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Structure development in PP/$CaSO_4$ composites

Part I *Preparation of the filler by an* in situ *technique*

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The structure, growth and morphology of calcium sulphate prepared *in situ* of a polymer has been investigated using polyethylene oxide as the growth medium. The structure was predominantly the dihydrate type with monoclinic configuration for these samples as compared to the anhydrite type with orthorhombic structure obtained in commercial samples. The crystal morphology consisted of sharp needle shape, having aspect ratio of more than 10. The concentration of the polymer used had a profound effect on the crystal size and its distribution. The size distribution became narrow and the average crystal size reduced with the increase of polymer concentration. Highly oriented crystals could be obtained with application of a small shearing force on the samples. These results have been explained on the basis of polymer mediated crystallization and large interaction between the filler and the matrix. © *1998 Chapman & Hall*

1. Introduction

Amongst the various particulate filled composites, those based on polypropylene (PP) have attracted much attention over the past few years [1–4]. This is mainly because polypropylene is extensively used in a large number of applications and its properties can be modified by a variety of additives [5–9]. There are various types of mineral fillers which show reinforcing effect, nucleation of certain crystalline forms and even epitaxial growth/transcrystallinity in PP. For example talc and wollastonite are reported to give some reinforcement to PP leading to better mechanical properties [10, 11]. Mineral fillers such as mica cause transcrystalline growth while talc induces the growth of the α phase and chalk the β phase in PP [12, 13]. The various effects are associated with the filler morphology as well as its interaction with the polymer matrix and/or its particular crystalline phase. However, because these minerals occur in different locations and in a number of crystalline polymorphic forms, it is difficult to keep track of these and correlate the property enhancement with structure development in such cases. It is known that for high reinforcing efficiency the filler should have high aspect ratio and it should preferably have fibrous morphology [14, 15]. Such a morphology is readily obtained in calcium sulphate ($CaSO_4$) and it can be synthesized easily by a simple precipitation route at room temperature. Additionally, polymer-mediated growth can modify the morphology of the crystals to a great extent, as has been reported by us for a number of compounds such as $CuCl_2$, $CaCO_3$, CdS etc. [16–18]. Apart from aspect ratio, $CaSO_4$ is also known to impart flame retardancy when incorporated in polymers [9]. It was hence thought that it could be possible to grow the $CaSO_4$ crystals by an *in situ* deposition technique under controlled conditions and use the same for making the PP/$CaSO_4$ composites. In this paper, the preparation of the filler, $CaSO_4$, by an *in situ* technique and the resulting new morphological features observed in them are discussed, while the effects of incorporation of such fillers on the structure development in PP are described in a subsequent communication [20].

2. Experimental procedure

The $CaSO_4$ was prepared by the *in situ* deposition technique in the same manner reported elsewhere for other compounds [14–16]. This essentially consisted of first forming a complex of calcium chloride ($CaCl_2$) with polyethylene oxide (PEO, WSR-N750, BDH, MW 3×10^5) by dissolving the two components in desired proportions in methanol. This was allowed to react for 10 h. Appropriate stoichiometric amounts of potassium sulphate (K_2SO_4) dissolved in distilled water were added to the above complex slowly without stirring. The whole reaction mixture was allowed to digest at room temperature for 20 h when the ions diffused through the PEO and formed a white gel-like precipitate which was filtered, washed lightly and dried. The $CaSO_4$ powder was characterized for structure and morphology by X-ray diffraction (XRD) and a optical polarizing microscope (Leitz 12POL D) coupled to an image analyser system (VID PRO-32, Leading Edge, Australia). The particle size and shape analysis could be directly obtained from this equipment. Details of the characterization by XRD and

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microscopy have been given elsewhere [21, 22]. In one set of experiments, the $CaSO_4$ powder was mixed with PEO in different concentrations ranging from 10 to 40 wt % and the wet thick slurry subjected to shearing between glass slides. These samples were allowed to dry and then studied for structure and morphology in the same manner as before.

3. Results and discussion

The white precipitate obtained after reaction of calcium chloride with potassium sulphate in the presence of different concentrations of PEO was analysed for crystal structure by X-ray diffraction. Fig. 1 shows the XRD scans for the $CaSO_4$ prepared by the *in situ* technique (curve A) together with that of commercially available $CaSO_4$ (curve B). It is evident from the figure that $CaSO_4$ prepared by the *in situ* technique is distinctly different from the commercial grade. The detailed analysis of the XRD and the assignment of various reflections is given in Table I. There are a number of crystalline forms for $CaSO_4$ existing in both anhydrous and hydrated states. Amongst these, the anhydrite and dihydrate forms are the most commonly found [23, 24, 25]. From the various reflections observed in the commercial sample, it appears that it contains mainly the anhydrite form (88%) with a small amount of dihydrate ($CaSO_4 \cdot 2H_2O$) and some hemihydrate ($CaSO_4 \cdot 0.5\ H_2O$). The hydrated forms may have been formed by absorption of moisture in these commercial samples over a long period of storage. The *in situ* deposition technique on the other hand yields exclusively the dihydrate form of $CaSO_4$. All the major reflections of curve A could be assigned to the $CaSO_4$ dihydrate crystalline form with monoclinic structure having the lattice parameters of $a = 0.567$ nm, $b = 1.515$ nm, $c = 0.651$ nm and $\beta = 118.23$ [26]. There are some weak reflections which correspond to the complex of PEO with calcium chloride for which the structure was reported earlier by us [17]. The presence of this small unreacted component of the complex in these samples could be caused by strong coupling between the calcium ions and oxygen moities of PEO which could not be dissociated by the sulphate ions; and/or penetration of PEO complex was restricted to some extent because of its large size. (There was no such PEO–$CaCl_2$ complex found to be present after the formation of calcium carbonate [17]).

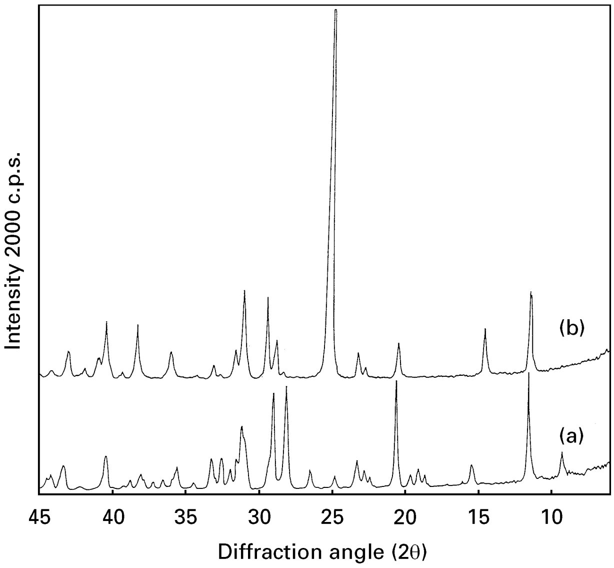

Figure 1 X-ray diffraction scan for different grades of calcium sulphate: (a) prepared by *in situ* technique and (b) commercially available grade.

In order to study the effect of PEO on the structure and morphology of the $CaSO_4$ formed *in situ*, the reaction was carried out with different concentrations of PEO in the PEO–$CaCl_2$ complex. Fig. 2 shows the

TABLE I XRD analysis of $CaSO_4$ prepared by *in situ* technique

Commercial $CaSO_4$		Assignment (h k l)	*In situ* 30 % PEO–$CaSO_4$		Assignment (h k l)
d (obs)	I/I_o		*d* (obs)	I/I_o	
7.62	22	Dihydrate (0 2 0)	7.59	$\underline{100}$	Dihydrate (0 2 0)
6.03	13	Hemi-hydrate			
4.31	9	Dihydrate $(1\,2\,\bar{1})$	4.30	96	Dihydrate $(1\,2\,\bar{1})$
3.90	3	Anhydrite (1 1 1)			
3.82	7	Dihydrate (0 3 1/0 4 0)	3.82	25	Dihydrate (0 3 1/0 4 0)
3.52	$\underline{100}$	Anhydrite (0 0 2/0 2 0)			
3.13	2	Anhydrite (2 0 0)	3.16	92	Dihydrate $(1\,1\,\bar{2})$
3.08	10	Dihydrate $(1\,4\,\bar{1})$	3.07	85	Dihydrate $(1\,4\,\bar{1})$
3.02	21	Hemi-hydrate			
2.87	23	Anhydrite (2 1 0), Dihydrate (0 0 2)	2.86	56	Dihydrate (0 0 2)
2.82	8	Anhydrite (1 2 1), Dihydrate $(2\,1\,\bar{1})$			
2.70	4	Dihydrate (0 2 2/0 5 1)	2.69	26	Dihydrate (0 2 2/0 5 1)
2.48	7	Anhydrite (0 2 2)			
2.34	14	Anhydrite (2 0 2/2 2 0)			
2.22	15	Anhydrite (2 1 2)	2.23	30	Dihydrate $(1\,5\,\bar{2})$
2.19	6	Anhydrite (1 0 3)			
2.09	7	Anhydrite (1 1 3)			
1.87	12	Anhydrite (2 3 0)			

Ref. Anhydrite 6-0226 (ASTM), dihydrate 1-0385 (ASTM), hemi-hydrate 1-0999 (ASTM).
Underlined reflections to bring out the comparison of d-values for strongest peak.

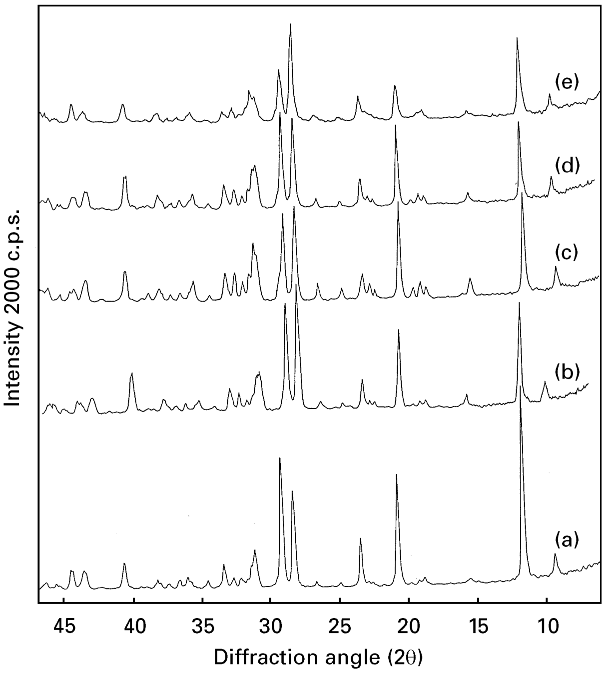

Figure 2 XRD scans for $CaSO_4$ prepared by *in situ* method with different concentrations of PEO: (a) to (e) correspond to PEO concentrations of 10, 20, 30, 40 and 50 wt % in solution, respectively.

XRD scans for $CaSO_4$ samples prepared with PEO concentrations of 10 to 50 wt %. It is interesting to note that although the basic structure of $CaSO_4$ formed is the same, the relative intensities of the peaks change considerably, especially in the 2θ region of 10° to 30°. The intensity of the reflections corresponding to $0\,2\,0$, $1\,2\,\bar{1}$, $1\,1\,\bar{2}$ and $1\,4\,\bar{1}$ show large variations with the increase of concentrations of PEO. These aspects will be discussed later in the paper.

The morphology of the $CaSO_4$ prepared by an *in situ* technique was distinctly different from that observed for the commercial sample, as seen in Fig. 3 which shows the optical micrographs for these samples. The $CaSO_4$ prepared by an *in situ* technique has long needle-shaped morphology whereas the commercial sample has small globular particle shape. The aspect ratio for the former case was 9 to 10 while for latter case it was 1.0. The concentration of PEO used during the *in situ* preparation of $CaSO_4$ also had a profound effect on the particle size distribution. Figs 4, 5, 6 and 7 show the size distribution of particles in $CaSO_4$ prepared with PEO concentrations of 10, 20, 30 and 40 wt%. It can be observed from Fig. 4 that there are large numbers of particles having sizes ranging from 20 to 60 μm. A few particles have size even greater than 70 μm. Thus the size distribution is quite broad in this case. The increase of PEO concentration to 20% leads to a decrease of the number particles having size greater than 60 μm (see Fig. 5) and the distribution curve becomes narrower than that for 10 wt % PEO. Further increase of concentration of PEO gives rise to the formation of some particles having small size (< 10 μm) and the distribution becomes increasingly narrow. Thus it is seen that the particle size distribution becomes narrow and the peak shifts towards smaller particle size with the increase of concentration of PEO.

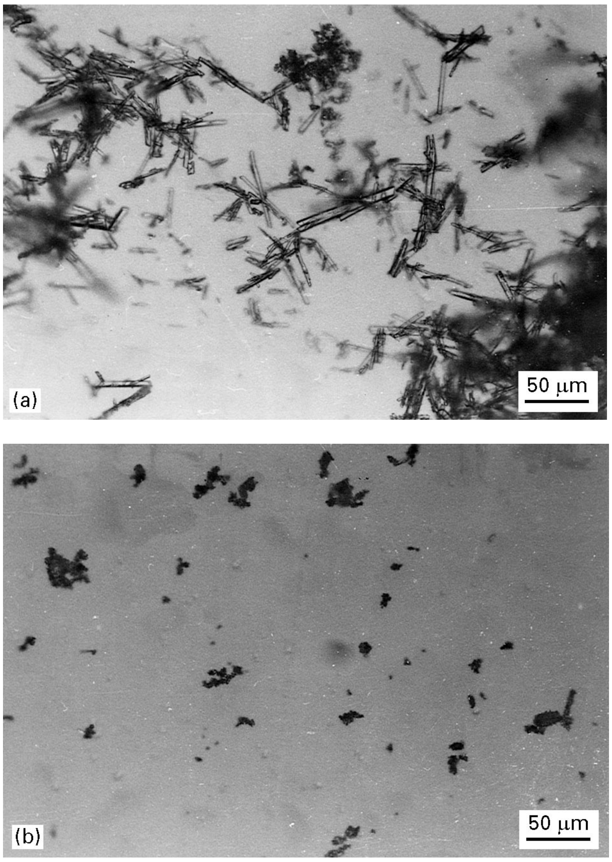

Figure 3 Morphology of $CaSO_4$ particles prepared by *in situ* method (a) and that of the commercial grade (b).

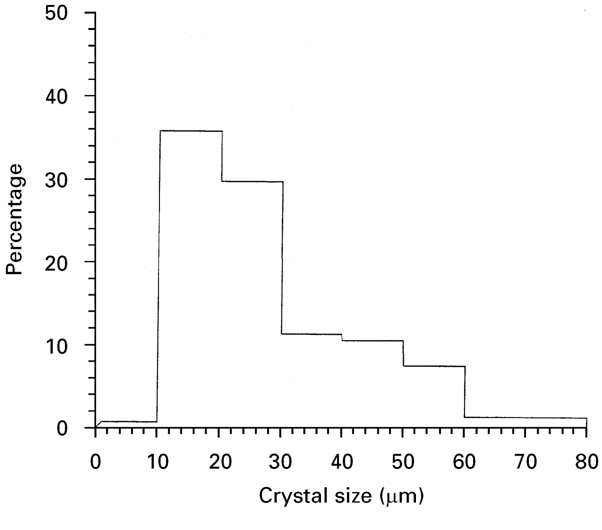

Figure 4 Crystal size distribution in $CaSO_4$ prepared *in situ* of PEO with concentration of 10 wt % in solution. Size distribution was obtained directly from image analyser.

In order to understand the above results one has to first look into the various processes involved in the *in situ* deposition technique. Firstly, the calcium salt forms a complex with the PEO polymer in which the calcium ions are bound within the "cage" of oxygen atoms of the polymer [27, 28]. This is then reacted with potassium sulphate during which sulphate ions diffuse into the polymer. Since the calcium ions are bound by the polymer chain, the formation of $CaSO_4$ can take place only at certain sites which are dependent

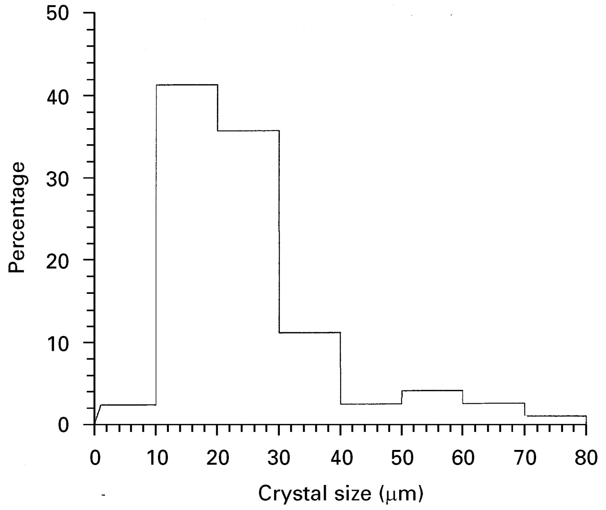

Figure 5 Same as Fig. 4 but with PEO concentration of 20 wt %.

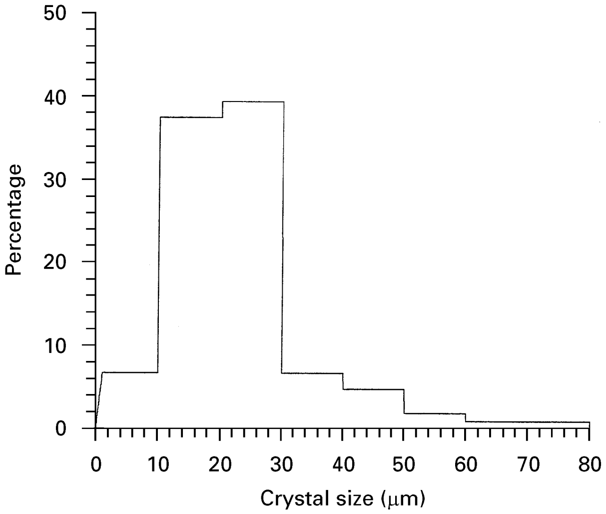

Figure 6 Same as Fig. 4 but with PEO concentration of 30 wt %.

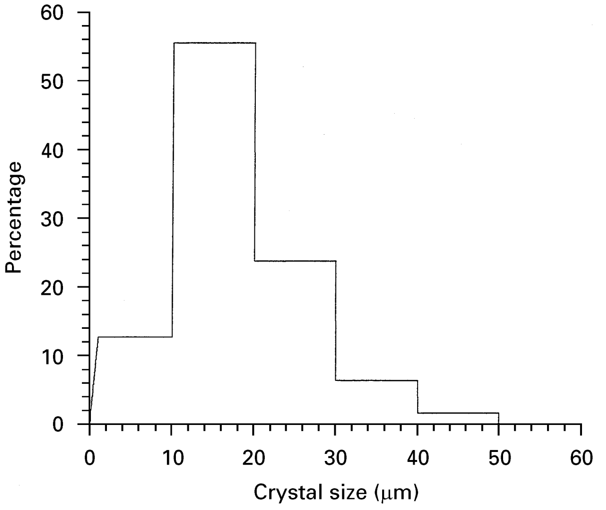

Figure 7 Same as Fig. 4 but with PEO concentration of 40 wt % in solution.

on the relative concentration of the polymer. The distance between these sites would depend on whether the PEO–$CaCl_2$ complex is in the ratio of 2 : 1, 4 : 1 or 16 : 1 etc. The proximity of such molecules would ultimately determine how the crystals would grow. Thus the polymer matrix (in gel form) surrounding the

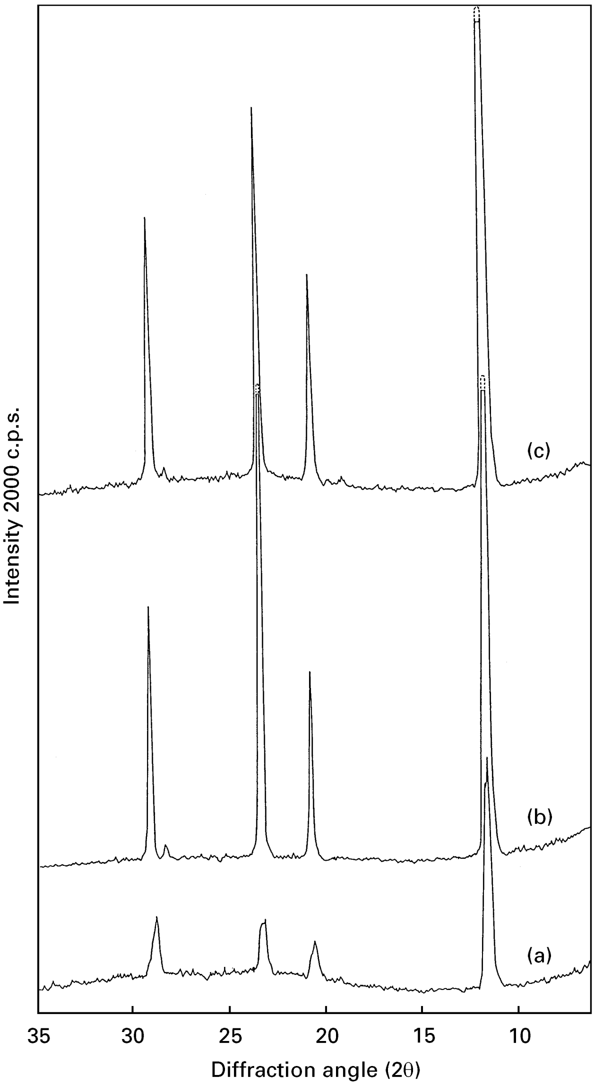

Figure 8 XRD scans for $CaSO_4$ prepared by *in situ* method using PEO after shearing between glass slides. Curves (a), (b) and (c) correspond to PEO concentrations of 10, 20 and 30 wt % respectively.

$CaSO_4$ moities influences its crystalline growth. The above findings regarding the increase or decrease of intensities of certain reflections suggest that the growth of certain crystalline faces has been inhibited. The decrease in the particle size with the increase of PEO content is also in agreement with the above hypothesis.

The filler particles are subjected to shear stress during processing of composites. This may cause alignment of fibres, giving better reinforcement to the material. In order to study the effect of shearing on the $CaSO_4$ needle-shaped crystals, the material synthesized by the *in situ* technique was sheared in the semi-wet state (made wet by a few drops of water) between two glass slides. The structure and morphology of these samples were investigated as before. Fig. 8 shows the XRD scans for these samples. Curves (a), (b) and (c) correspond to PEO concentrations of 10, 20 and 30 wt%, respectively. It is interesting to note that the intensities of some reflections increase enormously while for others there is decrease of intensity after shearing with the increase of PEO content. The detailed analysis and assignment of the XRD peaks is given in Table II. It is seen that whereas the

TABLE II WAXD analysis of sheared samples (PEO/$CaSO_4$)

10% PEO		20% PEO		30% PEO		$CaSO_4 \cdot 2H_2O$[a]		
d(obs)	I/I_o	d(obs)	I/I_o	d(obs)	I/I_o	d(obs)	I/I_o	h k l
7.76	100	7.76	100	7.76	100	7.7	020	50
4.33	23	4.33	7	4.33	16	4.29	$12\bar{1}$	100
3.85[b]	22	3.83	23	3.83	27	3.81	031/040	15
3.11	35	3.09	9	3.09	20	3.06	$14\bar{1}$	63

[a] as per monoclinic structure of $CaSO_4 \cdot 2H_2O$, Ref.ASTM 1-0385.
[b] also 1 1 2 reflection of PEO ($d = 3.81$).
$a = 0.567$ nm, $b = 1.515$ nm, $c = 0.651$ nm and $\beta = 118.23$.
WAXD, wide angle X-ray diffraction.

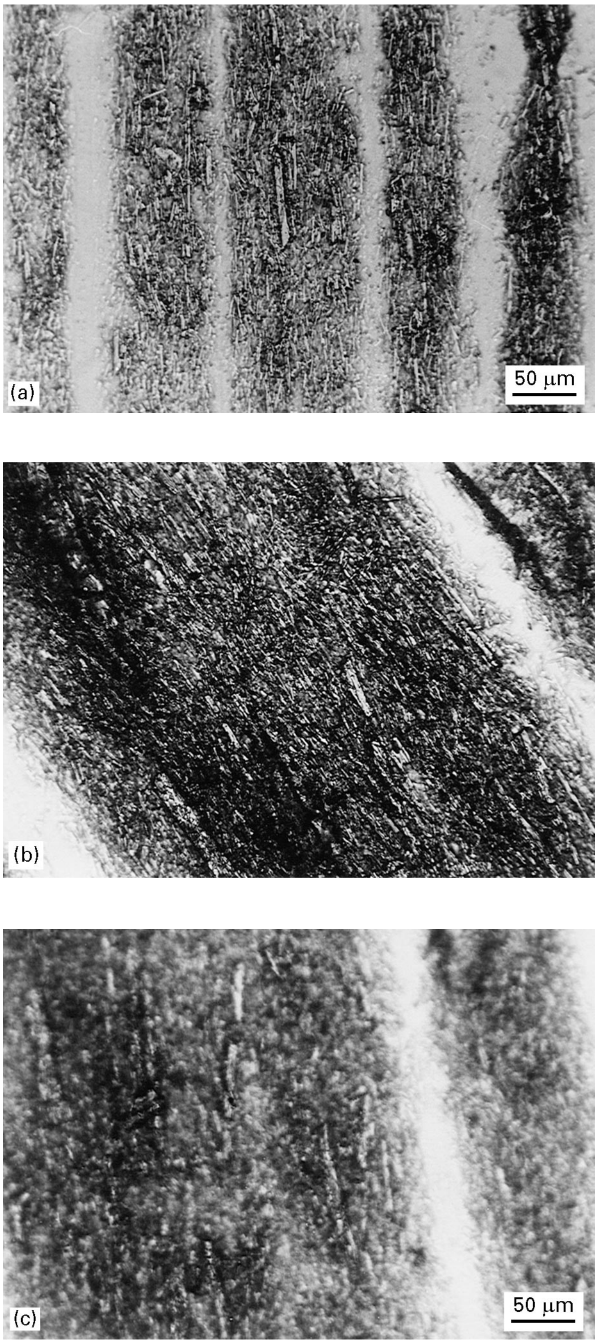

Figure 9 Optical micrographs of $CaSO_4$ samples after shearing: (a), (b) and (c) correspond to PEO concentrations of 10, 20 and 30 wt %, respectively.

intensity of the 0 2 0 reflection, which is of medium intensity in ordinary hydrated $CaSO_4$, increases tremendously, those of the 1 2 1 and 1 4 1 reflections decrease considerably in sheared samples. These changes in the intensities of XRD peaks can be associated with the orientation of the crystals with respect to the substrate surface during the shearing of the samples. Fig. 9 shows the optical micrographs of the sheared samples, and it is quite evident that the $CaSO_4$ crystals are aligned such that their long axis is parallel to the direction of shearing/polymer flow. These findings are important from the point of view of processing of polymers filled with $CaSO_4$ prepared by the *in situ* technique.

4. Conclusions

The structure and growth morphology of $CaSO_4$ prepared in a polymer matrix (PEO) was studied. The samples were prepared by first complexing $CaCl_2$ with PEO and then reacting the same with K_2SO_4. The presence of PEO had a profound effect on the crystal structure and the morphology of the crystals. Large variations in the intensities of various reflections in the XRD were noted. The particle size distribution became narrow and the mean particle size became smaller with the increase of PEO content. Sheared samples exhibited a high degree of orientation of the needle-shaped $CaSO_4$ crystals.

These studies indicate that it is possible to use the polymer-mediated growth for controlling the crystal morphology. Such materials have distinctly different morphological features from the commonly available ones, and these may provide useful applications in improving the properties of polymers such as PP. Our studies on the effect of such fillers on the structure development in PP will be described in the next part of the paper.

References

1. C. VASILE and R. B. SEYMOUR, "Handbook of polyolefin" (Dekker, New York, 1993) Ch. 5, 9.
2. M. FUJIYAMA and T. WAKINO, *J. Appl. Polym. Sci.* **43** (1991) 97.
3. Y. SUETSUGU, *Int. Polym. Process.* **5** (1990) 184.
4. V. MALPASS and J. KENPTHRON, *Plas. Compd.* **12** (1989) 55.
5. K. T. KOLLINGTON in Polypropylene The Way Ahead, Proceedings in Conference, Madrid, Spain, PRI London, 1989, p. 81.

6. J. KRAGER KOCSIS, "Polypropylene structure, blends and composites" (Chapman & Hall, London, 1995).
7. F. RYBNIKAR, *J. Appl. Polym. Sci.* **27** (1982) 1479.
8. T. KOWALESKI and A. BALESKI, *ibid.* **32** (1986) 2919.
9. K. MITSUISHI, S. UENO, S. KODAMA and H. KAWASAKI, *ibid.* **48** (1991) 204.
10. R. B. SEYMOUR, in "Developments in plastic technology" Vol. 2, edited by A. Whelan and J. L. Craft (Elsevier Applied Science, London, 1985) p. 219.
11. P. J. WRIGHT, in "Developments in plastic technology" Vol. 3, edited by A. Whelan and J. L. Craft (Elsevier Applied Science, London, 1986) p. 119.
12. S. F. XAVIER and Y. N. SHARMA, *Angew. Makromol. Chem.* **127** (1985) 145.
13. M. FUJIYAMA and T. WAKINO, *J. Appl. Polym. Sci.* **42** (1991).
14. D. HULL, "Introduction to composite materials" (Cambridge University Press, Cambridge, 1981).
15. W. V. TITOW and B. J. LANHAM, "Reinforced thermoplastics" (Applied Science Publishers, London, 1975) p. 12.
16. S. RADHAKRISHNAN and J. M. SCHULTZ, *J. Cryst. Growth* **116** (1992) 378.
17. S. RADHAKRISHNAN and D. R. SAINI, *ibid.* **129** (1993) 191.
18. S. RADHAKRISHNAN, *ibid.* **141** (1994) 437.
19. C. SAUJANYA and S. RADHAKRISHNAN, *J. Mater. Sci.* **33** (1998) 1069.
20. J. V. MILEWSKI and H. S. KATZ, "Handbook of reinforcements for plastics" (Van Nostrand Reinhold, New York, 1987).
21. S. RADHAKRISHNAN, C. R. RAJAN and V. M. NADKARNI, *J. Mater. Sci.* **21** (1986) 597.
22. S. RADHAKRISHNAN, K. KANE, K. KADU and H. P. NATU, *J. Appl. Polym. Sci.* **58** (1995) 571.
23. ASTM Diffraction files 1-0999, 2-0134, 2-0675, 6-0046, ASTM, Washington, 1995.
24. E. C. S. DICKSON and S. W. BINKS, *Phil. Mag.* **2** (1952) 114.
25. G. C. H. CHENG and J. ZUSMAN, *Acta Cryst.* **16** (1963) 767.
26. R. W. G. WYCKOFF, "Crystal structures" Vol. 3 (John Wiley, New York, 1968) p. 18 and 642.
27. J. M. G. COWIE and S. H. CREE, *Ann. Rev. Phys. Chem.* **40** (1989) 85.
28. C. A. VINCENT, *Prog. Solid State Chem.* **17** (1987) 145.

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