NOTE

Effect of Calcium Fluoride Concentration on Nylon 6,6 Crystallization Behavior and Morphology

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ABSTRACT: Nylon 6,6 (polyamide 6,6) heterogeneously nucleated with *ca.* 65 ppm calcium fluoride exhibits crystallization behavior and morphology characteristic of much higher levels of nucleating agent. This is shown using differential scanning calorimetry and polarized optical microscopy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1675–1678, 1998

Key words: heterogeneous nucleation; crystallization behavior; morphology; Nylon 6,6; CaF_2

INTRODUCTION

Heterogeneous nucleating agents are used in industry to improve optical properties (such as transparency) and mechanical properties (such as impact resistance, tensile strength, and elongation at break). This is achieved through increasing the nucleation density, resulting in spherulite size reduction.[1–8] For industrial applications, heterogeneous nucleating agent loadings are commonly in the fractional to 1% range. The present work shows that calcium fluoride (CaF_2) at levels less than 100 ppm affect the recrystallization behavior of Nylon 6,6 similarly to much higher loadings. Furthermore, it shows that the change in recrystallization behavior occurs over a narrow loading range.

EXPERIMENTAL

Nylon 6,6 samples containing CaF_2 were prepared by taking precursor Nylon 6,6 salts and various loadings of CaF_2 and polymerizing the Nylon 6,6 in a laboratory autoclave. Autoclave conditions were similar to those used for the Monsanto commercial Nylon 6,6 plant production. The procedure is described in detail in an earlier publication.[6] Table I lists the CaF_2 concentrations added initially and determined in the final samples by ion-selective electrode analysis for fluorine. The crystallization temperature upon cooling from the melt (T_{mc}) was measured using a Perkin-Elmer model 7 DSC at a cooling rate of 10°C min^{-1} after a 10-min anneal at 300°C. Four-micron-thick sections were cut at room temperature from samples generated by the differential scanning calorimetry (DSC) analyses and examined by polarized optical microscopy (POM). A Nikon Diaphot

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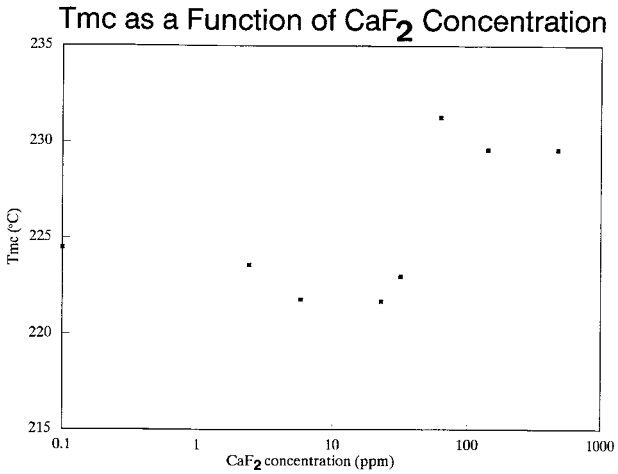


Figure 1 T_{mc} as a function of CaF_2 concentration.

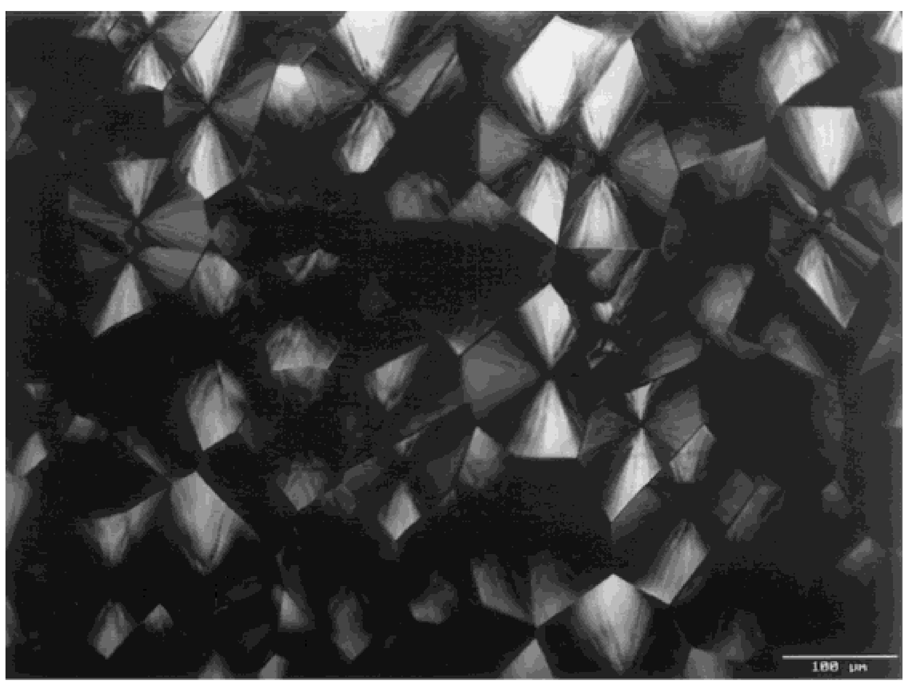
inverted microscope coupled to a BioRad 600 confocal microscope system was used. More details regarding experimental procedures are outlined elsewhere.[6,7,9]

RESULTS AND DISCUSSION

T_{mc} as a function of CaF_2 level is shown in Figure 1. The T_{mc}, like the overall crystallization rate, is affected by factors such as the addition of nucleation agents. It can thus be used to monitor changes in crystallization behavior. Similar analyses were used by Khanna and coworkers and Nadkarni and coworkers in their research.[3–7,9–11] At CaF_2 concentrations below *ca.* 35 ppm, the T_{mc} value is *ca.* 223°C. At CaF_2 concentrations of 65 ppm and higher, the value of T_{mc} increases to *ca.* 230°C. Allowing for experimental variation of ±1°C in T_{mc}, this difference is significant. It shows that a CaF_2 loading level of 65 ppm is sufficient to induce an increase in T_{mc}, which is characteristic of much higher loadings. This difference is also the same as that ob-

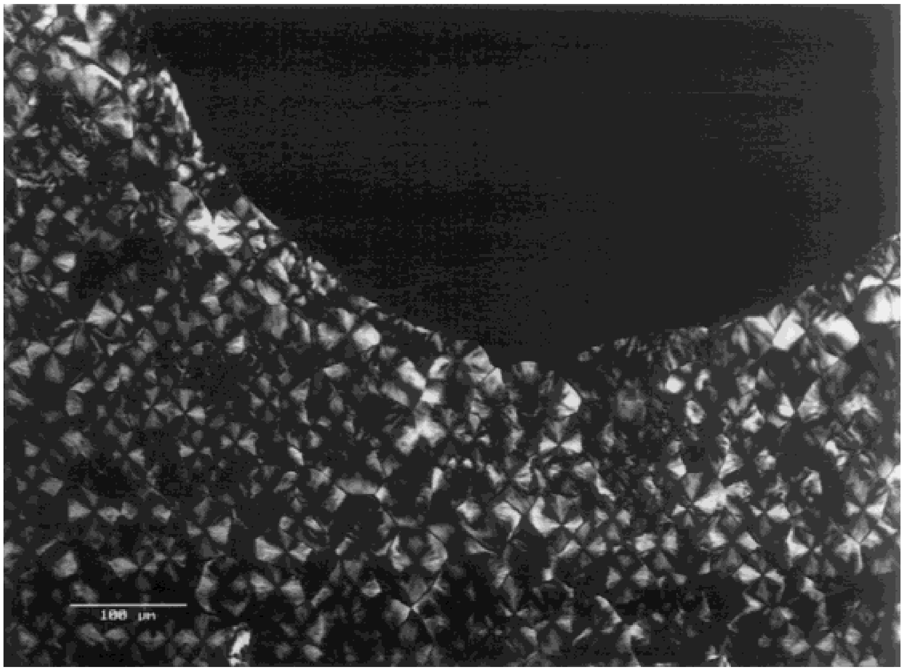
Table I CaF_2 **Concentrations Initially Added and Determined in the Final Samples Using Ion-Selective Electrode Analysis for Fluorine**

Sample	CaF_2 Added (ppm)	CaF_2 Measured (ppm)
1	0	< 1
2	5	6
3	10	6
4	25	24
5	50	34
6	100	65
7	250	144
8	1000	480



(A)

Figure 2 Polarized optical micrographs for Nylon 6,6 annealed at 300°C for 10 min, followed by controlled cooling at a rate of 10°C min^{-1}. (A) Sample containing *ca.* 35 ppm CaF_2. (B) Sample containing *ca.* 65 ppm CaF_2. Scale bar is 100 μm.



(B)

Figure 2 (*Continued from the previous page*)

tained for a Monsanto commercial nucleated and an unnucleated Nylon 6,6 molding resin.[12] A similar observation regarding this type of behavior was reported by Beck and Ledbetter[13] regarding the supercooling of polypropylene with aluminum dibenzoate as the heterogeneous nucleating agent. The calculated level of nucleating agent, *ca.* 2500 ppm, was much lower than expected.[13] Furthermore, the CaF_2 level range over which this transition occurs is *ca.* 30 ppm or less. Additional supporting evidence by POM for this effect is shown in Figure 2. Figure 2(A) and Figure 2(B) are micrographs of Nylon 6,6 morphologies containing CaF_2 loadings of *ca.* 35 and 65 ppm, respectively. The impinged spherulite size in Figure 2(B) is approximately an order of magnitude smaller than that in Figure 2(A). This reduction in size is comparable with that observed between a Monsanto commercial unnucleated and nucleated Nylon 6,6 molding resin.[14] Figure 2(A) and Figure 2(B) are also representative of the morphologies observed for samples with CaF_2 levels less than 35 ppm or more than 65 ppm, respectively.

CONCLUSIONS

In summary, this work shows by DSC and POM that Nylon 6,6 containing 65 ppm CaF_2 exhibits crystallization behavior and morphology characteristic of higher levels of heterogeneous nucleating agent. Furthermore, it shows that the CaF_2 loading range over which the transition from unnucleated to nucleated behavior occurs is between *ca.* 35 to 65 ppm.

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