JOURNAL OF MATERIALS SCIENCE **35** (2000) 2319–2323

Structure and properties of PP/$CaSO_4$ composite

Part III: *Effect of the filler grade on properties*

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The mechanical properties viz.impact strength and tensile modulus of polypropylene (PP) containing two different types of calcium sulphate (prepared by *in situ* method under controlled conditions in a polymer matrix i.e. polyethylene oxide in the composition range 0–25 wt% of filler were studied. Increase of impact strength together with high crystallinity and improved tensile modulus was observed in one of the grades of $CaSO_4$ filled composite as compared to pure PP. This could be associated with the long needle shaped $CaSO_4$ crystals and the change in the structure and morphology induced by the same in the PP matrix. © *2000 Kluwer Academic Publishers*

1. Introduction

The enhancement of properties of commodity plastics by modification of structure, orientation and morphology has received considerable attention in recent years [1–4]. In this context polypropylene (PP) has been studied extensively after incorporating it with many mineral fillers or additives which provide a simple route to improving the properties such as tensile modulus and impact resistance of the polymer [5–8]. However in these reports it has been observed that fillers in PP generally increased stiffness, tensile strength and dimensional stability but their impact strength, elongation and creep resistance deteriorated. It is well known that fillers having high aspect ratio and fibrous morphology influence the properties and performance of PP composites [9, 10]. As calcium sulphate exhibits needle like morphology with high aspect ratio under certain conditions of growth, it was thought that this filler could enhance the properties of PP as compared to other particulate fillers. In part–I of this series of papers on PP/$CaSO_4$, preparation and characterization of $CaSO_4$ having high aspect ratio has been described [11] while the part–II describes the effect of $CaSO_4$ on the structure development of PP [12]. In the present paper, we report a study on the mechanical properties of PP/$CaSO_4$ composites using different types of $CaSO_4$ synthesized by *in situ* deposition technique. These exhibited both high impact and high tensile strength and these have been correlated with structure and morphology of composites.

2. Experimental

The preparation of $CaSO_4$ by the *in situ* deposition technique was carried out in the same manner as described in the earlier report [11] by first complexing $CaCl_2$ with polyethylene oxide (PEO) and then reacting the same with K_2SO_4. Two types of $CaSO_4$ was prepared: one containing PEO and the other after complete washing out of the PEO. These have been designated as $CaSO_4$-I and $CaSO_4$-II respectively in the Table IA. The effect of filler on the crystallization and morphology of PP/$CaSO_4$ composites were investigated as described in the earlier report [12]. The PEO concentration of 10% was used for preparing both the grades of $CaSO_4$ which were used for the present study on the properties of these composites. The PP/$CaSO_4$ samples were obtained by compounding the filler with polypropylene pellets in the composition range 0 to 25 wt% under the conditions given in Table IB.

At least five samples were tested for each composition and the average values obtained for the different parameters are reported here in this paper. Tests were performed at ambient temperature (30°C) and humidity conditions. The complete details of specification of techniques used for investigation of properties were same as described elsewhere [13, 14].

3. Results and discussion

Modification of structure and morphology due to the additives present affects the properties of polymer matrix. In order to correlate the structure development in PP/$CaSO_4$ composites to properties, the effect of filler on the crystallization and morphology of PP is described here in brief. The details of the same has been reported in our earlier papers [11, 12]. Figs 1 and 2 show the WAXD scans for the melt crystallized samples (115°C) of PP containing $CaSO_4$ I (with PEO) and $CaSO_4$ II respectively. Curves A to D correspond to filler concentration of 10, 20, 30 and 40% by weight respectively for both the grades of $CaSO_4$. From the comparison of the figures it can be surmised that with the increase of filler concentration the β phase of PP is

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TABLE IA Characteristics of materials used in PP/$\mathrm{CaSO_4}$ composites

Polypropylene	Indothane SM85N, MFI 12, IPCL, India
Polyethylene oxide	WSR-N750, BDH England, M. W. 3 × 10^5
$\mathrm{CaSO_4}$-I	Prepared in lab by *in situ* technique using PEO (10%), Average size 10–30 μm
$\mathrm{CaSO_4}$-II	Prepared as above but with thorough washing out of PEO.

TABLE IB Conditions used for compounding and moulding and the specifications of impact and tensile testing

	Brabender plasticorder single screw extruder	Injection moulding conditions
Feed zone	150°C	210°C
Transition zone	175°C	195°C
Metering zone	190°C	205°C
Die temperature	210°C	215°C
Screw Speed	16–18 rpm	200 rpm
Injection pressure	—	1905 bar
	Impact testing	Tensile testing
	Izod impact tester (Ceast)	Instron 4204
ASTM	D- 256	D- 638
Hammer weight	7.5 Kg	—
Crosshead speed		50 mm/min
Extensometer gauge length		50 mm
Specimen gauge length		115 mm
Thickness		12.5 mm
Width		3.2 mm

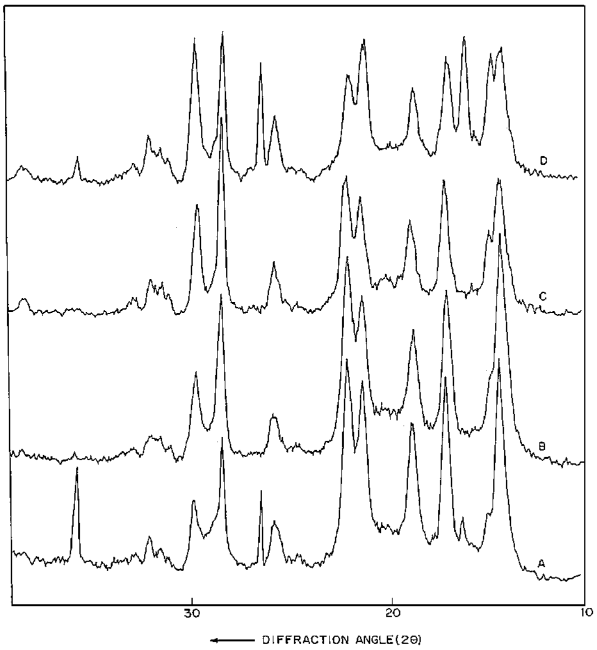

Figure 1 Wide angle X-ray diffraction scans for the isothermal melt crystallized samples (115°C) of PP containing different concentration of $\mathrm{CaSO_4}$-I (with PEO) ranging from 10, 20, 30 and 40% by wt.

TABLE II Crystallinity and β phase content in PP/$\mathrm{CaSO_4}$

Composition $\mathrm{CaSO_4}$ (wt%)	β content (%) $\mathrm{CaSO_4}$-I	β content (%) $\mathrm{CaSO_4}$-II	Ci (%) $\mathrm{CaSO_4}$-I	Ci (%) $\mathrm{CaSO_4}$-II
10%	17	85	77	77
20%	—	79	75	80
30%	13	75	75	79
40%	51	65	71	71

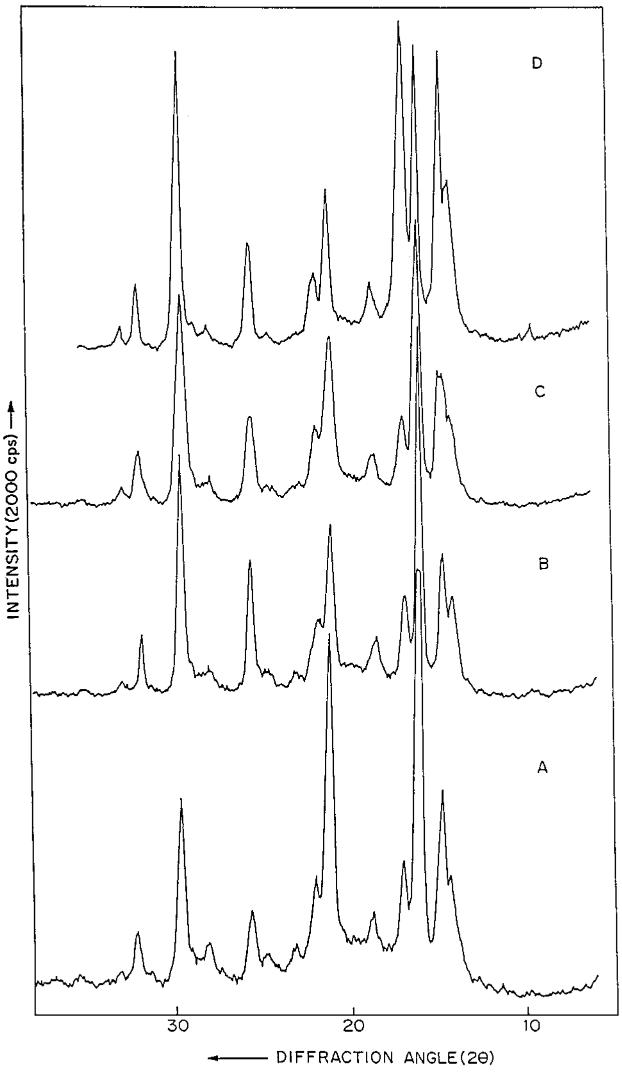

Figure 2 Wide angle X-ray diffraction scans for the isothermal melt crystallized samples (115°C) of PP containing different concentration of $\mathrm{CaSO_4}$-II ranging from 10, 20, 30 and 40% by wt.

developed in case of PP/$\mathrm{CaSO_4}$-II giving a sharp peak at $2\theta = 16^\circ$ which corresponds to (040) reflection whereas for PP/$\mathrm{CaSO_4}$-I a major peak is observed which corresponds to (110) reflection of α phase of PP. The detailed analysis of XRD data is reported in our earlier papers [12]. The β content and the crystallinity (Ci%) in these composites was determined from the XRD scans. The β content was determined from the ratio of intensities of major reflection from the β phase ($2\theta = 16^\circ$) to those from major reflection of α phase ($2\theta = 14^\circ$) as ($I_\beta/I_\alpha + I_\beta$). Table II indicates the β content and the crystallinity value with respect to composition for both the grades. It can be seen from the table that β content is quite high in case of PP/$\mathrm{CaSO_4}$-II as compared to PP/$\mathrm{CaSO_4}$-I. Also the high crystallinity of the order of 75% was observed for both the grades as compared to pure PP which typically has a Ci value of 62%. These various findings can be attributed to strong nucleation by $\mathrm{CaSO_4}$ crystallites giving rise to preferential

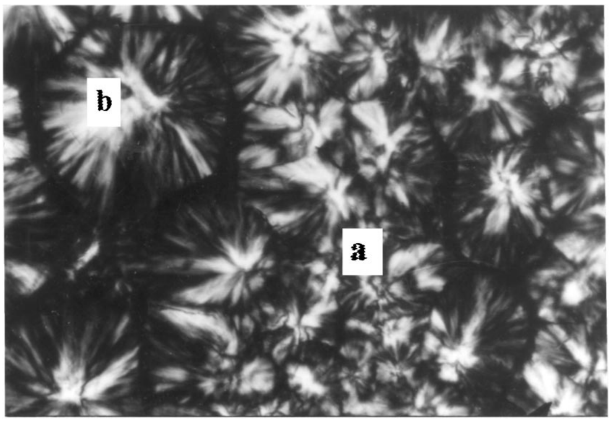

Figure 3 Optical polarising micrograph of PP containing $CaSO_4$-II melt crystallized at 115°C.

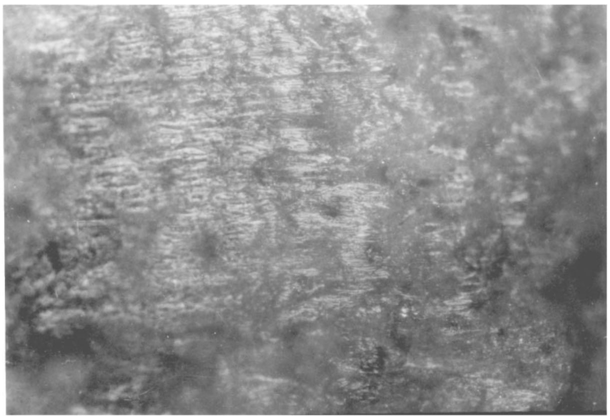

Figure 4 Optical polarising micrograph of a section of injection moulded PP/$CaSO_4$-II in the reflection mode.

growth of small β spherulites in case of PP/$CaSO_4$-II as compared to PP/$CaSO_4$-I where the presence of PEO surrounding the $CaSO_4$ crystallites inhibits the nucleation and generation of β phase. This is evident in Fig. 3 which shows the optical photomicrograph of PP/$CaSO_4$-II taken under cross polar condition in the microscope. It is interesting to note that a set of closely nucleated small β spherulites occurs near the $CaSO_4$ crystals while large spherulites occur at points far from these crystals.

The orientation of crystallites was also investigated for PP/$CaSO_4$-II. Fig. 4 shows the optical photomicrograph taken in reflection mode of the section of injection moulded sample along the machine or melt-flow direction. It reveals the needle shaped $CaSO_4$ crystals most of which are aligned with the long axis along the direction of flow.

With this brief discussion of structure development in the PP/$CaSO_4$ composites, we now describe the effect of the same on the properties viz. tensile modulus and impact strength of the composites.

The mechanical properties such as tensile modulus, elongation etc. were measured by standard techniques. The various values such as displacement at maximum load, stress at maximum load, stress at auto break, load at maximum load etc. are indicated in the Table III for the two cases of $CaSO_4$-I and II along with the unfilled PP. It is seen from the comparison of these different values that there is a slight decrease of elongation at break for high filler concentration but otherwise it remains more or less same. On the other hand, $CaSO_4$-II is effective in increasing the tensile strength of the composite which also exhibits a significant improvement in the impact strength up to a filler concentration of 10–15 wt% which will be discussed later in the paper.

The variation of tensile modulus with composition of filler is shown in Fig. 5. Curve A corresponds to the

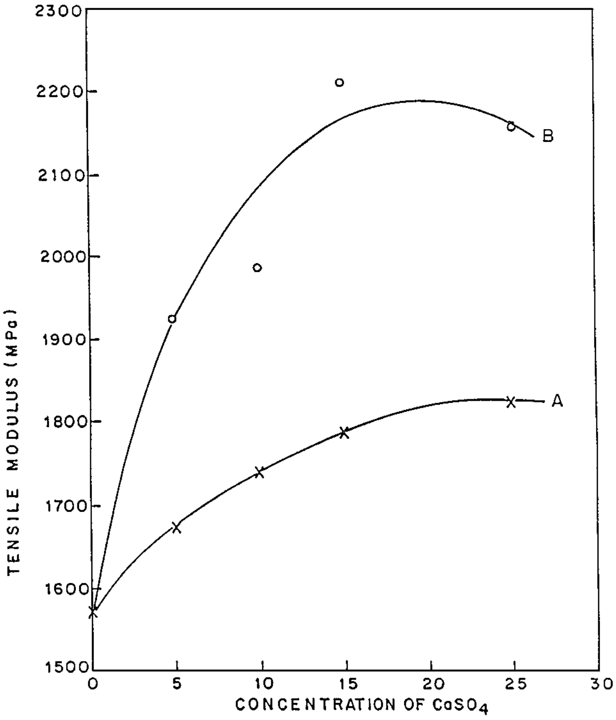

Figure 5 Variation of tensile modulus with filler concentration for both types of $CaSO_4$ added to PP.

TABLE III Mechanical properties of PP/$CaSO_4$ composites

	Pure PP	$CaSO_4$-I				$CaSO_4$-II			
		5%	10%	15%	25%	5%	10%	15%	25%
Displ. at max. load (mm)	4.04	3.04	2.96	2.78	0.14	2.98	2.88	2.56	2.19
% Strain at max. load (%)	8.10	6.13	5.93	5.56	4.61	5.96	5.76	5.14	4.38
Load at max. load (KN)	1.25	1.22	1.18	1.13	1.07	1.17	1.10	1.14	0.98
Stress at max. load (MPa)	31.8	31.1	30.1	29.1	27.4	30.6	28.6	29.4	26.5
% Strain at auto break (%)	13.2	10.3	12.7	11.2	8.13	13.4	15.3	10.6	7.51
Stress at auto break (MPa)	13.8	29.4	27.5	26.7	25.8	27.1	25.7	26.7	24.7
Tensile Modulus (MPa)	1566	1674	1743	1790	1827	1925	1986	2212	2158

tensile modulus of $CaSO_4$-I and curve B for $CaSO_4$ II composites respectively. It is interesting to note that tensile modulus increased to almost 1.5 times for PP/$CaSO_4$-II as compared to pure PP. It increased with increase of filler concentration up to 20 wt% above which it showed a tendency to decrease with the increase of filler loading. On the other hand $CaSO_4$ I had only slight improvement in the tensile modulus as compared to unfilled PP. These various results can be explained on the basis of various factors such as crystalline phase, orientation, filler-matrix interaction and the aspect ratio of filler which govern the tensile strength in thermoplastic polymers [15, 16].

The increase in tensile modulus values for PP/$CaSO_4$ II may be associated to preferential growth of β phase of PP. This is because the type of crystalline phase has an influence on the tensile modulus of the composite. It is well known that the α phase of PP has a monoclinic structure with lattice parameters of $a = 6.66$ Å, $b = 20.78$ Å and $c = 6.49$ Å and $\beta = 99.6^\circ$ while the β phase of PP has a hexagonal structure with lattice parameters of $a = 12.74$ Å and $c = 6.35$ Å. In the latter case, the chains are packed in much closer configuration than the former, which are therefore difficult to displace with respect to each other. Moreover the spherulites in the β phase are smaller and volume filling (see Fig. 3). These have more densely packed crystalline lamellae as compared to α phase which have loose and widely spaced lamellae in their internal morphology. The latter can be discerned from the well defined radial branches seen in the large α type spherulites. It is also reported that the β phase nucleated PP using quinacridone has much higher tensile strength than the normal [13]. Thus the presence of β phase in PP can lead to higher tensile modulus values than the normal PP.

The second factor governing the tensile strength is the orientation of crystallites. It is well known that tensile strength is more if the crystals are more aligned along the main axis as against the transverse direction of the tensile specimen [17, 18]. This has been depicted in Fig. 4 which reveals the needle shaped crystals of the additive are mostly oriented along the long axis for PP/$CaSO_4$-II type composites. These exhibited an increase of tensile modulus value as compared to PP.

The third factor affecting the tensile strength is the interaction between the filler and the matrix. Greater is the strength of bond between the filler and matrix, higher is the tensile strength. In case of PP/$CaSO_4$-I the presence of PEO surrounding the crystallites undergoes deformation easily when the load is applied due to its low T_g and more flexibility than PP [19]. Therefore it prevents the transfer of load from the matrix on to the filler thus making the filler-matrix bond weak and this results in a lowering of tensile strength values as compared to $CaSO_4$-II. On the other hand, in case of PP/$CaSO_4$-II there is good interfacial bonding due to the nucleated PP crystallites around the additive and the tensile load is transmitted from the matrix to crystallites giving rise to an increase of tensile strength values. However, with high filler loading above 25 wt% the tensile strength has a tendency to decrease. This could be due to agglomeration of $CaSO_4$ crystals giving rise to weak points at which there is poor inter-crystallite adhesion.

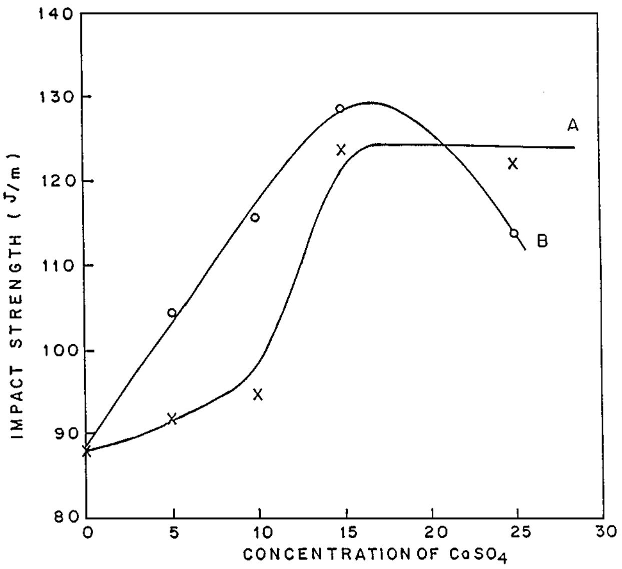

Figure 6 Variation of impact strength with filler concentration for both types of $CaSO_4$ added to PP, A($CaSO_4$-I) and B($CaSO_4$-II).

Lastly, the aspect ratio of crystallites also affects the tensile strength of the composite. Higher aspect ratio of the additive gives good reinforcing effect and hence higher tensile strength. In case of PP/$CaSO_4$-I the slight improvement in the tensile strength as compared to pure PP could be due to this factor. However, this improvement is quite small as compared to other factors mentioned above.

The impact properties of these composites (notched impact values) were measured by the Izod impact tester. Fig. 6 shows the variation of impact strength with the filler concentration ranging from 0 to 25 wt% for both the types of $CaSO_4$ added to PP. The impact strength increases with the filler content up to 15 wt% for both the types of $CaSO_4$ in the composite (120 J/m) as compared to pure PP which shows an impact strength of 85 J/m. It can be seen that the impact strength is much higher for PP/$CaSO_4$-II than for PP/$CaSO_4$-I at low filler concentration while at high filler concentration both the types have same value of impact strength. These results can be explained on the basis of different factors such as the crystallinity of the matrix, crystallite or spherulite size, bonding between the filler and the matrix and also the defects or stress points in the thermoplastic material which affect its impact strength.

Generally in semicrystalline polymers, it has been observed that higher is the crystallinity lower is the impact strength. However, we have been able to achieve high impact strength together with high crystallinity in PP/$CaSO_4$ composites. This is apparent in the Table II which indicates that the β content and the crystallinity to be higher for both the types of PP/$CaSO_4$ systems as compared to pure PP. This rather surprising result can be attributed to the size of the spherulites.

The spherulite size also plays a significant role in governing the value of impact strength. Smaller is the size of spherulites, higher is the impact strength. In the case PP/$CaSO_4$-II where the smaller β phase spherulites are mainly observed, the impact strength is higher while in case of PP/$CaSO_4$-I the presence of PEO surrounding the crystallites inhibits the nucleation and generation of β phase and accordingly the impact strength is lower.

The presence of stress points or defects in the specimen also affects the impact strength and this can take place especially at high filler loading. As the notched specimens were used for impact strength measurements it may be noted that crack propagation rather than crack initiation will be the main deciding factor for impact strength. The presence of defects can give rise to an easy path for crack propagation. From the Fig. 6 it can be seen that the impact strength shows a tendency to decrease at high filler loading greater than 25 wt% especially for $CaSO_4$-II. On the other hand, the impact strength for the PP/$CaSO_4$-I composite may remain more or less constant even at high filler loading greater than 25 wt%. This can be due to the presence of PEO surrounding the crystallites which acts as an effective absorber of the impact force. The PEO content in the composite would be higher at high filler loading and hence its effect is predominantly seen at concentrations >20 wt%. Thus although the impact strength in this case is lower than PP/$CaSO_4$-II due to the presence of large spherulites, the impact strength may remain same at high filler concentration which is could be advantageous for practical applications.

4. Summary and conclusions

The properties viz. tensile modulus and impact strength of PP containing two different types of $CaSO_4$ have been studied. The presence of β crystalline phase for $CaSO_4$ II enhanced the tensile modulus to almost 1.5 times than pure PP. The slight improvement in the tensile modulus values for $CaSO_4$-I could be due to the high aspect ratio of $CaSO_4$ needles. The impact strength increased for both the types than the unfilled PP, with higher impact strength for PP/$CaSO_4$-II than PP/$CaSO_4$ I. At high filler loading greater than 25 wt% the impact strength may remain steady for PP/$CaSO_4$-I due to the presence of PEO which acts as a good energy absorber.

These studies clearly indicate that improved properties of PP composites can be obtained by modifying the structure and morphology of filler using *in situ* technique having high aspect ratio. These can be effectively used for making better particulate filled polypropylene composites.

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Received 6 April 1998
and accepted 28 September 1999