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Synthesis of a hydroxyapatite/poly(methyl methacrylate) nanocomposite using dolomite

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Hydroxyapatite/poly(methyl methacrylate) (HA–PMMA) nanocomposites are extensively used in biomedical fields. Therefore, the design and development of low-cost and industrially viable novel methods are essential to synthesize HA–PMMA nanoparticles. In this letter, we report such an economical, simple and industrially applicable novel method to synthesize nanosized HA–PMMA composite particles using extensively distributed dolomite.

Hydroxyapatite [HA, Ca₁₀(PO₄)₆(OH)₂], also known as a bio-ceramic, is the major component of human bones and teeth (hard tissues) and is chemically compatible with synthetic HA nanoparticles.¹ Hence, synthetic HA nanoparticles are extensively employed in biomedical fields due to their excellent biocompatibility.^{2,3} In the preparation of artificial bones or bone cement, it is important to maintain the mechanical properties of the materials in order to mimic natural bones.⁴ However, HA alone cannot perform all the requirements of clinical applications due to the brittleness and stiffness of HA nanoparticles.^{5,6} Therefore, many researchers have developed HA/polymer nanocomposites to enhance the bioactive properties and mechanical properties of the artificial bone or bone cement. Poly(methyl methacrylate) (PMMA) has become one of the attractive and frequently used polymers in the synthesis of bone cements. Poly(methyl methacrylate) (PMMA) is the first synthetic polymer used in biomedical applications in 1937.^{7–9} HA can be combined with PMMA in order to synthesize HA/PMMA nanocomposites. When PMMA is associated with HA, it increases the biocompatibility, osteoconductivity, and mechanical properties of the nanocomposites. Therefore, PMMA–HA nanocomposites have good ability to fill dental cavities and also to generate a strong bond between the bone and the prosthesis.^{10,11} Numerous methods have been developed to synthesize HA–PMMA composites.^{10–12} For instance, Teodora *et al.* (2009) described the biocompatibility of HA–PMMA composites which

indicates the better cell adhesion on the synthesized HA–PMMA composites.¹³ Andrei *et al.* (2016) synthesized HA–PMMA composites for application in dentistry with a better biocompatibility¹⁴ and Nieto *et al.* (2012) used the HA–PMMA composite as a coating material for polythene substrates for use in biomedical applications while increasing mechanical properties.¹⁵ Therefore, HA–PMMA composites can be used in different biomedical applications such as bone filler materials, bone cements, bone implants and dental implants. However, simplicity and economic factors are timely needed requirements for the industrial scale manufacture of HA–PMMA. Therefore, in this manuscript, we report a novel, economical and potential industrially applicable method to synthesize HA–PMMA composites using readily available and extensively distributed dolomite as a calcium source. This method is industrially important due to the usage of readily available cheap naturally occurring dolomite as a raw material rather than using expensive chemicals and due to the involvement of a one pot *in situ* synthesis route.^{16,17}

Herein, sucrose, potassium persulphate (K₂S₂O₈), ammonium dihydrogen orthophosphate ((NH₄)H₂PO₄) and methyl methacrylate (MMA) were purchased from Sigma-Aldrich to use as raw materials for the synthesis. First, a calcium sucrate solution was prepared by adding 5.00 g of calcined dolomite (CaO·MgO) into 0.5 M sucrose (100 mL) while stirring and by continuing the stirring for 6 h. The mixture was filtered under suction and the solution was collected.¹⁸ Then, 1.00 g of potassium persulfate was dissolved in 100 mL of 0.5 M prepared calcium sucrate solution in a three-neck rounded bottom flask and heated to 80 °C. 10 mL of freshly distilled MMA and 100 mL of 0.3 M ammonium dihydrogen orthophosphate were added (until Ca/P ratio of 1.67) to the reaction mixture using two dropping funnels while stirring. The mixture was further stirred for 12 h and filtered under suction to obtain a precipitate. The precipitate was washed with distilled water 3 times and allowed to dry under ambient conditions. The yield of the obtained HA was 84%.

X-ray diffraction (XRD) patterns of the synthesized products were obtained using a Siemens D5000 powder diffractometer. Fourier Transform Infrared (FT-IR) spectra of the products were

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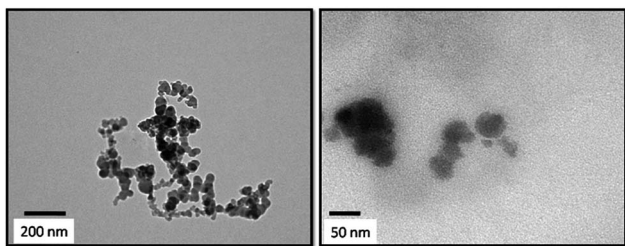


Fig. 3 TEM images of the HA-PMMA composite at two different magnifications.

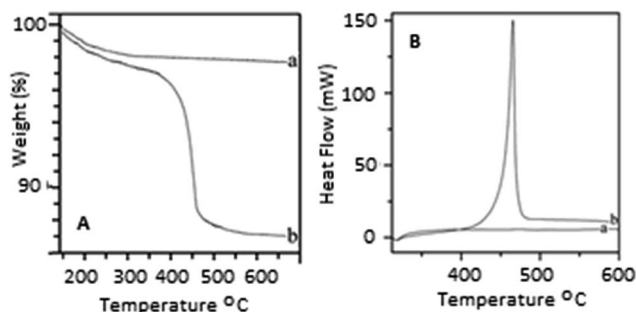


Fig. 4 [A] TGA curves of (a) HA and (b) the PMMA-HA nanocomposite [B] DSC curves of (a) HA and (b) the PMMA-HA nanocomposite.

PMMA (Fig. 4) shows a mass loss which reveals the combustion of PMMA. The DSC exothermic peak further confirms the presence of PMMA in the composite. Similarly, CaCO_3 -PMMA nanocomposites have been synthesized and characterized by Mantilaka *et al.* 2013 and the PMMA decomposition range in CaCO_3 -PMMA was 435–453 °C in their study.¹⁸ This indicates the increment of thermal properties of PMMA during the formation of PMMA composites. Also, several studies have been carried out to demonstrate the increment of decomposition temperature with the formation of PMMA composites.^{11,25,26}

Conclusions

A nanosized HA-PMMA composite was prepared by a novel, simple and industrially applicable method using dolomite. The synthesized HA-PMMA nanocomposite was 30 nm in size and had a spherical morphology with 84% yield.

Conflicts of interest

There are no conflicts of interest.

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Notes and references

1 Y. Tseng, C. Kuo, Y. Li and C. Huang, *Mater. Sci. Eng., C*, 2009, **29**, 819.

- 2 Y. Han, S. Li, X. Wang, I. Bauer and M. Yin, *Ultrason. Sonochem.*, 2007, **14**, 286.
- 3 B. Cengiz, Y. Gokce, N. Yildiz, Z. Aktas and A. Calimli, *Colloids Surf., A*, 2008, **322**, 29.
- 4 K. E. Tanner, *Proc. Inst. Mech. Eng., Part H*, 2010, **224**, 1359.
- 5 Z. Dong, Y. Li and Q. Zou, *Appl. Surf. Sci.*, 2009, **255**, 6087.
- 6 Y. Fujishiro, H. Yabuki, K. Kawamura, T. Sato and A. Okuwaki, *J. Chem. Technol. Biotechnol.*, 1993, **57**, 349.
- 7 R. Murugan and S. Ramakrishna, *Compos. Sci. Technol.*, 2005, **65**, 2385.
- 8 M. K. Singh, P. A. Marques, A. C. Sousa, J. Gracio, V. Silva, P. Goncalves and S. Olhero, *Int. J. Nano Biomater.*, 2009, **2**, 442.
- 9 D. Gnanasekaran, K. Madhavan and B. S. R. Reddy, *J. Sci. Ind. Res.*, 2009, **68**, 437.
- 10 A. S. Hamizah, M. Mariatti, R. Othman, M. Kawashita and A. R. N. Hayati, *J. Appl. Polym. Sci.*, 2012, **125**, 661.
- 11 Y. Wang, Y. Xiao, X. Huang and M. Lang, *J. Colloid Interface Sci.*, 2011, **360**, 415.
- 12 S. Zebarjad, S. Sajjadi, T. Sdrabadi, S. Sajjadi, A. Yaghmaei and B. Naderi, *Engineering*, 2011, **3**, 795.
- 13 T. G. Tihan, M. D. Ionita, R. G. Popescu and D. Iordachescu, *Mater. Chem. Phys.*, 2009, **118**, 165.
- 14 A. T. Cucuruza, E. Andronescu, A. Ficai, A. Ilie and F. Iordache, *Int. J. Pharm.*, 2016, **510**, 516.
- 15 V. M. Nieto, C. H. Navarroya, K. J. Moreno, A. A. Morquecho, A. C. Valdez, S. G. Miranda and J. F. L. Hernández, *Prog. Org. Coat.*, 2013, **76**, 204.
- 16 Y. R. Somarathna, M. M. M. G. P. G. Mantilaka, D. G. G. P. Karunaratne, R. M. G. Rajapakse, H. M. T. G. A. Pitawala and K. G. U. Wijayantha, *Cryst. Res. Technol.*, 2016, **51**, 207.
- 17 M. M. M. G. P. G. Mantilaka, W. P. S. L. Wijesinghe, H. M. T. G. A. Pitawala, R. M. G. Rajapakse and D. G. G. P. Karunaratne, *J. Natl. Sci. Found. Sri Lanka*, 2014, **42**, 221.
- 18 M. M. M. G. P. G. Mantilaka, D. G. G. P. Karunaratne, R. M. G. Rajapakse and H. M. T. G. A. Pitawala, *Powder Technol.*, 2013, **235**, 628.
- 19 W. P. S. L. Wijesinghe, M. M. M. G. P. G. Mantilaka, E. V. A. Premalal, H. M. T. U. Herath, S. Mahalingam, M. Edirisinghe, R. P. V. J. Rajapakse and R. M. G. Rajapakse, *Mater. Sci. Eng., C*, 2014, **42**, 83.
- 20 C. H. Navarro, K. J. Moreno, A. C. Valdez, F. L. Hernández, J. S. G. Miranda, R. Lesso and A. A. Morquecho, *Wear*, 2012, **282**, 76.
- 21 A. Angelopoulou, E. K. Efthimiadou, N. Boukos and G. Kordas, *Colloids Surf., B*, 2014, **117**, 322.
- 22 S. Koutsopoulou, *Inc. J. Biomed Mater Res*, 2002, **62**, 600.
- 23 C. A. Zamperini, R. S. André, V. M. Longo, E. G. Mima, C. E. Vergani, A. L. Machado, J. A. Varela and E. Longo, *J. Nanomater.*, 2013, 174398.
- 24 K. J. Thomas, M. Sheeba, V. P. N. Nampoori, C. P. G. Vallabhan and P. Radhakrishnan, *J. Opt. A: Pure Appl. Opt.*, 2008, **10**, 055303.
- 25 A. Singhal, A. Dubey, Y. K. Bhardwaj, D. Jain, S. Choudhury and A. K. Tyagi, *RSC Adv.*, 2013, **3**, 20913.
- 26 N. W. Elshereksi, S. H. Mohamed, A. Arifin and Z. A. M. Ishak, *J. Phys. Sci.*, 2014, **25**, 15.

