

Efficiency of Nucleating Additives in Polypropylene

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Synopsis

Investigation of the nucleating ability of selected nucleating agents in various commercial types of isotactic polypropylene revealed that the efficiency of individual additives is not equal for all types of polypropylene. As to the nucleation mechanism, it can be supposed that in most cases the added nucleating agents act mainly secondarily, activating the heterogeneities originally present in the polymer.

Numerous efforts to modify some properties of crystalline polymers by means of controlled nucleation have been made in recent years. It is usually stated that the spherulite size influences many physical properties of polymers.¹⁻⁶ In an earlier paper we arrived at the conclusion, that some properties of crystalline polypropylene do not primarily depend on spherulite size, but rather on the dimensions and quality of basic crystalline formations constituting the spherulites.⁷ The size and perfection of these crystallites is determined both in nucleated and normal samples only by the crystallization conditions (temperature and time), the influence of nucleating additives being only secondary. The nucleating agents enable the nucleated polymer to crystallize under comparable conditions at a higher rate or higher temperature than the polymer alone without nucleating additive.

There are two possible ways of modifying the number of heterogeneous crystallization nuclei: by means of the melting process or by adding artificial nucleating agents. The second way is more useful in the practice and therefore has been the center of interest in the most investigations concerning controlled nucleation.^{1-3,6,9,10} The greatest attention has been paid to isotactic polypropylene, where many compounds of different kind (organic and inorganic) were examined, among which some proved to be nucleating agents. Aromatic and aliphatic carboxylic acids and their Na, K, Mg, and Al salts are particularly effective.¹⁰ The present knowledge is mostly empirical, and an unambiguous correlation between chemical composition, crystal structure, or physical properties of the nucleation additive and polymer has not yet been established. Likewise, problems of the nucleation mechanism have not yet been solved, even though it was shown that the heterogeneous nucleation mechanism may be of two types.¹¹

All published papers concerning nucleating ability of additives in poly-

propylene presume *a priori* that the results obtained with one type of polypropylene may be generalized. Contrary to this, our measurements will show that the situation is far more complicated.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene from various sources were used. The characteristics of the samples are summarized in Table I.

TABLE I
Characteristics of the Polypropylene Samples

No. ^a	Sample	Viscosity number, ml/g	Extract, %		Ash, %
			Naph- thalene- ether	Naph- thalene- chloroform	
1	KM-61	199		3.9	0.06
2	AT-50	192	2.8	6.0	0.09
3	AD-50	314			0.1
4	AS-50	164			0.09
5	M-14	459	6.2		0.06
6	HSM-36	222			0.11
7	HPE-35	257			0.12
8	LWF-31	192	2.8	6.5	0.11

^a Sample 1 is Carlona (Shell Co., USA), samples 2-5 are Moplene (Montecatini, Italy), samples 6-8 are Propathene (I.C.I., England).

Nucleation Ability

Microscopic and DTA methods were used for the evaluation of nucleation ability. The mean spherulite size of crystallized films prepared from solution was measured by means of the microscopic method. The nucleating agent was added to a 4% solution of polypropylene in xylene (dissolving in 6 hr at 125°C), warmed to 128°C, and mixed 10 min. The polypropylene solution with additive was dropped on a clean microscopic cover slide and the solvent evaporated at room temperature. After this, the film was melted 15 min at 195°C and crystallized 30 min at 120°C in a CO₂ atmosphere. The mean size of spherulites in the crystallized film was measured microscopically between crossed polarizers and compared with film prepared from the polypropylene sample without nucleating agent.

We used a DTA apparatus of our own design and construction. In a silver, electrically heated cylindrical block (3 cm in diameter, 5 cm in height) are symmetrically located two cylindrical specimen holders made from silver (7 mm in diameter, 15 mm in height) for the sample and reference material (Al₂O₃). The iron-constantan differential thermocouple (0.2 mm thick) junctions are arranged longitudinally and reach 1 mm above the bottom of the wells. The sample temperature is measured with a laboratory milli-

voltmeter (0–15 mV), and ΔT recorded on the time-base strip chart recorder (–1 to +1 mV).

A 50-mg portion of the pulverized polypropylene with nucleating agent was placed in the sample cell between two layers of Al_2O_3 (total weight 50 mg), the second cell contained 100 mg Al_2O_3 . Both cells were placed in the block, heated up to 200°C, the heating switched off, the differential thermocouple inserted, and the heating block freely cooled down to room temperature. At this point, another cycle of heating to 200°C and free cooling was performed and the temperature and ΔT recorded. The temperature values for the exothermic maxima T_c for the maximum crystallization rate are means of two measurements which differed no more than $\pm 0.5^\circ\text{C}$. If under the described conditions the measured T_c value of the polymer containing 1% of additive is 6.5°C or more higher than that of the polymer alone, we rate the nucleating efficiency high; if the difference amounts to 5– 6.5°C , the efficiency is medium; for a difference of 3– 5°C the rating is low. This evaluation of nucleating ability agrees on the whole with the classification according to the spherulite size by microscopic method (mean size of spherulites less than 50 μ , high nucleating efficiency; 50–100 μ , medium; 100–200 μ , low).

RESULTS AND DISCUSSION

The nucleating efficiency of 1% (by weight) of six nucleating additives (phthalic acid, benzoic acid, aluminum phthalate, sodium salicylate, carbon black P-1250, and the pigment Irgalilechtbrilant blau (Geigy Switzerland) was evaluated for eight commercial types of isotactic polypropylene (listed in Table I) by using the DTA and microscopic methods. The results of measurements are summarized in Table II.

The reported results are interesting from several points of view. It is evident that most of the nucleating agents used do not exhibit a universal nucleating effect for all types of isotactic polypropylene examined. During further investigations we have verified that the same additive may exhibit substantial differences in nucleating efficiency even in the individual grades of the same polypropylene type, e.g., for one grade of AT-50 benzoic acid was strong nucleating agent, whereas in another grade it did not show any nucleating effect. Therefore, it is clear that no generally valid conclusions about the nucleating ability and structure, or chemical nature of polypropylene and additive can be made, unless the differences among individual polypropylene types are stated. As far as we could judge from the available data, the differences in nucleating ability for a given nucleating agent were not correlation with the molecular weight, ash content, and atactic or stereoblock fraction of polypropylene.

It may be seen in some cases listed in Table II that the results of classification of the nucleating efficiency by means of DTA and microscopy disagree, e.g., in polypropylene AD-50 containing sodium salicylate, or polypropylene LWF-31 containing benzoic acid or sodium salicylate. In order

TABLE II
Nucleating Efficiency of Additives Measured by the Microscopic and DTA Method in Various Types of Isotactic Polypropylene^a

Polymer	Additive													
	Phthalic acid		Benzoic acid		Al phthalate		Na salicylate		Carbon black P1250		Irga-blau		Polymer alone	
	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ	DTA $T_g, ^\circ\text{C}$	Micr. μ
AT-50	130.8	2	120.3	170	131.8	7	131.3	40	127	100	130.5	5	119.7	600
AD-50	130.8	27	120.8	550	129.3	30	131.5	550 ^b	127.5	60	128	25	121.3	500
AS-50	132	40	120.8	600	131	50	122.3	350	128.5	170	127.8	25	118	650
HPE-35	130	135 ^b	118	70 ^a	127	110	118	650	127	125	128	220	118	600
HSM-36	130.8	40	118	150	129.3	60	119.8	550	127	75	129.9	25	118	550
LWF-31	130.8	85	124	15 ^c	130.8	85	124	10 ^c	130.8	5	130	5	124	440
KM-61	128	550 ^b	121.8	550	124.5	75	119.8	550	119.3	450	127	35	119.3	550
M-14	119.3	125	117.8	45	122.5	125	119	450	125	1	125.5	10	116	600

^a Classification of nucleating efficiency: by DTA, $\Delta T_g \geq 6.5^\circ\text{C}$, high; $\Delta T_g = 5-6.5^\circ\text{C}$, medium; $\Delta T_g = 3-5^\circ\text{C}$, low; by microscopy, mean size of spherulites $\geq 50 \mu$, high; $50-100 \mu$, medium, $100-200 \mu$, low.

^b Fine spherulitic structure was found in the sections of samples after DTA measurement.

^c Large spherulites were found in the sections of samples after DTA measurement.

to elucidate the origin of these differences a comparison was made of the spherulitic structures in the samples prepared from xylene solution and in the sections of the samples being measured by the DTA method. It appeared that the results obtained by the DTA method are in agreement with the dimensions of spherulites observed on thin sections of identical samples (Figure 1). The differences in structure of the samples prepared from xylene solution are related to the process of film preparation and the effect of solvent. Also the effect of oxidation by atmospheric oxygen absorbed in polymer film during solvent evaporation on air cannot be excluded. Some nucleating agents possibly may aid this process. For these reasons the results of the microscopic method for samples prepared from solution must be judged with caution. For practical needs the evaluation of nucleating efficiency of additives by the DTA method is more favorable, because of the absence of interfering influences of the solvent and preparation method and because the process of measurement is closely similar to technological conditions of processing.

For some polymer-additive pairs, two peaks corresponding to two T_c values can be noticed on thermograms (Fig. 2). This signifies that the

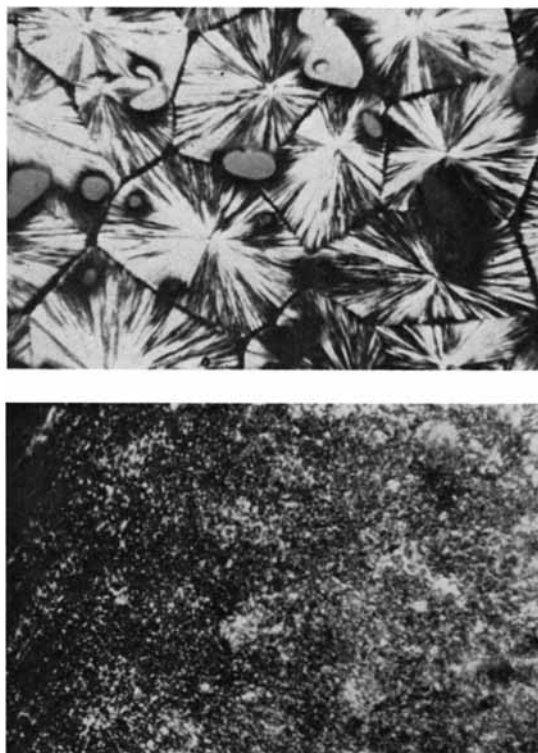


Fig. 1. Comparison of spherulite size in polypropylene AD-50 samples containing 1% of sodium salicylate and prepared (a) from xylene solution, (b) by sectioning the sample after DTA measurement. Crossed polarizers, magnification 180 \times .

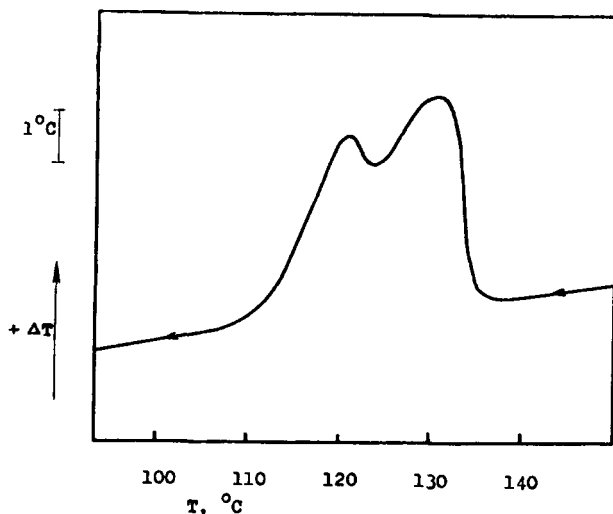


Fig. 2. Thermogram of crystallization during cooling of melted sample AT-50 containing 1% of phthalic acid, which is characteristic of two-stage crystallization.

course of crystallization showed two distinct stages. On the micrographs of sections of these samples the bright optically negative spherulites of type III according to the classification of Padden and Keith¹² were recognized in an enhanced proportion in addition to the optically positive spherulites.

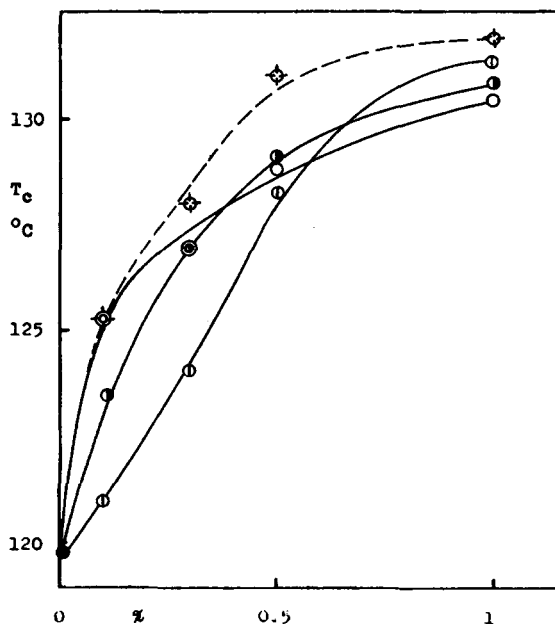


Fig. 3. Effect of nucleating agent concentration on crystallization temperature, measured by the DTA method: (1) aluminium phthalate; (2) sodium salicylate; (3) phthalic acid; (4) Irgalilechtbrilant blau.

It is thus demonstrated that some nucleating agents exert a specific morphological activity which leads to formation of specific spherulite structures.

The above results indicate that the nucleation mechanisms in the presence of additives are quite complicated. In most cases simple interaction of the solid additive with the polypropylene on a chemical or structural basis must be excluded, partly because some active additives (benzoic acid) are not in the solid state under crystallization conditions; further there is no reason why various types of polypropylene should react differently with the same additive. Rather it should be considered that the proper heterogeneities may be other substances originally present in the polymer which aid the heterogeneous nucleation or represent the places where crystalline nuclei can survive the melting process. These are possibly remainders of the catalytic system, occasional impurities, or various ingredients. The nucleating agents may activate the originally present heterogeneities (e.g., by improving the wetting) and thus may enhance their nucleating effect. This concept explains why the number of heterogeneous nuclei cannot be arbitrarily increased by raising the concentration of nucleating agents, as can be seen in Figure 3.

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