JOURNAL OF MATERIALS SCIENCE **33** (1998) 1069–1074

Structure development in PP/$CaSO_4$ composites

Part II *Effect of filler on crystallization and morphology*

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The structure development in melt crystallized polypropylene (PP) containing different types and concentration of calcium sulphate has been studied by X-ray diffraction and optical polarizing microscopy. The commercial $CaSO_4$ containing mostly the anhydrite form gives the α form of PP while the $CaSO_4$ prepared by *in situ* method yields the β form of PP. This takes place first by conversion of the dihydrate form of $CaSO_4$ to the τ form which preferentially nucleates the β form of PP. The crystallization behaviour in the latter case clearly reveals two processes. The presence of PEO which is used for the *in situ* preparation of $CaSO_4$, however, is found to hinder the rate of crystallization and nucleation of the β form of PP but it gives a high degree of orientation of the $CaSO_4$ needle-like crystals during extrusion of the PP–$CaSO_4$ composites. © *1998 Chapman & Hall*

1. Introduction

The crystallization behaviour and structure development in polypropylene (PP) has received considerable attention in recent years because it has potential applications in many areas as equivalent to some of the engineering polymers [1–5]. Modification of structure and morphology by the use of additives is a simple route to improving the properties such as tensile strength and impact resistance in PP [6–8]. Amongst others, mineral fillers such as talc, mica, calcium carbonate and wollastonite have been found to have a significant effect on the structure development in PP [9–11]. It is also known that the fillers having high aspect ratio and fibrous morphology give reinforcing effects to the polymer [12–13]. Calcium sulphate ($CaSO_4$) is known to have needle-shaped morphology with high aspect ratio under certain conditions of growth [14–16]. Hence, it was thought that this filler could be better than other particulate fillers for bringing about the improvements in properties of PP. In Part I of this series, the preparation and characterization of $CaSO_4$ having high aspect ratio was described [17]. The effect of this additive on the structure development of PP is discussed in the present paper.

2. Experimental procedure

The preparation of $CaSO_4$ by the *in situ* technique was carried out in the same manner as described in the earlier report [17]. Three types of calcium sulphate were used in the present experiments, namely commerically available, prepared by the *in situ* method with polyethylene oxide (PEO) and the same after washing out the PEO. These have been designated as $CaSO_4$ grade CM, IS and ISW, respectively. The characteristics of these three types of $CaSO_4$ are given in Tables I and II. Polypropylene (Indothane SM85N, MFI 12, IPCL, India) powder was obtained after precipitation of its solution followed by thorough washing with acetone and drying. The desired amount of $CaSO_4$ was mixed with the PP powder and dry mixed in an agate pestle and mortar. A small quantity of the mixed powder was isothermally melt crystallized on the hot stage of the microscope. It was also compression moulded in a single ended die at 29 MPa pressure for 30 s to form thin discs (12 mm diameter, 2 mm thick) which were subsequently subjected to the same melt crystallization process as before (melt temperature 190 °C, crystallization at 115 °C, time 15 min). The crystallization behaviour was investigated by recording the growth of the spherulites as well as the transmitted light intensity (grey scale) in the cross-polar mode of the optical polarizing microscope (Leitz, Germany) coupled to the image analyzer system (VID PRO32, Leading Edge, Australia). The details of the techniques used for the investigation of structure, growth and morphology were the same as described elsewhere [19, 20].

3. Results and discussion

The wide angle X-ray diffraction (XRD) scan for PP containing commercial $CaSO_4$ (10%) is indicated in Fig. 1 for the diffraction angle (2θ) region of 5 to 30° in which the major reflections of PP are known to be observed. It is seen that there are five prominent peaks in this region which are typically observed for the α form of PP [20]. The additional peak at 2θ of 26° corresponds to the 0 0 2/0 2 0 reflection of the anhydrite form of $CaSO_4$ [17]. On the other hand, the most interesting results were obtained in the case of PP containing $CaSO_4$ (ISW) prepared by the *in situ* method. Fig. 2 shows the XRD scans for these

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TABLE I. XRD analysis of PP/$CaSO_4$ composites

PP + 10% $CaSO_4$ (commercial)		Assignment	PP + 10% $CaSO_4$ *in situ* (ISW)		Assignment
d (obs)	I/I_o	(h k l)	*d* (obs)	I/I_o	(h k l)
6.32	100	α PP (1 1 0)	6.33	17	α PP (1 1 0)
			6.11	29	τ $CaSO_4$ (1 0 0)
			5.57	100	β PP (3 0 0)
5.31	82	α PP (0 4 0)	5.31	19	α PP (0 4 0)
4.82	64	α PP (1 3 0)	4.82	12	α PP (1 3 0)
4.23	77	α PP (1 3 1)	4.25	50	α PP (1 3 1), β PP (3 0 1)
4.10	79	α PP (0 4 1)	4.10	17	α PP (0 4 1)
3.53	83	α PP (0 6 0), $CaSO_4$ anhydrite (0 0 2/0 2 0)	3.51	12	α PP (0 6 0), β PP (4 1 0) τ $CaSO_4$ (1 1 0)
3.14	15	α PP (2 2 0)	3.21	8	β PP (4 1 1)
3.04	17	$CaSO_4$ anhydrite (1 0 2)	3.04	28	β PP (1 1 2), τ $CaSO_4$ (2 0 0/1 1 1)
2.88	13	α PP (1 6 1) $CaSO_4$ anhydrite (2 1 0)	2.81	9	β PP (6 0 0), τ $CaSO_4$

TABLE II. XRD data reported for PP and $CaSO_4$

α PP (Ref.)			β PP (Ref.)			τ $CaSO_4$ (Ref.)		
d	I/I_o	h k l	*d*	I/I_o	h k l	*d*	I/I_o	h k l
6.34	100	1 1 0						
						6.05	100	(1 0 0)
			5.56	100	3 0 0			
5.32	70	0 4 0						
4.84	56	1 3 0						
4.25	40	1 3 1	4.25	28	3 0 1			
4.10	58	0 4 1						
3.5	20	0 6 0	3.56	4	4 1 0	3.48	60	(1 1 0)
3.13	8	2 2 0	3.19	2	4 1 1			
			3.09	2	1 1 2	3.01	90	(2 0 0/1 1 1)
2.86	2	1 6 1	2.88	2	3 3 1			
2.74	2	2 0 1	2.78	2	6 0 0	2.80	90	(1 0 2)

Underlined reflections indicate the strongest reflection to bring out the comparison of d-values for same.

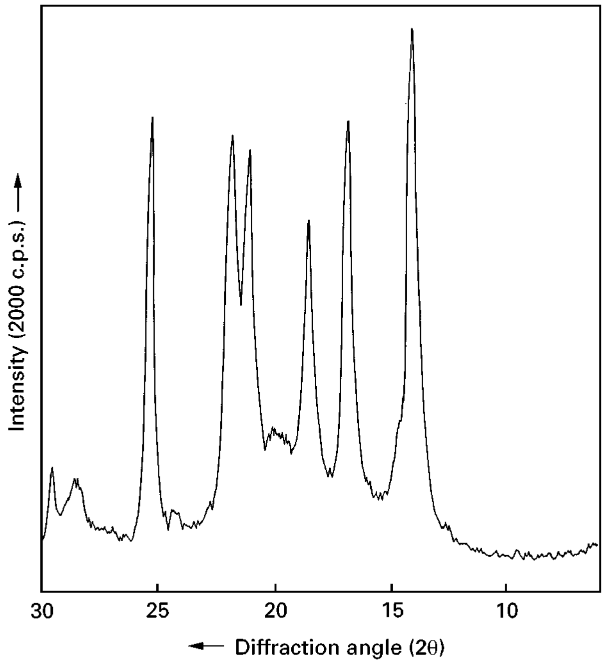

Figure 1 X-ray diffraction scan for PP containing commercial $CaSO_4$ (10 wt %). Samples isothermally crystallized from melt at 115 °C.

melt-crystallized samples containing different concentrations of $CaSO_4$ (ISW). The dramatic changes in the XRD pattern are evident especially at 2θ of about 16°, where a sharp and intense peak appears. It may be noted that $CaSO_4$ does not exhibit any reflection in this region and all the changes can be attributed to the structure modification of PP. The detailed analysis of the XRD data is given in Table III, from which it can be surmised that the β phase of PP is developed in these samples. Another interesting feature to be noted is that the $CaSO_4$ also gets transformed from its monoclinic dihydrate form to the hexagonal τ phase during the melt crystallization process.

The β content of the total crystallinity in the polymer was determined from the ratio of the intensities of the major reflection from the β phase to those from the α phase ($I_\beta/(I_\alpha + I_\beta)$). Table IV indicates the β content with respect to composition for the PP/$CaSO_4$ composites with different grades of the additive. It is seen that the β content is very high in the case of $CaSO_4$ (ISW) as compared to $CaSO_4$ (IS) or $CaSO_4$ (CM). The effect of PEO surrounding the $CaSO_4$ prepared *in situ* on the structure development of PP was also investigated. Fig. 3 shows the XRD scans for

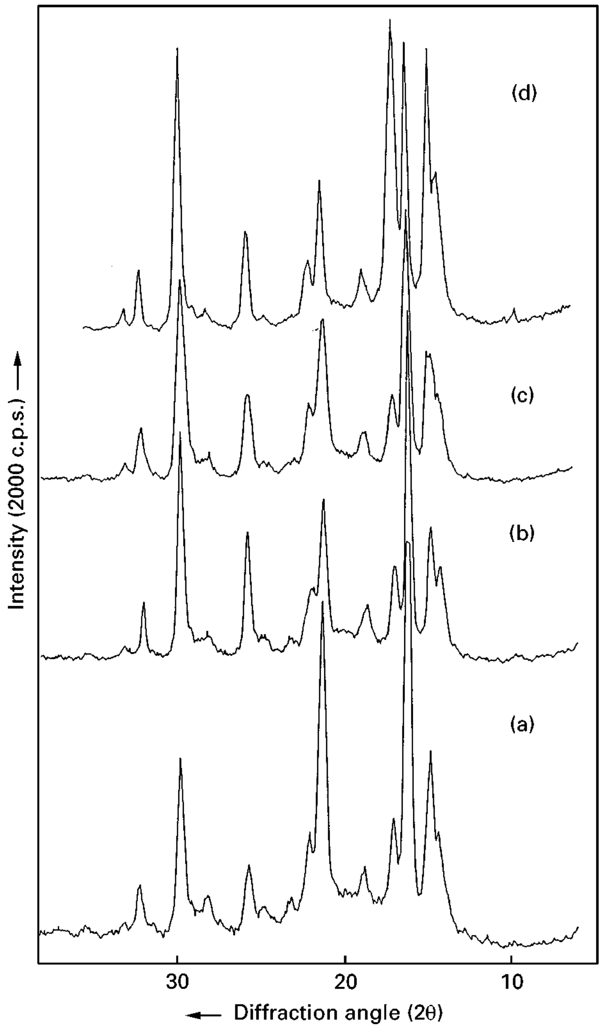

Figure 2 XRD scans for PP containing $CaSO_4$ (ISW) prepared by *in situ* method. Curves (a) to (d) correspond to the additive concentration of 10, 20, 30 and 40 wt %, respectively. Samples melt-crystallized at 115 °C.

TABLE III. The β-phase content in PP/$CaSO_4$ composites

Composition		β content		Ci
$CaSO_4$ (wt %)	With PEO (%)	Without PEO (%)	With PEO (%)	Without PEO (%)
10	17	85	77	77
20	–	79	75	80
30	13	75	75	79
40	51	65	71	71

PP/$CaSO_4$ composites containing the additive prepared by the *in situ* technique but containing different concentrations of $CaSO_4$ with 10% PEO (PEO was used during the preparation of filler and it was allowed to be retained in the filtered product without washing it out). It can be observed that there are some minor changes in the intensities of various reflections but the overall pattern remain more or less same for the additive content up to 30 wt %. A new peak is observed at $2\theta \approx 16^\circ$ only in the curve (D). This may be compared with the results depicted in Fig. 2 wherein dramatic changes were observed. The detailed analysis of these XRD peaks is indicated in Table III.

TABLE IV. WAXD analysis of *in situ* $CaSO_4$ (40 %) with PED in PP

d	I/I_o	Assignment[a] (h k l)
6.37	92	α PP (1 1 0)
6.15	86	τ $CaSO_4$ (1 0 0) [b]
5.61	<u>100</u>	β PP (3 0 0)
5.31	86	α PP (0 4 0)
4.82	66	α PP (1 3 0)
4.25	98	α PP (1 3 1), β PP (3 0 1)
4.10	75	α PP (0 4 1)
3.51	48	α PP (0 6 0), β PP (4 1 0)
3.41	82	τ $CaSO_4$ (1 1 0)
3.19	56	β PP (4 1 1)
3.16	36	α PP (2 2 0), β PP (3 3 0)
3.04	98	β PP (1 1 2), τ $CaSO_4$ (2 0 0/1 1 1)
2.82	34	β PP (6 0 0), τ $CaSO_4$ (1 0 2)

[a] As per reported structure (Ref. 20).
[b] As per hexagonal structure of τ $CaSO_4$.
$a = 0.699$ nm, $c = 0.634$ nm (Ref. 21).

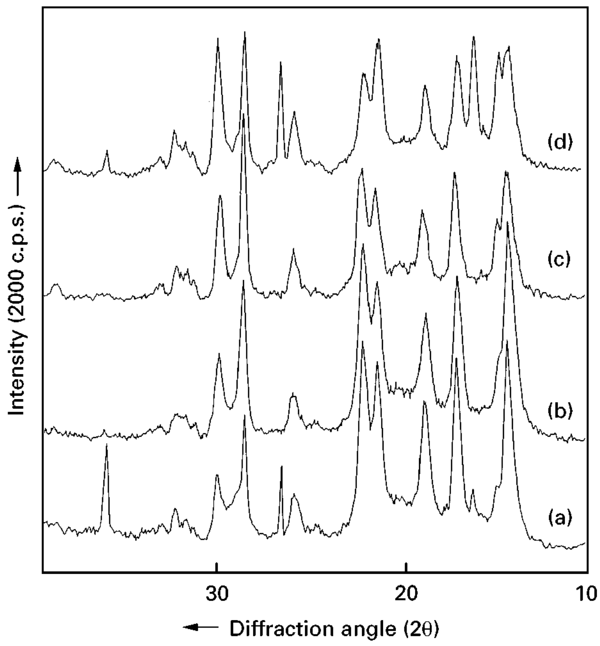

Figure 3 XRD scans for PP containing $CaSO_4$ (IS) with PEO. Curves (a) to (d) correspond to PEO concentrations of 10, 20, 30 and 40 %, respectively. Other conditions same as Fig. 2.

It can be noticed that in this case the PP is in α form with practically no β content. Thus, it appears that the presence of PEO surrounding the $CaSO_4$ crystals prevents the nucleation of the β phase of PP in the PP/$CaSO_4$ composites.

The crystallization behaviour of PP containing different types of $CaSO_4$ was monitored by observing the growth of spherulites. This could be carried out by observing the transmitted intensity through the specimen under cross Fl polar condition in the microscope. Figs 4 and 5 are plots of intensity against time obtained from the image analyser for PP containing 2% of $CaSO_4$ prepared *in situ* with and without (fully washed out) PEO, respectively. Samples were isothermally crystallized at 115 °C. It can be seen that in the case of $CaSO_4$ with PEO as the additive (Fig. 5) the

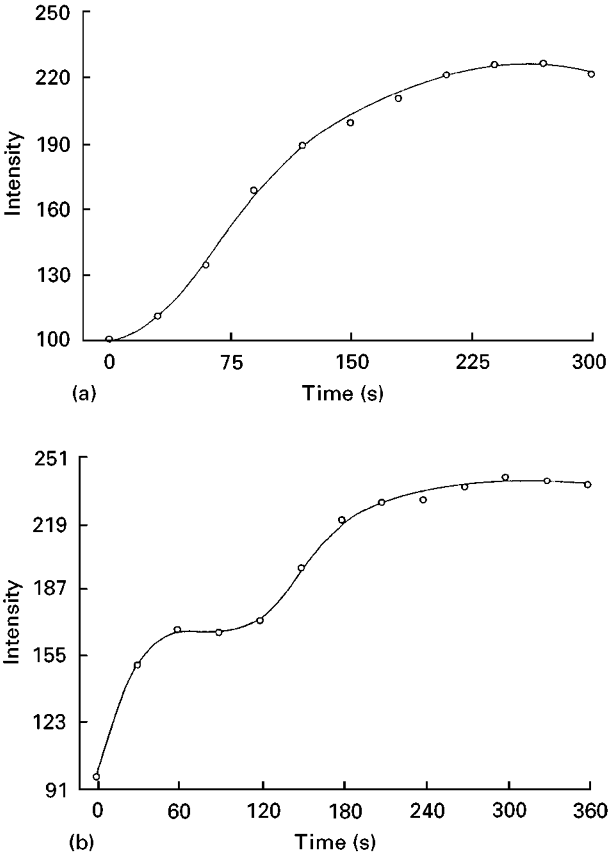

Figure 4 Isothermal crystallization curve for PP containing $CaSO_4$ (IS) with PEO (a) and $CaSO_4$ (ISW) grade without PEO (b). Crystallization temperature 115 °C.

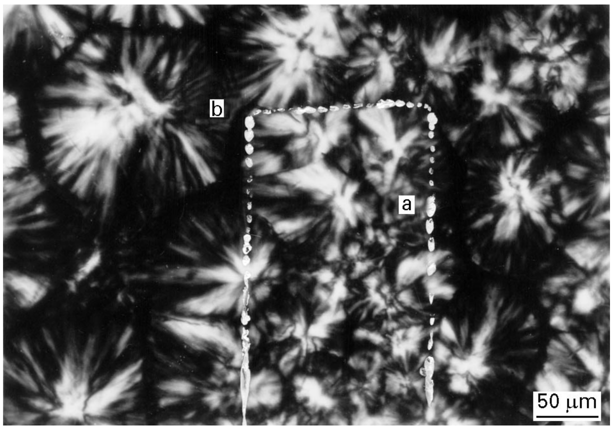

Figure 5 Optical polarizing micrograph of melt-crystallized PP with $CaSO_4$ (ISW). The white dotted line is drawn guidance to delineate the portion nucleated on $CaSO_4$ needle (a) and that away from it (b). Magnification 300 ×.

crystallinity of PP increases monotonically and the crystallization half time (1/2) is about 100 s. On the other hand, crystallization in PP with 2% of $CaSO_4$ grade ISW is quite different: it takes place in two stages (see Fig. 6) in which the first process is rapid and completes in 70 s while the second is slow and continues until 200 s. This suggests that there are two types of crystals growing in these PP/$CaSO_4$ samples. The morphology of these samples (shown in Fig. 6) consists of a set of closely nucleated small spherulites near the $CaSO_4$ crystals together with large spherulites spaced far from these crystals. These observations are in agreement with the above findings in XRD data, namely the existence of two crystalline phases (α and β) in the PP/$CaSO_4$ samples containing *in situ* prepared $CaSO_4$ (PEO).

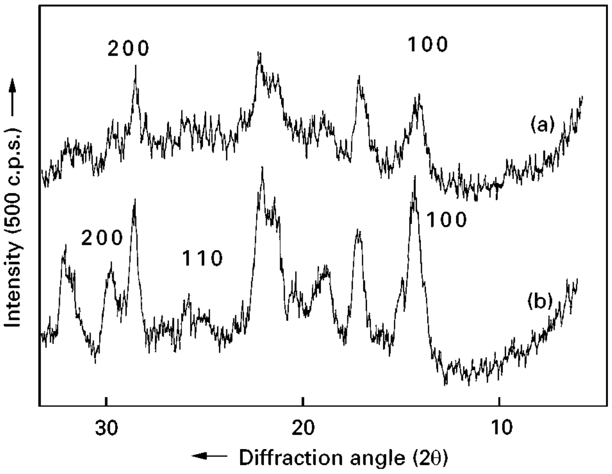

Figure 6 XRD scans for the melt-extruded samples of PP–$CaSO_4$ (IS) composite. (a) Samples sectioned perpendicular and (b) sectioned parallel to the machine direction.

The effect of processing on the orientation of the additive fibres in thermoplastic composites is known and reported for a few systems in the past [21, 22]. In the present case, even at a mild extrusion rate as obtained from a melt indexer, the extrudate was found to consist of $CaSO_4$ crystals oriented with their needle axis parallel to the extrusion direction. Fig. 6 shows the XRD of samples sectioned parallel and perpendicular to the direction of extrusion. There are appreciable changes in the intensities of reflections corresponding to 2 0 0, 1 1 0 and 1 0 0 from $CaSO_4$ crystals when the direction of the section is changed. This is mainly due to the orientation of the $CaSO_4$ crystal parallel or perpendicular to the sectioned surface. Similar variation in the intensities of the samples was observed in the case of shear oriented samples, as reported in Part I of this series [17]. The sectioned samples were observed under the microscope in reflection mode and this revealed the needle-shaped $CaSO_4$ crystals, most of which were oriented with their long axis lying along the direction of extrusion (see micrograph in Fig. 7).

These various results on the structure development in PP/$CaSO_4$ composites can be understood in terms of nucleation, growth and crystallographic interaction between the polymer and the additive. According to the crystal lattice mismatch theory, the substrate influences the growth of another substance on it if the lattice parameters for the substrate and the growing phase are close to each other. The lattice mismatch δ is defined as [23, 24]

$$\delta = |ml_s| - |nl_g|/|l_s|$$

where l is the lattice parameter along any axis, m and n are integers and the subscripts s and g represent substrate and growing media, respectively. If the mismatch parameter is below 15% (i.e. $\delta \ll 15\%$) then the substrate can influence the growth of the crystals in the medium in contact with it. Such an influence can

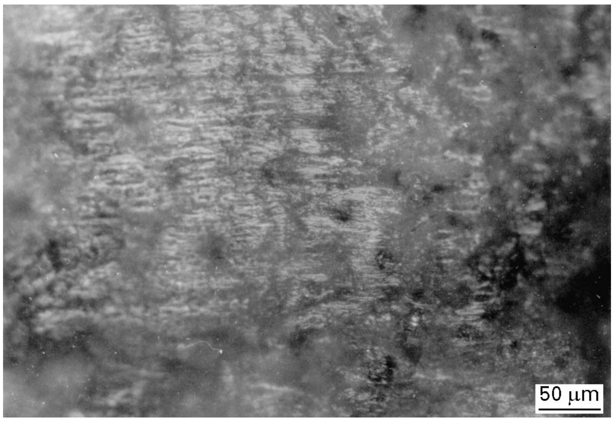

Figure 7 Optical micrograph of the melt extruded PP–$CaSO_4$ samples sectioned parallel to the extrusion direction taken in reflection mode from top surface. Magnification 200 ×.

give rise to the nucleation of a certain crystalline phase, as for example in polyvinylidene fluoride or polypropylene, wherein certain additives alone give the β phase [25, 26]. In the present case, $CaSO_4$ exists in a number of crystalline phases and those obtained in the commercial as well as *in situ* grade have been identified by us. The commercial grade is mostly the anhydrite type: with $a = 0.6328$ nm, $b = 0.6991$ nm and $c = 0.6996$ nm, while that prepared by the *in situ* technique is dihydrate type with $a = 0.567$ nm, $b = 1.515$ nm, $c = 0.651$ nm, $\beta = 118.23$. The τ $CaSO_4$ has hexagonal configuration with $a = 0.699$ nm and $c = 0.634$ nm. The polypropylene has four types of crystallographic form in which the α and β are most common. The α type PP has monoclinic configuration with $a = 0.665$ nm, $b = 2.098$ nm, $c = 0.65$ nm and $\beta = 99.3°$. On the other hand the β PP is hexagonal with $a = 1.274$ nm and $c = 0.635$ nm. If one compares the lattice parameters between the commercial grade $CaSO_4$ and α PP the lattice mismatch is $\delta = 6.2\%$ for *a* axis and 7.63% for *c* axis. On the other hand the lattice mismatch between β PP and the commerical grade $CaSO_4$ is $> 10\%$ for all axes. Hence, the PP–$CaSO_4$ containing the commercial grade additive is not likely to contain the β phase PP. If a similar comparison is made between the τ phase of $CaSO_4$ and β PP, which are both hexagonal, one obtains the lattice mismatch of 0.15% for the *c* axis and $|a_g| - |2a_s|/|a_s|$ as 9.7%. This clearly suggests that the τ $CaSO_4$ can nucleate the β phase. The dihydrate $CaSO_4$ also has smaller lattice mismatch values with β PP. Thus, it appears that in PP/$CaSO_4$ composites containing $CaSO_4$ prepared by the *in situ* technique, the melt crystallization process (melt temperature 190 °C, crystallization at 115 °C) gives rise to first the formation of τ $CaSO_4$, which in turn nucleates the β phase of PP. This close crystallographic interaction is essential for the β phase, as can be surmised from the crystalline content of PP–$CaSO_4$ composite made with the additive containing PEO. The surrounding PEO matrix prevents the interaction between PP and $CaSO_4$ and decreases the nucleation efficiency of the filler for generation of the β phase of PP (see Fig. 3 and Table II). The slight reduction in the β content at higher concentration of the additive can be understood in terms of filler particle aggregation giving rise to a smaller effective surface area for nucleation. The high degree of orientation of the $CaSO_4$ crystals during extension of the PP–$CaSO_4$ composite also confirms the close crystallographic interaction between the additive and the polymer.

4. Conclusions

The structure development in PP/$CaSO_4$ composite containing various types of $CaSO_4$ has been studied. The commercial grade of $CaSO_4$ containing mostly the anhydrite form gives the α form of PP, while the $CaSO_4$ prepared by the *in situ* technique gets transformed from the dihydrate to the τ form of $CaSO_4$, which in turn nucleates preferentially the β form of PP during isothermal melt crystallization at 115 °C. The presence of PEO surrounding the $CaSO_4$ has a major effect on the crystallization rate as well as the crystalline form developed in PP. The α form of PP is mainly obtained in the presence of PEO, which decreases the nucleating effect of the $CaSO_4$.

These studies clearly indicate that the additives can bring about large changes in the structure development in thermoplastic composites of semicrystalline polymers. Further, the same additive but in different crystallographic forms behaves differently as regards nucleation, crystallization and growth of certain crystalline phases in PP. The modification of the filler can be carried out by preparation of the filler using the *in situ* technique, and such modified fillers, having a large aspect ratio, can be effectively used for making better particulate-filled polypropylene composites. The mechanical, electrical and other properties of these composites are being investigated and these results will be published in the near future.

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Received 25 July 1996
and accepted 12 September 1997