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CARBON NANOPARTICLES AS EFFECTIVE NUCLEATING AGENTS FOR POLYPROPYLENE

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The effect of four nucleating agents on the crystallization of isotactic polypropylene (iPP) was studied by differential scanning calorimetry (DSC) under isothermal and non-isothermal conditions. The nucleating agents are: carbon nanofibers (CNF), carbon nanotubes (CNT), lithium benzoate and dimethyl-benzylidene sorbitol.

Avrami's model is used to analyze the isothermal crystallization kinetics of iPP.

Based on the increase in crystallization temperature (T_c) and the decrease in half-life time ($\tau_{1/2}$) for crystallization, the most efficient nucleating agents are the CNF and CNT, at concentrations as low as 0.001 mass%. Sorbitol and lithium benzoate show to be less efficient, while the sorbitol needs to be present at concentrations above 0.05 mass% to even act as nucleating agent.

Keywords: *carbon nanofibers, carbon nanotubes, dimethyl-benzylidene sorbitol, isothermal kinetics, lithium benzoate, nucleating agents, polypropylene*

Introduction

Polypropylene is a semi-crystalline polymer, extensively used in the packaging industry, due to its good balance of physical and mechanical properties. Additionally, isotactic polypropylene (iPP) is easy to process and has a relative low cost [1].

iPP has normally a slow crystallization rate, forming large spherulites. Therefore, heterogeneous nucleation is amply used to enhance the mechanical properties and/or to provide consistent optical properties.

The crystallization behavior of iPP can be described by the stages of nucleation and crystal growth [2]. Nucleation can be homogeneous or heterogeneous. Homogeneous nucleation is the process in which nuclei form spontaneously in the PP melt as it cools down [3]. This crystallization will not occur before the melt is supercooled well below the equilibrium melting temperature. On the other hand during heterogeneous nucleation the crystallite growth is initiated by foreign bodies within the molten phase. In this case, crystallization will tend to occur at higher temperatures. These foreign bodies are called nucleators or nucleating agents [4]. In the case of polypropylene, solids, liquids and even gas bubbles have been used as nucleators [5].

The mechanism of heterogeneous nucleation is still not precisely known, it has been suggested that, apart from the dispersion of the agent, the mechanism is controlled by the polymer–nucleator interactions, and these can be chemical or physical [3], or even related to Van der Waals attractions [6].

The two main effects of a nucleator on the crystallization of PP are, to increase the crystallization temperature, which decreases the moulding process cycle time, and to decrease the crystal size, which considering evenly sized crystals, would improve the optical and mechanical properties of the polymer [7].

The effect of the nucleator is assessed for individual substances more or less on try-and-error basis. Different methods have been used to determine the nucleating efficiency of a substance on the crystallization of iPP. Among these methods, the following can be mentioned: a) measurement of the increase in the crystallization temperature (T_c), being this a heterogeneous nucleation the polymer crystallizes at higher temperatures, b) determination of the increase in the crystallization rate, this can be calculated by the half-life time ($\tau_{1/2}$) – defined as the time taken for 50% of the total crystallization to occur [8], c) the agent also reduces the fold surface energy (σ_e), making the formation of crystals easier, d) by providing sites for crystallization the density of actual nuclei can also be estimated from the radial growth rate of spherulites, e) the nucleation free energy [9] or the direct observation of the reduction of crystal size by optical means [10], are also used to determine the action of the nucleator and finally, f) the nucleating efficiency calculated by taking the ideal situation of auto-nucleation of the polymer has also been reported [3].

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The purpose of this study was to assess the nucleating ability of very small loads of CNT and CNF on iPP as well as two recognized commercial nucleating agents: dimethyl-benzylidene sorbitol (Millad) and lithium benzoate (LiBe).

While most studies on the nucleating efficiency of CNT and CNF [11, 12] deal with high loads of the nucleating agents, the present study is devoted to investigate the effect of using the minimum amounts of nucleating agent. The nucleating ability was determined from the increase in T_c and the decrease in the crystallization rate.

Experimental

Materials

iPP used in this study is a commercial grade supplied in pellet form by Total Petrochemicals USA, with an experimental average molecular mass M_w of 150000 and MFI of 15 g 10 min^{-1}.

The nucleating agents included in this study, were: carbon nanofibers, Pyrograf™ III, from Applied Sciences, Inc., multi-walled carbon nanotubes from NanoLab®, Inc., lithium benzoate from Micronisers Pty Ltd., and 1,3:2,4-*bis*(3,4-dimethyl-benzylidene sorbitol), Millad® 3988, from Milliken Chemical.

A series of compositions with 0.001, 0.01, 0.05 and 0.1 mass% of the nucleating agent were prepared by melt mixing samples of 250 g for 10 min, at 438 K and 50 rpm, in a Brabender torque rheometer mixing chamber. Plain iPP was also passed through the mixer to produce blank samples. To prepare the samples with the lower nucleating agent concentrations, i.e. 0.001 and 0.01%, the compound with 0.05% was used as a master batch and diluted as necessary.

Methods

All DSC analysis was performed on a Perkin Elmer DSC 7, Pyris. All samples, of 8±1 mg were analyzed under a nitrogen atmosphere.

Isothermal measurements

These were carried out at various isothermal temperatures ranging from 383 to 410.5 K in 2.5 intervals. All samples were first heated to 473 K at 10°C min^{-1} and held there for 2 min to erase the previous thermal history. Subsequently, they were cooled at 50°C min^{-1} to the desired isothermal temperature and held at that temperature until complete crystallization.

Dynamic measurements

All samples were heated to 473 K at 10°C min^{-1} and maintained there for 2 min and further cooled down to 323 K, at 10°C min^{-1}.

Results and discussion

The effect of the different nucleating agents as a function of the concentrations investigated during this study on the crystallization temperature (T_c) of iPP is presented in Fig. 1. It can be observed that both carbon nanofibers and carbon nanotubes are the ones that exert the greatest increase – more than 10 K in the T_c of iPP – which indicates a very good nucleating effect of these two materials.

The excellent nucleating effect of the CNFs and CNTs can be explained in terms of the greater chemical affinity that the non polar nanotubes and nanofibers present towards the polymer as compared to the sorbitol and the benzoate, which count with polar carbonyl groups in their structure. Additionally, the great surface area of the CNFs and CNTs may induce a better interaction with the polymer, as it has been reported before [12, 13].

In Fig. 1 can be observed that the sorbitol (Millad) shows no nucleating effect at concentrations of and below 0.05%, this behavior has already been reported [14–16] and attributed to the fact that, at this concentrations the sorbitol acts more as a low molecular mass diluent, decreasing the melting and crystallization temperatures of the polymer. In the present study, the nucleating effect of the sorbitol was achieved already at the concentration of 0.1%. The T_c value for the sorbitol at 0.1% concentration is comparable to the value obtained with the CNT and CNF at the same concentration.

Other authors [3, 13, 14] report the nucleating effect of this specific sorbitol at concentrations higher

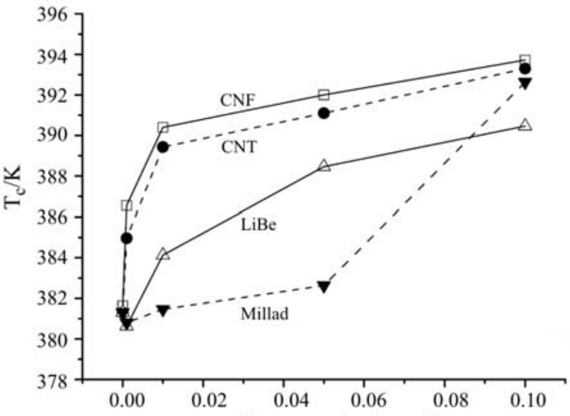

Fig. 1 T_c of iPP as a function of the nucleating agent concentration

than 0.2%. Our results, however, are in agreement with Iguchi [9], who reports a value for a free-energy parameter for the nucleation of Millad® 3988 to be very good already at 0.1 mass%.

No higher concentrations were tried since the aim of this study was to find the minimum load of agent to accomplish the nucleating effect.

Even though lithium benzoate has been used as a nucleating agent in other investigations [2, 17] during the present study the lithium benzoate was found to be the less effective as nucleating agent, even though it does induce a steady increase in T_c with increasing concentration, the best result is obtained from the CNF. Figure 2 presents the increase in T_c as a function of the CNF concentration.

The overall crystallization of the nucleated iPP was also measured, the results indicate the systems present a slight increase in the overall crystallization, and this gain in crystallization is directly proportional to the increase in T_c. The results are presented in Table 1. For the calculation of crystallinity, the value of 209 kJ kg^{-1} was taken as the one corresponding to 100% crystalline PP [18].

The samples with a nucleating agent concentration of 0.1% were selected to make the analysis of the isothermal crystallization, this with the purpose of including the sorbitol agent, which presented a nucleating effect only at 0.1%. Figures 3 and 4 show the crystallization isotherms taken from the DSC, for the pure iPP and iPP nucleated with carbon nanotubes, respectively. From the isothermal curves the effect of the temperature on the crystallization rate of iPP and iPP/CNT is observed.

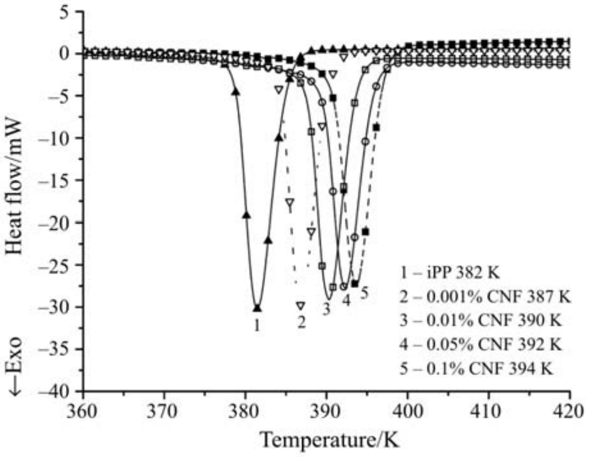

Fig. 2 Effect of CNF concentrations on the crystallization temperature of PP

Table 1 Crystallinity of iPP as a function of nucleating agent concentration

Conc./ mass%	Crystallinity/%			
	iPP–CNT	iPP–CNF	iPP–Millad	iPP–LiBe
0.0	42.51	42.51	42.51	42.51
0.001	43.25	43.43	41.96	43.25
0.01	44.00	43.98	42.54	43.40
0.05	44.71	44.94	42.64	44.23
0.1	44.29	45.03	43.80	44.78

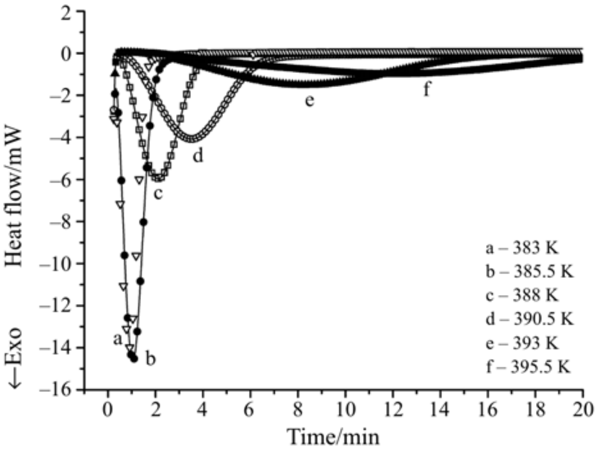

Fig. 3 DSC isotherms for plain iPP, at different crystallization temperatures

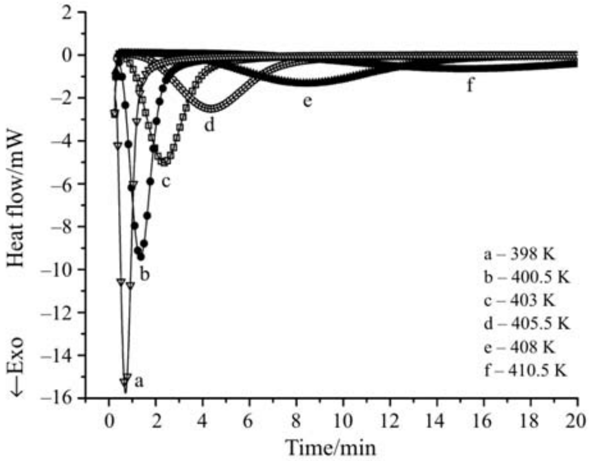

Fig. 4 Isotherms for iPP/CNTs (with 0.1 mass% CNTs)

The crystallization rates of iPP and nucleated iPP are strongly affected by crystallization temperatures. Figure 5 shows the crystallization formation for plain PP and the four nucleated iPP, at the selected temperature of 388 K. The nucleating agents dramatically accelerate the development of crystallinity.

The crystallization kinetics of iPP and nucleated iPP was carried out based on the Avrami's model. This theory has been often used to analyze the crystallization of iPP [19–21], even though the model does not account for the secondary crystallization or the change in volume, which are dominant at later stages of crystallization, in the case of iPP it has been

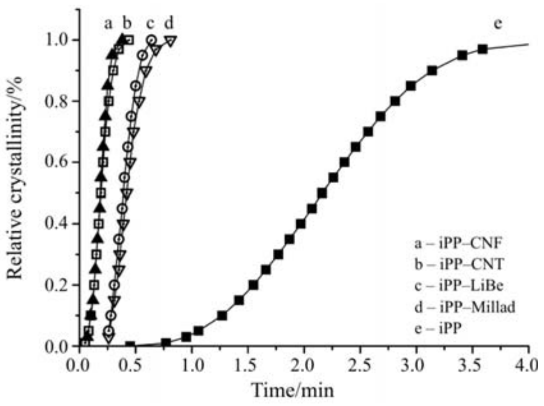

Fig. 5 Crystallinity development in iPP and nucleated iPP (with 0.1 mass%) at T=388 K

found [8] that secondary crystallization is not relevant in the crystallization process of this polymer.

To analyze the isothermal crystallization the following equation derived from the Avrami model was used:

$$\alpha(t)=1-\exp(-Kt^{n})$$

where $\alpha(t)$ is the fraction of mass that has been transformed from the amorphous to the crystalline state, as a function of the time t, where K is the Avrami's constant and n is the Avrami's exponent. The last two parameters are used to interpret the mechanism of nucleation, morphology and overall crystallization rate of the polymer. The parameters K and n are obtained from a

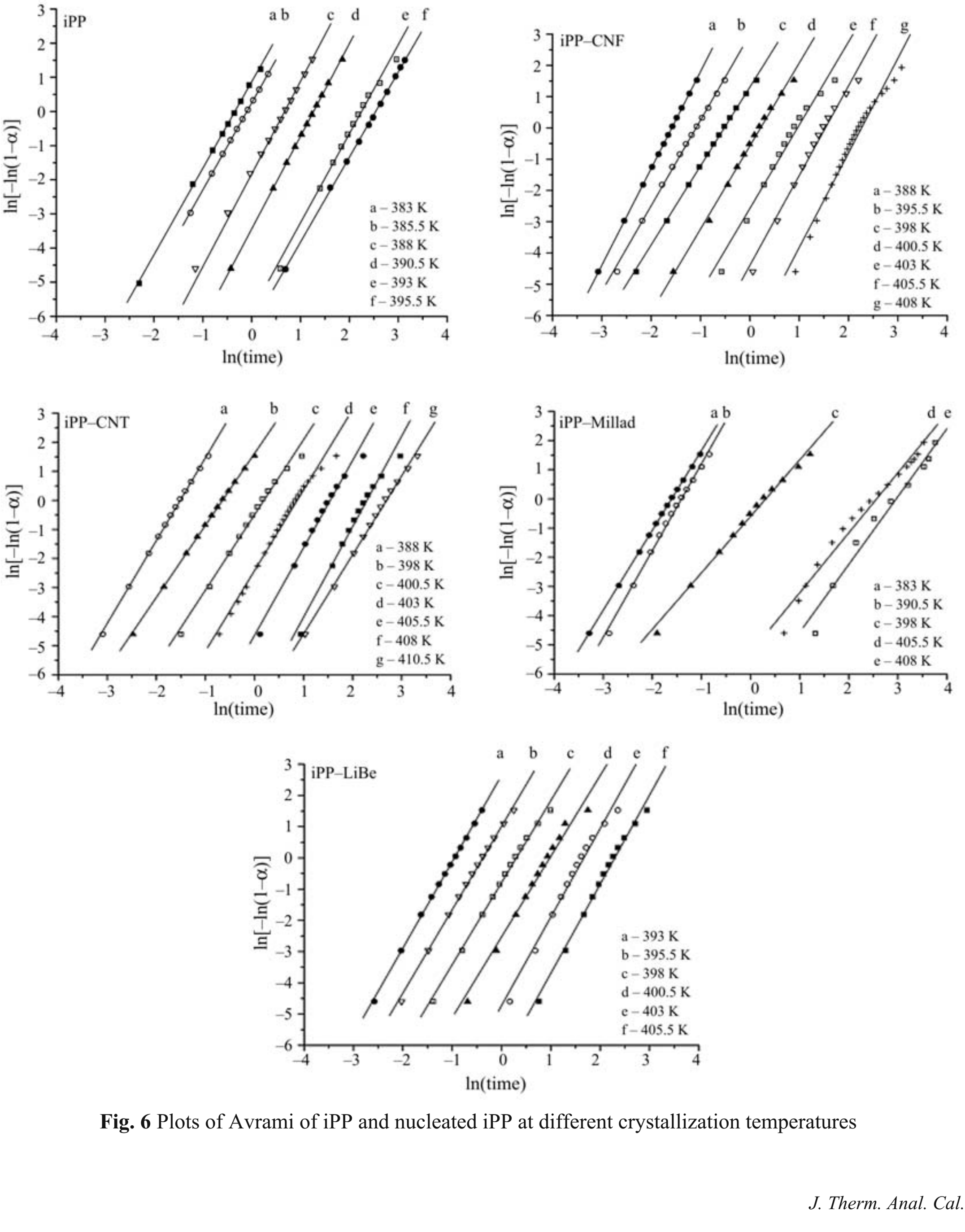

Fig. 6 Plots of Avrami of iPP and nucleated iPP at different crystallization temperatures

Table 2 Crystallization temperature T_c, Avrami's constant K, Avrami's exponent n and half-life time of crystallization $\tau_{1/2}$ for iPP and nucleated iPP, at different temperatures

Sample	T_c/K	K	n	$\tau_{1/2}$/min	Sample	T_c/K	K	n	$\tau_{1/2}$/min
iPP	383.0	2.47	2.57	0.61	iPP–Millad	383.0	80.84	2.73	0.17
	385.5	1.28	2.55	0.79		391.0	19.45	4.17	0.4
	388.0	0.17	2.58	1.7		393.0	9.14	2.5	0.4
	390.5	0.032	2.71	3.1		398.0	0.55	1.93	1.12
	393.0	0.002	2.61	8.2		405.5	0.005	2.05	10.9
	395.5	0.0018	2.49	10.9		408.0	0.001	2.32	16.58
iPP–CNT	388.0	74.11	2.84	0.19					
	393.0	52.19	2.74	0.21	iPP–LiBe	393.0	13.82	2.76	0.54
	398.0	5.002	2.48	0.45		395.5	2.74	2.67	0.88
	400.5	0.606	2.58	1.05		398.0	0.47	2.74	1.49
	403.0	0.0894	2.77	2.09		400.5	0.08	2.58	2.64
	405.5	0.0096	3.01	4.15		403.0	0.008	2.83	4.89
	408.0	0.0008	3.11	8.78		405.5	0.001	2.85	9.87
	410.5	0.0007	2.72	12.86					
iPP–CNF	388.0	134.32	3.1	0.18	iPP–CNF	403.0	0.076	2.66	2.56
	395.0	19.79	2.98	0.49		405.5	0.012	2.87	4.54
	398.0	3.7	2.52	0.81		408.0	0.001	3.02	8.64
	400.5	1.79	2.65	1.39					

plot of $\ln[-\ln(1-\alpha)]$, where α is the fraction of crystalline material, *vs*. ($\ln t$), where t is the time needed to attain the crystalline fraction α. Figure 6 shows the Avrami's plots for pure and nucleated iPP.

Once the Avrami parameters K and n are defined, the half-life time of crystallization can be determined. The half-life time of crystallization ($\tau_{1/2}$) is defined as the time needed to complete 50% of crystallization and can be calculated directly from the isotherm curves or from the measured kinetics parameters, with: $\tau_{1/2}=[(\ln 2)/K]^{1/n}$. The results for K, n and $\tau_{1/2}$, are reported in Table 2.

The results are in good agreement with the Avrami equation at temperatures below and near T_c – measured under dynamic conditions –, whereas at higher temperatures there is a slight deviation. The fractional n values are accounted in the Avrami theory assuming a partial time of overlapping of primary nucleation and growth [22].

The n values range between 2.0 and 3.0 for both the blank polymer and for the nucleated polypropylene. Values for n ranging between 2 and 3 have been previously reported for isotactic polypropylene [12, 13, 22–24].

The sorbitol shows less consistent n values, some of them being even as high as 4, this might be related to the dissolution effect of the agent [16].

The effect of the nucleating agents is clearly seen in the rate of the crystallization development (Fig. 5). The crystallization rate – measured by the half-life time of crystallization – for the given temperature of 388 K, indicates a reduction in the velocity of crystallization induced by the nucleating agent (Table 2). For the carbon nanoparticles this reduction has a magnitude of a factor 10, compared to the blank, while for the sorbitol and lithium benzoate the reduction is less.

The spherulitic growth rate and number of nuclei are reflected on the Avrami's constant K. This constant can be used to determine the nucleating ability of the nucleating agents, taking into account that the spherulitic growth rate depends on the crystallization temperature and is characteristic of each polymer, assuming the spherulitic growth rate is not influenced by the nucleator [2]. Avrami's constant follows an Arrhenius type relationship, which can be observed in Fig. 7. In this case, the higher K values imply a higher number of nuclei for iPP–CNFs and iPP–CNTs than for pure iPP. A slightly higher number of nuclei are seen for the CNF systems, this is in agreement with the also slightly higher T_c measured for the CNF, im-

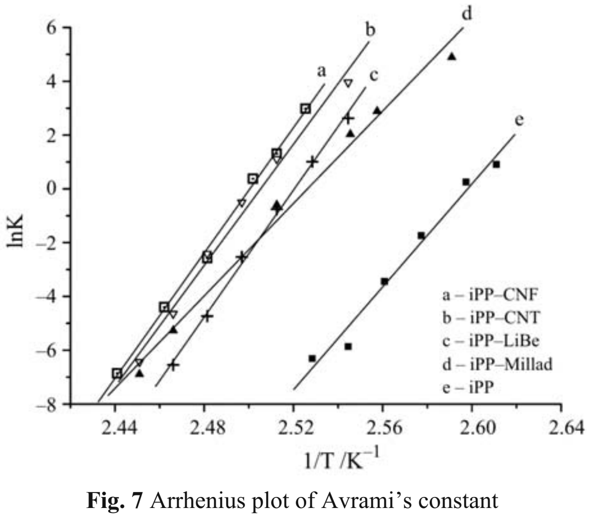

Fig. 7 Arrhenius plot of Avrami's constant

plying a slightly better nucleating effect from the carbon nano fibers than the carbon nano tubes, this is also true when comparing the half-life time of crystallization for both nucleators. On the other hand, Millad shows very similar results to lithium benzoate.

Conclusions

From the above results, the following conclusions can be deduced:

- The carbon nanofibres and carbon nanotubes were able to enhance the crystallization rate by increasing the nuclei sites, as a result a raise in the crystallization temperature of the polypropylene is observed.
- Lithium benzoate shows steady and consistent good results at raising the crystallization temperature of iPP, reducing the half-life time of crystallization and increasing the nuclei density in the polymer, while the dimethyl-benzylidene sorbitol gives good results only at the highest studied concentration of 0.1% in mass, and the results obtained from T_c and $\tau_{1/2}$ are comparable to those from lithium benzoate.

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