

EFFECT OF BOTH TALC FINENESS AND TALC LOADING ON HETEROGENEOUS NUCLEATION OF BLOCK COPOLYMER POLYPROPYLENE

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Abstract

The heterogeneous nucleation behavior of block copolymer polypropylene modified with fine talc is discussed as a function of talc fineness and loading in polymer matrix. Specifically, three talc samples having different particle size distributions were used to modify the resin. Non isothermal and isothermal nucleation were studied and mechanical performances were evaluated as well. It's been demonstrated the higher nucleation efficiency can be observed for the finer talc sample at the higher concentration evaluated in experimental work. Isothermal crystallization study showed a visible reduction of crystallization half time when talc was introduced in block copolymer polypropylene and kinetic parameters from Avrami models on isothermal tests confirmed efficiency of talc as nucleating agent. Besides process advantages in nucleating block copolymer polypropylene (in general, lower cycle time in injection molding), an evident advantage in mechanical properties was observed. The addition of talc in small amount enhanced rigidity and lowered molding shrinkage, with no significant variation in impact resistance properties. .

Introduction

Crystallization is a process in which the molten polymer is cooled below its melting temperature such that the crystalline order begins to re-establish. Crystallization occurs essentially in two stages, nucleation and crystal growth. Nucleation is a process in which the loose coiled polymer chains orient themselves into the proper conformation and align into a perfect three-dimensional pattern. The site at which the nucleation starts is called the nucleus. During crystal growth polymer chains orient to the three-dimensional pattern on the nucleus and mostly form a spherical crystal cluster which is called a spherulite.

Nucleation in polymers may be homogeneous or heterogeneous. Homogeneous nucleation occurs at high super-cooling in pure polymers. Heterogeneous nucleation occurs at relatively low super-cooling, when a foreign body is present in the melt which reduces the free energy barrier for nucleation. These foreign bodies are called nucleating agents or nucleators. A third kind of nucleation called self-nucleation also occurs in polymer crystallization which is caused due to the presence of partially melted polymer, which acts as a nucleus.

Nucleators raise the crystallization temperature. They also shorten time required for crystallization, thus reducing the cycle time in injection molding processes. Nucleators increase the number of crystallization sites in a polymer thus reducing the process time.

Talc is generally used as nucleating agent in several semi-crystalline polymers, especially in isotactic polypropylene, where it's efficiency is well known^[1]. Using talc as nucleating agent involves modification in crystallization of the resulting composite, inducing an increase of its overall mechanical properties. This modification was attributed to a preferential orientation of talc particles and PP in composite^[2,3,4]. isotactic polypropylene can crystallize in 3 polymorphic components: α , β forms and more rarely in γ .^[5] Talc induces α form in polypropylene.^[5]

The low ethylene content block copolymer polypropylene (PP) are commercially important for their high impact resistance, especially at low temperature, exhibiting a lower glass transition temperature than isotactic polypropylene. For these materials, the modification with nucleating agents is a useful method to tailor the stiffness-toughness balance and to shorten the molding cycle time. Nucleation of block copolymer polypropylene is becoming more and more important from industrial standpoint, but there is very little experimental data concerning primary nucleation of such materials. For block copolymer polypropylene, primary nucleation behavior differs from homopolymer because of the presence of non-crystallizable copolymers units that interrupts or terminate crystal growth in the molecular chain direction, resulting more difficult than in isotactic polypropylene.

The purpose of this work is to evaluate the heterogeneous nucleation that occurs in block copolymer polypropylene when fine talc is added.

Experimental

Materials

A block copolymer polypropylene (PP) resin was used for the experimental work and it was manufactured by Repsol, Spain. The melt flow rate (MFR) was 20 dg/min (230°C, 2.16 kg) and density was 0.905 g/cm³. The resin was not nucleated.

As nucleating agents, three different talc grades were used and they were manufactured by IMIFabi Spa, Italy

Talc is natural mineral and it can be identified as a hydrated magnesium sheet silicate. All samples were produced by using the same ore body (>99% white talc) and micronized into different particle size distributions (PSD). The median diameters, determined by sedimentation technique, were 2.4 μm , 1.5 μm and 0.6 μm respectively. In Figure 1 PSD data are shown, while in Table 1 some other data are highlighted.

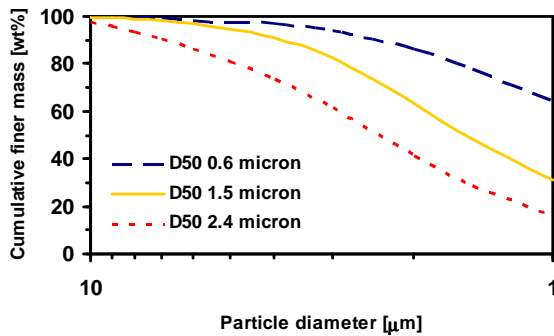


Figure 1. Particle size distribution (PSD) data of the talc samples.

	unit	D ₅₀ 2.4 μm	D ₅₀ 1.5 μm	D ₅₀ 0.6 μm
Physical properties				
Median diameter D ₅₀	μm	2,4	1,5	0,6
Specific surface B.E.T.	m^2/g	8,2	10,1	13,9
Chemical composition				
SiO ₂	wt%		61,0	
MgO	wt%		32,0	
CaO	wt%		0,2	
Fe ₂ O ₃	wt%		0,4	
Al ₂ O ₃	wt%		0,4	
LoI @ 1050°C ^(*)	wt%		6,0	

^(*)LoI = loss on Ignition

Table 1. Physical and chemical properties of talc samples used for block copolymer polypropylene nucleation. Chemical composition has been determined via atomic absorption technique.

Sample preparation

All examined samples were processed under the same identical conditions. PP resin was extruded into a 25mm co-rotating twin screw extruder, adding different percent weight of each talc sample (0.25, 0.5 and 1) and 0.1% of glycerol monostearate (GMS) as wetting agent, used to prevent talc segregation in dry-blend. Neat resin was extruded and modified with GMS too. Main process conditions were: screws speed 200rpm, barrel temperature 150–210°C, throughput 6kg/h. Extruded materials were molded into ISO specimens by using temperature profile

of 190–210°C and by holding mold temperature at 50°C. Total cycle time was 48 seconds and injection speed was set at minimum over 17 seconds.

Analysis

Differential scanning calorimetry (DSC, TA instruments Q200) was used to study crystallization during continuous cooling and under isothermal conditions. Heating and cooling cycles were performed at 10°C/min under nitrogen purge. 10 mg samples were used. Isothermal crystallizations were measured after holding samples at 200°C per 3 min and cooling at 10°C/min down to 135°C. Half times for crystallization were calculated. The temperature of 135°C was determined after a preliminary evaluation on part of examined samples. All analyzed samples were sourced from molded specimens.

Mechanical testing

ISO specimens were tested after 72 hours from molding. Samples were aged at constant temperature or 23°C and tested at such temperature if not diversely indicated

Tensile properties were measured according to ISO 527 by using a crosshead speed of 1 mm/min. Impact strength was measured using an Izod instrument on standard notched specimens (according to ISO 180/A) at -20°C. Vicat temperatures were determined according to ISO 306 A/50. Molding shrinkage data was determined evaluating final longitudinal dimension of tensile specimen in relation with mold cavity dimension.

Results and discussion

Crystallization

The presence of talc as heterogeneous nucleators in block copolymer polypropylene enhances crystallization temperature of not modified resin. In Figure 2, crystallization temperatures (T_c) versus talc loading are shown. Each line represents a different talc PSD.

T_c varies with both talc loading and talc fineness. A finer talc is identified by a smaller median diameter (D_{50}) and, by examining data listed in Figure 2, it is possible to highlight an increment of T_c with talc content as well as with smaller D_{50} . Trend is not linear and it leads to a plateau-like behavior: with higher loading than 1%, increment of T_c becomes very small.

Crystallization under isothermal conditions provides different information about polymer cooling behavior. Crystallization half time gives an idea about the fastness of the crystallization process at a certain given temperature. In Table 2, The crystallization half time

values (after subtraction of the induction time) are highlighted.

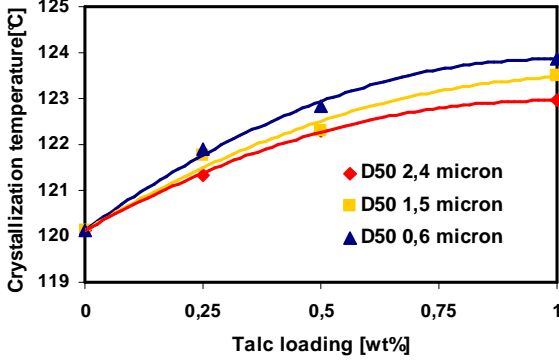


Figure 2. Crystallization temperatures of different talc samples versus loading in block copolymer polypropylene

$t_{1/2}$ [min] @ 135°C			
talc loading	median diameter, D_{50} [μm]		
	2.4	1.5	0.6
	$t_{1/2}$ [min]	$t_{1/2}$ [min]	$t_{1/2}$ [min]
none (neat PP)	12.1	12.1	12.1
0,25%	6.1	5.9	5.7
0,50%	4.8	4.7	4.4
1,00%	4.0	3.7	3.3

Table 2. Crystallization half time ($t_{1/2}$) under isothermal conditions at 135°C. Induction time has been subtracted before calculating $t_{1/2}$.

In Figure 3, the crystallization fraction (X_t) of PP modified with talc having median diameter equal to 1.5 μm at 135°C is shown, which obtained from the thermal analysis results of the DSC. The crystallization fraction was determined as follows:

$$X_t = \frac{\int_0^t (dH / dt) dt}{\int_0^\infty (dH / dt) dt} \quad (1)$$

where X_t is the crystallization fraction after time t . A numerator is the heat generated after time t and a denominator is the heat generated after time goes infinite. From Figure 3, it is observed that crystallization fraction shifts to shorter crystallization time with the increase of talc loading, indicating that talc modified PP samples crystallize faster than neat PP and that talc loading affects crystallization speed.

The crystallization kinetics of the analyzed samples under isothermal conditions were determined by the following Avrami equation ^[6,7]:

$$\theta = \exp(-kt^n) \quad (2)$$

where t is the fraction of the crystallizable polymer not yet crystallized at time t , k is the crystallization rate constant and n is a parameter varying with the type of nucleation and growth processes. Being

$$\theta = 1 - X_t \quad (3)$$

the double-logarithm form becomes:

$$\log(-\ln(1 - X_t)) = \log k + n \log t \quad (4)$$

A plot of the $\log(-\ln(1 - X_t))$ versus $\log t$ is linear and it yields the Avrami parameters k (antilog of intercept) and n (slope). Graphical data for talc with D_{50} equal to 1.5 μm are plotted in Figure 4, while Avrami parameters for all examined samples are summarized in Table 3.

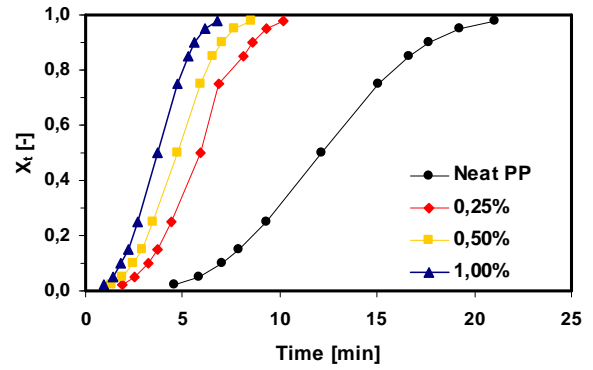


Figure 3. Crystallization fraction (X_t) of the D_{50} 1.5 μm talc nucleated block copolymer polypropylene at 135°C.

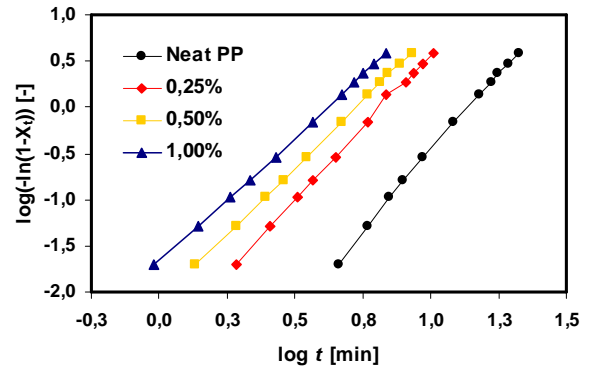


Figure 4. Avrami plots of the D_{50} 1.5 μm talc nucleated block copolymer polypropylene at 135°C.

The increment of talc loading led to a general reduction of constant n and to an increment of crystallization rate constant k . Similar behavior can be

observed, at same loading, when talc fineness is incremented (smaller median diameter). The latter has a weaker effect than talc loading effect. In Figure 9 and Figure 10, isothermal crystallization curves for three different talc D_{50} 1.5 μm loadings and isothermal crystallization curves for same loading (0.5%) of three different talc samples are shown. It appears evident the stronger effect in crystallization behavior achievable with higher talc loading rather than by using a finer talc.

Physical properties

Results of mechanical characterization are collected in Table 4, Table 5 and Table 6.

In general, an increment of properties with both talc loading and talc fineness was observed. With reference to tensile modulus, in Figure 5, rigidity values versus talc loading are plotted for the three different talc samples, used as nucleators. Stiffness trend is linear with both talc loading and talc fineness: finer talc, with smaller median diameter, provides higher rigidity. Stiffness enhancement effect of talc having D_{50} 0.6 μm is evident: 0.5% of such talc provided higher stiffness of 1% of coarser talc (D_{50} 2.4 μm).

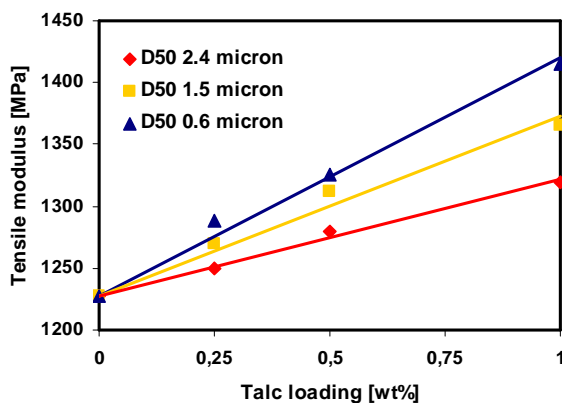


Figure 5. Crystallization fraction (X_t) of the D_{50} 1.5 μm talc nucleated block copolymer polypropylene at 135°C.

In general, a raise in stiffness is associated with a reduction in impact resistance. For talc nucleated block copolymer polypropylene, such statement is not true. For most of examined samples, IZOD impact resistance exhibited similar values as per not modified PP. Specifically, the higher loading of finer talc (D_{50} 0.6 μm) recorded an increment in impact resistance at room temperature versus neat PP. The presence of talc increased the crystallization temperature of composite and decreased the average spherulite size. The decreased crystal size is preferred for toughness, though the talc tends to drive properties in opposite directions^[8]. In Table 5, IZOD impact data are shown. In Figure 6, an example of quenched neat PP and nucleated PP is highlighted: it is

possible to detect a lower number of spherulites than in the talc nucleated sample. It is also evident a higher disorder in spherulite organization on neat PP.

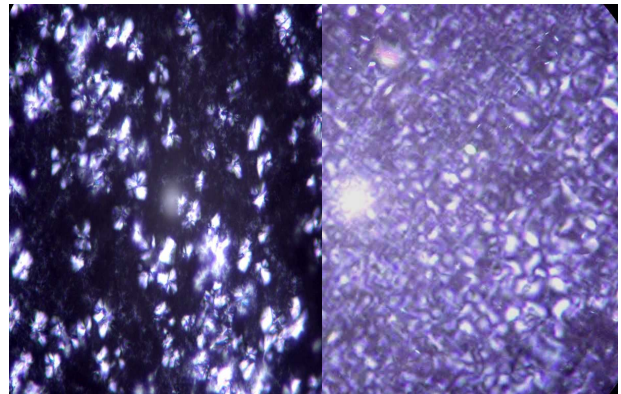


Figure 6. Spherulites on quenched samples of neat block copolymer PP (left) and PP modified with 1% of talc D_{50} 1.5 μm (right). Samples have been heated at 230°C and quenched in cold water. Images have been obtained in cross polarized light.

As further indication of improved spherulite organization with nucleation, molding shrinkage data can be used. A general reduction in shrinkage was observed for increasing talc loading and for decreasing talc PSD. For semi-crystalline polymers, as block copolymer polypropylene, molding shrinkage is rather high and the presence of a nucleator can significantly lower such value. The presence of talc as nucleator allows to enhance overall molding shrinkage in molded item (in both longitudinal and transversal directions) minimizing warpage phenomenon^[9]. In this work, only longitudinal shrinkage was measured. In Figure 7, experimental data are plotted.

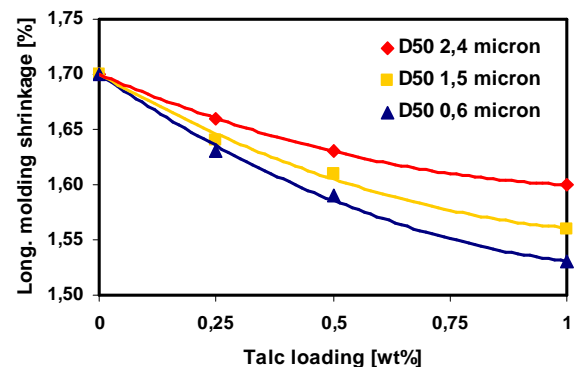


Figure 7. Crystallization fraction (X_t) of the D_{50} 1.5 μm talc nucleated block copolymer polypropylene at 135°C.

Concerning Vicat temperature, a certain increment was recorded, with a similar behavior recorded for stiffness. In figure 8, Vicat temperatures data are shown.

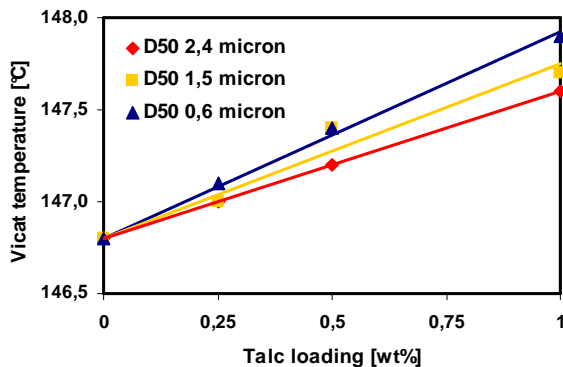


Figure 8. Crystallization fraction (X_t) of the D_{50} 1,5 μ m talc nucleated block copolymer polypropylene at 135°C.

Conclusions

Both crystallization properties and mechanical properties were analyzed in this work. A general increment in crystallization kinetics was observed modifying block copolymer polypropylene with talc. It was observed a stronger effect of talc loading rather than talc fineness. In terms of mechanical properties, the overall behavior is different: 0,5% loading of finer talc equalized 1% amount of coarser nucleator. A significant increment in stiffness with minor or no variation in impact resistance was recorded.

The usage of fine talc as nucleator in block copolymer polypropylene provides is efficient and efficacious:

crystallization properties are enhanced and stiffness to toughness balance is optimized. In general a higher talc loading, such as 1%, is preferred for PP nucleation not only because of the overall properties, but also because of the better possibility of dispersion into the PP matrix.

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Key Words: Block copolymer polypropylene, heterogeneous nucleation, talc, DSC, Avrami

talc loading	Talc D ₅₀ =2.4µm			Talc D ₅₀ =1.5µm			Talc D ₅₀ =0.6µm		
	n [-]	K [min ⁻¹]	t _{1/2} [min]	n [-]	K [min ⁻¹]	t _{1/2} [min]	n [-]	K [min ⁻¹]	t _{1/2} [min]
none (neat PP)	3.4	1.3·10 ⁻⁴	12.1	3.4	1.3·10 ⁻⁴	12.1	3.4	1.3·10 ⁻⁴	12.1
0,25%	3.1	2.4·10 ⁻³	6.1	3.2	2.6·10 ⁻³	5.9	3.2	2.8·10 ⁻³	5.7
0,50%	3.0	7.1·10 ⁻³	4.8	2.9	7.9·10 ⁻³	4.7	2.9	8.9·10 ⁻³	4.4
1,00%	2.7	1.7·10 ⁻²	4.0	2.7	2.1·10 ⁻²	3.7	2.6	3.3·10 ⁻²	3.3

Table 3. Isothermal (135°C) crystallization kinetics for block copolymer polypropylene nucleated with different talc samples on Avrami analysis.

talc loading	Talc D ₅₀ =2.4µm			Talc D ₅₀ =1.5µm			Talc D ₅₀ =0.6µm		
	Tensile modulus [MPa]	Yield strength [MPa]	Elong. at Yield [%]	Tensile modulus [MPa]	Yield strength [MPa]	Elong. at Yield [%]	Tensile modulus [MPa]	Yield strength [MPa]	Elong. at Yield [%]
none (neat PP)	1227	24.3	7.1	1227	24.3	7.1	1227	24.3	7.1
0,25%	1250	24.4	7.0	1270	24.7	6.9	1288	24.8	6.8
0,50%	1280	24.9	6.7	1312	24.7	6.7	1326	25.3	6.6
1,00%	1320	25.2	6.4	1366	24.8	6.4	1415	25.4	6.3

Table 4. Tensile properties of block copolymer polypropylene nucleated with different talc samples, according to ISO 527 at 23°C, crosshead 1 mm/min. Specimens were tested after 72h from injection molding.

talc loading	Talc D ₅₀ =2.4µm		Talc D ₅₀ =1.5µm		Talc D ₅₀ =0.6µm	
	@ 23°C [kJ/m ²]	@ -20°C [kJ/m ²]	@ 23°C [kJ/m ²]	@ -20°C [kJ/m ²]	@ 23°C [kJ/m ²]	@ -20°C [kJ/m ²]
none (neat PP)	8.2	4.9	8.1	4.9	8.2	4.9
0,25%	8.2	4.9	7.9	4.9	8.2	4.9
0,50%	7.9	4.9	8.1	4.9	8.1	4.9
1,00%	8.0	4.9	8.0	4.9	8.5	4.9

Table 5. IZOD notched impact properties of block copolymer polypropylene nucleated with different talc samples, according to ISO 180/A. Tests were performed at two different temperatures: 23°C and -20°C. Specimens were tested after 72h from injection molding.

talc loading	Talc D ₅₀ =2.4µm		Talc D ₅₀ =1.5µm		Talc D ₅₀ =0.6µm	
	Shrinkage [%]	Vicat 50/A [°C]	Shrinkage [%]	Vicat 50/A [°C]	Shrinkage [%]	Vicat 50/A [°C]
none (neat PP)	1.70	146.8	1.70	146.8	1.70	146.8
0,25%	1.66	147.0	1.64	147.0	1.63	147.1
0,50%	1.63	147.2	1.61	147.4	1.59	147.4
1,00%	1.60	147.6	1.56	147.7	1.53	147.9

Table 6. Longitudinal molding shrinkage and Vicat temperature of block copolymer polypropylene nucleated with different talc samples. Molding shrinkage was calculated as ration between the dimensional difference from mould to tensile specimen and mold cavity. Vicat temperature was tested according to ISO 306 A/50. Specimens were tested after 72h from injection molding.

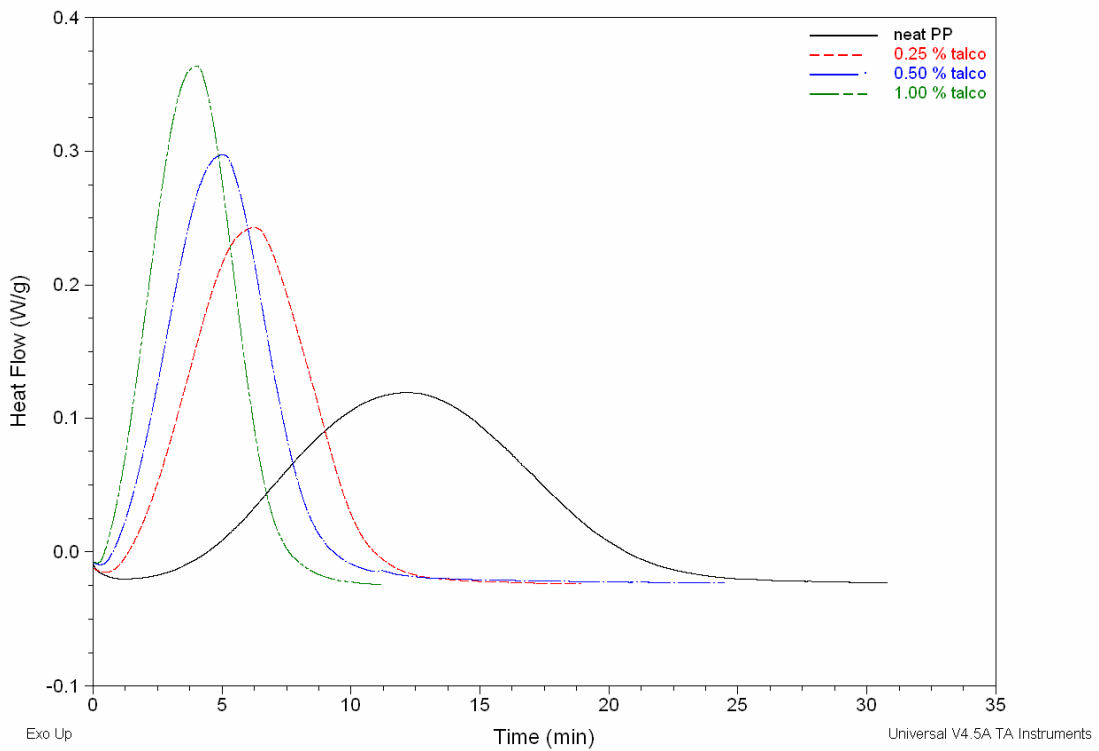


Figure 9. Isothermal crystallization, performed at 135°C, of block copolymer polypropylene modified with different loadings of talc having median diameter (D_{50}) of 1.5 μm .

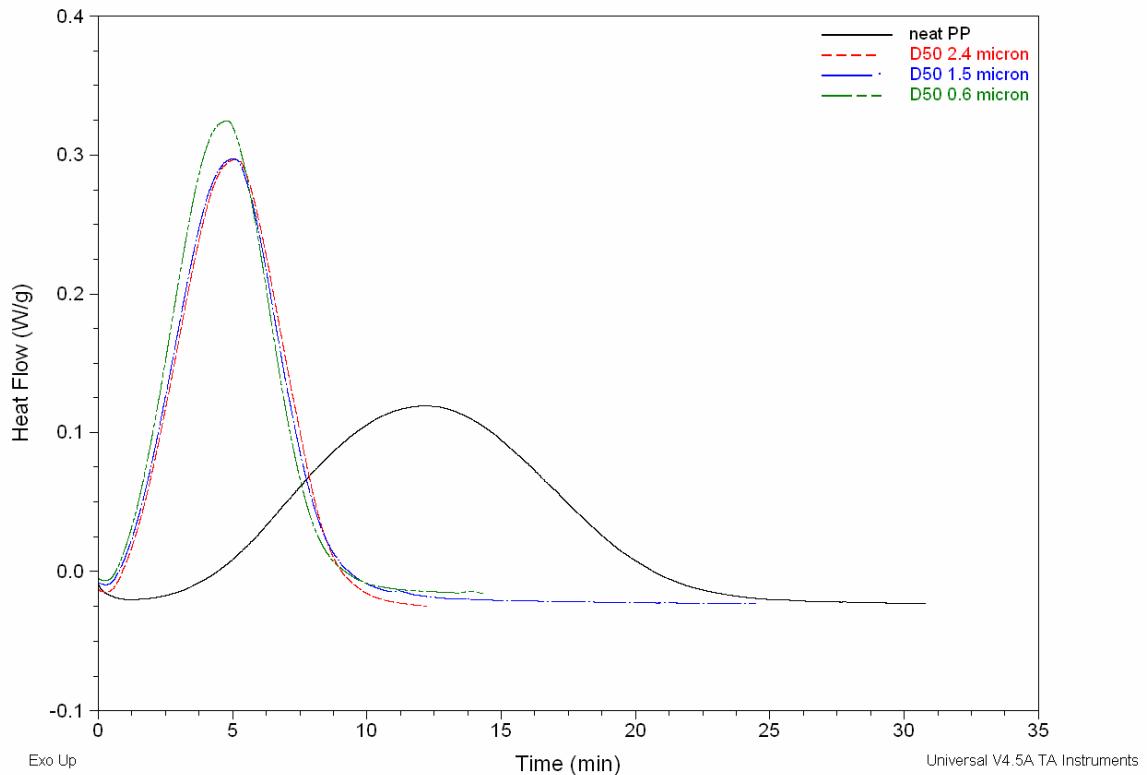


Figure 10. Isothermal crystallization, performed at 135°C, on block copolymer polypropylene modified with 0.5% of talc samples having different particle size distributions.