

Carbon Nanoparticles As effective Nucleating Agents for Polypropylene

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1. Abstract

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. The efficiency of the four agents on the nucleation of the iPP was assessed based on the increase in crystallization temperature (T_c), the decrease in half-life time ($\tau_{1/2}$) for crystallization, and the crystal size. The most efficient nucleating agents are the CNF and CNT, at concentrations as low as 0.001 wt %. Sorbitol and lithium benzoate show to be less efficient, while the sorbitol needs to be present at concentrations above 0.05 wt % to even act as nucleating agent.

2. Introduction

Polypropylene is a semi-crystalline polymer, extensively used in the packaging industry, due to its good balance of physical and mechanical properties^[1].

iPP has normally a slow crystallization rate, forming large spherulites, therefore considerable efforts have been aimed to increase the crystallization rate of the polymer^[2]. The crystallization of iPP is described by the stages of nucleation and crystal growth^[2]. Nucleation can be homogeneous or heterogeneous. During homogeneous nucleation, nuclei form spontaneously in the PP melt as it cools down^[3], when heterogeneous nucleation the crystallite growth is initiated by foreign bodies within the molten phase, occurring this at higher temperatures. These foreign bodies are called nucleators or nucleating agents^[4].

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 and lithium benzoate.

The nucleating ability is assed using three parameters: a) increase in the crystallization temperature (T_c), b) increase in the crystallization rate, - calculated by the half-life time ($\tau_{1/2}$),

defined as the time taken for 50% of the total crystallization to occur - ^[5], and c) effect in the crystal size.

3. Experimental

3.1 Materials

Polymer: iPP supplied by Total Petrochemicals USA, Mw of 150000 and MFI of 15g/10 min. Nucleating agents: CNF, PyrografTMIII, multi walled CNT from NanoLab®, Inc., lithium benzoate from Micronisers Pty Ltd., and 1,3:2,4-bis(3,4-dimethyl-benzylidene sorbitol), from Milliken Chemical.

3.1.1. Sample preparation

Compositions with 0.001, 0.01, 0.05 and 0.1% by weight of the nucleating agent were prepared by melt mixing samples of 250g for 10 min, at 165°C and 50 rpm, in a Brabender torque rheometer mixing chamber.

3.2 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. Samples were heated to 200° C at 10°/min and held there for 2 min. Subsequently, cooled at 50°C/min to the desired isothermal temperature and held at that temperature until complete crystallization.

Dynamic measurements. Samples were heated to 200°C at 10°C/min and maintained there for 2 min and further cooled down to 50°C, at 10°C/min.

Optical Microscopy. The microscopy was performed on a Metler Toledo FP900, coupled to a contrast phase microscope, from Zeiss, additionally the microscope is coupled to a Samsung video camera model SCC-131A. The amplification used was 10X times 100X.

4. Results and Discussions

Figure 1 presents the effect of the nucleating agents on Tc. Both CNF and CNT are the ones that exert the greatest increase – more than 10°C in the Tc 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 ^[6,7].

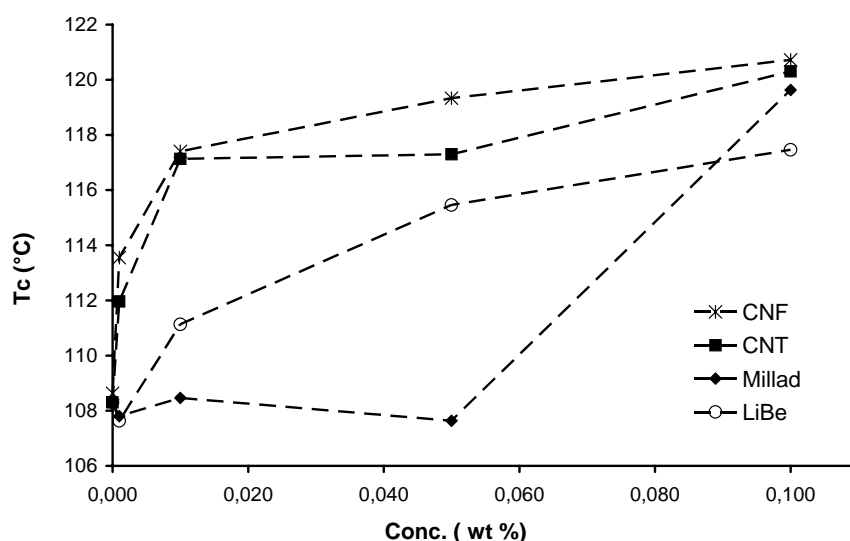


Figure 1. T_c of iPP as a function of the concentration of the nucleating agents

The effect of the four nucleating agents (at 0.01% wt) on the half-time of crystallization ($\tau_{1/2}$) on the iPP is presented in table 1.

Sample	T_c [°C]	$\tau_{1/2}$ [min]
iPP	108.3	12.05
PP-CNT	117.1	1.40
PP-CNF	117.4	1.5
PP-BeLi	111.3	4.22
PP-Sorbitol	108.5	16.68

The results confirm that both CNF and CNT are the ones inducing the greatest increase in the crystallization rate of iPP. While the sorbitol based agent at this low concentration does not act as a nucleating agent, since it does not increase either T_c or the crystallization rate.

Figure 2 presents the crystal growth of the samples at 0, 5, 10, 20 and 30 minutes, from top to bottom and blank PP, Millad, LiBe, CNT and CNF from left to right, at 0.01% wt.

The picture shows how the crystal size of the sorbitol nucleating (Millad) agent remains unchanged, while lithium benzoate induces a decrease in the crystal size, showing the carbon nanoparticles the smallest crystal size.

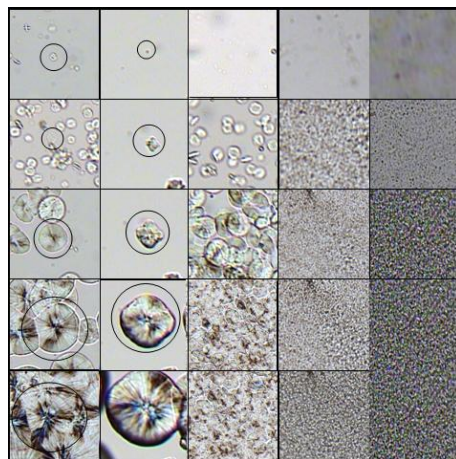


Figure 2. Crystal Tc of iPP as a function of the concentration

5. Conclusions

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

- The carbon nanofibres and carbon nanotubes were the most efficient at nucleating the polymer, being 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, as well as a reduction in the crystal size.
- Lithium benzoate shows steady and consistent good results at raising the crystallization temperature of iPP, reducing the half-life time of crystallization, increasing the nuclei density in the polymer and decreasing the crystal size, while the dimethyl-benzylidene sorbitol acts as a nucleating agent only at the highest studied concentration of 0.1% in weight.

6. References

- 1 W. J. Kissel and J.A. Meyer, Handbook of Polypropylene and Polypropylene Composites, Haruton G. Karian RheTech, Inc. p. 11.
- 2 K. Nagarajan, K. Levon, and A.S. Myerson, J. Thermal. Anal. Cal. 59 (2000) 497.
- 3 C. Marco, G. Ellis, M.A. Gomez and J.M. Arribas, J. Thermal. Anal. Cal. 68 (2002) 61.

- 4 E. P. Moore, Polypropylene Handbook, Hanser/Gardner Publications, Inc. 1996, p. 190.
- 5 Y. Feng, X. Jin and J.N. Hay, J. Applied Polymer Science 69 (1998) 2089.
- 6 J. Sandler, G. Broza, M. Nolte, K. Schulte, Y.-M Lam, and M. S. P. Shaffer, J. Macromolecular Science, Part B: Polymer Physics, B42 (2003) 479.
- 7 E. Assouline, A. Lustiger, A. H. Barber, C. A. Cooper, E. Klein, E. Wachtel, and H. D. Wagner, J. Polymer Science, Part B: Polymer Physics, 41 (2003) 520.