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Control of nanoparticle size of fillers by polymer blend technique

C. Saujanya, Ashamol, S. Padalkar, S. Radhakrishnan*

Polymer Science & Engineering, National Chemical Laboratory, Pune 411008, India

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Abstract

Nanosize particles of calcium phosphate were prepared by a new technique based on matrix mediated control of growth and morphology using polymer blends. The particle size could be reduced down to the order of 10 nm at a certain composition of the blend. These particles were stabilized and could be handled easily due to the polymer matrix surrounding them. Their crystal structure and size was confirmed by X-ray diffraction and electron microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanoparticle; Filler; Calcium phosphate

1. Introduction

The matrix-mediated control of growth and morphology has drawn considerable attention among various groups of researchers since it offers a new route to material synthesis [1–4]. Amongst the various methods which have been established for the synthesis of nanosize particles, the sol–gel technique has been studied extensively [5–7]. However, this method is cumbersome to use and difficult to apply to all types of materials which can range from oxides, ceramics, etc to organic compounds which are desired in nanoparticulate form. Different types of materials such as $CaCO_3$, $CuCl_2$, K_2CO_3, CdS, $CaSO_4$, etc. have been prepared in situ within a polymer matrix such as polyethylene oxide (PEO) which modified or controlled the morphology, crystalline phase, orientation and growth habit of these compounds [8–11]. In the present work, we have exploited this method by using blending technique to prepare nanosize particles of calcium phosphate that gave better control on the particle size. Such nanosize fillers are important in making nanocomposites with thermoplastics and offer exceptionally high gas barrier properties, optical transparency, thermal stability and stiffness [12–16].

2. Experimental

The nanosized calcium phosphate filler particles were synthesized using in situ deposition technique as follows. First, a complex of calcium chloride with polyethylene oxide in desired proportions was prepared in methanol. This complex was then blended by mixing it with amorphous polymer such as polyvinyl acetate (PVAc) solution (dissolved in methanol) after which it was allowed to stabilize over a period of 10 h. The composition of the blend was varied from 20 to 80% PVAc in PEO/PVAc blends. An appropriate stoichiometric amount of trisodium phosphate in distilled water was added to the blended complex slowly without stirring. The whole mixture was allowed to digest at room temperature for 20 h when both the chloride and phosphate ions diffused through the PEO and formed a white gel like precipitate, which was filtered, washed and dried. The crystal structure and particle size were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques in the same manner as reported elsewhere [17,18].

3. Results and discussion

Fig. 1 shows the XRD scans for calcium phosphate synthesized in PEO alone (curves B–F representing increasing level of polymer) and that prepared without any polymer (curve A). The XRD scans were recorded on a Philips (PW 1730) model using CuKα radiation with β-Ni filter ($\lambda = 1.542$ Å) at a scan rate of 4°/min. Amongst the large number of crystalline forms that have been reported for calcium phosphate (in both anhydrous and hydrated states) the material prepared without PEO (curve A) appears to be composed of a mixed phase of calcium orthophosphate dihydrate (major phase) and β-calcium orthophosphate (minor phase). In the presence of PEO, (curves B–F) a

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* Corresponding author.

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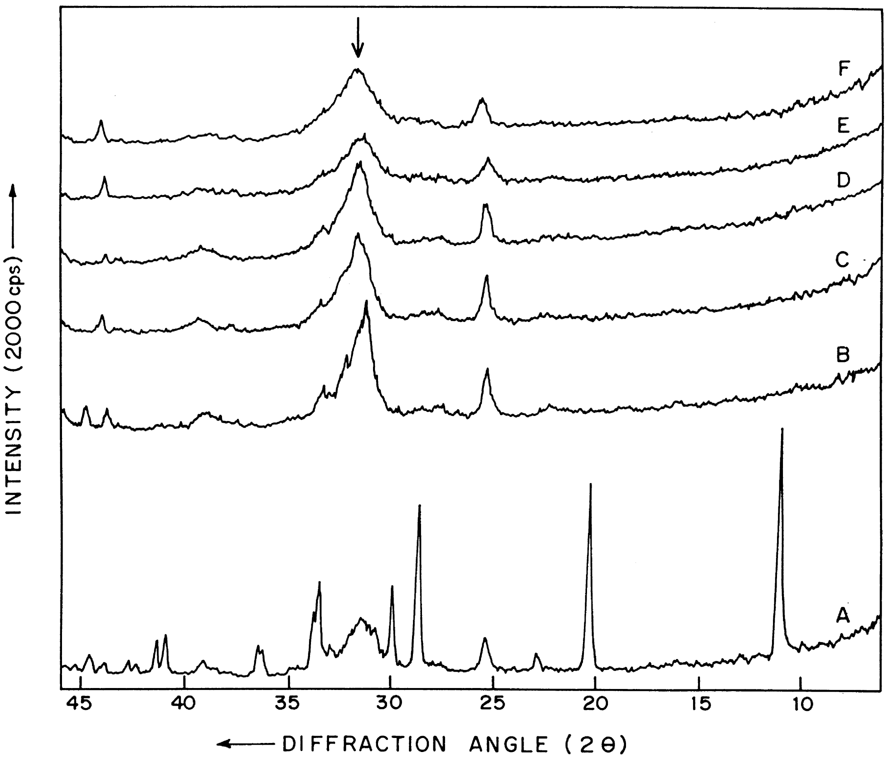

Fig. 1. XRD scans for calcium phosphate synthesized in PEO alone (curves B–F). Representing increasing level of polymer and that prepared without any polymer (curve A).

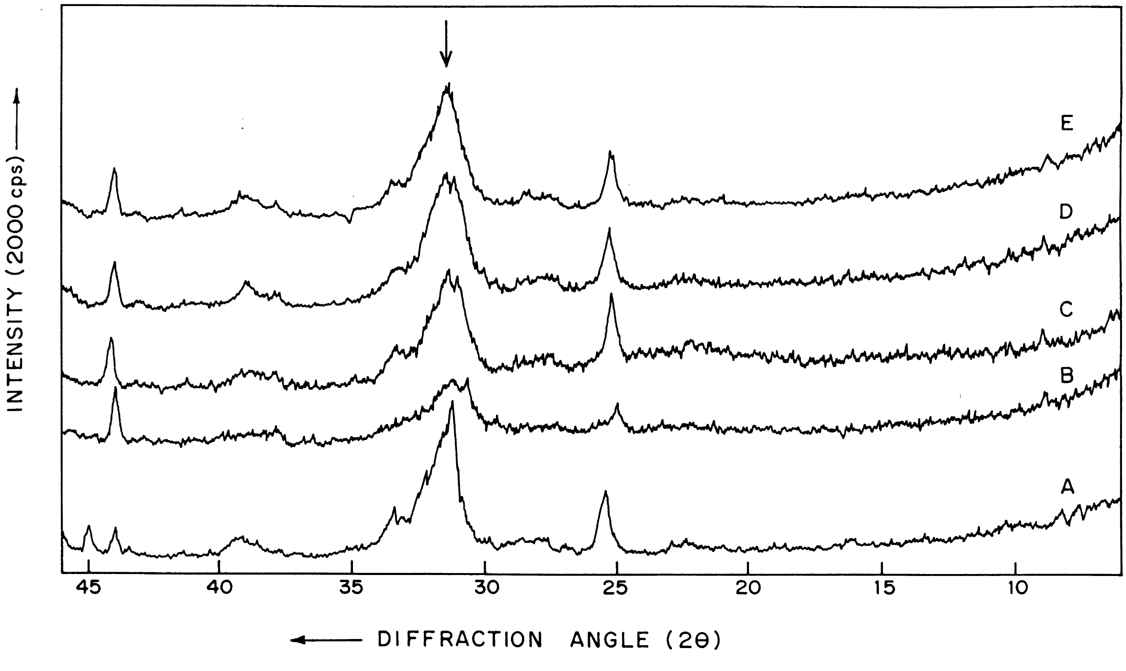

Fig. 2. XRD scans for calcium phosphate synthesized in PEO/PVAc blends. Curve A corresponds to that prepared in PEO only, while curves B–E correspond to PEO/PVAc blend with PVAc concentration of 80, 60, 40 and 20%, respectively.

Table 1
Particle size of calcium phosphate obtained by blend technique

Composition	Crystallite size (L) in nm[a]
PEO (0%)	83
PEO:PVAc (100:0)	12
PEO:PVAc (80:20)	9
PEO:PVAc (60:40)	8
PEO:PVAc (40:60)	8
PEO:PVAc (20:80)	7

[a] Determined from Scherrer's formula.

drastic change in the diffraction patterns is observed with a number of peaks suppressed compared to curve A. The detailed analysis of the various peaks shows the exclusive formation of β-calcium orthophosphate. It is also interesting to note that with the increase of PEO concentration (curves B–F), the XRD peaks broaden suggesting a decrease in the particle size. The strong influence of the polymer matrix on the structure and growth behavior of calcium phosphate crystals is clearly seen in these data. Since calcium chloride is first complexed with PEO, the calcium atoms are strongly held within the polymer chains. The growth of subsequent formation of calcium phosphate crystals is therefore restricted to only certain crystalline phase as compared to large number of phases developed in normal solution precipitation.

The most outstanding feature of the present work can be observed in Fig. 2, which shows the XRD scans for calcium phosphate synthesized in PEO/PVAc blends. Curve A corresponds to that prepared in PEO only while curves B–E represent PEO/PVAc blend with PVAc concentration of 80, 60, 40 and 20%, respectively. The formation of exclusively single phase of β-calcium orthophosphate is seen even in this case. The change in composition of the blend reflected on the peak broadening and hence particle size of the inorganic product formed in the matrix.

The particle/crystallite size was estimated from the full-width at half-maxima of the XRD peak (marked by arrow in Figs. 1 and 2 at $2\theta = 31.5°$) using Scherrer's formula [19,20] and the results are given in Table 1. It can be surmised that the calcium phosphate prepared without any polymer has an average particle size of 83 nm while the presence of PEO causes lowering of the particle size (12 nm). This gets further reduced to few nanometers level in the case of blends. This reduction in size can be as low as 7 nm. This is because the PEO/$CaCl_2$ is immiscible with PVAc and as composition becomes PVAc rich, the domain size of the dispersed phase (PEO complex) is very small. The calcium phosphate formation during subsequent reaction is then restricted within such domains leading to drastic reduction in their particle size.

Fig. 3a shows the TEM micrograph of calcium phosphate crystals in PEO/PVAc (60/40) blend and Fig.3b represents the selected area electron diffraction pattern recorded at an accelerated voltage of 100 kV. The sample shows an average particle size of less than 10 nm. Higher magnifications were attempted but the images were unstable and diffused due to the damage of the polymer matrix caused by high accelerated electron beam voltage impinging on the same. The detailed analysis of selected area diffraction results reveals β-calcium orthophosphate having monoclinic crystalline structure, which is in good agreement with the structure obtained from the XRD data. There is some aggregation of the particles seen which can be during the precipitation process when the polymer itself forms agglomerates otherwise the particles are well dispersed. These results are consistent with the result described above for XRD data.

4. Conclusions

The present work demonstrates that nanoparticles of calcium phosphate can be synthesized by a novel route using the blend technique. This method is quite different from that currently used by few groups working on polymer

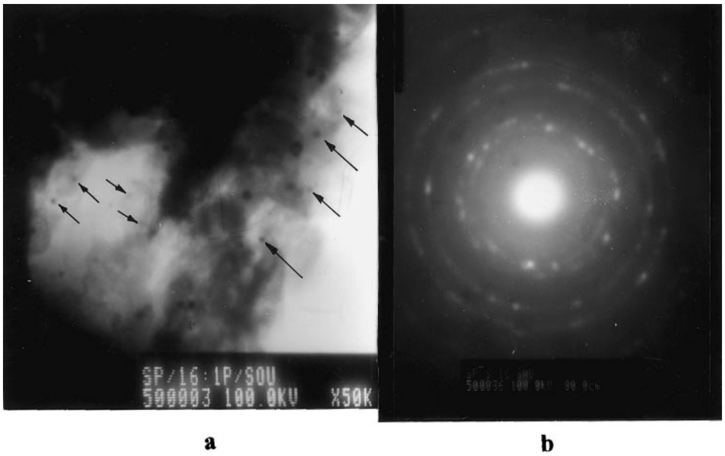

Fig. 3. (a) TEM micrograph of calcium phosphate crystals in PEO/PVAc (60/40) blend (the arrows indicate the particles). (b) The selected area electron diffraction pattern recorded at an accelerated voltage of 100 kV.

nanocomposites wherein exfoliation of clay particles during polymerization is used for reduction of the particle size. In the present case the particle size, shape, crystalline phase and the dispersion is stabilized and controlled by using polymer blends as growth media. It is also much simpler than the conventional sol–gel technique used for inorganic materials in which first the metal ions are entrapped/reacted with gel forming siloxane and then further treated so as to form nanoparticles. The present technique can provide a simple method for generation of particles of other inorganic fillers as well, which may be useful in nanocomposites. The application of these particles in forming thermoplastic nanocomposites is an important area of research. Further studies in this direction are being carried out which will be published soon in the near future.

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