Optimization of the crystallinity of polypropylene/submicronic-talc composites: The role of filler ratio and cooling rate

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Received 31 July 2015; accepted in revised form 12 October 2015

Abstract. Micronic and submicronic mineral fillers recently appeared as efficient reinforcing agents for polyolefins in addition to the benefit of bypassing the exfoliation/dispersion problem encountered in the case of incorporation of nanoscopic fillers such as clay. Submicronic-talc, designated as μ -talc, belongs to this kind of new fillers. This work was aimed at searching to optimize the crystallinity ratio of isotactic polypropylene in the presence of μ -talc in relation to the filler ratio of the composites and the cooling rate from the melt. In order to highlight the efficiency of the μ -talc on the crystallization of polypropylene comparison has been made with PP composites containing conventional talc particles. The study has been carried out on samples having μ -talc weight fractions covering the range 3–30%. In the context of optimizing the crystallinity ratio of the polypropylene matrix in the composites, calorimetric experiments have been planned using a full factorial design. The results were statistically processed by analysis of the variance via mathematical models for predicting the crystallinity ratio in relation to the cooling rate and the filler ratio. Contour graphs have been plotted to determine the effect of each parameter on crystallinity. The cooling rate proved to have a significantly stronger influence on crystallinity than the type and content of filler.

Keywords: polymer composites, polypropylene composite, micro-talc, crystallinity, ANOVA method

1. Introduction

Isotactic polypropylene (iPP) filled with mineral particles such as calcium carbonate (CaCO_3) or with short glass fibers has been the subject of a lot of research [1–8]. The role of fillers in polymer based composites is multiple: it helps reducing the composite cost as it is generally less expensive than the polymer, but it also contributes to improving the mechanical performances and the physical properties if properly dispersed in the polymer matrix.

Isotactic polypropylene (iPP) is one of the most widely used semi-crystalline polymer for structural applications in the automotive industry, household appliances, construction, packaging, ropes, etc.

Mineral fillers proved to provide a toughening effect on iPP bulk pieces due to the ability to initiate elementary plasticity processes at the particle-matrix interface [3–8].

Since the early 80's, profuse studies have been devoted to the mechanical reinforcement of iPP by nanofillers such as clay [9–11]. Such kinds of nanofillers were shown to noticeably improve the fire-resistance of thermoplastic polymers [12] in addition to the mechanical performances. In the case of polymer matrices such as iPP having poor if any interaction with the nanofillers, surface treatment techniques of the nanoparticles were required as well as

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specific preparation methods involving the use of compatibilizing agents.

Among mineral fillers, talc proved to have a good potential of development for iPP-based composites, noticeably in the automotive industry [13–17]. It appeared very soon that talc displayed a strong nucleating effect for iPP [14, 19–23] due to specific physico-chemical interactions between the filler and the polymer matrix that promote epitaxial crystallization [14, 24–27]. This effect was significantly more pronounced than for other common fillers such as CaCO_3 or kaolin and therefore give rise to better improvement of mechanical properties [14, 18]. This property makes talc able to be easily incorporated in iPP matrix without the use of a chemical surface treatment [14, 17, 22], though the use of such treatment was reported to be efficient for dispersion of very fine particles at high loading [28–34].

It is worth noticing that talc reduces the efficiency of heat-stabilizing agents in iPP-based composites and by the way the fire-resistance of these composites [35, 36]. However, a significant advantage of talc compared to CaCO_3 or kaolin from a practical viewpoint is that it is much less abrasive for the extruder during the compounding and injection-molding stages.

Works regarding the mechanical reinforcement of iPP with talc have been orientated towards sub-micronic powders, i.e. intermediate size between conventional and nanometric fillers [15–17]. Using such filler particles with sub-micronic size enables to increase the specific area of the filler with respect to the former kind of fillers and to overcome the quite common problem of exfoliation and dispersion of the second kind of fillers. Besides, unlike CaCO_3 and kaolin, μ -talc has been developed as a lamellar-like filler thanks to a specific delamination technique from the producer that provides better reinforcing capacities at equivalent volume fraction [17, 37], owing to a very good dispersion that prevents the detrimental formation of aggregates [38]. It was shown in a previous study that the combination of the nucleating effect and the lamellar-like shape of μ -talc particles generates a rigid percolating network of polymer crystallites and filler particles that contributes to the enhancement of the composite stiffness [36]. However, a possible drawback of the nucleation ability of talc on iPP is a reduced toughness due to the increase of crystallinity [39].

Therefore, it appears that the structure-property relationships of μ -talc-reinforced iPP deserved further studies. The aim the present work was to investigate the effect of incorporation of μ -talc on the crystallization potential of an iPP matrix in comparison with conventional PP composites with standard talc particles having a 3-times lower specific surface area. The cooling rate from the melt is also under concern in this study since it is well known to significantly influence the crystallization capabilities of semi-crystalline polymers, especially polypropylene [40–42]. A numerical analysis of the data has been used to optimize the composite crystallinity in relation to the filler ratio and the cooling rate.

2. Experimental

2.1. Materials

The polymer under investigation in this work is an isotactic polypropylene (iPP) from Solvay (Brussels, Belgium) with an isotacticity index of 96% according to the manufacturer. The weight-average molar mass was $M_w = 380\,000$ g/mol and the polydispersity index $IP = 12$, as determined by size exclusion chromatography. The sub-micronic size talc (μ -talc) without any surface treatment was supplied by Imerys Talc (Luzenac, France) under trade name HAR[®]Talc (High Aspect Ratio Talc). This new kind of filler was produced by delamination milling instead of grinding or micronizing. Standard talc (S-talc) was also used for the sake of comparison. The specific area of the present μ -talc is $17\text{ m}^2/\text{g}$ as compared to $6\text{ m}^2/\text{g}$ for S-talc, using the Brunauer-Emmett-Teller method, according to the manufacturer. The average aspect ratio of the platelets, 5.5 and 1.3 for μ -talc and S-talc respectively, was determined by scanning electron microscopy. All the composites were compounded by Multibase/Dow Corning (Saint Laurent du Pont, France) without compatibilizing agent using a Clextral BC21 twin screw extruder (Firminy, France) of length 1200 mm and diameter 25 mm, the temperature being 180–210 °C between feeder and die. The composites were finally injection-molded into 2 mm thick sheets.

The actual filler ratio of the various composites was precisely determined after compounding by means of thermogravimetry [37]. The actual ratio was very close to the nominal value adjusted at the stage of compounding, the standard deviation not exceeding 1%, so that the nominal values were taken into account in this study.

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG60 apparatus (Kyoto, Japan) under nitrogen gas flow. The heating rate was 10 °C/min over the temperature range 25–650 °C. The sample weight was about 10 mg.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out on a SETARAM apparatus (Lyon, France), model LABSYS evo. The temperature and heat flow scales were calibrated using high purity indium at a heat rate of 10 °C/min. The samples of about 10 mg were heated up from 25 to 210 °C and held at 210 °C for 5 min in order to erase surviving iPP nuclei and thermal history due to processing. This methodology enabled determining the actual nucleating effect of μ -talc. The samples were then cooled down to 25 °C at various cooling rates in the range 2–40 °C/min. Subsequent heating was performed at 10 °C/min in order to record the melting endotherm and determine the melting enthalpy. The crystal weight fraction was then computed from Equation (1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \quad (1)$$

where ΔH_f is the melting enthalpy of the polymer and $\Delta H_f^0 = 207 \text{ J/g}$ is the melting enthalpy of perfectly crystalline PP in the α -crystal form [43]. In the case of composites, the actual weight fraction of the matrix polymer was taken into account.

2.4. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) experiments were carried out at room temperature in transmission mode on a laboratory bench equipped with a Rigaku rotating Cu-anode (Tokyo, Japan) operated at 100 kV and 40 mA. The X-ray beam was collimated with Göbel mirrors from Xenocs (Grenoble, France) that provided a monochromatic Cu-K α radiation (wavelength = 0.154 nm) and parallel point focusing thanks to two pairs of anti-scattering slits. The 2D-WAXS patterns were recorded on a SCX2D-CCD camera from Princeton Instruments (Trenton NJ, USA). Data corrections were performed for transmission coefficient and background scattering. Azimuthal integration of the 2D patterns was performed using FitD2 software in order to get intensity profiles as a function of the scattering angle. This enabled to characterize the crystalline texturing of the samples

Figure 1. Schematic of the injection-moulded sheet and characteristic directions

induced by the injection-molding process in addition to the identification of their crystalline form. The samples were punched out from the sheets as shown in Figure 1. All samples were analyzed with the X-ray beam parallel to each of the 3 main directions, i.e. injection, transverse and thickness directions.

2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) experiments were performed on a JOEL JSM 840A apparatus (Tokyo, Japan) in topographic mode at an acceleration voltage of 20 kV. Observations were made from the metal-coated surface of samples broken in liquid nitrogen. The microscope was equipped with an energy-dispersive X-ray (EDX) device that enabled identifying the elements from the talc platelets.

2.6. Design and planning of experiments

A design of experiments (DOE) approach was adopted for optimizing the crystallinity ratio, the two variables being the filler ratio and the cooling rate. The aim of this analysis was to identify the statistical relevance of the factors under investigation and their interactions and consequences on the response [44–47]. The ANOVA variance analysis was used to determine the mathematical law. The 3D response surfaces (RS) were constructed by using the Design-Expert-8 statistics software.

Using the RS method enables 1) to model the response Y under consideration as a function of the independent variables $X_1, X_2, \dots, X_i, \dots$ and 2) to determine the interaction of these variables and their respective influence on the response Y . The second order regression used for the modelling is given by Equation (2):

$$Y = a_0 + \sum_{i=1}^k a_i X_i + \sum_{i=1}^k a_{ii} X_i^2 + \sum_{i < j}^k a_{ij} X_i X_j \quad (2)$$

where k is the number of independent variable parameters. In the present study, the response Y is featuring the crystallinity ratio while the independent variables X_1 and X_2 hold for the cooling rate, C_R , and the filler ratio, F_R .

The strategy of planning of the experiments aims at carrying out the experiments in an optimal way for the modelling. The number of trials, N , is related to the number of variables, k , and the level of variation of these variables, q , via Equation (3):

$$N = q^k \quad (3)$$

In the present study, $k = 2$ and $q = 7$ according to Table 1 data, so that $N = 49$. The variable values for the trials are listed in Table 1.

Table 1. Data of the planning of experiments

Level	C_R [°C/min]	F_R [%]
1	2	0
2	5	3
3	10	5
4	15	7
5	20	10
6	30	20
7	40	30

3. Experimental results

In the previous study it was clearly shown that iPP/ μ -talc composites exhibit significantly enhanced mechanical properties as compared to iPP/S-talc composites, at equivalent filler loading [36]. Only the thermal and structural behavior of the iPP/ μ -talc composites will be addressed here, in comparison with the iPP/S-talc relatives.

3.1. Thermogravimetric analysis

Figure 2 shows the loss of mass plotted versus temperature. The residual mass of the samples after heating beyond 550 °C is very close to that expected from the weight fraction of filler introduced at the processing stage, for all composites. Another observation from Figure 2 is that the curves gradually shift to higher temperature with increasing talc content indicating an improved resistance to thermal decomposition. Moreover, the shift of the curves for the μ -talc composites is more notable than those for the industrial talc composites at the same filler loading. This

Figure 2. Weight loss of the iPP/ μ -talc composites as a function of temperature

emphasizes the benefiting effect of μ -talc compared to conventional talc from the viewpoint of fire-resistance owing to its higher specific surface area that enhances the intumescence activity [26].

3.2. Structural characterization

Figure 3 reports the DSC cooling traces of iPP and iPP/ μ -talc composites containing 10 and 30% of μ -talc. The gradual shift to higher temperature of the crystallization exotherm with increasing μ -talc content clearly reveals the nucleating effect of the talc particles that promotes an early initial crystallization of the PP matrix. Regarding the peak of the exotherm that is more relevant to the global crystallization rate including nucleation and growth, the very slight difference between the 10 and 30% μ -talc composites (Figure 3) suggests that a hindrance to the global crystallization occurs at high μ -talc loading. Such a phenomenon has been reported to occur in nanocom-

Figure 3. DSC crystallization curves of pure iPP and the composites iPP/10% μ -talc and iPP/30% μ -talc upon cooling at 10 °C/min from 210 °C

posites as well as conventional composites based on various semi-crystalline polymer matrices [48–54]. The current explanation is that at high loads the filler particles generate a physical barrier to the crystal lamella growth and thus limit the crystallization efficiency. This point will be further discussed regarding the effect of μ -talc content on the crystallinity ratio.

The nucleating effect of μ -talc is compared in Figure 4 to that of S-talc through the DSC cooling traces of the composites for the same filler loading value $F_R = 20\%$ and same cooling rate $C_R = 10^\circ\text{C}/\text{min}$. The shift to high temperature of the crystallization exotherm is slightly greater for μ -talc, indicating better nucleating effect of the latter one due to its 3-fold higher specific surface area compared to S-talc.

The WAXS intensity profiles along 3 directions of the parallelepipedic samples of iPP and the iPP/7% μ -talc composite are reported in Figures 5 and 6. Only the main reflections of the monoclinic α -form of iPP are observed for both the pure sample and the composite. This is consistent with previous reports that talc is an α -nucleating agent for iPP [19–27]. The 3 intensity profiles of the pure iPP display a great similarity relevant of a structural isotropy (Figure 5). In contrast the strongly different profiles along for the iPP matrix in the iPP/7% μ -talc composite are indicative of a strong crystalline texturing due to both the injection-molding and nucleating effect (Figure 6). Particularly, the very weak intensity of the (040) reflection of iPP in the WAXS profile through the thickness is a clear indication that the iPP chains are lying in the sample plane [23–27]. Moreover, the total absence of the

Figure 4. DSC crystallization curves of pure iPP and the composites iPP/20% μ -talc and iPP/20% S-talc upon cooling at $10^\circ\text{C}/\text{min}$ from 210°C

Figure 5. WAXS intensity profiles of pure iPP (injection-molding)

(002) reflection of talc on the WAXS profile through the sample thickness (Figure 6) reveals that the talc platelets are also lying within the sample plane. Indeed, the (002) planes characteristic of the silicate sheets of talc stand along the larger dimensions of the talc platelets. The combination of this crystallographic characteristic of the talc platelets and their nucleating effect results in an orientation of the iPP crystals nearly normal to the talc platelets [23–27]. This concomitance of orientation of the chains and the talc platelets is a common feature of injection-molded composites reinforced with filler of high aspect ratio which tend to align along the flow direction [27, 33, 55–57]. In the case of composites with lamellar fillers, this phenomenon is enhanced by the so-called shear-amplification effect [58].

The shear-induced nucleation can compete with filler-induced nucleation [59] and may even prevail on it [33]. In the present study, the thermal treatment

Figure 6. WAXS intensity profiles of the iPP/7% μ -talc composite (injection-molding)

of the samples at $T = 210^\circ\text{C}$ for 5 min prior to the DSC crystallization experiments was carried out in order to erase any shear-induced chain orientation due to processing. Therefore, the sensitivity of the crystallization kinetics of the iPP/ μ -talc composites to the filler content can be assigned to the μ -talc surface nucleation due to favorable surface free energy [26]. Scanning electron microscopy was also used for further structural characterization of the composites. Figure 7 shows a SEM image from the fracture surface

Figure 7. SEM image (a) from the center of a cross-section of an injection-molded iPP/30% μ -talc and corresponding EDX images of the Si (b) and Mg (c) atomic distributions in the talc platelets

of an iPP/30% μ -talc composite. The talc platelets appear to be fairly well dispersed and aligned along the injection direction. Better identification of the talc platelets and confirmation of both their dispersion and orientation is provided by the corresponding EDX images showing the distributions of the Si and Mg elements from talc.

3.3. Crystallinity versus talc loading and cooling rate

Crystallinity has been determined for the 49 samples of the series, i.e. pure iPP together with 6 composites of different μ -talc loadings crystallized at 7 different cooling rates. All the X_C data are reported in Table 2. An examination of these data reveals that X_C decreases with increasing C_R for a given F_R . Less time is afforded to the iPP matrix for crystallizing in its optimal temperature range ($110 < T_c^{\max} < 130^\circ\text{C}$, see Figure 3) when C_R is high. Conversely, X_C increases with F_R at a given C_R since higher F_R provides more particle surface for iPP nucleation. However, it can be seen in Table 2 that the X_C evolution is different if considering the sensitivity to C_R of the various materials. At low cooling rate, i.e. $C_R = 2^\circ\text{C}/\text{min}$, the rather high X_C data increase quickly in a first step with increasing F_R then tend to level off for $F_R > 7\%$. In contrast, at high C_R , i.e. $C_R = 40^\circ\text{C}/\text{min}$, the significantly lower X_C values display a roughly linear increase with F_R without leveling off. As proposed in the previous subsection, and borrowing from several reports regarding polymer-clay nanocomposites, this finding may be attributed to a physical barrier effect or steric hindrance of the μ -talc platelets to the growth of iPP crystal lamellae at high F_R and low C_R when crystallinity is high. The barrier effect of the μ -talc platelets would be less effective at high C_R due to less steric hindrance to the crystal growth when crystallinity is low.

For the sake of comparison, crystallinity data for S-talc composites are reported in Table 2 as a function of C_R , for two F_R values 3 and 20%. Though differences are not dramatic between the two kinds of composites, the X_C data are systematically higher for the μ -talc composites, irrespective of C_R and F_R , which confirms the better nucleating effect of μ -talc due to higher specific area.

3.4. Statistical analysis and modeling

The statistical analysis of the response to any kind of experiment is a useful tool for probing the incidence

of the various experimental or entry parameters on the response. A numerical relation can be established between the response and the entry parameters [16, 43–45]. The numerical values of the response can be

Table 2. Crystallinity data from experimental plan (μ and S superscripts hold for μ -talc and S-talc composites)

Run	C_R [°C/min]	F_R [%]	X_C^μ [%]	X_C^S [%]
1	2	0	53.8	–
2	2	3	54.3	54.0
3	2	5	55.0	–
4	2	7	59.2	–
5	2	10	59.6	–
6	2	20	61.2	58.2
7	2	30	62.2	–
8	5	0	51.4	–
9	5	3	53.7	52.7
10	5	5	54.2	–
11	5	7	56.7	–
12	5	10	59.4	–
13	5	20	61.0	(58.5)
14	5	30	61.9	–
15	10	0	49.2	–
16	10	3	51.5	50.5
17	10	5	53.2	–
18	10	7	53.4	–
19	10	10	53.5	–
20	10	20	54.9	53.5
21	10	30	58.8	–
22	15	0	44.5	–
23	15	3	47.4	46.1
24	15	5	49.8	–
25	15	7	50.2	–
26	15	10	53.0	–
27	15	20	53.5	52.8
28	15	30	57.2	–
29	20	0	43.9	–
30	20	3	44.0	43.6
31	20	5	45.1	–
32	20	7	46.9	–
33	20	10	48.4	–
34	20	20	52.2	48.2
35	20	30	55.9	–
36	30	0	35.2	–
37	30	3	37.3	36.4
38	30	5	38.5	–
39	30	7	42.4	–
40	30	10	42.6	–
41	30	20	43.9	42.1
42	30	30	48.8	–
43	40	0	34.5	–
44	40	3	36.6	35.7
45	40	5	37.0	–
46	40	7	37.6	–
47	40	10	37.9	–
48	40	20	39.3	37.8
49	40	30	43.4	–

then compared to the experimental data. The Design Expert 8 software was used in this study in combination with the ANOVA variance analysis.

The numerical expression for the crystallinity as a function of the experimental parameters derived from Equation (2) is given by Equation (4):

$$X_C = + 53.77850 - 0.42080 \cdot C_R + 1.02231 \cdot F_R + 3.89570 \cdot 10^{-3} \cdot C_R \cdot F_R - 0.015739 \cdot C_R^2 - 0.047613 \cdot F_R^2 - 3.31598 \cdot 10^{-4} \cdot C_R^2 \cdot F_R + 3.35287 \cdot 10^{-4} \cdot C_R \cdot F_R^2 + 3.52478 \cdot 10^{-4} \cdot C_R^3 + 7.63055 \cdot 10^{-4} \cdot F_R^3 \quad (4)$$

with a regression coefficient $R^2 = 98.5$.

The residuals reported in Figure 8 for the 49 experiments or runs do not exceed 2.5% of the X_C value and are randomly distributed about the X_C value of every run. Moreover, Figure 9 shows that the residues fairly obey a normal law distribution.

On Figure 10 is shown the 2D mapping of the predicted crystallinity as a function of C_R and F_R together with the experimental data. The blue to red color range accounts for the full crystallinity range of the present study $34.5\% < X_C < 62.2\%$. The iso-color domains stand for the C_R/F_R coupling that results in iso-crystallinity.

Figure 11 is a 3D diagram of X_C versus C_R and F_R . This figure shows that, in the experimentally accessible ranges of C_R and F_R , X_C is much more sensitive to C_R than to F_R . Indeed, in the high X_C domain, the red zone extends more along the F_R range than along the C_R range. Similarly, in the low X_C domain,

Figure 8. Residuals for the crystallinity ratio from the statistical analysis (same Run N° as in Table 2; symbol color holds for the crystallinity ratio)

Figure 9. Residual distribution of the crystallinity ratio (same color scale as in Figure 8)

Figure 10. 2D mapping of the predicted crystallinity ratio versus C_R and F_R (the full lines stand for iso-crystallinity curves; symbols hold for experimental data)

the blue zone extends more along the F_R range than along the C_R range.

Figure 11 also reveals that at high talc loading, i.e. $F_R \geq 20\%$, X_C tends to saturate at its maximum value for $C_R \leq 5^\circ\text{C/min}$ as judged from the nearly zero slope of the predicted X_C variation versus F_R . Therefore, one cannot expect $X_C > 62.2\%$ even with μ -talc loadings $F_R \gg 30\%$. Similarly, the very low slope of the predicted X_C variation with C_R at low C_R values suggests that one may hardly expect $X_C > 62.2\%$ even if using $C_R \ll 2^\circ\text{C/min}$.

Figure 11. 3D surface plot of X_C versus C_R and F_R

4. Conclusions

The thermal, microscopic and crystallographic study of iPP/ μ -talc composites showed that μ -talc is actually a nucleating agent of the iPP matrix, irrespective of potential shear-induced effects due to processing. This nucleating effect is somewhat more pronounced than for standard talc having a surface area about 3 times lower than that of μ -talc. The combination of this nucleating effect with the injection-driven orientation of the platelets generates a strong texturing of the samples.

The use of ANOVA analysis of a set of experimental data of crystallinity (X_C) for various values of the cooling rate (C_R) and various values of the filler content (F_R) allowed to draw a numerical 3D surface $X_C = f(C_R, F_R)$ for predicting the crystallinity of the composites for any cooling rate and filler content with a confidence level greater than of 95%. This 3D surface clearly shows the greater X_C sensitivity to C_R compared to F_R . It also clearly showed the X_C saturation at low cooling rates ($C_R \leq 5^\circ\text{C/min}$) and high talc loading ($F_R \geq 20\%$). Moreover, it appears that the strong sensitivity of iPP matrix to F_R does not shortcut the intrinsic sensitivity of iPP to C_R , the two effects being clearly additive.

Acknowledgements

The authors are indebted to Multibase/Dow Corning (Saint-Laurent du Pont, France) for the supply of the composites and the characteristics of the components, and to Dr. Patrick Prele from Multibase for fruitful discussions.

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