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Synthesis and study of thermal, mechanical and biodegradation properties of chitosan-g-PMMA with chicken egg shell (nano-CaO) as a novel bio-filler

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ABSTRACT

The important objective of this study is to evaluate the effect of chicken eggshell (nano-Cao) as a functionalized bio-filler on the mechanical strength and thermal stability of acrylic based bionanocomposite of chitosan grafted with poly(methyl methacrylate)(PMMA). The chitosan grafted PMMA adsorbed with functionalized biofiller was prepared via emulsion polymerisation technique and physicochemically characterized as bone graft substitute. The so prepared grafted bioactive bone cement (BBC) bionanocomposite (BNC), chitosan-g-PMMA/nano-CaO was characterized by FTIR, XRD, FESEM and TGA. The water uptake, retention ability, their biodegradability and the nanosize particle arrangement in the polymeric BBC-BNCs were undertaken. These preliminary investigations of the BNCs will open the door for their use in bioadhesive bone cement implants in future.

1. Introduction

The effectiveness of the chicken eggshell (ES) biowaste is strongly encouraged in our society for green environmental and economic reasons. Most ES waste are discarded in landfills without further processing. The valuable organic and inorganic components in it are utilized in commercial products by designing new value in these waste materials. This study reflects a useful bio-filler derived from ES waste and its potential role in the coating industry [1–3]. ES contains about 95% calcium carbonate in the form of calcite and 5% organic materials such as collagen, sulfated polysaccharides, and other proteins [4–6]. The chemical composition and availability makes ES a potential source of filler for polymer composites. Better attention has been given to the study of bio-filler reinforced bio-polymer composites [7]. Therefore, there is a pressing need for more reliable and abundant bone substitutes to replace or repair bone filling the defect with either PMMA or bio-absorbable bone graft substitutes - ceramics - in cement defects in clinics. PMMA individually has not gained wide acceptance when used for fracture treatment in the extremities because of its inability to remodel and possible inhibition of fracture healing [8]. Among other bone cement materials, PMMA or its derivatives has been used successfully in orthopedic surgeries. PMMA was first introduced as bone cement in the early 1960s by Charnley and Smith [9]. PMMA conforms to the shape of its surroundings, allows even distribution of implant loads, and forms a strong mechanical bond with implants. However, its widespread use is limited by several complications. For example, PMMA adheres insufficiently to bone surfaces (no bioactivity) [10]. It is weaker than cortical bone [11]. It has a high exothermic reaction temperature [12,13]. It exhibits the monomer toxicity [14]. To address the concerns regarding PMMA and modified PMMA several investigations of different BBCs have been conducted [15] by adding hydroxyapatite (HA) powder. Other researchers have added bone particles and growth hormones to PMMA cement [16,17]. Another potential additive is chitosan which is biodegradable, soluble in organic acid solutions and resistant to alkali environments. Chitosan is a co-polymer of glucosamine and N-acetylglucosamine deacetylated from the natural polymer chitin. Chitosan also has a high resistance to heat due to its intramolecular hydrogen bonds [18]. Chitosan based PMMA composite exhibits biological properties such as biodegradability, biocompatibility, immunological and antibacterial activities. Although improvements have been realized, many fundamental problems with PMMA remain unresolved. Polymer with layered CaO represents a new class of high performance material and is of great academic and industrial interest [19]. Nano-CaO is one of the most common spherical nanoscale filler used in preparation of nano composites [20,21]. Exfoliated structures, however, formed because of extensive penetration of polymer into the CaO resolution in the determination of the CaO layers, and therefore, a loss of the ordered structure. The purpose of this study was to develop novel BBC, from nano-CaO of egg shell and chitosan, for use in orthopedic surgeries such as a bone filler. The addition of nano-CaO of egg shell to a BBC is an innovative study that has not yet been reported in the literature.

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2. Materials and methods

2.1. Materials

The deacetylated chitosan and the initiator, ammonium persulfate, were purchased from HIMEDIA, Mumbai, India. MMA was purchased from SRL India Ltd., The egg shells were collected from a breakfast shop on the university campus and washed with demineralised water for 3 times and then oven dried at 120 °C for 2 h. The filler nano-CaO of egg shell was prepared in the laboratory as follows:

2.1.1. Preparation of nano-CaO

The clean and dry egg shells were dried in oven once again over 24 h at 120 °C. Then the dried egg shells were crushed and grinded in a mechanical attritor. The egg shell powder was reduced by adding 10% o-phosphoric acid and then the sample was heated in a furnace at a temperature of 900 °C for 8 h. Upon cooling, the sample was stored in a desiccator. The $CaCO_3$ at about 900 °C was completely decomposed and turned to nano-CaO [22].

2.2. Deacetylation of chitosan

To increase the amine content of chitosan, chitosan with 76% of deacetylation degree was further deacetylated according to the modified procedure to increase the deacetylation degree above 90%. Degree of deacetylation or $\%NH_2$ group is determined by potentiometric titration method as per the report [23,24,25] described below. An accurate excess of hydrogen chloride is added to a known amount of chitosan and the remaining amount of hydrogen chloride is back titrated with a sodium hydroxide solution. The resultant titration curve shows two equivalence points: the first one corresponds to the excess hydrogen chloride, while the second corresponds to the protonated chitosans. Thus, the difference between them would correspond to the free deacetylated amino groups. A titration curve of pH vs. NaOH titration volume was generated. The curve's inflection points were found for each indicated transition. The volume of NaOH at the each inflection point was applied to the equation. The polymers deacetylation is calculated using Eq. (1).

Degree of deacetylation (DA) or NH2% = 16.1 (y − x) f/w. Chitosan (0.5 g) was dissolved in 20 mL of 0.3 N hydrochloric acid. After adding 400 mL of distilled water, this solution was titrated with a 1 N NaOH solution. A titration curve of pH vs. NaOH titration volume was generated. The inflection points of the curve were found for each indicated transition. The volume of NaOH at the each inflection point was applied to the equation: NH2% = 16.1 × (y − x)/M [26,27,28]. Degree of deacetylation (DA) = 16.1 (y − x) f/w. 1 N NaOH = 1 M NaOH = f = 1, W = M means weight of chitosan (hence disappearance of f = 1 does not affect the equation). Degree of deacetylation (DA) or NH2% = 16.1 (y − x) f/w = 16.1(y − x) × 1/w = 16.1 (y − x) f/w = 16.1(y − x)/w = 16.1 × (y − x)/M. NH2% = 16.1 × (y − x)/M. where: y, higher inflection point (mL); x, lower inflection point (mL); f, molarity of the NaOH solution (mol/L); m, chitosan weight (g); 16.1:NH_2 content(g) in 1 L of 0.1 M HCl.

2.3. Preparation of chitosan-g-PMMA graft copolymer and chitosan-g-PMMA/nano-CaO BNC

To make the grafted copolymer i.e. chitosan-g-PMMA (BBC1): chitosan (0.25 g), monomer (MMA), initiator (APS) along with complex $CuSO_4$ and glycine (1:1) and surfactant sorbitol (0.05 g) were added sequentially to the reaction vessel under N_2 atmosphere. Then a different set of nano-CaO based graft composite samples were prepared, taking the same quantity of monomer MMA and chitosan in the reaction vessels followed by addition of nano-CaO (BBC2 = 0.10%, BBC3 = 0.20%, BBC4 = 0.35%, BBC5 = 0.75% and BBC6 = 0.90%) to each vessel as shown in Table 1. The mixtures were stirred overnight around 14 h for complete insertion of monomer into the chitosan at 25 °C. Under N_2 atmosphere desired quantity of initiator APS, complex $CuSO_4$ and glycine (1:1) along with the surfactant were added at 55 °C. Then the reaction was continued with stirring for 3 h and then ceased by quenching the vessel in ice water. The graft copolymer was washed thrice in distilled water followed by Soxhelet extraction using acetone as solvent to remove the homopolymer PMMA until a constant weight was obtained for the graft copolymer and the additive based graft nanocomposite was washed with hot water and acetone thrice and were oven dried at 70 °C for 3 h and kept in the desiccator for 1 h to make moisture free and then weighed. The material so prepared was shown in the Scheme 1.

2.4. Calculation of grafting parameters

Yield of grafting (%) = [(wt. of graft copolymer − wt. of chitosan)/wt. of chitosan] × 100.

2.5. Characterization

The PMMA grafted chitosan samples and nano-CaO based bionanocomposites BBCs were characterized by XRD, FTIR, FESEM and TGA. The insertion of PMMA into the chitosan was confirmed by using an XRD monitoring diffraction angle 2θ from 10° to 90° on a Philips PW-1847 X-ray crystallographic unit equipped with a Guinier focusing camera with CuKα radiation (λ = 0.15059 nm) with a 0.02 2θ step size and a 2-s count time. Nanoscale structure of grafted samples was investigated by means of a FESEM accelerating voltage of 5.00 kV. The ultrathin section (the edge of the sample sheet perpendicular to the compression mold) with a thickness of 1 μm and 200 nm was microtomed at −80 °C on Zeiss Mevlin SEM Instrument (FESEM). Thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 600 °C at a heating rate of 10 °C/min. The IR spectra of samples, in the form of KBr pellets, were recorded with a Perkin–Elmer model Paragon-500 FTIR spectrophotometer.

2.6. Properties

2.6.1. Testing of mechanical properties

The prepared BBCs were pressed between two glass plates for 1 h. After the cement had hardened, it was pulled out of the plates and stored at room temperature. The specimens for the tensile tests were prepared of (75 × 5 × 3) mm dimension [29].

Table 1
Variation of reacting components and the percentage (%) of grafting.

Sample code	Chitosan gm	[MMA] mol/dm^3	[APS] mol/dm^3	[$CuSO_4$] $\times 10^{-3}$ mol/dm^3	[Glycine] $\times 10^{-3}$ mol/dm^3	Sorbitol, gm	nano-CaO	% of grafting
BBC1	0.25	0.093	0.01	6.0	6.0	0.05	–	89.6
BBC2	0.25	0.031	0.01	6.0	6.0	0.05	0.10	–
BBC3	0.25	0.062	0.01	6.0	6.0	0.05	0.20	–
BBC4	0.25	0.093	0.01	6.0	6.0	0.05	0.35	–
BBC5	0.25	0.124	0.01	6.0	6.0	0.05	0.75	–
BBC6	0.25	0.155	0.01	6.0	6.0	0.05	0.90	–