Nucleating and Clarifying Agents for Polyolefins

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Summary: Nucleating agents are used in semi-crystalline polymer systems (mainly polyolefins) to increase the rate of crystallization. These agents increase degree of crystallinity and lamellae thickness and, hence, improve stiffness and strength. In addition to altered mechanical characteristics, clarifying agents do also improve optical properties.
This paper provides a brief overview on nucleating / clarifying agents. The efficiency of such products (e.g. Na-benzoate, sorbitol acetals) for polypropylene (PP homopolymer, PP copolymer) is evaluated.
The clarifiers Irgaclear D ((1,3:2,4)-dibenzylidene sorbitol) and Irgaclear DM (1,3:2,4-Bis-(p-methylbenzylidene) sorbitol) provide a 3-dimensional fibrillar structure upon cooling from the polymer melt. This magnified nucleation density yields spherulites with reduced size (< 1micron) - in comparison to non-nucleated products. Addition of Irgaclear to polypropylene leads to increased clarity, reduced haze and enhanced stiffness of molded parts. Higher recrystallization temperatures results in shorter cycle times and increased throughput during the molding process.

Introduction

The necessity of an adequate stabilization for polymers in general, polypropylene in particular, is well established[1-3]. Various processing, heat and light stabilizers are used to ensure the long term properties (e.g. prevention of discoloration, deterioration, microbial attack).

In PP[4,5], nylon, crystalline polyethylene terephthalate (CPET), and thermoplastic PET[6] molding compounds the polymer morphology and crystallization behavior can be modified by the incorporation of nucleating agents. Use levels are typically below 1%, although CPET uses higher levels. By addition of these compounds the polymer's crystallization temperature, spherulite size, optical properties (e.g. haze, clarity), mechanical properties[7-9] (e.g. E-modulus) and cycle time to get the final product are changed. In HDPE[10], nucleating agents are not very effective due to its extremely high crystallization rate. In LLDPE, the influence of nucleating agents is more pronounced due to disturbance of PE- backbone by the incorporation of 1-olefins.

Nucleating agents increase the rate of crystal nucleation by acting as heterogeneous nuclei. It is known that an existing foreign surface within the polymer melt greatly reduces the free energy for the formation of a critical nucleus and, consequently, an increase in the rate of crystallization is observed[11-14)]. In the case of isotactic polypropylene, the use of nucleating agents is particularly important owing to its low rate of crystallization.

For a polymer to crystallize, the following requirements must be met[7)]:

* 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

The exact correlation between polymer type and chemical / physical nature of the nucleating agent is not fully understood. Organic compounds, to be used as nucleating agents, should fulfill the following five attributes[7,15)]:

* Crystal structure should be similar to that of the polymer. Increasing compatibility of crystal structure promotes crystal growth
* Nucleating agent should be insoluble in the polymer
* m.p. of nucleating agent should be above the m.p. of polymer
* Nucleating agent should be non volatile and inert towards environment (polymer, oxygen, humidity, other additives, etc.)
* Nucleating agent has to be well dispersed in the polymer

The chemical nucleating agents have various structures[16,17):]

* substituted sorbitol acetals are used in polyolefins, particularly PP
* organic salts (e.g. NUC-1) are primarily used in nylon and PP[18)]

* low molecular weight polyolefins are used in CPET for rapid crystallization
* ionomer resins are used to control crystallization in PET engineering resins

In addition, a variety of mineral fillers (talc, etc)[19] and pigments are used primarily in nylon and PBT. These non-chemical nucleating agents have to be dispersed, are inexpensive, and typically available "on-site" since they are commonly used as reinforcing agents and fillers.

Nucleating agents are primarily used in injection molding applications. However, they can also be found in blow molding, sheet extrusion, and thermoforming. Due to the faster crystallization of the polymer, the cycle time for processing of the final article can be reduced, this leads to an increase of industrial productivity.

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 (see Fig. 1).

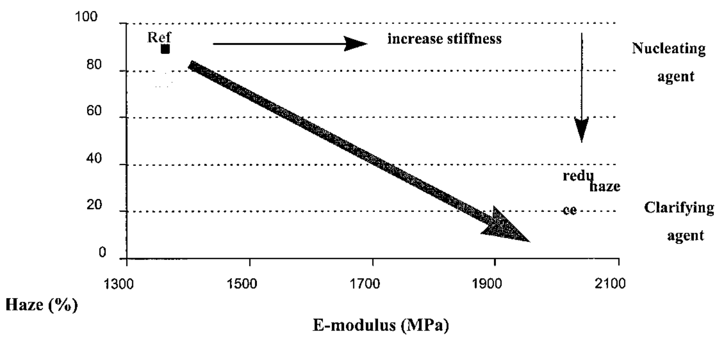

Fig. 1: Behavior of nucleating and clarifying agents.

The major application for clarifying agents is clarified PP, e.g. transparent containers. The major class of clarifying agents (sorbitol acetals) dissolve in the PP melt during processing. Upon cooling from the melt, a fibrous network of clarifying agent is formed. This magnified nucleation density yields spherulites[20,21] with reduced size (< 1 micron) - in comparison to non-nucleated products. Traditional nucleating agents (e.g. NUC-1) are primarily used in PP homopolymer, improving nucleation rate without improvement of optical properties in terms of haze.

The efficiency of such products (e.g. NUC-1, sorbitol acetals) on the mechanical and optical properties and morphology of polypropylene homopolymer and polypropylene co-polymer will be discussed in more detail.

Experimental

Polymer: Two grades of polypropylene were used in the investigations: (1) Montell PP Profax 6501 (PP Homo-polymer), MFR 3 g/10 min, powder; (2) Borealis PP Daplen KFC 2008 (PP Co-polymer), MFR 1 g/10 min, powder.

Sample preparation: 100 wt-% polymer, 0.15 wt-% B1 and 0.10 wt-% Ca-stearate were mixed with / without x wt-% NUC using a high speed mixer (Fa. Henschel). The powder blends were compounded using a twin screw extruder (Fa. Berstorff) at max. 250°C. Injection-molded specimen were prepared on an Arburg 320 S ($T_{max.}$ 240°C, mold temp. 45°C)

Testing equipment: Differential Scanning Calorimetry (Mettler DSC 30, nitrogen, heating / cooling rate: 10 K / min, sample mass: 10 mg), Optical Microscopy: Leitz Aristomet; Mechanical behavior: Zwick tensile test; Optical Properties (Haze)[22]: BYK GARDNER haze guard plus.

Results and Discussion

Fig. 2 shows the influence of nucleating agents on E-modulus. Stiffness of PP homopolymer is increased up to 30 % by the addition of 0.20 % NUC-3. Similar results are obtained with NUC-4, the 3,4-dimethyl derivative of dibenzylidene sorbitol. Even at low concentration (0.10%) NUC-1 is a very efficient nucleating agent in terms of E-modulus by increasing the degree of crystallinity.

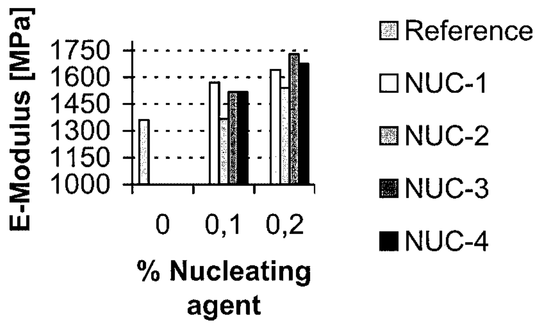

Fig. 2: E-modulus of clarified PP homopolymer, test samples: 2 mm inj. molded plaques.

Nucleating agents, which boost optical properties of PP in terms of haze and clarity, are referred to as clarifiers. Fig. 3 and 4 display the optical properties of nucleated PP homo- and copolymer. Only the highly efficient sorbitol derivatives NUC-3 and NUC-4 reduce haze from 90 % to 28% accompanied by superior clarity. In contrast, NUC-1 does not improve the optical properties.

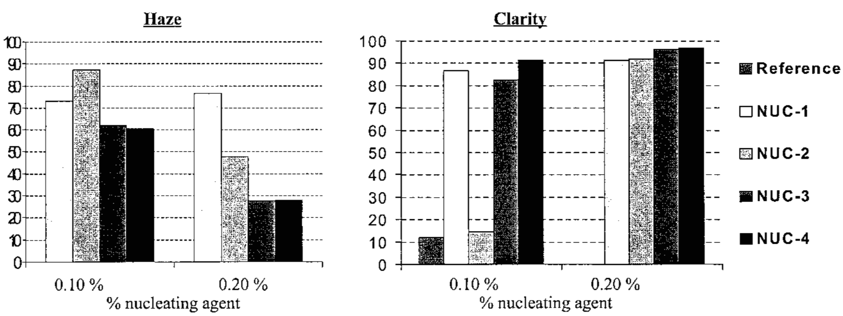

Fig. 3: Optical properties of clarified PP homopolymer.

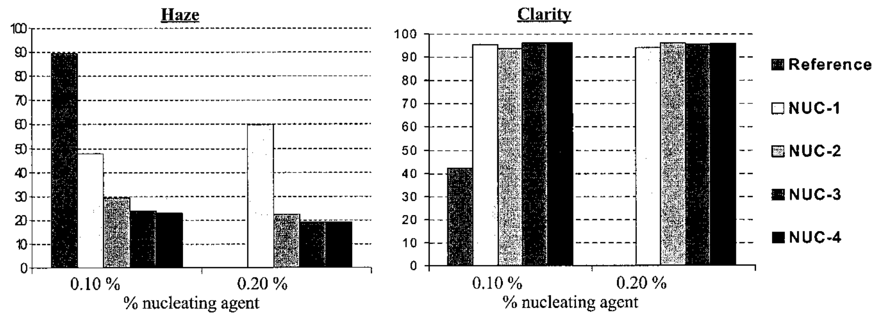

Fig. 4: Optical properties of clarified PP copolymer.

Sorbitol-acetal based clarifying agents do not only alter optical properties, they are also able to reduce cycle time (up to 30 %) during injection molding. Fig. 5 shows the optical performance of different clarifying agents as a function of injection molding time.

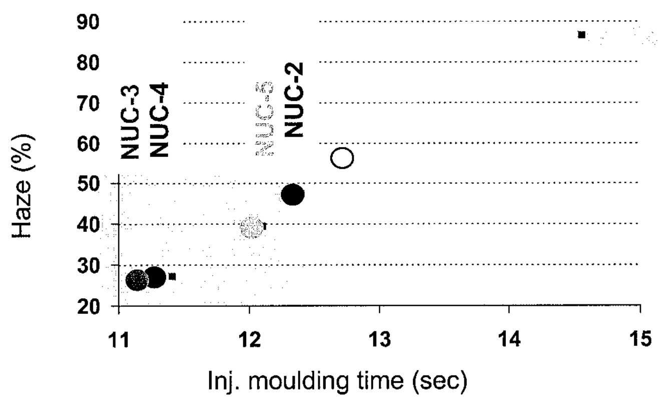

Fig. 5: Correlation haze / injection molding time of PP homopolymer (0.20 % nucleating agent); Test samples: 2 mm inj. molded plaques.

Shepard et al[23] investigated the fibril structure of self-organized sorbitol acetals by transmission electron microscope (see Fig. 6). The formation of a 3-dimensional fibril network is also observed by dynamic rheological experiments (PP compound containing 0.2% NUC-3). Upon cooling the dynamic viscosity η' of the PP melt increased moderately. At 156°C a significant rise in viscosity occurs. This rise is due to the formation of NUC-3 fibrils, driven by self-organization of NUC-3 in the PP melt. At higher concentrations a 3-dimensional network is formed. Upon heating this self-organization can also be destroyed (194°C) indicating the reversibility of this transition from self-organized to dissolved NUC-3.

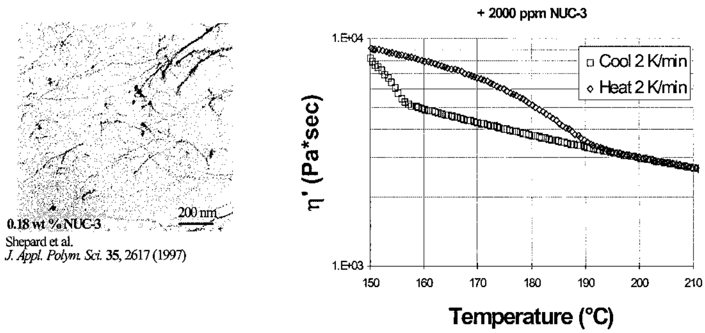

Fig. 6: Formation of 3-D network, crystallization sites for PP; Extrusion: Twin screw, max. 250°C, Rheometrics RDAII:F=1 rad/sec, S=5%,DT=2K/min.

The fibril formation (at 156°C, i.e. above the crystallization temperature) thus generates a 2-phase system providing nucleation sites for PP, i.e. crystallization of PP is induced. This leads to a significant increase in PP crystallization temperature T_{cr}[24,25] which can be detected by DSC measurements. T_{cr} increases from 120°C for non-nucleated PP to 135°C for PP containing 0.2% NUC-3.

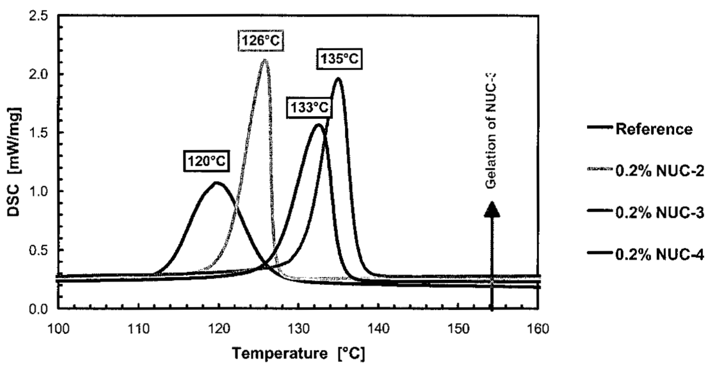

Fig. 7: Crystallization temperature of PP homopolymer (2 mm inj. molded plaques).

Conclusions

The sorbitol clarifying agents broaden the application range of PP. Clarified PP penetrates markets which up to day were reserved for amorphous thermoplastics, e.g. styrenics. These effect additives meliorate the optical and mechanical properties of isotactic PP homo and PP copolymer. Addition of Irgaclear D and Irgaclear DM to polypropylene leads to increased clarity, reduced haze and enhanced stiffness of molded parts. Higher recrystallization temperatures results in shorter cycle times and increased throughput during the molding process.

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Appendix: Product Key

B 1	Irganox B 215 (Irgafos 168 : Irganox 1010 = 2 : 1)
NUC	Nucleating Agent
NUC-1	Na-benzoate
NUC-2	Irgaclear D
NUC-3	Irgaclear DM
NUC-4	Millad 3988
NUC-5	1,3:2,4-Bis-(m-methylbenzylidene) sorbitol