

Investigation of Silane Coupling Agent on The Performance Properties of Biocomposite Hydrogels

D. S. Franklin¹ and S. Guhanathan^{2*}

¹Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli-627 012, Tamilnadu, India

¹Department of Chemistry, C. Abdul Hakeem College of Engineering and Technology, Melvisharam-632 509, Tamilnadu, India, E-mail: loyolafrank@yahoo.co.in

^{2*}PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore-632 002, Tamilnadu, India

Corresponding author E-mail: sai_gugan@yahoo.com, Telephone: +91 9894053917

Abstract— Ethylene glycol (EG) based citric acid (CA) and acrylic acid (AA) containing pH sensitive biopolymeric hydrogels were synthesized using solvent free green approach. Incorporation of hydroxyapatite (HA) prepared from waste egg shells with ACE resulted biocomposite (ACE-HA). Synthesized biocomposite hydrogel was subjected various characterization viz., spectral, thermal and morphological. Further, HA was surface treated with two different silane based coupling agents, namely 3-aminopropyltrimethoxy silane (AMS) and vinyl triethoxysilane (VES) on performance properties of biocomposite hydrogels. The outcomes of the studies reveal that VES treated ACE-HA found to possess superior properties than AMS and untreated ACE-HA on overall properties of biocomposite hydrogels.

Key words: Ethylene glycol; citric acid; hydrogel; biocomposite; coupling agent

I. INTRODUCTION

Hydroxyapatite (HA) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, the inorganic constituent of bone and hard tissues is one of the most widely used biomaterials for reconstruction of the skeleton. The disposal of waste egg shells found to deliver a greater environmental task. To overcome such setbacks, the utilization of egg shells by recycling into a valuable product [1]. The combination of hydroxyapatite with smart polymeric architectures seems to be a promising route to the design of biomaterials. Compared with artificial method of synthesizing HA, obtained from natural sources like waste eggshells many advantageous feature as a filler in polymer matrix. They are low in cost, environmentally friendly, renewable, biodegradable and available in large quantities. Polymers with hydroxyapatite has long been an interesting theme of research and industrial applications as the incorporation of hydroxyapatite can reduce production cost and improve the performance of material. Hydrogels are a class of polymers that can imbibe water, biological fluids and swell several times as their volume based on several environmental conditions [2]. Such environment sensitive hydrogels were also called “smart” or “intelligent hydrogels”.

Citric acid (CA) is a renewable resource, mainly manufactured for fermentation of carbohydrate viz., starch or glucose. CA was chosen as a poly functional monomer because of its nutritionally harmless by nature. Since, it is a nontoxic, readily available and cost effective monomer. Ethylene glycol (EG) was chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility. Acrylic acid (AA) was also used to synthesis pH sensitive hydrogels and also AA interactions utilize strong influence along the swelling behavior of hydrogels and there is a great potential for their application in pharmaceutical formulations, particularly in drug delivery systems [3]. Lin et al. [4] contributed biocomposite hydrogel from Poly (ethylene glycol) and hydroxyapatite for the controlled drug delivery applications. Improved performance behavior of polymer composites by the addition of silane based coupling agents [5]. Silane are a group of organo-functional compounds that has the ability to react chemically to promote adhesion between polymer and hydroxyapatite.

Based on careful analysis of literature, the present investigation is being concentrated on the synthesis of new type of biocomposite hydrogels. The structure, thermal stability and morphologies of synthesized biocomposite hydrogels were identified by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction studies (XRD), thermal studies (TGA, DTG) and the scanning electron microscopy (SEM). Furthermore, the effect of silane based coupling agent on their performance of biocomposite hydrogels have also been investigated.

II. EXPERIMENTAL

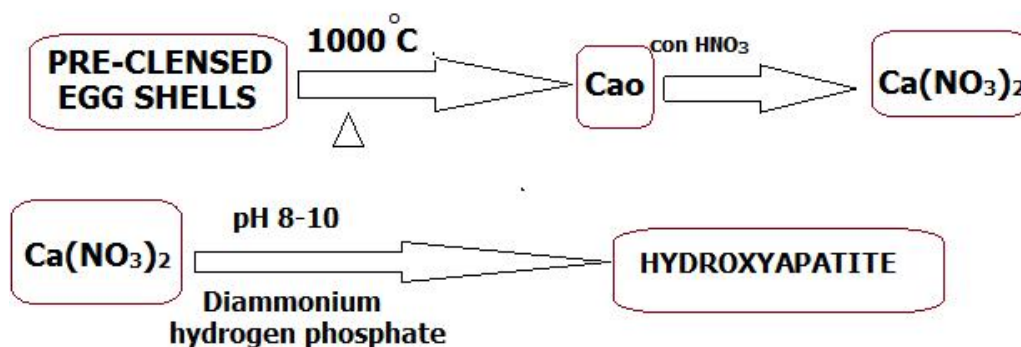
Materials and Physio-chemical characterisation

The monomer anhydrous citric acid (CA), acrylic acid (AA) were purchased from Sigma Aldrich Chemical Company (Bangalore, India). Prior to use, AA was vacuum distilled at 54°C/ 25 mm Hg to remove the inhibitor hydroquinone. Ethylene glycol (EG) was purchased from Merck (India). Waste egg shells were collected domestically. Demineralized water was used for the preparation of the buffer solutions. 3-Aminopropyltrimethoxysilane (AMS), and Vinyl triethoxysilane (VES) were received from Sigma-Aldrich (St. Louis, MO). Methanol from Merck (India) was also employed in this investigation.

FT-IR spectra of composites and hydrogels were recorded on a FTIR-8400 S, Shimadzu spectrophotometer in KBr medium at room temperature in the region of 4000-500 cm^{-1} . SEM was performed on dried biocomposite hydrogel samples were carried out using Hitachi, Model: S-3400. The samples were mounted on the base plate and gold-sputter coated to render them electrically conductive, the scanning was synchronized with a microscopic beam to maintain the small size over a large distance relative to the specimen. Thermo gravimetric Analysis (TGA) and DTG using a Perkin Elmer (Diamond) with simultaneous (TA Instruments) were used to characterize the thermal properties of the different polymeric biocomposite hydrogels. Both TGA and DTG curves were recorded in the temperature range from ambient to 500°C at a heating rate of 10°C min^{-1} , under N_2 atmosphere.

Preparation of hydroxyapatite from waste egg shells

Hydroxyapatite used in the present investigation were summarized in the scheme 1.



Scheme 1: Conversion of waste egg shells to hydroxyapatite

Surface treatment of HA

1% solution of the silane coupling agent solution (AMS and VES) was prepared using methanol. 10 ml of 1% solution was added to 0.2 g of dried hydroxyapatite in a closed container with constant stirring for an hour. The surface treated HA was subjected to evaporation to dryness at room temperature for 24 h to complete removal of methanol. The resultant compounds were named as HA-AMS and HA-VES respectively.

Synthesis of ACE-HA, ACE-HA-AMS and ACE-HA-VES biocomposite hydrogels

The hydrogels (ACE) was synthesized according to our previous contribution [3]. Briefly, the citric acid (0.025 mol) dissolved in 1% solution of hydrochloric acid was taken in a round bottomed flask fitted with a mechanical stirrer and nitrogen inlet. Ethylene glycol (0.025 mol) was added drop wise using a dropping funnel. The content was stirred for 1 h at 140 °C in a nitrogen atmosphere. The completion of the reaction was noticed by the formation of a white colored sticky gel-like compound (CE). Acrylic acid (0.025 mol) was added to prepolymer CE at 140 °C with constant stirring for 2 h in the nitrogen atmosphere. The formation of glassy gel (ACE) implies the completion of the reaction. Subsequently, 0.2 g of each HA and surface treated HA were added to a separate reaction vessel which contain biopolymeric hydrogel (ACE) resulted biocomposite hydrogels ACE-HA, ACE-HA-AMS and ACE-HA-VES respectively.

III. RESULTS AND DISCUSSION

FT-IR Spectral studies of biocomposite hydrogels

The FT-IR spectra of hydroxyapatite prepared from egg shells has been demonstrated in Fig. 1(a) The strong absorption band observed at 1085.92, 1018.41 cm^{-1} and 833.25, 570.93 cm^{-1} corresponds to stretching and bending vibration of phosphate groups in hydroxyapatite respectively. The broad band at 2900-3700 cm^{-1} was

assigned to OH stretching. The observed absorption bands at 1099, 952, 839, 563 cm^{-1} ascribed to the phosphate group in HA while the stretching band approximately between 2900-3700 cm^{-1} . The sharp and separated peaks 602 and 566 cm^{-1} were attributed to the bending of group of HA. This clearly shows the formation of hydroxyapatite from egg shells. The FT-IR spectra of the synthesized biocomposite hydrogel (ACE-HA) was recorded in Fig. 1(b), a strong absorption band at 1713.68 cm^{-1} , which is a characteristic absorptions of C=O stretching vibration and C-O stretching was observed at 1117.61 cm^{-1} of ester groups indicating formation of polyesters. The spectra clearly marked, broad stretching at 3442.09 cm^{-1} suggested the presence of hydrogen-bonded hydroxyl group. The peaks centered at around 2926.01, 2860.43 cm^{-1} .

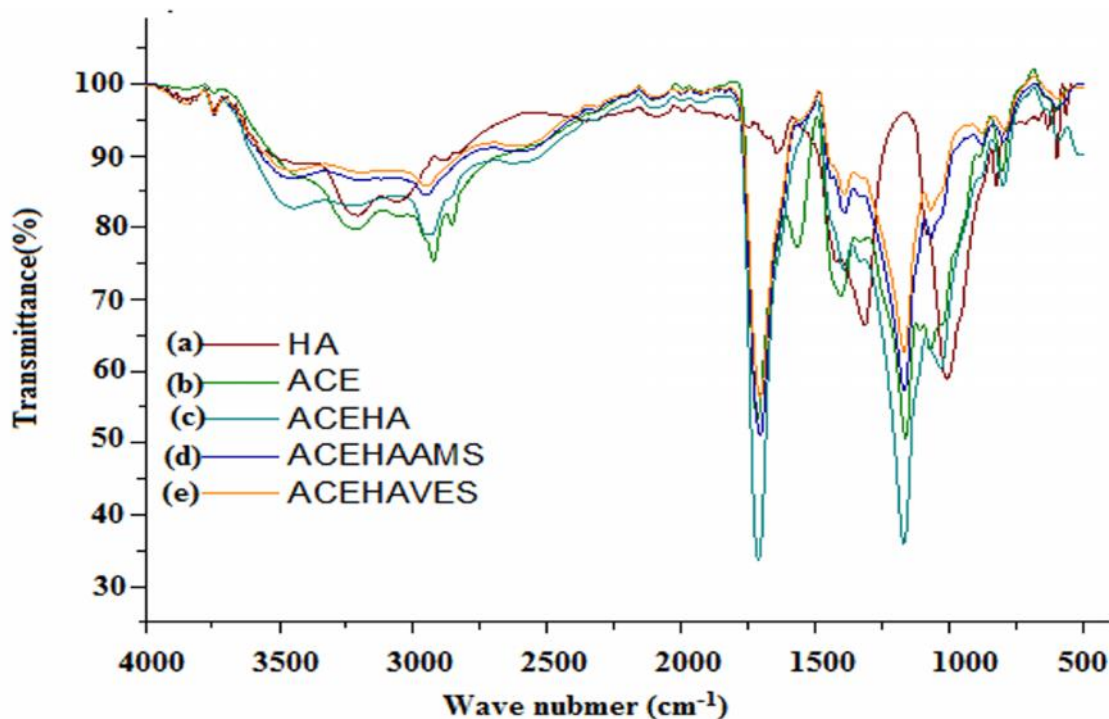


Figure 1. FT-IR spectra of (a) HA from egg shells (b) ACE (c) ACE-HA (d) ACE-HA-AMS (e) ACE-HA-VES

Further, the characteristics absorption band of ACE-HA at 1395.91, 1033.54, 580.02 cm^{-1} bands of PO_4^{3-} indicated the existence of HA in ACE hydrogels. There are slight shifts in the status of absorption bands for hydrogel compared with biocomposite hydrogels which indicated the interaction formed between HA and respective hydrogels. Bajpai et al. also observed peaks at 602.09, 962.02, and 1035.01 cm^{-1} for Gelatin-hydroxyapatite based composite. Fig. 2(a) and Fig. 2(b) showed the FT-IR spectrum of ACE-HA-AMS and ACE-HA-VES. ACE-HA-AMS biocomposite hydrogels showed the broad absorption band observed in the range of 3450 cm^{-1} (OH stretching) and relatively new bands was appeared at 880.34 cm^{-1} which may be attributed to Si-O bending vibration. The peaks appearing at 2958.09 cm^{-1} may be attributed to CH_2 stretching of Si (CH_2)₃ stretching frequencies. The spectral characteristics of ACE-HA-VES hydrogels presented in Fig. 2(b), revealed the C=O stretching vibration of ester carbonyl groups appeared at 1717.17 cm^{-1} and the stretching vibration of C-O observed at 1166.20 cm^{-1} . In addition, the characteristics absorption band of COO^- was observed at 1445.00 and 1526.22 cm^{-1} for symmetric and asymmetric stretching. A broad absorption band was appeared for -OH in the range of 3444.69 cm^{-1} . In addition, new band was also observed at 880.51 cm^{-1} , which may be attributed to Si-O bending vibration and PO_4^{3-} stretching was observed at 1394.21. An absorption band with a weak shoulder peak around 2930.84 cm^{-1} , which correspond to the stretching of aliphatic - CH_2 -, C-H, - CH_3 groups, respectively. The peak at 2950.09 cm^{-1} might be attributed to CH_2 stretching of Si (CH_2)₃ stretching frequencies were also observed for their polymer composites.

Morphologies of biocomposite hydrogels

Fig. 2 shows the SEM image of dried ACE, ACE-HA, ACE-HA-AMS and ACE-HA-VES biocomposite hydrogel. As shown in Fig. 5(a), the surface morphology of the hydrogels (ACE) were extremely smooth and porous, which might be related to the perfect homogeneity among the ingredients.

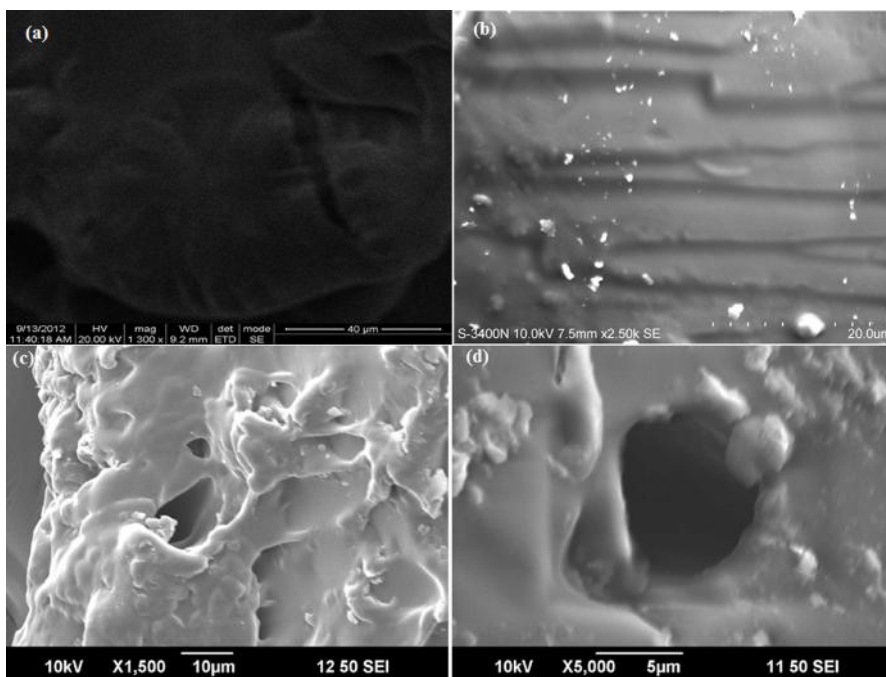


Fig. 2. Scanning electron microscope picture of (a) ACE (b) ACE-HA (c) ACE-HA-AMS (d) ACE-HA-VES.

Fig. 2(b) showed ACE-HA biocomposite hydrogel reveals that the spherical shape and porous nature in their surfaces. The presence HA particles are dispersed inside the polymer matrix. Incorporation of HA into the ACE polymer matrix reduces the crystallinity and alters the original polymer structure by increasing the swelling of biocomposite hydrogel. As witnessed in the Fig. 2(c), ACE-HA-AMS obtained from the fracture and exhibited mostly circular and elliptical pores, which may find better swelling at various buffer solutions. It has been recognized from Fig. 2(d) that ACE-HA-VES biocomposite hydrogel with uneven dispersed HA particle were present, which tunes the irregular large pores and channels within the biopolymer matrix. Furthermore, it encouraged the fluid to easily enter into the gaps, leading to a significant increment of the absorption than of ACE-HA and ACE-HA-AMS biocomposite hydrogels.

Thermal characterization of biocomposite hydrogels

It could be seen from Fig. 3(a), ACE-HA biocomposite hydrogel presents two stages of degradation. The first stage ranges between 220-380°C corresponding to 40% loss in weight. This may equate to the loss of absorbed water. The second stage weight loss started at 380°C and progressed up to 540°C with weight loss 40% might be related to the cleavage of yet another composition of biocomposite hydrogel and carbonization of the polymeric materials. TGA curves of ACE-HA-AMS biocomposite hydrogels shown in Fig. 3(b). In general, the mass loss occurs in three stages: the first stage was the loss of structural water of the hydrogels 120-170 °C with weight loss of 6.0%. The second stage might be the decomposition occur at (207-315 °C), with 42.00% weight loss due to the thermal degradation of the polymeric chains and the third stage at (425-475 °C) with corresponding weight loss of about 31.00 % was due to the carbonization of the polymeric materials. The thermograph of the ACE-HA-VES (Fig. 3(c)) shows that the first stage of decomposition has been observed from 202-235 °C with 8% weight loss, might be due to moisture. Second stage decomposition started at 235 °C and proceeded up to 360 °C with 34% weight loss. Third stage decomposition started at 380 °C and continued up to 460 °C with 29.5% weight loss.

The DTG curves of ACE-HA, ACE-HA-VES and ACE-HA-AMS were depicted in Fig. 3, which supported the TGA results of synthesized biocomposite hydrogels. The DTG curve of ACE-HA illustrated two separate degradation steps. The foremost and second decomposition peak was observed at 230.67 and 413.83 °C with maximum weight loss. ACE-HA-AMS three stages decomposition was occurring at 92.34, 2321.02 and 426.02 °C. ACE-HA-VES showed at 255.07, 323.68 and 412.68 °C. Altogether the three stages decomposition in TGA curves was well supported by DTG curves. The improved thermal stability was observed in general, for silane surface modified hydroxyapatite than untreated one.

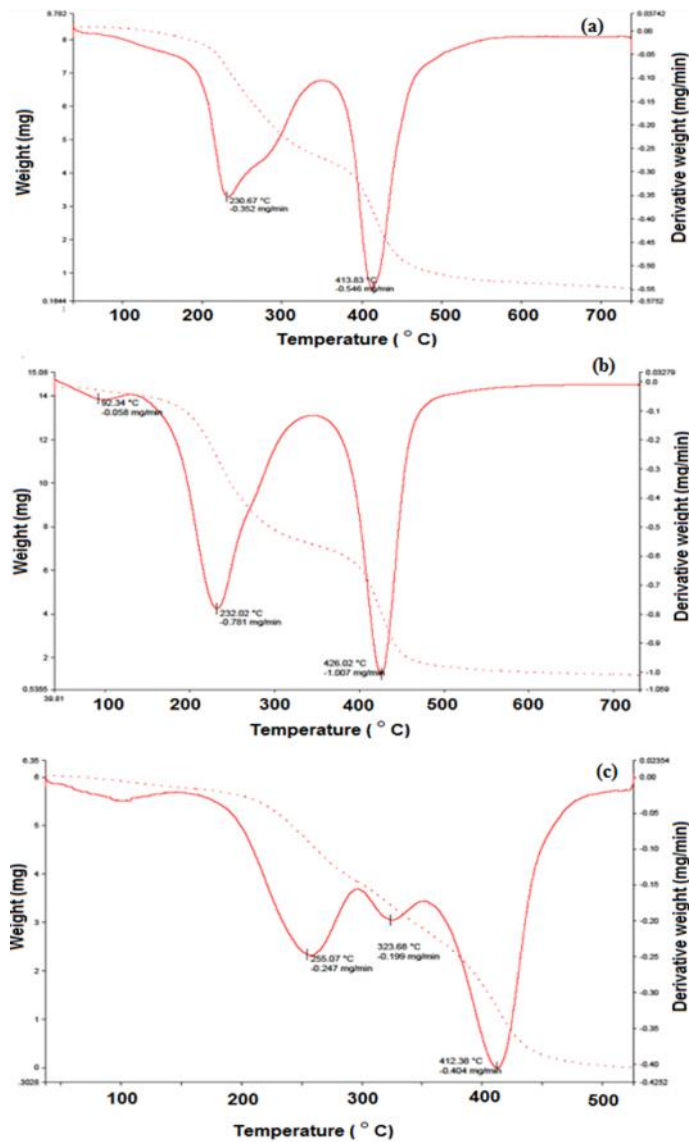


Fig 7. DTG Curve of (a) ACE-HA (a) ACE-HA-AMS (b) ACE-HA-VES.

IV. CONCLUSIONS

In this study, citric acid and glycol based hydrogels and their composites were synthesized in a greener direction. The incorporation of hydroxyapatite and formation of composites clearly improved the surface morphologies and thermal properties. VES treated HA with ACE was found to possess superior properties than AMS and untreated ACE-HA on overall properties of biocomposite hydrogels.

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