfgang Neißl*

Borealis GmbH, St. Peterstr. 25, A-4021 Linz, Austria

Summary: The interaction between the type of nucleating agent and base polymer was investigated for a combination of three commercial nucleants and polypropylenes each. Both the crystallisation behavior under DSC conditions and the mechanical and optical properties were determined for all materials. For both the influences of the nucleant and of the base polymer, the present study has provided qualitative indications as to the triggered crystal morphology and shear-induced superstructure. Especially the latter can be related to the differences between optical and mechanical effects of the nucleation process.

Introduction

External nucleation systems, frequently used to improve the properties of polypropylene, produce a significantly different combination of external properties (shrinkage, anisotropy, mechanics, optics), the reasons for whichare not always well-known[1]. There are several possible sources for these differences. One of these is the polymorphic nature of polypropylene, which can crystallize in three different modifications (α-, β- and γ-form)[2]. While the mechanically very different β-modification cannot be nucleated by the same substrates as the α- and the γ-form[3], the latter two can be enhanced by the same nucleants. Another source of variation is the crystalline superstructure developed in conversion processes[4].

Other differences result from the nature of the nucleating agent, which must, for achieving high efficiency, combine a high degree of lattice matching for the epitactic structure formation[5] with a certain adhesion to the polymer matrix in molten state to allow a fine dispersion of the nucleant particles. Finally, the polymer structure which determines not only the spherulithic growth rate and intrinsic nucleation density of the material[6] but also the preference for a specific crystal modification[7] strongly affects the result of a nucleation process.

 CCC 1022-1360/00/$ 17.50+.50/0

Background and earlier investigations

PP parts produced in injection molding show complex crystalline superstructures, due to the nonhomogenous cooling of the molded part and the occurrence of flow-induced crystallization[8,9]. Not only does the degree of crystallinity and the amount of orientation vary along the cross section of a part, but also the distribution of the different crystalline modifications depends on the actual position (see Figure 1). Both processing conditions and the molecular structure of the polymer itself – through the crystallization behavior - affect the development of these crystalline superstructures.

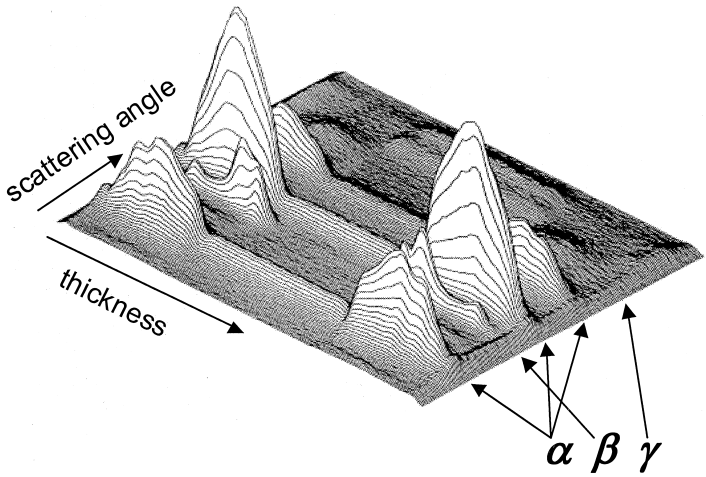

Figure 1 – Distribution of crystallinity and crystal modifications in an injection-molded PP plaque (PP homopolymer, reactor grade with MFR 8 similar to RE-H in present series; plaque thickness 2 mm) recorded with wide-angle X-ray diffraction using a Kratky slit camera in flow direction (data courtesy of Prof. Peter Zipper, Graz University)

An important factor for the skin-layer formation is the molecular weight distribution (MWD) of the polymer. Higher skin-layer thickness has been found to result from broad MWD[8,10], while a reduction of these oriented structures can be achieved by reducing broadness or the average molecular weight directly[11,12]. Other structural parameters of the polymer generally affecting the crystallization behavior[1] have also been found to affect skin-layer formation. While materials with higher isotacticity show an increasing amount of oriented structures[13], the opposite has been found for random and heterophasic ethylene-propylene copolymers[14].

A strong increase of the skin-layer formation was furthermore found with external nucleation[8,15,16] , which should be more closely investigated in the present study. Similar effects were also found in mineral-filled PP, especially with plate-like fillers like talc[17].

Finally, also the parameters of the injection molding process are decisive for the morphology of the part. A reduction of the melt temperature positively affects skin-layer formation[4,18], the same holds for an increase of the wall temperature in the mold[10,13].

Table 1 - Summary of most relevant characterization results for all investigated materials (Tc(DSC) = peak value in cooling at $\partial T/\partial t$ = -10 K/min; NIS Charpy = impact strength (fracture work) in ISO 179 1eA at +23°C; S2* = normalized small angle light scatter in transparency measurement)

Nucleating agent	Conc. ppm	Tc (DSC) °C	Flex.mod. MPa	NIS Charpy kJ/m²	S2* %
RE-H					
none	0	115,8	1461	3,29	48,3
Talc	5000	124,9	1746	3,72	58,4
NA11	1000	129,5	1968	2,41	34,6
M 3988	2000	130,4	1760	2,89	19,6
CR-H					
none	0	114,2	1256	3,96	52,8
Talc	5000	122,6	1508	4,64	43
NA11	1000	127,2	1627	3,9	20,4
M 3988	2000	128,2	1534	3,67	9,2
CR-R					
none	0	96,6	656	8,88	39,3
Talc	5000	105,7	723	8,27	40,6
NA11	1000	128,6	806	9,1	12,6
M 3988	2000	125,7	767	8,93	3,4

Experimental work

Three different base polymers, all having the same melt flow rate (MFR according to ISO 1133; 230°C/2,16kg) of 8 g/10min, were selected for the study: A reactor-grade homopolymer (RE-H), a "Controlled rheoloy"-(CR)-grade hompolymer (CR-H) and a CR-grade random copolymer with 7 mol% ethylene (CR-R). The molecular weight distributions (MWDs) of the two CR-grades are very similar ($M_W/M_N \sim 3$), the reactor grade has a significantly wider MWD ($M_W/M_N \sim 5$). Both homopolymers are based on the same catalyst system and have a comparable isotacticity of 0,97 according to the IR-method[19]. These polymers were combined with three different nucleating agents, namely talc (Luzenac A7, average particle size 2,5 µm), a sorbitol derivative (Milliken

Millad 3988 or DMDBS; 1,3 : 2,4 Bis(3,4-dimethyl-benzylidene) sorbitol) and an organophosphate (Asahi NA11; Sodium 2,2'- methylene bis-(4,6-di-tert. butylphenyl) phosphate).

The crystallization behaviour of the melt compounded materials was tested in DSC with heating and cooling rates of 10 K/min according to ISO 3146; the increase of the apparent crystallisation temperature $\Delta(T_C)$ was used to quantify the nucleation effect despite a nonlinear correlation to the crystallinity as calculated from the melting enthalpy H_M using a theoretical value of 209 J/g for the enthalpy of a completely crystalline PP[20] as obvious from Figure 2. Mechanical properties – flexural modulus according to ISO 178 and Charpy notched impact strength according to ISO 179 1eA at +23°C – were determined on bar specimens of 80x10x4 mm, optical properties (transparency and turbidity according to internal standards) as well as the formed crystalline morphology on plaque specimens of 60x60x2 mm. In both cases, the specimens were injection-molded according to ISO standard conditions (melt temperature 250°C, mold temperature 50°C). For the morphology investigation, polarizing light microscopy (PLM) was used. In selective cases, also details of the crystalline structure were investigated using transmission electron microscopy (TEM) of specimens contrasted with RuO_4.

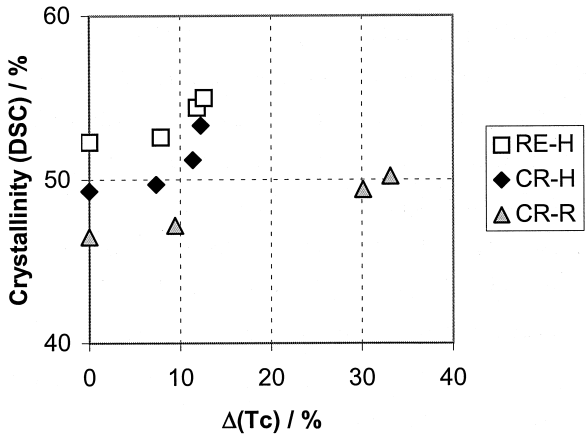

Figure 2 - Correlation between the crystallisation temperature effect and the crystallisation enthalpy of the samples (points on y-axis denote non-nucleated materials)

Results and discussion

The efficiency of a nucleating agent is mostly judged by the increase of the crystallisation temperature in a DSC experiment. It becomes obvious from Table 1 already that the random copolymer (CR-R) has a somewhat special position in the series. This is confirmed by attempts to establish correlations between the DSC-effects and the mechanical behavior (see Figures 3 and 4). While the differences between the two homopolymers can be understood from the differences in original nucleation density resulting from the MWD[1,6], the much stronger nucleation effect for the random copolymer points to a partial suppression of crystallization for the base polymer resulting from the disturbed chain structure. In injection molding, the shift of solidification to higher temperatures also can lead to a change in the distribution between the different crystal modifications, as these have different maxima of the growth rate on the temperature scale ($\gamma < \alpha < \beta$) and also different melting points.

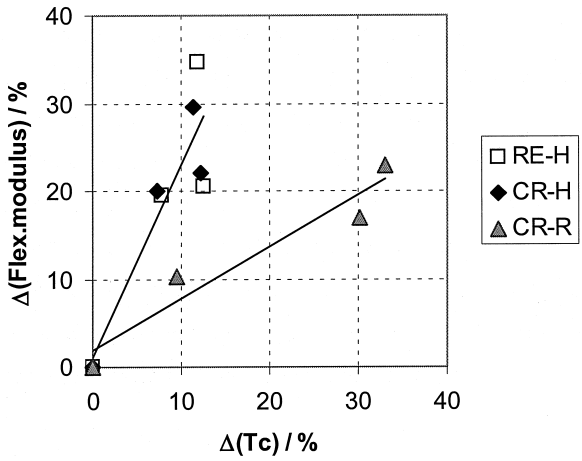

Figure 3 - Correlation between the crystallisation temperature effect and the stiffness increase achieved by nucleation

For the toughness the random copolymer shows a behaviour normally found rather for lower MFR, where nucleation frequently even increases the impact strength. Generally, no direct correlations between crystallinity and impact strength are possible. A deeper understanding of the fracture processes occuring in PP requires consideration of MWD and chain structure on the one hand and morphology and crystal modifications on the

other hand[21].

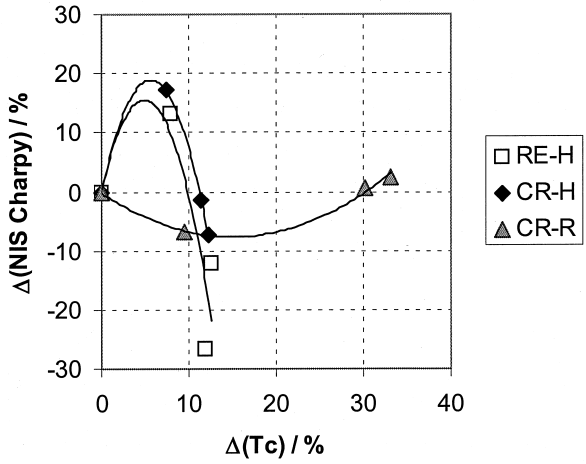

Figure 4 - Correlation between the crystallisation temperature effect and the change in impact strength achieved by nucleation

The situation becomes even more complex when expanding the considerations to optical properties, which are frequently the target of PP nucleation[22]. On top of the well-known fact that the sorbitol derivative gives the best transparency improvement, while falling behind the performance of the organophosphate in stiffness increase[23] also here a significant effect of the base polymer is found (see Figure 5). No correlation at all exists between stiffness and transparency increase.

While for explaining the differences in efficiency between NA11 and talc the change in nucleation density as determined before for pure polymers[1,6] can be used, no such simple explanation is possible for the difference between Millad 3988 and NA11. A possible explanation for the superior optics of the sorbitol-nucleated mixtures is the combination of the network-like structure of the nucleant [24] with the locally twisted nature of the sorbitol-fibrils resulting from the "butterfly"-structure of the molecule.

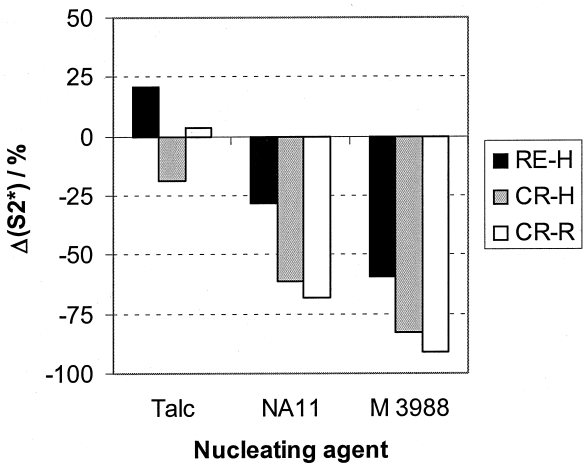

Figure 5 – Nucleation and polymer effects on the relative change in transparency

For understanding the effects of the polymer structure a closer look at the developed morphology is necessary. The dimensions of the oriented superstructures at the specimen surface were determined from PLM as shown in Figure 6. While the skin layer is an assembly of shear induced (shish-kebab) crystallites nucleated and crystallised in shear flow, the following fine grained layer is only nucleated in shear and is sometimes oriented perpendicular to the flow direction[25]. As outlined before, both layers are enhanced by nucleating agents[1,11,26]. Only limited effects on details of the oriented layers by the nucleating agents were found in the TEM investigations, which confirmed earlier results[25,26].

A possible explanation based on simulations using recoverable strain as key parameter for the formation of shear-induced crystal structures has recently been given by Zuidema[27,28]. The positive interaction between the formation of primary crystallites, which is strongly enhanced by external nucleation, and a gelation effect changing the rheological behavior of the polymer gives at least a qualitative reason for the formation of the highly oriented layer.

As Table 2 shows, the degree of enhancement of the skin layer is, however, strongly affected by the nature of the base polymer. While most oriented structures are developed for the material with the highest stiffness increase (RE-H), the opposite is found for the material with the best transparency improvements in nucleation (CR-R).

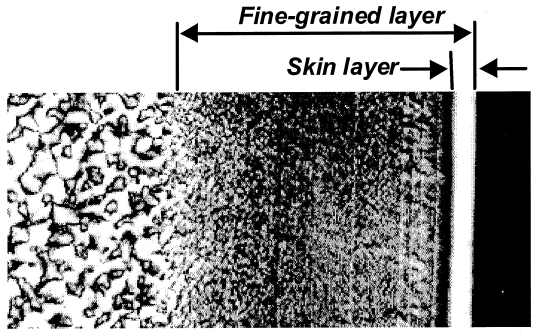

Figure 6 - Schematic presentation of the oriented crystalline structures at the surface of the injection molded specimens

Table 2 - Thickness of the oriented crystalline structures at the surface of the injection molded specimens (thickness of oriented layer – T(OL) – is the sum of the thicknesses of skin and fine-grained layer)

Nucleating Agent		RE-H		**CR-H**		**CR-R**	
		skin	fine-grained	skin	fine-grained	skin	fine-grained
	ppm	µm	µm	µm	µm	µm	µm
none	0	11	139	8	84	< 5	20
Talc	5000	30	160	20	94	10	60
NA11	1000	50	150	38	85	28	54
M 3988	2000	47	149	35	79	15	61

Various correlations between the morphology and mechanical as well as optical properties were tried subsequently. Generally, the best correlations can be found to the total thickness of skin and fine-grained layer together. The exact definition as well as the differentiation between these two layers has not always been made clearly in the past[11,13,17] and is an important point in comparing data from different sources.

While, however, the mechanical properties (mainly the stiffness increase) can be nicely correlated within one material, such correlations can only be found within one type of nucleating agent for the transparency improvement (see Figure 7).

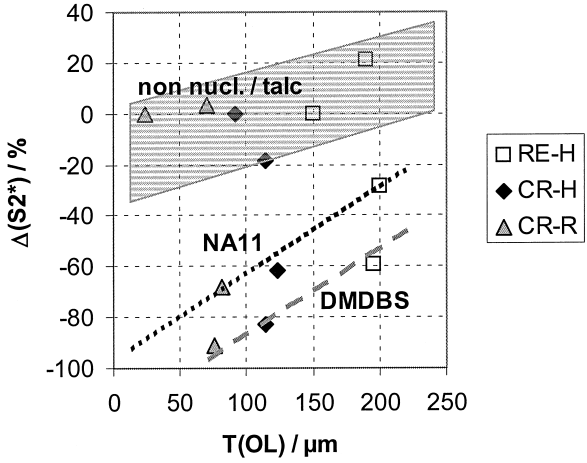

Figure 7 – Correlation between the thickness of the combined skin and fine-grained layers (T(OL)) and transparency increase

If a similar diagram is drawn for the modulus effect (see Figure 8), the outstanding performance of the organophosphate in terms of stiffness becomes obvious as well as the massive contribution of the base polymer. A positive interaction can especially be concluded for the material with broad MWD, RE-H.

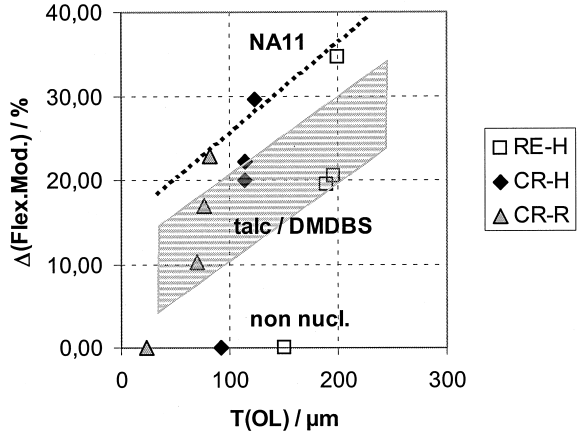

Figure 8 – Correlation between the thickness of the combined skin and fine-grained layers (T(OL)) and modulus increase

Conclusions

For nucleated polypropylene grades the efficiency of the nucleation and especially the achieved effect on the property profile – mechanical and optical properties as well as shrinkage – is effectively determined by the nature of the nuclating agent as well as of the polymer. For both influence factors, the present study has yielded at least qualitative indications, which relate to the formed morphology and crystalline superstructures (shear-induced layers). Especially the latter can be related to the differences between optical and mechanical effects of the nucleation process. Depending on the application in question and the desired property improvements, "ideal" combinations of nucleant and polymer will have to be found. In any case, also processing conditions and part geometry will strongly affect the ultimate applivcation properties.

The fact that the best transparency values were reached for the sorbitol-nucleated random copolymer can most probably be additionally explained with the higher amount of γ-modification, which is even favored by the nucleation in case of PP-homopolymers with reduced isotacticity or EP-random copolymers[6,7,29].

Acknowledgements

The authors are grateful to Ms. Annabel Bordman and Prof. Bernard Lotz of ICS Strasbourg, France, for support in designing and performing the experimental investigations, Ms. Ewa Ratajski and Prof. Hermann Janeschitz-Kriegl of J. Kepler University Linz, Austria, for helpful discussions. The microscopic investigations were supplied by Mr. Walter Achleitner, Borealis Linz, Austria (PLM) and Ms. Elisabeth Ingolic, ZFE Graz, Austria (TEM).

[1] M. Gahleitner, J. Wolfschwenger, K. Bernreitner, W. Neißl, C. Bachner, *J.Appl.Polym.Sci.* **1996**, *61*, 649.
[2] J. Varga, in : "*Polypropylene : Structure, blends and composites*", J. Karger-Kocsis, Ed., Chapman&Hall, London 1995, p.56.
[3] J. Karger-Kocsis, J. Varga, G. Ehrenstein, *J.Appl.Polym.Sci.* **1997**, *64*, 2057.
[4] D. Jarus, A. Scheibelhofer, A. Hiltner, E. Baer, *J.Appl.Polym.Sci.* **1996**, *60*, 209.
[5] J.C. Wittmann, B. Lotz, *Prog.Polym.Sci.* **1990**, *15*, 909.
[6] M. Gahleitner, C. Bachner, E. Ratajski, G. Rohaczek, W. Neißl, *J.Appl.Polym.Sci.* **1999**, *73*, 2507.
[7] R. Thomann, H. Semke, R.-D. Maier, Y. Thomann, J. Scherble, R. Mühlhaupt & J. Kressler, *Polymer* 2000, *42*, 4597.
[8] S. Liedauer, G. Eder, H. Janeschitz-Kriegl, P. Jerschow, W. Geymayer, E. Ingolic, *Intern.Polym.Proc.* **1993**, *8*, 236.
[9] S. Liedauer, G. Eder, H. Janeschitz-Kriegl, *Intern.Polym.Proc.* **1995**, *10*, 243.
[10] D. Tartari, M. Bramuzzo, *Kunststoffe* **1993**, *83*, 460.
[11] M. Fujiyama, T. Wakino, *J.Appl.Polym.Sci.* **1991**, *42*, 2749.
[12] M. Demiray, A. Isayev, *Proc. of SPE ANTEC* **1996**, *54*, 1576.
[13] R. Phillips, G. Hebert, J. News, M. Wolkowicz, *Proc. of SPE ANTEC* **1994**, *52*, 1425.
[14] J. Varga, J. Karger-Kocsis, *J.Polym.Sci.B:Polym.Phys.* **1996**, *34*, 657.
[15] M. Fujiyama, T. Wakino, *Intern.Polym.Proc.* **1992**, *7*, 84.

[16] M. Gahleitner, J. Wolfschwenger, K. Bernreitner, W. Neißl & C. Bachner, *J.Appl.Polym.Sci.* **61**, 649-57, 1996
[17] M. Fujiyama, *J.Appl.Polym.Sci.* **1991**, *43*, 97.
[18] M. Gahleitner, J. Fiebig, C. Paulik, J. Wolfschwenger, H. Zuidema, G. Dreiling, *Proc. 15th Int. PPS Conf.*, 's Hertogenbosch / NL 1999, # 008 (CD-ROM edition).
[19] T. Sundell, H. Fagerholm, H. Crozier, *Polymer* **1996**, *37*, 3227.
[20] J. Brandrup, E.H. Immergut, Eds.), *"Polymer Handbook"*, 3rd ed., Wiley, New York 1989
[21] J.H. Bheda, J.E. Spruiell, *Polym.Eng.Sci.* **1986**, *26*, 736.
[22] P. Tordjeman, C. Robert, G. Marin, P. Gerard, *Eur.Phys.J.E* **2001**, *4*, 496.
[23] K. Wang, K. Mai, H. Zeng, *J.Appl.Polym.Sci.* **2000**, *78*, 2457.
[24] T.A. Shepard, C.R. Delsorbo, R.M. Louth, J.L. Walborn, D.A. Norman, N.G. Harvey, R.J. Spontak, *J.Polym.Sci.B:Polym.Phys.* **1997**, *35*, 2617.
[25] P. Jerschow, H. Janeschitz-Kriegl, *Rheol.Acta* **1996**, *35*, 127.
[26] P. Jerschow, H. Janeschitz-Kriegl, *Intern.Polym.Proc.* **1997**, *12*, 72.
[27] H. Zuidema, *"Flow Induced Crystallization of Polymers – Application to Injection Moulding"*, PhD thesis, TU Eindhoven / NL 2000
[28] H. Zuidema, G.M.W. Peters, H.E.H. Meijer, *Macromol.Theory Simul.* **2001**, *10*, 447.
[29] E. Perez, D. Zucchi, M.C. Sacchi, F. Forlini & A. Bello, *Polymer* **1999**, *40*, 675.