IMPROVING MOLDING PRODUCTIVITY AND ENHANCING MECHANICAL PROPERTIES OF POLYPROPYLENE WITH NUCLEATING AGENTS

James H. Botkin, Neil Dunski, and Dietmar Maeder[+]*
Ciba Specialty Chemicals Corporation, Tarrytown, New York
**Ciba Specialty Chemicals Corporation, St. Louis, Missouri*
[+]Ciba Specialty Chemicals Inc., Basel, Switzerland

Introduction

Polypropylene-based materials are widely used in automotive applications due to their excellent balance of properties and low cost. Further improvements in properties can be achieved through the use of nucleating agents. These additives function by promoting the crystallization of polypropylene during molding, providing a wide range of benefits including improved molding productivity, increased modulus without sacrificing impact strength, enhanced thermal properties, and improved clarity for special visual effects. This paper presents an overview of the various types of nucleating agents and compares the effects they provide.

Overview of Nucleating Agents

The first scientific studies on the nucleation of polypropylene were conducted by Beck[1] and Binsbergen[2-5]. Based on this work it can be concluded that nucleating agents act by introducing a heterogeneous surface to the supercooled polymer melt, making crystallization more thermodynamically favorable. As a result of the nucleating effect, the temperature at which the polymer begins to crystallize is increased, as are the rate of nucleation and overall rate of crystallization. Nucleating agents also promote the formation of smaller and more numerous spherulites, resulting in enhanced properties.

A variety of nucleating agents have been used in polypropylene[6]. Talc and carboxylate salts (e.g. sodium benzoate, NaOBz) were among the first additives used for this purpose and are still widely used today. In the 1980's, sorbitol acetals came into use. These additives can produce spherulites smaller than the wavelength of visible light, providing transparent polypropylene. Nucleating agents that provide this effect are commonly referred to as *clarifiers*. More recently phosphate ester salts have been introduced as high performance nucleating agents. Pigments (organic & inorganic) used as colorants in polymers can also produce nucleating effects. Structures of representative nucleating agents are given in the Appendix.

The efficacy of nucleating agents is typically evaluated by determining the peak crystallization temperature (T_c) on cooling the polymer melt using differential scanning calorimetry. T_c is defined as the temperature at the peak of the crystallization exotherm. An example of the effect of nucleation on the crystallization exotherm of polypropylene is shown in Figure 1. Alternatively, the crystallization half-time can be determined upon rapid cooling of the polymer melt to the temperature of interest.

Nucleation Effects

Crystallization Effects and Implications for Molding Productivity

Nucleating agents increase the temperature at which the supercooled polymer melt begins to crystallize on cooling (Figure 2). They also serve to increase the overall rate of crystallization (Figure 3). As a result, shorter cooling cycles can often be used in injection molding, enabling shorter molding cycles and a significant improvement in molding productivity. The high performance phosphate ester salt IRGASTAB® NA 11 UH is notable in that it shows a significant effect even at low concentrations.

Figure 1. Effect of Nucleation on the Crystallization of PP Homopolymer on Cooling (10°C/min) from the Melt.

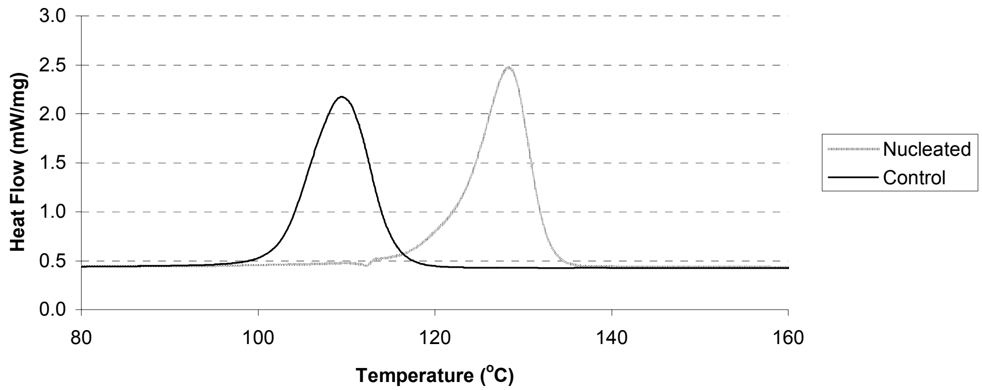


Figure 2. Effect of Nucleating Agents on the Crystallization Temperature (T_c) of PP Homopolymer.

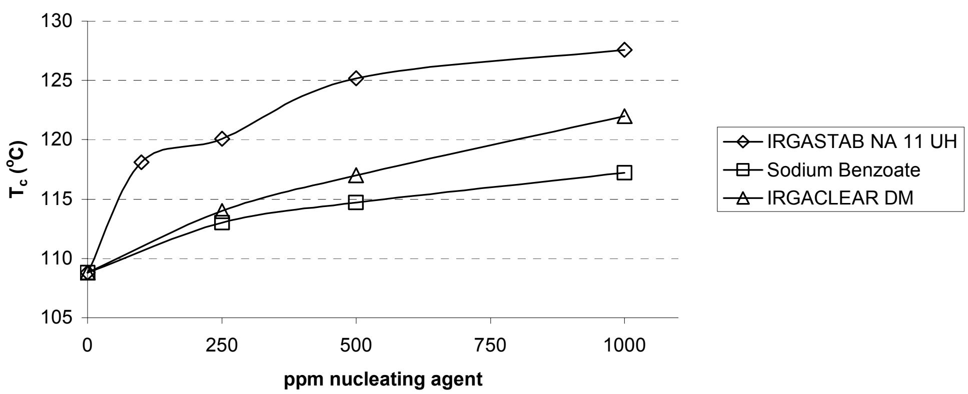
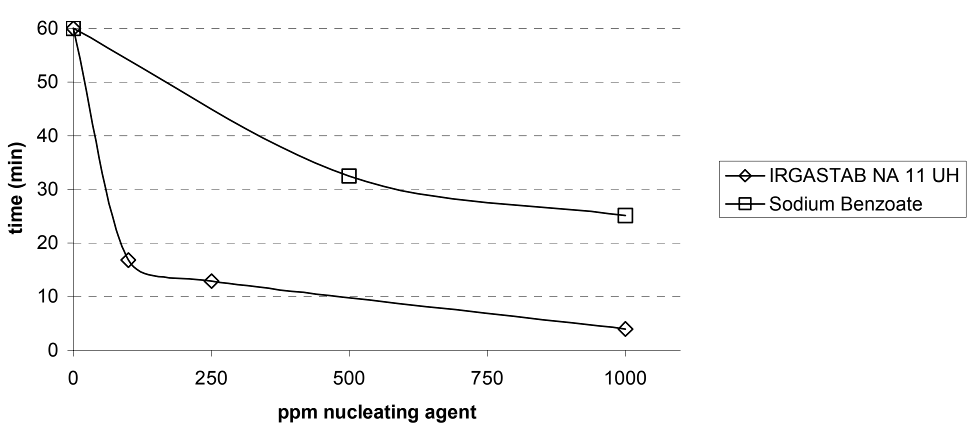


Figure 3. Effect on Crystallization Half Time (140°C) in PP Homopolymer.



Mechanical & Thermal Properties

The formation of a larger number of small spherulites in the molding of nucleated polypropylene results in increased modulus (Figure 4) without sacrificing impact strength, leading to a superior stiffness/impact balance (Figure 5). IRGASTAB® NA 11 UH was most effective at increasing modulus. A similar increase in modulus has been observed in polypropylene copolymer[7]. This effect can help to enable the thinwalling of automotive parts such as bumper fascia.

Figure 4. Effect of Nucleating Agents on Modulus in PP Homopolymer.

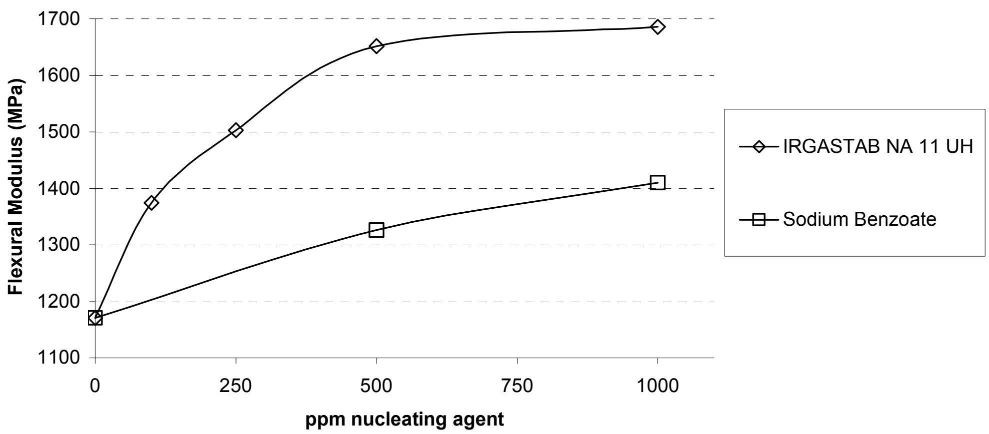
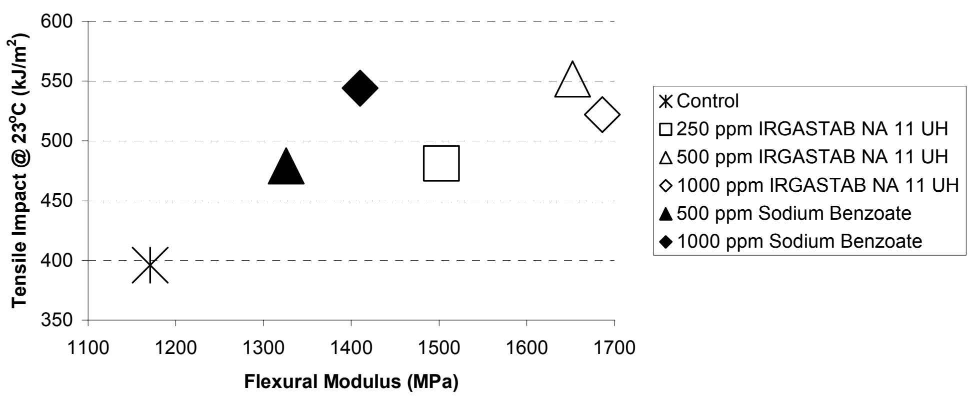


Figure 5. Effect of Nucleating Agents on Stiffness/Impact Balance in PP Homopolymer.



Nucleated polypropylene also exhibits improved thermal properties, such as heat deflection temperature (Figure 6) and Vicat softening temperature (Figure 7). IRGASTAB® NA 11 UH provided superior performance vs. sodium benzoate. Improving thermal properties is important for under-the-hood applications as well as for interior applications with high thermal demands, such as instrument panel structures.

Figure 6. Effect of Nucleating Agents on Heat Deflection Temperature in PP Homopolymer.

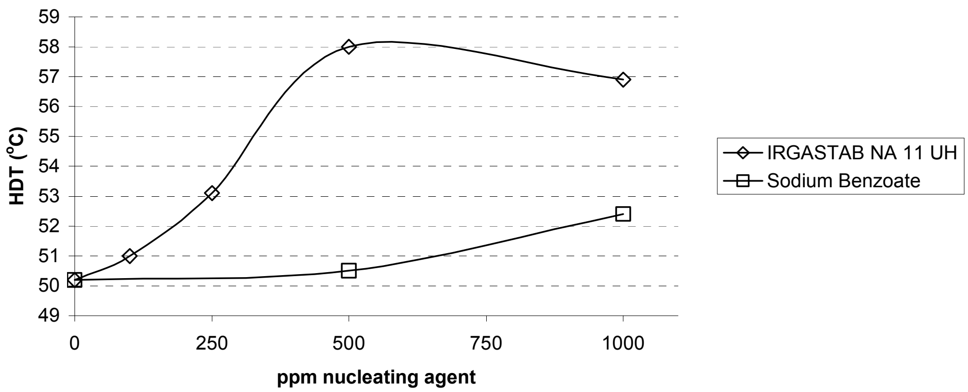
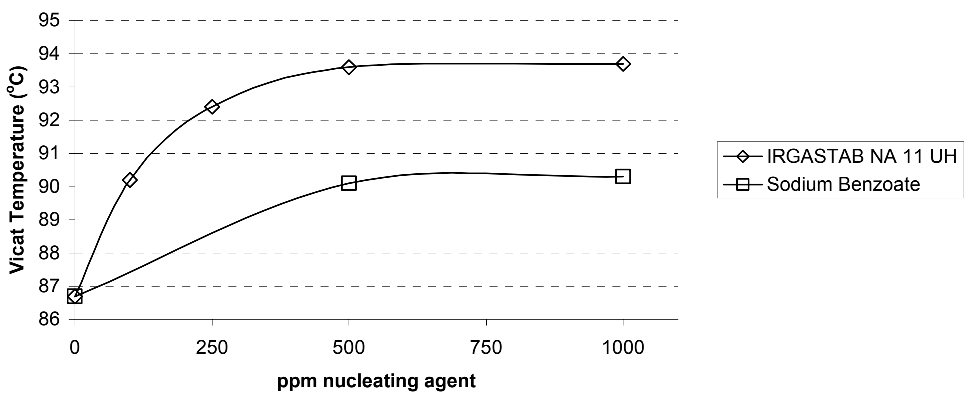


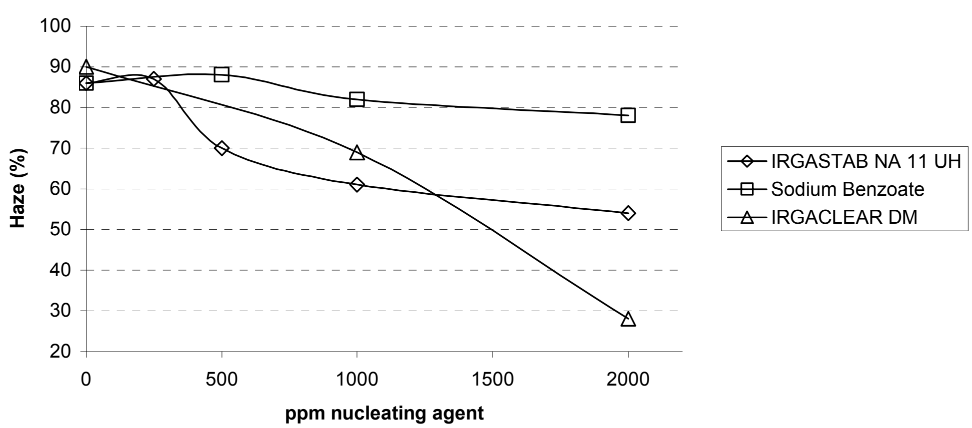
Figure 7. Effect of Nucleating Agents on Vicat Softening Temperature in PP Homopolymer.



Clarity

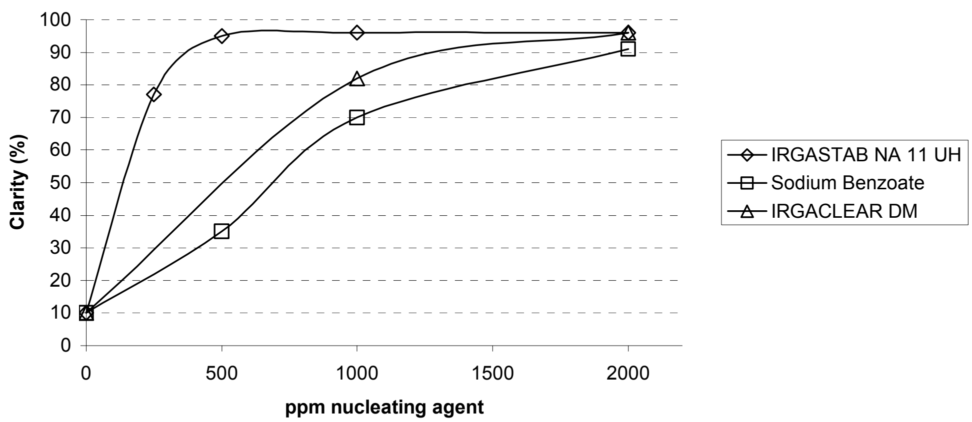
Another consequence of reducing the size of spherulites in polypropylene is an improvement in transparency. Haze is decreased (Figure 8) and clarity is increased (Figure 9) by the addition of

Figure 8. Effect of Nucleating Agents on Haze in PP Homopolymer.



nucleating agents. At higher concentrations (~0.2%), sorbitol-based nucleating agents such as IRGACLEAR® DM give the best results and are commonly used to produce transparent polypropylene for applications such as food packaging. In automotive applications, increasing the clarity of polypropylene-based materials may be valuable to provide enhanced colorability or special visual effects.

Figure 9. Effect of Nucleating Agents on Clarity in PP Homopolymer.



Other Considerations

As heterogeneous additives, the particle size and dispersion of nucleating agents in the polymer are crucial. Nucleating agents are available in a variety of particle sizes. In general, provided they are properly dispersed, finer particles give better results. The benefit of using finer nucleating agents must be weighed vs. potential disadvantages, such as handling characteristics. Even sorbitol-based clarifiers which are soluble in polypropylene must be properly dispersed for optimal results. However, additive packages containing nucleating/clarifying agents are available in feedable forms which alleviate handling, conveying and feeding difficulties while achieving appropriate dispersion in the resin.

Sodium benzoate is a highly reactive nucleating agent capable of reacting with other formulation components, including calcium stearate (Table 1). This coadditive is widely used as an acid scavenger and lubricant in polyolefins. This problem can be avoided by substituting a hydrotalcite-based acid scavenger. Interaction with calcium stearate is not an issue with higher performance sorbitol acetal and phosphate ester salt nucleating agents.

Table 1. Effect of Coadditives on the Crystallization of PP Homopolymer Nucleated with Sodium Benzoate.

Formulation	T_c (°C)
1000 ppm NaOBz 1000 ppm Calcium stearate	117
1000 ppm NaOBz 500 ppm HYCITE® 713	129

Conclusions

Nucleating agents provide many benefits for polypropylene-based materials in automotive applications, including:

- Improved molding productivity through increased crystallization temperature and crystallization rate of the supercooled polymer melt,
- Enhanced stiffness/impact balance to enable thinwalling of parts,
- Improved thermal properties for high temperature applications, and
- Improved clarity for enhanced colorability and special visual effects.

Common nucleating agents include carboxylate salts (sodium benzoate, NaOBz), sorbitol acetals (IRGACLEAR® DM), and phosphate ester salts (IRGASTAB® NA 11 UH). The use of the phosphate ester salt IRGASTAB® NA 11 UH is particularly recommended to improve physical properties and molding productivity, while the sorbitol acetal IRGACLEAR® DM is recommended as a clarifier.

Experimental

Substrate

Polypropylene homopolymer, nominal MFR 4 dg/min.

Additives

Except where noted, all formulations contained 0.05% IRGANOX® 1010 + 0.10% IRGAFOS® 168 + 0.10% calcium stearate as base stabilization. The sodium benzoate used (IRGASTAB® NA 02) had a maximum particle size of 20 μm and mean particle size of <3 μm; IRGASTAB® NA 11 UH had a mean particle size of 6-8 μm.

Compounding

Polymer and additives were blended using a high speed mixer (Henschel). The powder blends were compounded using a twin screw extruder (Berstorff) at a maximum temperature of 250°C.

Injection Molding

Injection-molded test specimens were prepared on an Arburg 320 S (maximum temperature 240°C, mold temperature 45°C).

Differential Scanning Calorimetry

A TA instruments DSC 2920 was used. Crystallization temperature (T_c) was determined using a heating/cooling rate of 10°C/min under nitrogen. Crystallization half-time ($T_{1/2}$) was determined isothermally at 140°C after rapid cooling from the melt under nitrogen. Sample size: 10 mg.

Measurement of Polymer Properties

Property	Test Method	Notes
Flexural Modulus	ISO 178	Zwick tensile tester
Tensile Impact Strength	ISO 8256	
Heat Deflection Temperature	ISO 75	Method A (1.80 MPa stress)
Vicat Softening Temperature	ISO 306	
Haze	ASTM D1003-61	BYK Gardner Haze Guard Plus
Clarity	ASTM D1003-61	

References

1. Beck, H. N. *J. Appl. Pol. Sci.,* **1967**, *11*, 673.

2. Binsbergen, F. L. *Polymer*, **1970**, *11*, 253.

3. Binsbergen, F. L. and DeLange, B. G. M. *Polymer*, **1970**, *11*, 309.

4. Binsbergen, F. L. *J. Poly. Sci.*, **1973**, *11*, 117.

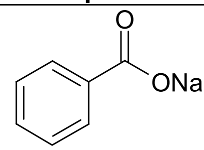
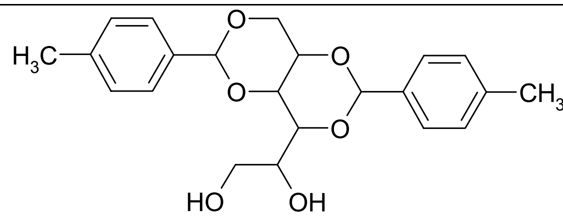
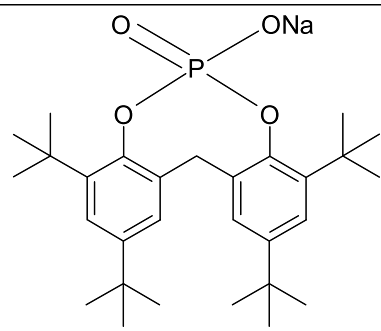
5. Binsbergen, F. L. *J. Poly. Sci., Poly. Symp.*, **1977**, *59*, 11.

6. Kurja, J. and Mehl, N. A. in "Plastics Additives Handbook", 5th ed.; H. Zweifel, Ed.; Hanser Gardner Publications, Inc.: Cincinnati, 2001; Ch. 18.

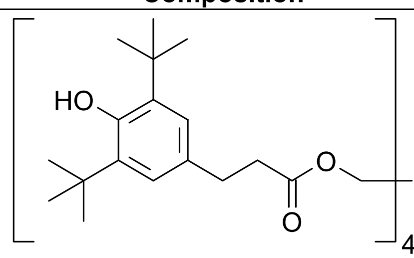
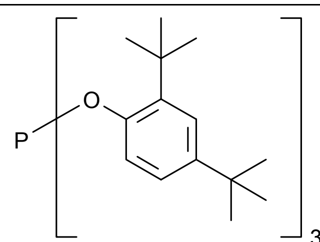
7. Pukanszky, B.; Mudra, I.; Staniek, P. *J. Vinyl Add. Tech.*, **1997**, *3*, 53.

Appendix

Nucleating Agents

Class	Composition	Tradename
Carboxylate salt (Sodium benzoate)		IRGASTAB® NA 02 IRGASTAB® NA 04
Sorbitol acetal		IRGACLEAR® DM
Phosphate ester salt		IRGASTAB® NA 11 UH

Other Additives

Class	Composition	Tradename
Hindered phenol		IRGANOX® 1010
Phosphite		IRGAFOS® 168

IRGACLEAR®, IRGAFOS®, IRGANOX®, and IRGASTAB® are registered trademarks of Ciba Specialty Chemicals Inc.