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Influence of the cooling rate on the non-isothermal crystallization of isotactic polypropylene modified with sorbitol derivative and silsesquioxane

RAPID COMMUNICATION

Summary — The influence of 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) and tetrasilanolphenyl silsesquioxane (phPOSS) on the modification of isotactic polypropylene (*i*PP) was investigated. In particular, dependency of crystallization behavior on the cooling rate was determined. To understand these effects the results of differential scanning calorimetry (DSC) measurements and the crystallization curves were analyzed.

Keywords: isotactic polypropylene, silsesquioxane, sorbitol derivative, crystallization.

OCENA WPŁYWU SZYBKOŚCI CHŁODZENIA NA PRZEBIEG NIEIZOTERMICZNEJ KRYSTALIZACJI IZOTAKTYCZNEGO POLIPROPYLENU MODYFIKOWANEGO POCHODNĄ SORBITOLU I SILSESKWIOKSANEM

Streszczenie — W niniejszym artykule opisano modyfikację izotaktycznego polipropylenu za pomocą 1,3:2,4-bis(3,4-dimetylobenzylideno)sorbitolu (DMDBS) oraz tetrasilanolofenylosilseskwioksanu (phPOSS). W szczególności zbadano zależność przebiegu procesu krystalizacji od szybkości chłodzenia w przypadku polipropylenu modyfikowanego układem DMDBS/phPOSS. W tym celu przeprowadzono badania metodą skaningowej kalorymetrii różnicowej (DSC) oraz analizowano przebieg krzywych krystalizacji.

Słowa kluczowe: polipropylen izotaktyczny, silseskwioksan, pochodna sorbitolu, krystalizacja.

INTRODUCTION

Recently the polyhedral oligomeric silsesquioxanes (POSS) have received a widespread interest because of being hybrid inorganic cage molecules functionalized with organic substituent groups which may be introduced into a polymer matrix as modifiers [1]. A number of studies were carried out to consider rheological behavior, thermal stability, crystallization, structure and mechanical properties of POSS-polymer composites. A considerable attention was given also to the question of miscibility with polymeric matrix and to the quality of homogeneous distribution of incorporated nanomodifiers during both polymerization *in situ* and polymer melt processing on laboratory scale, with the use of conventional mixing methods [2—5]. It was stated that modifying polymeric matrix with only POSS may fail to achieve satisfactory results [6—8]. Thus, to improve the modification efficiency, silsesquioxanes grafted with modifying agents have recently gained a substantial interest [9, 10].

The most effective, widely used in industry nucleating agents for isotactic polypropylene and its copolymers are derivatives of sorbitol, *i.e.* condensation products of aromatic aldehyde and sorbitol. The main advantage of sorbitol derivatives, used frequently as clarifying agent, is a high level of transparency of the polypropylene matrix. As it results from studies, sorbitol phase separates from the polymer matrix in a form of an oriented network [11]. Accordingly, the crystallization of isotactic polypropylene may be observed in a form of somehow oriented crystals on a highly oriented sorbitol network [12—14]. The crystalline nucleation that resulted from this structural effect led to a significant increase in crystallization temperature, and consequently caused viscosity increase in the polymer melt during the cooling process. This

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effect may finally disturb the processing of highly oriented products like films, fibers, *etc.* [15—18].

Thus, the aim of this work was to study the influence of the addition of POSS modified sorbitol derivatives on the crystallization behavior of isotactic polypropylene, and particularly on the slowing down of crystallization, observed as a suppression of a viscosity increase during cooling by melt processing.

EXPERIMENTAL

Materials

The following materials were used in the investigations:

— isotactic polypropylene (*i*PP), with trade name Moplen HP500N produced by Basell Orlen Polyolefins (Poland), with the melt flow rate $MFR_{2.16;230} = 10$ g/10 min;

— 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS), with trade name Millad 39881 which is the third generation of sorbitol derivatives, that is offered by the Milliken Chemical Company (USA);

— tetrasilanolphenyl-POSS ($C_{44}H_{44}O_{14}Si_8$), abbreviated phPOSS, which acts as a nucleating agent modifier, synthesized by the Department of Organometallic Chemistry UAM in Poznań (Poland).

Sample preparation

The *i*PP granules were ground into powder using a Tria high-speed grinder. A drying process of the nucleating agent and the modifier was carried out in a vacuum oven for 2 h at 120 °C. A mixing process of the polymer with DMDBS and phPOSS was performed using the rotary mixer Retsch GM 200, operating for 3 min with the rotation speed of 3000 rpm. The final stage of *i*PP homogenization with 0.25 wt. % of DMDBS and 0.25 wt. % of phPOSS was performed with molten state extrusion using the Zamak co-rotating twin-screw extruder (at 190 °C and 70 rpm). The granulation process was performed by pelletizing of the extruded rod in a water bath pelletizing system.

Methods of testing

The DSC measurements were performed by means of Netzsch DSC 204 F1 Phoenix®, using samples of about 5 mg placed in aluminum crucibles. The following heating-cooling temperature program was applied: first heating to 220 °C, the molten state held for 5 min at 220 °C to erase the thermal history, and final cooling to 60 °C with various cooling rates φ = 2.5, 5, 10 or 20 deg/min. All the experiments were performed in the nitrogen atmosphere. As a result, a set of DSC crystallization curves has been registered and analyzed [15—17].

The degree of crystallinity as a function of temperature has been presented for various cooling rates to examine the impact of pure DMDBS and DMDBS combined with phPOSS on the crystallization process. Based on these crystallization curves, the values of ΔT and ΔT^* presenting the difference in temperatures have been evaluated according to equations:

$$\Delta T = T_{PP/DMDBS} - T_{PP} \quad (1)$$

$$\Delta T^* = T_{PP/DMDBS} - T_{PP/DMDBS/phPOSS} \quad (2)$$

where: T_{PP}, $T_{PP/DMDB}$, $T_{PP/DMDBS/phPOSS\ S}$ — *the temperatures of pure iPP, iPP nucleated with DMDBS and iPP nucleated with DMDBS/phPOSS system, respectively, at particular values of crystallinity degree*.

The effect of the cooling rate on ΔT and ΔT^* was analyzed.

RESULTS AND DISCUSSION

The DSC calorimetric investigations were intended to describe the effect of phPOSS addition on a position of the nucleated *i*PP crystallization curves. In case of samples cooled with rate equal to 10 deg/min, it was found that a maximum rise of crystallization temperature, compared to pure *i*PP, was noted for *i*PP nucleated with DMDBS (about 10.9 deg). Comparing to the pure one, it was found that this value is also higher for polypropylene nucleated with DMDBS and phPOSS, and the difference is equal to about 7.5 deg.

Figure 1 presents the relative degree of crystallinity (X_{cr}) as a function of temperature for samples cooled at the rate of 2.5, 5, 10 and 20 deg/min. A decrease in the crystallization temperature with increasing cooling rate was observed for all samples. For the lowest cooling rate the X_{cr} = f(T) curve of *i*PP nucleated with the DMDBS/phPOSS system is at the same position as the pure one, *i.e.* both curves overlap. Furthermore, with increasing cooling rate the shift of DMDBS/phPOSS curves towards higher temperatures was noted.

To describe the shift of crystallization curves, the calculated data of ΔT and ΔT^* for three relative degrees of crystallinity, *i.e.* 20, 50 and 80 % are listed in Table 1.

Table 1. The values of ΔT and ΔT^* calculated for selected values of relative degree of crystallinity (X_{cr}) as a function of cooling rate (φ)

φ deg/min	ΔT for selected X_{cr} values deg			ΔT^* for selected X_{cr} values deg		
	80 %	50 %	20 %	80 %	50 %	20 %
2.5	10.5	10.5	10.5	10.0	10.5	11.5
5	11.0	11.0	11.0	5.5	6.0	6.0
10	10.5	11.0	11.0	4.5	4.5	3.5
20	10.0	11.0	12.0	0.1	0.3	0.6

An increase in the *i*PP crystallization temperature occurring due to the addition of DMDBS, presented by ΔT, and slightly influenced by a cooling rate was noted.

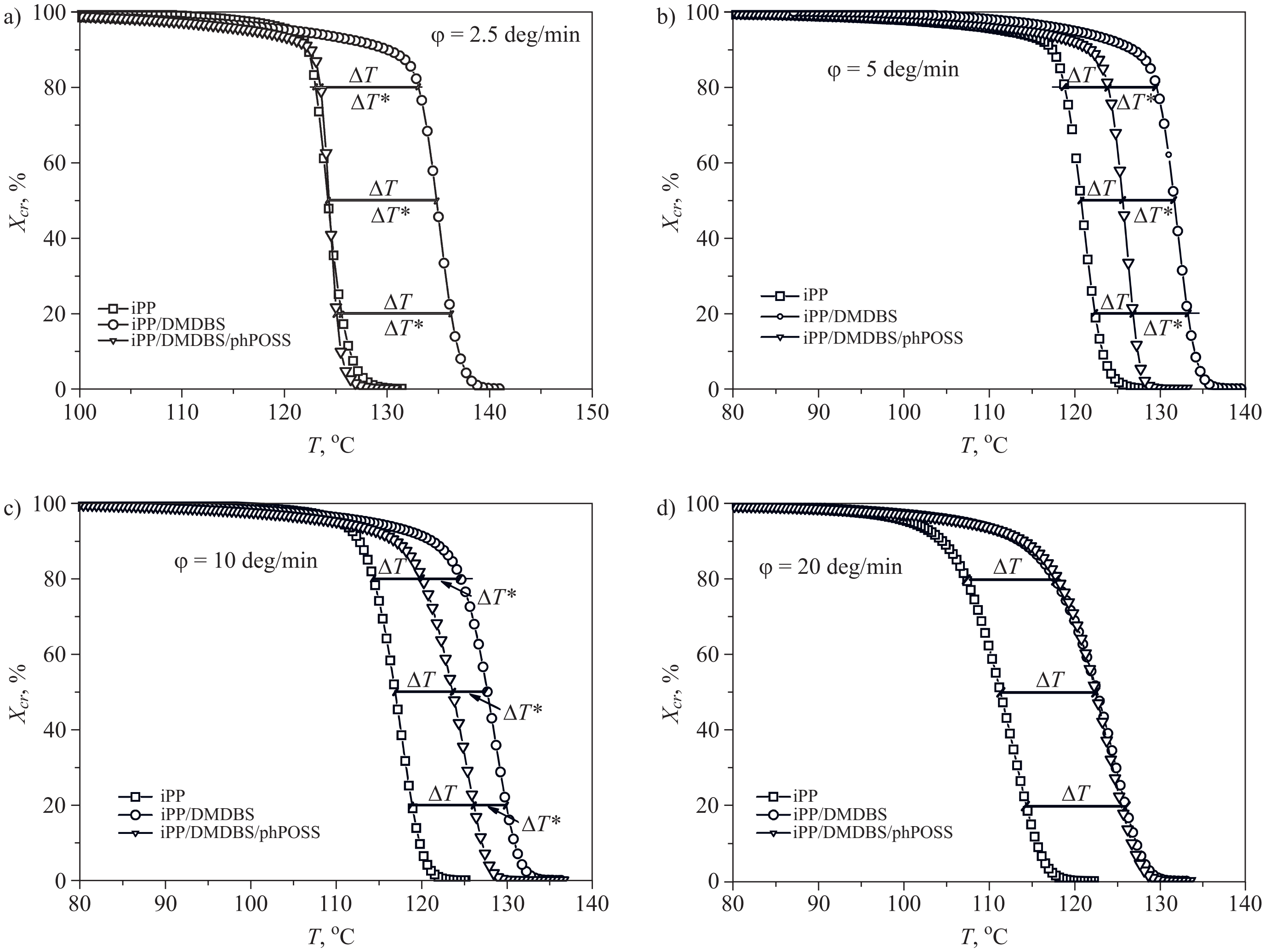

Fig. 1. The relative degree of crystallinity (X_{cr}) as a function of temperature (T) for samples cooled at rate of: a) 2.5 deg/min, b) 5 deg/min, c) 10 deg/min, d) 20 deg/min

However, the values of ΔT^* presenting the efficiency of phPOSS as a DMDBS modifier show a significant cooling rate dependency. As it was observed, the addition of phPOSS led to a suppression of DMDBS activity regarding the crystallization temperature (compare Fig. 1 for the lowest cooling rate). For the cooling rate of 2.5 deg/min, the ΔT^* value of about 10 deg was noted. A constant lowering of efficiency for higher cooling rates was observed. Finally, for the highest cooling rate of 20 deg/min, the *i*PP nucleated with DMDBS/phPOSS crystallization temperature occurs at the same position as the *i*PP nucleated with DMDBS, *i.e.* under these particular processing conditions the modification of sorbitol nucleating agent with POSS is negligible.

A similar cooling rate effect was observed by Varga [19] where a crystal phase formation of *i*PP, except an activity of nucleating agent, was strongly dependent on the cooling conditions. It was confirmed that a high cooling rate would lead to the formation of a monoclinic α phase in *i*PP, even if the polypropylene was modified with systems nucleating hexagonal form. As the derivatives of sorbitol form α-phase, a similar effect may be expected in this case.

Additives dependent shift of crystallization towards lower temperatures leads to a slowdown in the viscosity increase while cooling. This effect was observed during rheological studies performed using a cone and plate rheometer. These investigations, which are significant for processing meaning, like longer time for melt drawing during films and fibers production, due to the controlled crystallization behavior of *i*PP/DMDBS/phPOSS composites, will be published and analyzed elsewhere [20].

CONCLUSION

It was found that the application of a nucleation system consisted of 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol modified by tetrasilanolphenyl-POSS, in strictly controlled processing conditions, may result in an adjustment of crystallization behavior of *i*PP. This led to lowering of the crystallization temperature and consequently delayed a melt viscosity increase. This structural effect may be applied in various fields, *e.g.* in films and fibers production, especially in case where high transparency is crucial (and occurs due to a DMDBS clarifying activity) and in the same time the high melt drawing rates are supposed to be achieved.

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