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Green synthesis, swelling behaviour and orthopaedic application of polysaccharide based hydrogel

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The bio-composite material Taragum-g-P(MMA-co-AN)/CaO has excellent properties like superabsorbent, biodegradable and antibacterial property having interpenetrating network structures (IPNS) is prepared through the microwave-assisted synthesis method, in aqueous medium by using cobalt complex as the cross-linking agent and APS (Ammonium Persulphate) as an initiator. The maximum swelling percentage (%) is as observed in the different time interval in a vacuum having *p*H=7. The partial IPNS of the composite now converted into complete IPNS through the impregnation of Taragum chain both in acidic and also in natural conditions. The characterization such as FESEM, FTIR, XRD has been carried out for identification of both partial and complete IPNS structure. The tensile strength, biodegradability, swelling behaviour and antibacterial properties are studied by adopting the suitable procedure. The prepared material is biodegradable, superabsorbent, shows antibacterial property and biocompatibility for which it is used as an excellent material for orthopaedic implants and hard tissue engineering.

Keywords: Antimicrobial property, Biodegradability, Hydrogel, Super absorbent, Taragum.

The three-dimensional network polymeric materials or composites having hydrophilic nature shows the property of superabsorbent and it absorbs or retains huge volume of water generally 10 to 1000 times more weight in comparison to its original weight[1,2]. This is due to large number of gaps because of more cross-linking bonding in the prepared biocomposite material. The superabsorbent polymeric hydrogel materials are prepared by either emulsion polymerisation or co-polymerisation technique of hydrophilic vinyl monomers such as acrylic acid(AA), acrylonitrile (AN), acrylamide (AM), Methyl methacrylate (MMA), Ethyhexylacetate (EHA) having hydrophilic functional groups. Due to greater water absorption capacity and biocompatibility these materials are easily applicable in biomedical application, biosensor and agricultural field of water scarcity areas and also act as sorbents for removal of heavy metal ions from the industrial waste effluents and also act as a catalyst. The hydrogels prepared from vinyl monomers although have better water absorption capacity but these are non-biodegradable in nature and doesn't show antibacterial properties which is the major problem to our environment and to solve this problem we have to prepare superabsorbent hydrogel by taking the natural polymeric materials such as taragum, pectin, guargum, alginate, zein and materials of cellulose derivatives. It was reported that the composites of these materials shows better biodegradability property along with swelling behaviour and biocompatibility. Since this prepared polymeric composite material shows the property of non-toxicity, biocompatibility, antibacterial and biodegradability, therefore it can be efficiently applied in the treatment wound. Due to the excellent property of hydrophilicity, biocompatibility and non-toxicity, it can be used effectively in orthopaedic implants. Because of good biocompatibility, the prepared materials can also be utilized to replace some specific parts of the living system and it functions immediately and safely when is in contact with the living tissues. Due to this specific novel property, it can be applied in tissue engineering also. Nowadays, the scarcity of water is a global problem all over the world. But in the modern agriculture and horticulture system, we can use the superabsorbent hydrogel which not only solves the water scarcity problems but also the nutritional requirements of plants[3-6]. The sandy and sandy-loam soils generally have low water holding capacity and the plant growth in this kind of soil is difficult. Excessive drainage of rain water in high level areas is the cause of less water infiltration inside the soil and the fertilizers applied are also washed away from the soil. If hydrogel is

successfully applied in these areas, it improves the seed germination and also plants growth capability by increasing the water holding capacity. Taragum is commonly known as a South American gum and is a better biodegradable material. The biodegradation property of this material depends upon its hydrolytic degradation and breaking of the materials by enzyme-catalysed reaction[7-9]. Tara gum is a biopolymer and structurally similar to galactomannans and its properties are much similar to Indian guar gum. But it has many advantages like smooth flow rate, more natural and softer than guar gum. Tara gum is an odourless, tasteless and non-toxic material whereas the Indian guar gum has unpleasant odour with some disagreeable taste. The flavour released from Tara gum is much better than that of the guar gum. The addition of Tara gum increases gel elastic property and retain a much higher volume of water and also improves the stability of the prepared hydrogel. Tara gum retains stability and prevents the formation of crystal ice in ice cream. The present purpose of the study is to develop a smart biomaterial synthesized by a noble process by using water-soluble cobalt complex in the microwave assisted synthesized medium so that no toxic gases emitted into the atmosphere and it is completely a green synthesis process and can be industrially applied. The prepared smart material shows a high degree of biodegradability, super adsorbent, anti-microbial property and finally electrically conducting in nature. The major nobility of our work is to prepare smart biomaterial and hydrogel by using natural resources (chicken eggshell) in green synthesis method (irradiation by microwaves) which can be utilized in several of fields and also in broader applications with decreasing the pollution load of the environment[10-14].

Experimental Section

Preparation of Nano-CaO (Chicken eggshell)

Chicken eggshells were collected from different egg shops and Indian restaurants. After collection, it were properly washed with normal water for five times and then again washed with distilled water for two times and finally washed with alcohol for two times. After that, it was dried at about 50-60°C for 10 h in a hot air oven. Then the dried chicken eggshell were immersed in 70% dilute solution of acetic acid for about 48 h and after that it was thoroughly washed with the deionized water and completely dried in an air tight oven (at about 50°C) for two consecutive days. Then finally it was crushed and grinded in a mechanical grinder (Cuisinart DCG-12BC) to make it into powdered form. The mesh size of the powdered sample of the chicken eggshell was measured to be 100-350 μm. The chicken eggshell powder so obtained was completely purified by accumulation with 5% O-phosphoric acid and then washed with 5% NaOH solution, then after that the sample was incorporated into a specified blast furnace for heating at a temperature of about 200°C for 8 h to get Nano-CaO. After cooling, the samples were taken and stored in an airtight closed desiccator[15,16,18].

Preparation of $[Co\ (III)en_2(NO_2)_2]NO_3$ complex

Ethylene di-amine (en) 6.85 g was partially neutralized by 10 mL of distilled water with the simultaneous addition of 3 mL of conc. HNO_3. The solution so prepared was added in an 11.5 g of Co $(NO_3)_6.6H_2O$ and 6 g of $NaNO_2$ with 20 mL of H_2O. Then a stream of air was passed vigorously to the solution for about 8 h and after sometimes a yellow Trans $[Co(III)en_2(NO_2)_2]NO_3$ complex starts to be precipitated (after 30 min), then the mixture was cooled in an ice bath and finally filtered by using whattmann-42 filter paper. A yellowish crystalline solid mass was obtained after boiling with distilled water. The so prepared cobalt complex was finally washed with alcohol and dried in an airtight oven at a controlled temperature[19,20].

Taragum-g-P(MMA-co-AN)/CaO composite preparation

The required amount of three different types of monomers (Taragum, Methyl methacrylate, Acrylonitrile), freshly prepared Nano-CaO, sorbitol (surfactant) and distilled water along with freshly prepared APS solution (initiator) followed by the stock solution of the above prepared cobalt complex (slowly added with continuous stirring) were taken in a three necked reaction vessel and the temperature was maintained in the range of 70-80°C in an inert N_2 atmosphere. The freshly prepared complex (trans $[Co(III)en_2(NO_2)]NO_2$) catalyses the reaction and increases the kinetics of the reaction rate. This reaction is a complete complex catalysed microwave-assisted synthesis reaction and is eco-friendly to our environment. When the reaction almost completed after a few minutes the three-necked reaction vessel is taken from the micro-oven and kept in an ice bath for quenching the reaction. The sample now becomes gelatinous with pale yellow colour, which was cleaned by washing three times with a little hot

distilled water and then with alcohol followed by drying at 200°C for 6 h in an air tight oven. Finally, the synthesized copolymer Taragum-g-P (MMA-co-AN)/CaO was weighed and kept inside a desiccator for about one hour[21, 23].

Result and Discussion

Calculation of grafting parameters

The grafting parameter for Taragum-g-P (MMA-co-AN)/CaO composite was calculated by the given in equation (1) and presented in Table 1.

$$\text{Yield of grafting}(\%) = \frac{wt\ of\ graftcopolymer - wt\ of\ taragum}{wtoftaragum} \times 100 \quad \ldots (1)$$

Mechanism of hydrogel formation

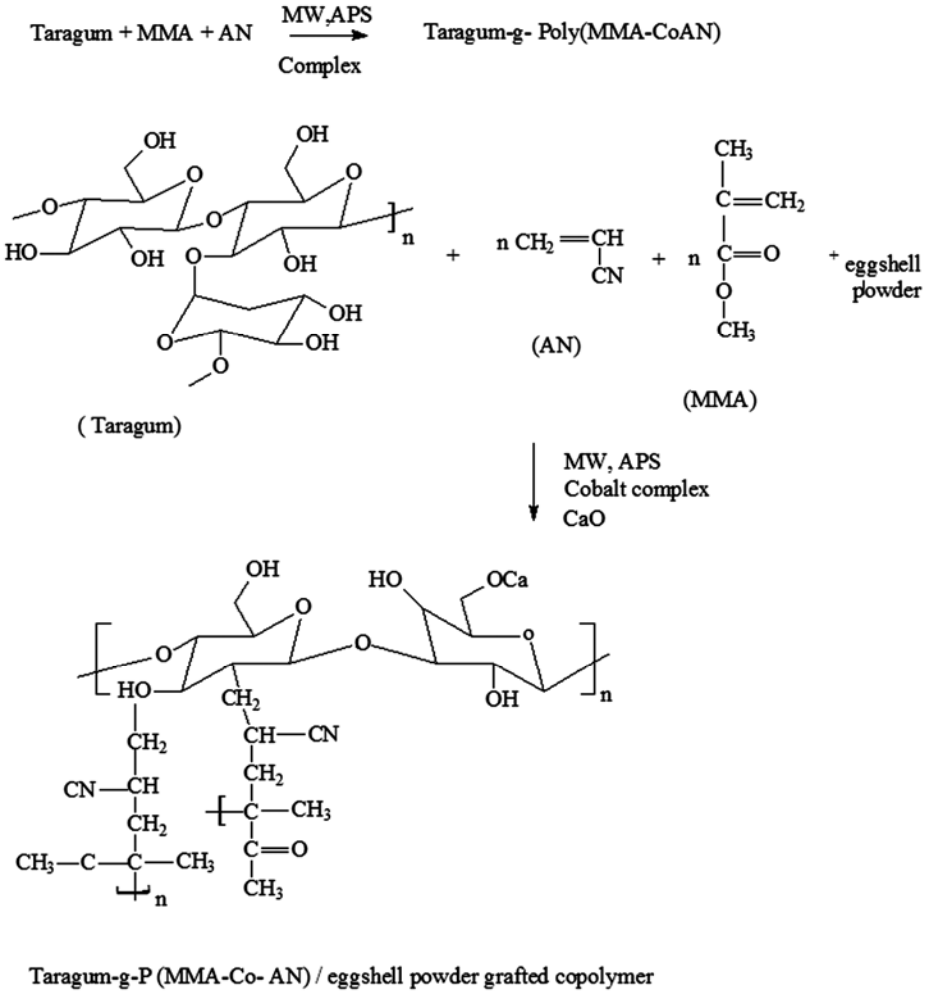
Hydrogel preparation is given in Scheme 1.

Biodegradation of hydrogel by the activated sludge

The biodegradability of the prepared composite material was analysed under the sludge area of Mahanadi basin. It was found that the rate of biodegradation of so formed hydrogel varies with

Table 1 — Grafting of taragum-g-P(MMA-co-AN) copolymer and taragum-g-P(MMA-co-AN)/nanoCaO composite hydrogel

Sample code	Taragumgm	MMA (mL)	AN Ml	APS (g)	Co(III) Complex (mL)	Sorbitol (g)	Nano CaO (g)	Grafting (%)
T1	0.2	2.0	1.0	0.65	1.0	0.02	0.5	88.9
T2	0.2	0.5	0.5	0.65	1.0	0.02	1.0	89.1
T3	0.2	1.0	1.0	0.65	1.0	0.02	1.5	91.6
T4	0.2	1.5	1.5	0.65	1.0	0.02	2.0	97.5
T5	0.2	2.0	2.0	0.65	1.0	0.02	1.5	92.0
T6	0.2	2.5	2.5	0.65	1.0	0.02	1.0	89.6



Scheme 1 — Taragum-g-p (MMA-Co-AN)/eggshell powder grafted copolymer

different time intervals. The sludgy wastewater was carefully put inside the container known as ampule. This sludgy water mostly contains dirty muds with different varieties of microorganisms like fungi, algae, bacteria, yeast, etc. which are the major causes of the biodegradation of the synthesized biomaterial. This waste sludge material was carefully collected and packed tightly into the polypropylene ampule bottle. A sample of about 0.5 g was dipped into the waste sludge water and incubated in a finely sterilized small vessel at normal room temperature of about 25±5°C for 1 day, 7 days, 1 month, 3 months, 6 months[24-26], which are shown in Fig. 1.

Tensile strength

The data gathered from the experiment shows that the tensile strength of the synthesized hydrogel increases from T1 to T4 and then gradually decreases to T6. The increasing trend of the tensile strength might be due to the enhancement of the crosslinking of the Nano CaO, PMMA and PAN with Taragum up to 54.3 MPa and after that the Nano-composite might become brittle due to higher crosslinking density as a result of after 54.3 MPa there is a decreasing trend of tensile strength[27], as shown in Fig. 2.

FESEM

The micrograph of FESEM of the prepared composite material Taragum-g-P(MMA-co-AN) and Taragum-g-P(MMA-co-AN)/CaO was shown in Fig. 3(a) and (b) with a magnification of 51X. From this micrograph, it was confirmed that the nano form of taragum powder is uniformly and compatibily inserted within the grafted form of copolymer P(MMA-co-AN). Hence the surface morphology of Taragum-g-P(MMA-co-AN) is homogenous as compared to the P(MMA-co-AN) with less gap and voids. But by insertion of chicken eggshell powder the composite Taragum-g-P(MMA-co-AN)/CaO formed is morphologically homogenous but the void

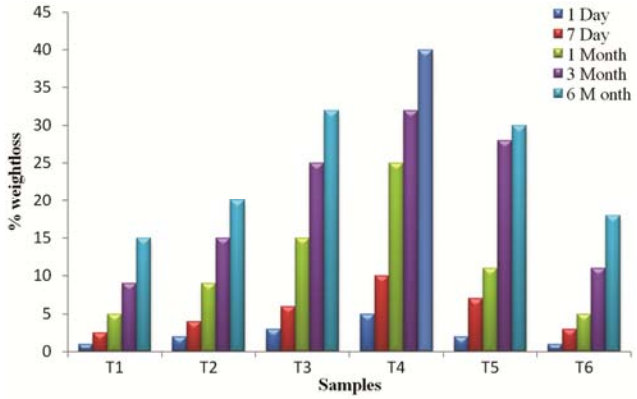


Fig. 1 — Biodegradation study of Taragum-g-P(MMA-co-AN)/CaO (T1 to T6)

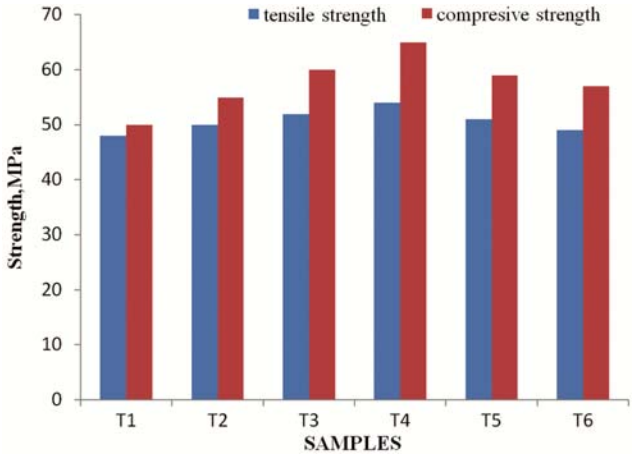


Fig. 2 — The compressive strength and tensile strength of Taragum-g-P(MMA-co-AN)/CaO

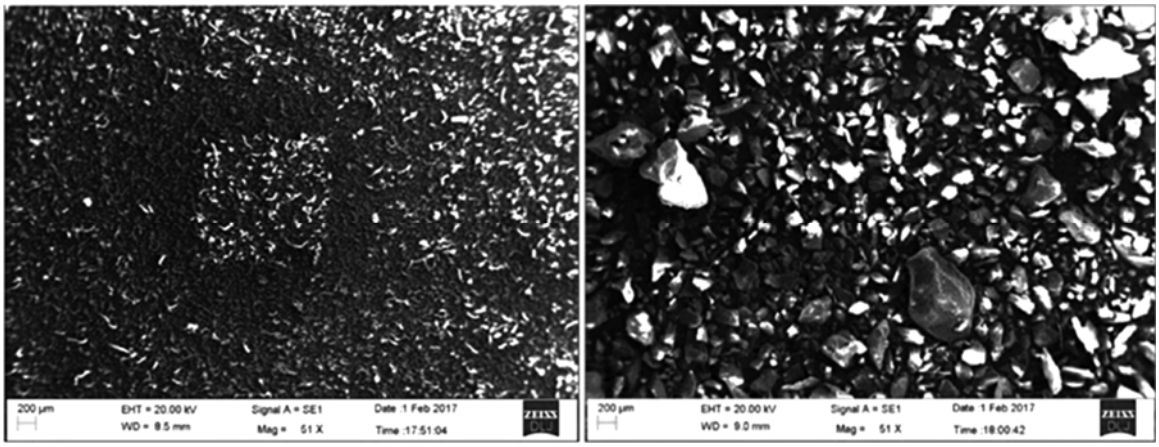


Fig. 3 — FESEM of (a) Taragum-g-P(MMA-co-AN), (b) Taragum-g-P(MMA-co-AN)/CaO

and gaps present in it becomes more than Taragum-g-P(MMA-co-AN) which is the cause of absorbing more water and the prepared composite material show the properties of superabsorbant and biodegradability.

FTIR

Tara gum grafted with the copolymer P(MMA-co-AN) and further crosslinking with chicken eggshell powder was confirmed in the spectra of FTIR study as shown in Fig. 4. The peak at 1680cm^{-1} indicates due to the absorption of carbonyl group present in the Tara gum-g-P(MMA-co-AN)/CaO composite. The peak at 1465cm^{-1} is the asymmetric stretching vibration because of the presence of Tara gum. The peak at 480cm^{-1} is due to bending mode of vibration of O-Ca-O and peak at 786cm^{-1} is due to Ca=0 group of Nanopowder form of chicken eggshell. The peak at 1100cm-1 is due to symmetric stretching and at 1400cm-1 is due to asymmetric stretching of Tara gum-g-P(MMA-co-AN)/CaO composite. The small peak at 1637cm-1 is due to the- bending vibration of the synthesized bio-nano composite.

XRD

The percentage of crystallinity of the composite material Taragum-g-P(MMA-co-AN)/CaO was confirmed by the study of X-ray diffraction shown in Fig. 5. The insertion of eggshell powder in the Nano composite Taragum-g-P(MMA-co-AN) decreases crystallinity which is observed because of the angle $2\Theta = 13.5^0, 22.4^0, 27.1^0$. The crystallinity of composite decreases because of the addition of the powder form of chicken eggshell due to the formation of more gaps and voids in between the layers present in the structure of the Taragum-g-P(MMA-co-AN)/CaO. Finally, it was confirmed that both taragum and chicken eggshell are successfully inserted in between the layers of the copolymer and made it environmentally friendly and superabsorbent.

Equilibrium water content

The equilibrium water content is calculated by using the formula given below.

$$EWC\% = \frac{Wt-Wo}{Wo} \times 100 \quad \ldots (2)$$

The equilibrium water content is mainly due to the addition of chicken eggshell powder in the prepared bio-Nano composite material. The maximum percentage of water absorption is found in the T4 sample because of the creation of more space due to the grafting of chicken eggshell powder (Fig. 6). Then with the further addition of more chicken eggshell powder the gaps in between the layers covered by eggshell powder decreases which result the decrease in the percentages of water absorbency in the prepared Taragum-g-P(MMA-co-AN)/CaO bio-Nano composite and increases the rigidity, crosslinking

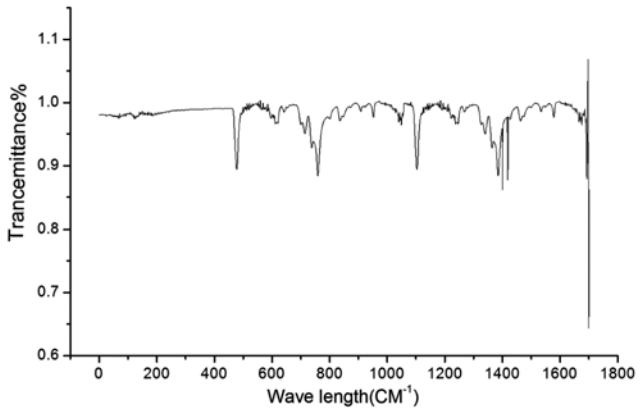


Fig. 4 — FTIR spectra of Taragum-g-P(MMA-co-AN)/ CaObionanocomposite

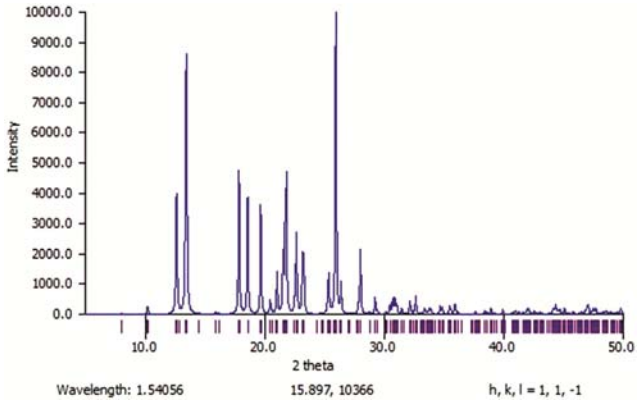


Fig.5 — XRD of Taragum-g-P(MMA-co-AN)/CaO

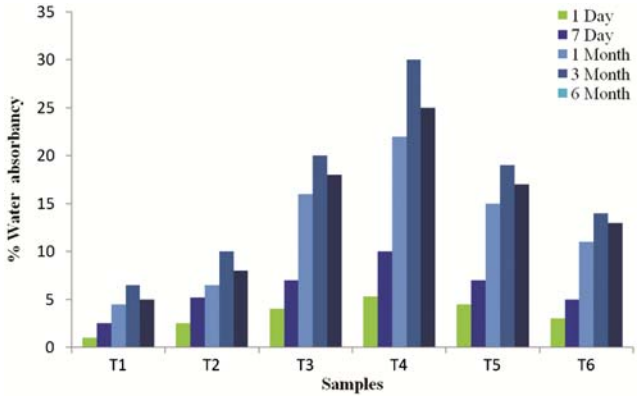


Fig.6 — Equivalent water content of Taragum-g-P(MMA-co-AN)/CaO (T1 to T6)

property and density with a decrease in water-retaining capacity[28].

Conclusion

The synthesized new material Taragum-g-P(MMA-co-AN)/CaO is synthesized by microwave-assisted polymerization method, in which the rate of polymerisation is much more than the conventional in-situ method of synthesis with less time requirement. No toxic gaseous components are eliminated so that it is sustainable to our environment. New Taragum based synthesized polymeric material showsexcellent swelling properties in water and aqueous solutions of urine. The synthesis of Taragum with PMMA and PAN composites are thecause of increasing crosslinking capacity which results in the increasing density and elastic modulus. Since it behaves as superabsorbent, therefore can be successfully used as diapers, agriculture and gardening in desert areas. The prepared copolymer is characterized by FESEM, FTIR, XRD, biodegradability, tensile strength and swelling behaviour. The materials show good tensile strength, EWC values tallies with the values of results obtained in biodegradation. This material also considered as an outstanding material used as bone cement implant in orthopaedic application. From the biodegradation study, it was found that sample T4 undergoes biodegradation of 42% in 6 months. The biodegradability is carried out in soil burial method. Due to the superabsorbent property, it can absorb potentially urine, blood, fluids of the body and therefore can be used commercially as some biomaterial products.

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