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Facile synthesis of hydroxyapatite (HA)-polymethylmethacrylate (PMMA) nanocomposites by a novel ex-situ polymerization method: morphology, thermal stability and formation mechanism of HA particles in nanocomposite

T.P. Gamagedara, H.M.N. Bandara and R.M.G. Rajapakse*

Postgraduate Institute of Science, University of Peradeniya, Sri Lanka,
Department of Chemistry, Faculty of Science, University of Peradeniya, Sri Lanka
**rmgr@pdn.ac.lk*

Demand for bone grafts in the global surgical market is very high due to frequent occurrence of bone defects either from traumatic or from non-traumatic destruction. Since bone is a typical example of a nanocomposite, designing a bone graft in the form of a nanocomposite can be advantageous over monolithic or microcomposite materials. Mainly due to the lack of clinical data supporting long-term performance and the prevalence of complex methodologies, the use of nanocomposites in bone grafting is very much less than expected. Therefore, in this study, clinically well-known substances, such as HA nanoparticles and methyl methacrylate (MMA) were used to synthesize HA-PMMA nanocomposites by a novel ex-situ polymerization method.

Nanosized HA spherical particles (~17 nm) were dispersed in PMMA matrix while PMMA was synthesized using its monomer (MMA) with the presence of $K_2S_2O_8$ initiator at 80 ^oC. The nanocomposite was characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Thermo-gravimetric analysis (TGA) and Differential scanning calorimetric (DSC) analysis.

Particle size of HA was calculated using the XRD pattern, applying Debye-Scherer formulae, giving the dimensions of the HA crystals to be 43 nm and 158 nm in the nanocomposite. According to the SEM images and obtained dimensions in the XRD patterns, spherical HA nanoparticles may self-assemble in the PMMA matrix to plate shaped particles. Initially, MMA may have strong interactions with spherical HA nanoparticles in the 'a' axis direction as 'c' axis direction ((001) surface) is considered as the non-dipolar surface of HA. Upon polymerization of MMA, HA nanoparticles may get closer in the 'a' axis direction and strong interactions with MMA may be released as radical polymerization is more favourable, so that allowing self-assemble into plate shape structures. TGA and DSC analysis shows that thermal stability enhanced in the HA-PMMA nanocomposite when compared with PMMA alone, showing existence of some strong interactions between HA nanoparticles and the PMMA matrix. Therefore, enhanced mechanical properties can be expected in the synthesized nanocomposite.

Thus, in the novel one pot synthetic route, HA-PMMA nanocomposite, with a higher thermal stability can be obtained, which can be used as a bone grafting material.

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