Journal of Thermal Analysis, Vol. 52 (1998) 355-361

COMPARATIVE STUDY OF EFFICIENCY OF NUCLEATING AGENTS IN PA-6

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(Received March 10, 1997; in revised form June 5, 1997)

Abstract

The isothermal and anisothermal crystallization of nucleated polyamide-6 (PA-6) was investigated by DSC. A comparative study was made of twelve potential nucleating agents, including some commercial products for PA-6 and polypropylene. The amide wax processing aid lubricant originally introduced into the polymer was found to exhibit a marked nucleation ability.

Keywords: crystallization, DSC study, nucleating agents, PA-6

Introduction

Polyamide-6 (PA-6) is a widely used, relatively cheap crystalline engineering thermoplastic which has a moderate crystallization rate similar to that of polypropylene (PP).

Nucleating agents are mostly used in these two polymers. These additives normally increase the rate of crystallization, which shortens the cycle time in injection moulding, improving the productivity of the process, decreases the spherulite size and results in the development of a more uniform structure with enhanced mechanical properties [1–4].

Thousands of different materials have been studied as potential nucleating agents in the case of PP, but a literature search reveals that less attention has been paid to the nucleation of PA-6. Nevertheless, a patent dealing with the fillers of PA-6 more than 50 years ago claimed an appreciable nucleating effect [2]. Numerous commercial nucleated PA grades are currently on the market, e.g. several materials of Allied Signal Co.; Adell; EMS; Nylon Corp.; Texapol; etc. [5]. In basic monographs, several materials are mentioned as efficient nucleating agents in PA-6:

- kaolin
- lead(II) phosphate

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

- sodium phenyl phosphinate
- polyethylene terephthalate
- polyamide 6,6
- colloidal silica
- molybdenum(IV) sulfide
- iron sulfide
- titanium(IV) oxide
- talc

The nucleating effects of some new materials have been verified:

- poly(4,4-diphenylsulfone terephthalamide) [6]
- polyvinylidene fluoride [7]
- montanates [8]
- phthalocyanine [9]
- fatty acid amide [10]
- metal diaryl phosphates [11]
- surface-treated montmorillonite [12]

An on-line literature search demonstrated that a great number of materials may be used as nucleating agents in PA-6, but their mechanisms are not known, and extensive studies to compare tens or hundreds of potential nucleating agents have not been made at all for PA-6.

The main aims of the present study were:

- a comparative study of some potential nucleating agents, with a commercial grade PA-6 as base polymer
- a check on the activity of some nucleating agents of PP in PA-6 (since more information is available on the mechanism and efficiency of nucleating agents in PP).

Experimental

The base polymer used was an injection moulding grade material produced by 'Viscosa RT' (Hungary), containing 0.5 wt% amide wax lubricant. The nucleating agent content was 0.1, 0.5 or 1.0 wt%. The additives were introduced into the polymer with a Brabender ZSK 42-7 twin-screw extruder at 250°C.

The nucleating agents studied and their abbreviations are listed below:

- Two different grades of calcium stearate (CAN and CAS)
- Polyethylene terephthalate (PET)
- Wyoming bentonite with high montmorillonite content (NAB)
- $CaCO_3$ with high surface area, precipitated (Socal, Solvay Co.) (SU)
- Colloidal silica, normal grade (Degussa Co.) (A200)
- Colloidal silica, surface-modified (Degussa) (R972)
- Talc (Luzenac Co.) (LT)

– A phosphorus compound, highly effective in PP (Palmarole) (NA11)
– An organic aluminium compound, a nucleating agent in PP (Sandoz AG) (S4030)
– Bruggolen, a commercial nucleating agent in PA-6 (Bruggeman AG) (VKB22)
– A commercial nucleating agent in PA-6 (Viba SpA) (VRF6)

Crystallization of the samples was followed by DSC. Anisothermal crystallization runs were carried out on a ~5 mg sample in nitrogen on a Perkin-Elmer DSC-7 instrument. Some samples were crystallized isothermally at 202°C. The crystallization temperature was reached at a cooling rate of 40°C min^{-1} after melting the sample at 280°C for 5 min. Flexural tests were carried out according to ISO 178 in order to investigate the structure – property relationship.

A knowledge of the upper limit of the effect of the best nucleating agent in a given polymer would be very important from both practical and theoretical aspects. The method developed by Fillon and co-workers mainly for PP [13] gives a possibility for determination of this value. The earlier methods used only one reference point, the crystallization peak temperature of the 'non-seeded' polymer. This value is compared with those measured for nucleated samples. In the Fillon method, two extreme reference points are applied: the peak temperature of the crystallization of the 'non-seeded' polymer (blank melt) gives the lower point, while the completely seeded material, i.e. the base polymer itself, possessing the maximum number of self-nuclei, but without a considerable crystalline phase content, gives the upper point. This latter state is achieved by limited melting of the sample before crystallization.

By means of the Fillon method, the two limiting temperatures of the base polyamide were determined in several DSC runs by varying the upper temperature (T_f) of melting before crystallization. With decreasing T_f, the crystallization peak temperature increases continuously as more and more self-nuclei survive the melting process. To verify that an increase in the number of self-nuclei is not accompanied by the presence of crystalline phase, a subsequent melting run is necessary. If an appreciable amount of crystalline phase survives the melting process relating to a give T_f, a very sharp peak appears at high temperature, superimposed on the main melting peak.

DSC runs according to the above method yielded the upper and lower limits as 192.2 and 187.7°C, respectively. This means that an increase of less than 5°C can be reached with the best nucleating agent in the peak temperature of crystallization. (The differences are in the range of 20–30°C in the case of PP.)

Crystallization characteristics obtained from the anisothermal DSC traces of samples containing 1 wt% additives are shown in Fig. 1 (T_{co}=onset temperature; T_{cp}=peak temperature; and T_{cf}=final temperature of crystallization).

The commercial material Bruggolen (VKB22) developed for this purpose is one of the best nucleating agents; the effect of the other commercial product, VRF6, is poorer. However, our data indicate that even the efficiency of Brug-

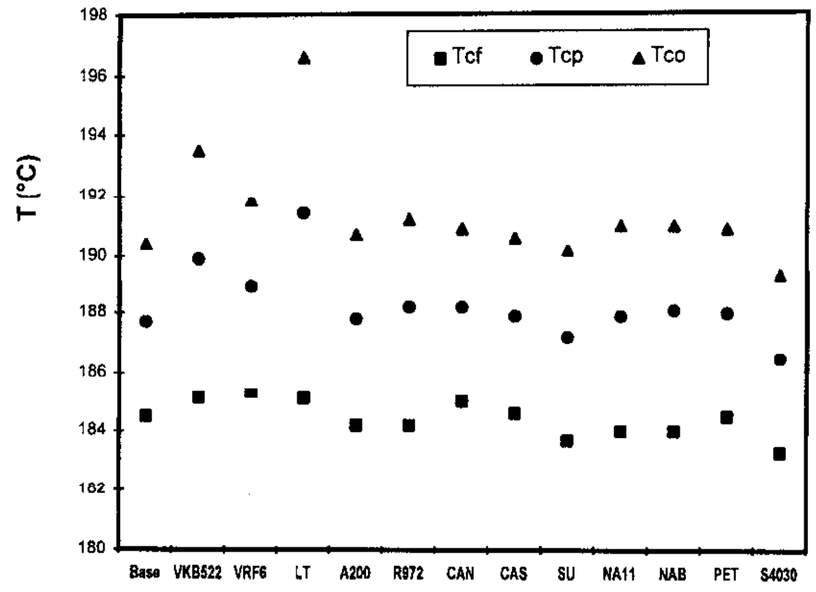

Fig. 1 Crystallization characteristics of PA-6 containing 1 wt% different additives

golen is surpassed by that of the cheap inorganic filler talc (mentioned, not surprisingly, in some newer patents). In the presence of talc, the crystallization interval is widened significantly, which is important for practical applications. As concerns the other additives, montmorillonite (NAB) (an excellent nucleating agent according to the literature) and the phosphate (NA11) (one of the best additives in PP) exert only minor effects. Similarly, PET and the aerosils (all effective nucleators according to some publications) increased the rate of crystallization to only small extents. Calcium stearate and $CaCO_3$ behave as inert compounds, although these particulate fillers with high specific surface areas are active nucleating agents in PP. The aluminium salt (S4030) strongly decreased the rate of crystallization. We have never met such a retardation of nucleation before, especially not at such a low concentration, which was only 1 wt%.

Further investigations were focused on determination of the dependence of the crystallization characteristics on the additive content, and checking of the validity of previous observations in isothermal crystallization experiments using only the interesting or promising materials (talc, VKB22, VRF6 and S4030). The results of anisothermal experiments can be seen in Fig. 2, where the characteristic temperatures of crystallization are plotted against additive content.

The basic tendencies remained the same as in the case of 1 wt% additive content. Talc is the best nucleating agent and the Al salt decreases the rate of crystallization at every concentration. The effectiveness of talc reaches saturation at about 0.5 wt%; its activity does not increase appreciably at higher concentrations. Saturation in PP occurs only at about 4 wt%.

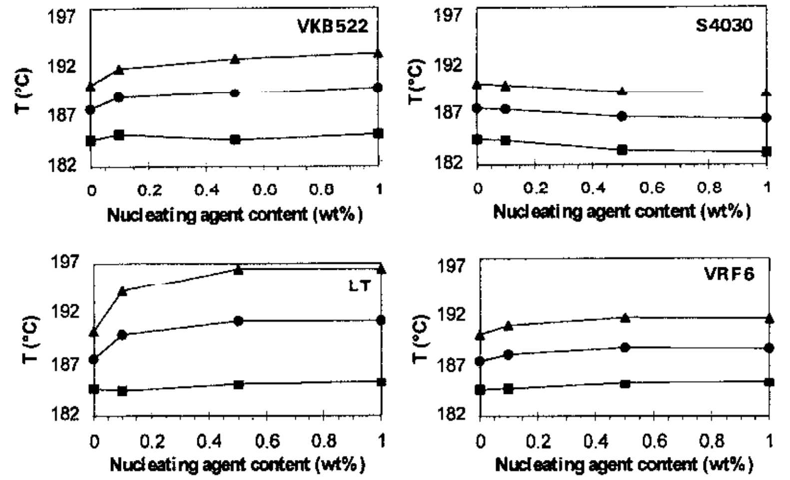

Fig. 2 Concentration dependence of crystallization characteristics of nucleated PA-6 (T_{co} ▲, T_{cp} ●, T_{cf} ■)

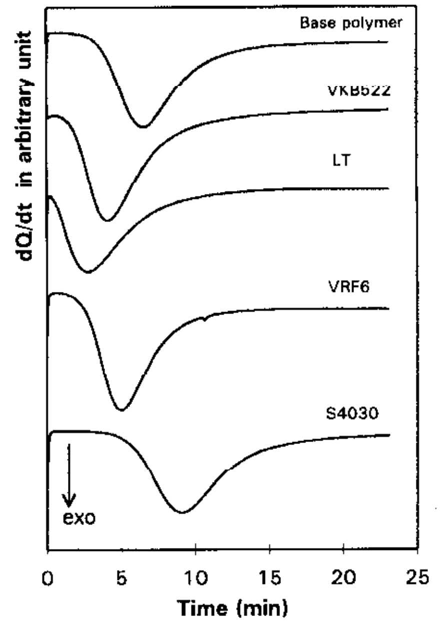

Fig. 3 Crystallization isotherms of PA-6 at 202 °C. Additive content 1 wt%

In isothermal runs (Fig. 3), the effects of nucleating agents on the crystallization process can be detected as a function of time. The sequence of the additives as regards nucleation activity remained the same as in the anisothermal crystallization experiments, but the differences between them were enhanced.

The poor performance of some nucleating agents, and above all the surprising retardation effect of the Al salt, led us to conclude that the lubricant originally present in the system as a processing aid is not inert from the aspect of crystallization. We received a true 'virgin' polymer (absolutely free from additives) from Viscose RT, and the results of our repeated experiments are given in Table 1.

Table 1 Crystallization characteristics of the base and the lubricant free grade PA-6 (ΔT: crystallization interval; ΔH: heat of crystallization

	T_{co}/°C	T_{cp}/°C	T_{cf}/°C	ΔT/°C	ΔH/J g^{-1}
Base polymer	190.3	187.7	184.6	5.7	63.7
Lubricant free polymer	182.7	174.5	168.5	14.2	63.0

Our assumption was confirmed. Under the same conditions, the virgin PA-6 crystallized at a temperature 10 °C lower than that for the 'base' polymer, so the amide wax lubricant plays a dual role in the system: as a lubricant and as a nucleating agent. We assume that some physical or chemical interaction occurs between the organoaluminium salt (S4030) and the lubricant, which causes a decrease in crystallization temperature for samples containing S4030.

Table 2 Flexural modulus of nucleated PA-6

Sample	Additive content/wt%	Flexural modulus/GPa
Base polymer	–	1.40
Bruggolen (VKB22)	0.05	1.63
	0.10	1.68
	0.50	1.60
Talc(LT)	0.05	1.69
	0.10	1.66
	0.50	1.65

In order to check the effects of the nucleating agents on the properties of the products, some mechanical tests were carried out. Table 2 lists the flexural moduli of the samples nucleated by talc and Bruggolen as a function of additive content. In spite of the moderate nucleating effects of these two additives, the increases in flexural modulus are surprisingly large.

Conclusions

DSC crystallization experiments have shown that some well-known and strong nucleating agents of PP are inactive in PA-6. Among them, talc is the only additive which exerts a marked nucleating effect. The amide wax lubricant behaves as a true nucleating agent; it can interact with other additives and lose its efficiency as a result. We are convinced that a detailed study of the interaction between S4030 and the amide wax lubricant would help towards an understanding of the mechanism of nucleation in PA-6.

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