



## Recent Progress on the Design and Applications of Guar Gum Based Nano Hydrogel “Guar Gum-g-P(HEMA-co-AM)/Chicken Eggshell” as Superabsorbent

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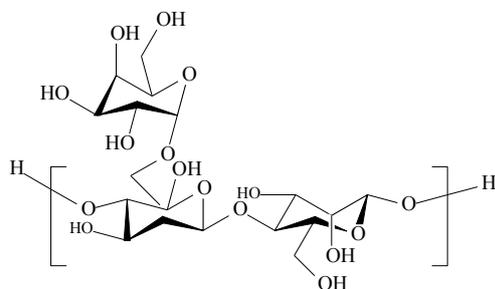


**G**UAR gum is water soluble non-ionic plant polysaccharide collected from the fruit seeds of *Cyamopsis tetragonoloba* and have been used to synthesize nanohydrogel with the introduction of 2-hydroxyethyl methacrylate (HEMA), acrylamide (AM) and chicken eggshell powder. The equilibrium water content (EWC) of the nanohydrogel were measured at a pH range of 3.6 –10.5 and an optima EWC has been reported at pH 8.4 for biomedical application. The egg shell based Nano hydrogel exhibited good biodegradability property. The prepared materials can be used as a probable super-adsorbent for numerous ionic contaminants present in waste water. The large water content capacities and with large pore sizes of the synthesized nanohydrogel have applications for water saving and prevention of soil erosion in desert localities.

**Keywords:** Biodegradability, EWC, Drug delivery, Grafting of copolymer, Nano-composite hydrogel (NCH), Super-absorbent.

### Introduction

Guar gum, also known as “Guaran” is a material obtained from guar beans has congealing and soothing assets. It is utilized in various industrial units such as food manufacturing unit, hydraulic manufacturing unit, etc. The guar fruit seeds are carefully dehusked, crushed and partitioned to get Guar gum which is a white coloured powder. It is a galactomannan, comprising of (1-4)- linked  $\beta$ - D -mannopyranose units with side chains of (1-6)-linked- $\alpha$ - D -galactopyranose .



(Guargum)



(Guargum powder)

In the era of nanomaterials the natural products like guar gum , gumghati and chicken egg-shell powder plays an important role in producing various nanocomposites. The guar gum based nanoparticles can be used to summarize the active compounds in drug delivery systems. Nano calcium oxide (Nano-CaO) produced from chicken egg shell is a group of materials with great performance for manufacture interest. These materials can be utilized for the preparation of small nanocomposite based thin film hydrogel [1]. Labelled and covered silicates with fibers show good reinforcement properties on several

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polymeric matrixes because of their high aspect ratio, but this kind of filler with a high aspect ratio does not markedly advance the roughness, and sometimes even decreases it. In contrast, sphere-shaped mineral nanoparticles are fairly dissimilar. Their low aspect ratio but high surface part could frequently result in a strong interfacial interface in between filler with polymeric matrix [2]. Guar gum based hydrogels especially play a very essential role in muco adhesion to the mucosal surface or pressure sensitive adhesive (PSA). This may behave as an ideal adsorbent surface for the drug release system. The Nano filler based bio-nanohydrogel for drug dissolution has potential applications especially in skin formulation behaviours such as biodegradability, immunological, antibacterial action and wound-healing activity. Hydrogels exhibit better potential activity very likely to the natural living tissues compared to any other different class of artificial biomaterials with its large water content capacities and stability. The important behaviours of the nanocomposites are significantly depends upon the filler's aspect ratio, surface modified area and exchanges in between the filler along with the polymer matrix [3, 4].

The present work describes the development of Guar Gum-g-P(HEMA-co-AM)/nano-CaO nanocomposite hydrogel (NCH) having possible use as biodegradable super absorbents as well as having adhesive properties.

## **Materials and Methods**

### *Materials*

Guar gum and ammonium persulfate (APS) were purchased from The Himedia, Mumbai. Ortho phosphoric acid, sorbitol and ethanol were purchased from Indian laboratories Ltd. Chicken egg shells were collected from an Indian restaurants and washed with demineralized water three times contineously and then dehydrated at 120°C for 3 hr in an air tight oven.

### *Preparation of cobalt complex*

6 g of ethylene diamine (en) was partially neutralised by 15ml of the distilled water (H<sub>2</sub>O), with simultaneous addition of 5 ml of conc. HNO<sub>3</sub> (nitric acid). The solution so prepared was added in a 11 g of Co(NO<sub>3</sub>).6H<sub>2</sub>O and 5 g of NaNO<sub>2</sub> in 25 ml of H<sub>2</sub>O. A stream of air was passed vigorously to the solution through a blow pipe. After sometimes a yellow complex of Trans[Co(III)en<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]

NO<sub>3</sub> starts to be precipitated (after 45 min), then after sometimes the mixture was cooled in an ice bath and finally filtered by using whattmann 42 filter paper. A yellow crystalline solid mass was obtained from the boiling H<sub>2</sub>O (distilled water). Then it was finally washed with alcohol and dried in an air tight oven at a controlled temperature. The prepared complex material was confirmed by UV-Visible spectroscopy.

### *Deacetylation of Guar gum*

The removal of acetyl group during the combination process of Guar gum, HEMA, AM in the presence of APS as initiator in N<sub>2</sub> atmosphere causes deacetylation. This process involves the breaking of acetyl group and forms another product. From pH analysis data, it was found that the basic and acidic groups involves in the deacetylation process. Guar gum with 75% of deacetylation was prepared by increasing the amine content in Guar gum with (Hydroxyethyl) methacrylate and acrylamide.

$$\text{Deacetylation Degree (DD)} = \frac{16.1(Y - X)}{FW}$$

Where, F= Molarity of base (NaOH taken) solutions, Y and X are two Inflection points, W = Weight of the sample.

### *Preparation of nano-CaO*

The dried chicken egg shells were crushed and ground in a mechanical attritor. The chicken egg shell powder was concentrated by accumulation with 5% O-phosphoric acid and the sample was incorporated into a blast furnace and heated at a temperature of about 200°C for 8 hr to get nano-CaO. After cooling, the samples were placed and stored in a air tight closed desiccator.

### *Preparation of hydrogel*

*Preparation of copolymer Guar gum-g-P(HEMA-co-AM)\nano-cao:* The essential amount of monomers units like Guar gum, HEMA, Acrylamide, freshly prepared nano-CaO, sorbitol (surfactant) and distilled water were taken in a reaction vessel. The temperature of the reaction medium was kept under 70-80°C in an inert N<sub>2</sub> atmosphere. The aqueous solution of the initiator ammonium persulphate (APS) was slowly added in the reaction vessel with continuous stirring. After 2 hr the reaction vessel is kept in a ice bath for quenching the reaction. The samples became gelatinous which were cleaned by washing three times with a little hot water followed by drying

at 300°C for 6h in an air oven. Finally, the copolymer P(HEMA-co-AM) was obtained, then it was kept inside a desiccator for 1 hr and finally weighed. The graft copolymer (GH4) and the nanocomposite hydrogel (GH16) NCH as shown in Table 1 were chosen for characterization. The mechanism of synthesis is shown in Scheme 1 given below [5-8].

#### Calculation of grafting parameters

Grafting patterns of Guar gum copolymers are calculated and was found by means of the subsequent experimental formula given below:

$$\text{Yield of copolymer grafting (\%)} = \frac{(\text{weight of grafted copolymer} - \text{weight of guar gum})}{\text{wt. of guar gum}} \times 100 \quad (1)$$

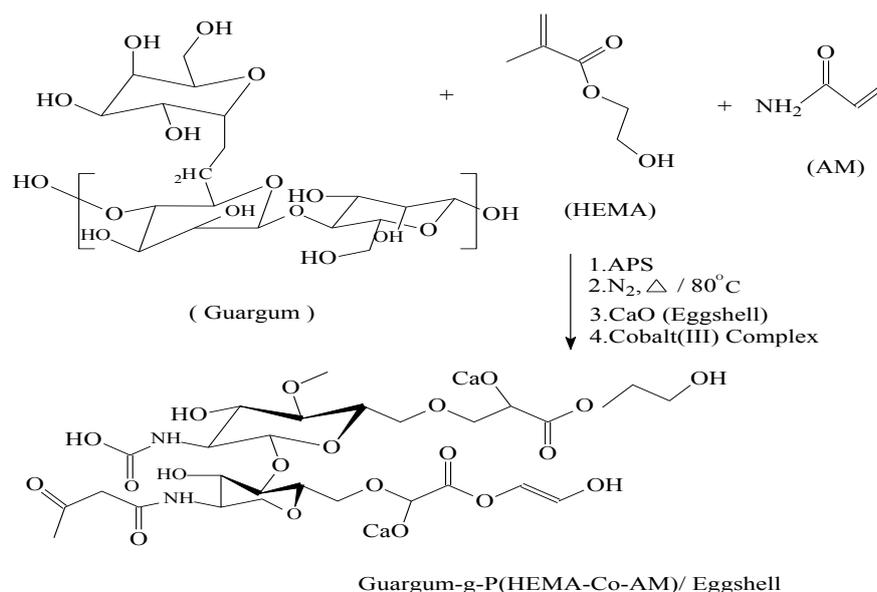
#### Characterization

The grafting of P(HEMA-co-AM) with the Guar gum was confirmed by using FTIR analysis. The FTIR spectrophotometer Perkin-Elmer based Paragon-500 model was recorded by the IR spectra in the method of KBr pellets. The dispersion of grafted copolymer into nano eggshell was studied using XRD with diffraction angle  $2\theta$  from  $10^\circ$  to  $90^\circ$  on a Bruker D8 Discover (Germany) instrument at 200C. X-ray having crystallographic part prepared with a Guinier concentrating camera with  $\text{CuK}\alpha$  irradiation ( $\lambda = 0.1498 \text{ nm}$ ) with a  $0.02 \text{ } 2\theta$  [16] step with size and 2 sec count time. Nanoscale form of grafted copolymer samples were observed by calculation with packing Brucker, Germany. FESEM operated

at microscopic investigations were obtained by using a field emission scanning electron microscope (FESEM) GEMINI®FE-SEM to get the surface morphological structure of the coated material. For FESEM observation, gold particle were coated on all samples and with a low beam of energy like 1.0 kV was activated to decrease the probability of coatings thermal destruction. Then ultrathin unit through a width of 150 nm was microtome at 80°C. Thermogravimetric analysis (TGA) were accepted due to detect the variations in thermal proceedings in the polymers by means of a Shimadzu DTA-500 scheme. It were carried out in atmospheric air from room temperature to 500°C at a heating system rate of 15°C/min [9].

#### Biodegradation study by activated sludge

Biodegradation of Cross-linked copolymer hydrogel and cross-linked NCH were studied under sludge water in order to link the extent of biodegradation at altered conditions. This sludgy waste water was carefully collected from a domestic waste water sludge area. This contains dissimilar categories of microbes (bacteria, fungi and yeast etc.) which are accountable for the biodegradation of the prepared materials. The sludge was collected in a polypropylene ampule, which was packed completely in a air tight bottle and used in the biodegradation study. 0.5 g of the prepared material were dipped in the sludge water incubated in a finely sterilized small vessel at normal room temperature ( $25 \pm 5^\circ\text{C}$ ) about 7days, 1 month, 3 months and 6 months [10-13] (Fig. 1).



Scheme 1. Guargum-g-P( HEMA-co-AM) graft copolymer.

TABLE 1. Variation of [HEMA],[AM],nano-CaO in Guar Gum-g-P(HEMA-co-AM)/nano-CaO-NCH.

Sample code	Guar gum (gm)	HEMA (mol/dm <sup>3</sup> )	AM (mol/dm <sup>3</sup> )	APS (mol/dm <sup>3</sup> )	Sorbitol (gm)	Nano-CaO	% of sample grafted	%, EWC at pH
GH1	1	0.070	0.034	0.01	0.05	1	83±1.33	314
GH2	1	0.071	0.068	0.01	0.05	1	86±1.33	321
GH3	1	0.141	0.087	0.01	0.05	1	92±1.33	341
GH4	1	0.177	0.104	0.01	0.05	1	98±1.33	365
GH5	1	0.178	0.122	0.01	0.05	1	94±1.33	343
GH6	1	0.224	0.034	0.01	0.05	1	91±1.33	335
GH7	1	0.141	0.034	0.01	0.05	1	93±1.33	342
GH8	1	0.072	0.104	0.01	0.05	2	89±1.33	331
GH9	1	0.177	0.087	0.01	0.05	1	91±1.33	335
GH10	1	0.142	0.122	0.01	0.05	1	93±1.33	342
GH11	1	0.214	0.104	0.01	0.05	1	96±1.33	359
GH12	1	0.071	0.139	0.01	0.05	1	91±1.33	335
GH13	1	0.178	0.104	0.01	0.05	0.1	86±1.33	406
GH14	1	0.178	0.104	0.01	0.05	0.25	92±1.33	411
GH15	1	0.178	0.104	0.01	0.05	0.5	98±1.33	419
<b>GH16</b>	<b>1</b>	<b>0.178</b>	<b>0.104</b>	<b>0.01</b>	<b>0.05</b>	<b>1</b>	<b>94±1.33</b>	<b>428</b>
GH17	1	0.178	0.104	0.01	0.05	1.25	91±1.33	415
GH18	1	0.178	0.104	0.01	0.05	1.5	93±1.33	412
GH19	1	0.071	0.068	0.01	0.05	1	89±1.33	389
GH20	1	0.142	0.087	0.01	0.05	1	91±1.33	407
GH21	1	0.071	0.104	0.01	0.05	1	93±1.33	371

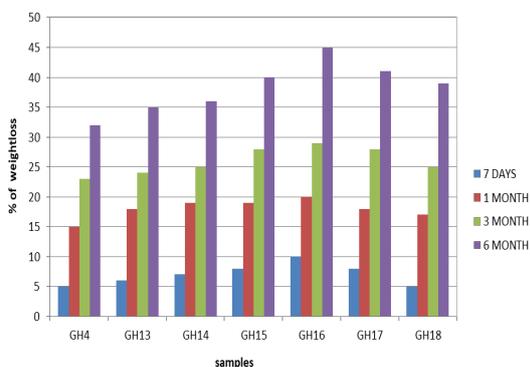


Fig. 1. Biodegradation of guar gum-g-P(HEMA-co-AM)(GH4) and guar gum-g-P(HEMA-co-AM)/nano-CaO NCH (GH13 to GH18). AM, acrylamide; HEMA, 2-hydroxyethyl methacrylate; NCH, nanocomposite hydrogel.

#### FTIR analysis

Functional groups along with the bonds distinguishes the superabsorbent study of the synthesised materials, which reveals that the

FTIR spectra was carried out by measuring the pellets with KBr. FTIR spectra in Agilent Cray 500 series spectrophotometer in the several ranges of 5000-500 cm<sup>-1</sup> was collected. The FTIR spectrum for natural Guar gum shows broad band in the region of 3453.8 cm<sup>-1</sup>, which is due to the stretching vibrational frequency of O-H bond and that shows the presence of many number of free -OH groups in the Guar gum backbone. Generally the finger print region of Guar gum consists of characteristic peaks from 875.1 to 1152.4 cm<sup>-1</sup> which shows the -C-O bond stretching. The bands at 1641.3 cm<sup>-1</sup> and 1084.1 cm<sup>-1</sup> are due to bending vibration of -OH and -CH<sub>2</sub> groups respectively. The sharp band at 2925.9 cm<sup>-1</sup> was due to -CH<sub>2</sub> group stretching. The spectra of Guar gum grafted HEMA and AM composite exhibited a broad peak at 3453.8 cm<sup>-1</sup> which indicates the -OH group with its stretching vibration, a smaller peak at 2925.9 cm<sup>-1</sup> is accredited to C-H stretching vibrations. The absorption band at 814.9 cm<sup>-1</sup> is due to

-C=O stretching vibrations. There is a different absorption band from  $1426.3\text{ cm}^{-1}$  to  $1084.1\text{ cm}^{-1}$  is due to C-O-C stretching vibrations. The band at  $1426.3\text{ cm}^{-1}$  recognizes to bending vibration of -C-H bonds of  $-\text{CH}_3$  groups. The peak at  $1025.7\text{ cm}^{-1}$  is due to coupling of -C-O stretching along with -O-H 'in plane' bending vibrations. The presence of the characteristic peaks clearly proves that HEMA and AM with egg shell filler material has been successfully grafted into the guar gum. [14-19] (Fig. 2).

#### FESEM analysis

SEM observations shows that the synthesised superabsorbent composite have a rough and uneven surface. From the figure analyzing surface modified morphology, it is clear that the synthesised composite materials has more irregular structure than SEM image of Guar gum, which is shown in Fig. 3. The SEM images of different magnification (500KX and 51KX) indicates the increase in surface roughness with addition of Nano-CaO. This results show the increase in pore size and causes of high water absorption property. The micrographs show the homogeneous addition of the grafted copolymer with the matrix of the chicken egg shell and reasonably give the machine-driven strengthening behaviour to the Guar gum based grafted copolymer for its biomedical uses. The surface deformed morphology after biodegradation with its initiated sludge was verified. This may be due to the decomposition or development by the micro- entities on the Guar gum-g-P(HEMA-co-AM)/nano-CaO-NCH resulting in

the rough surface before biodegradation (Fig. 3). Hence, the synthesised novel nanohydrogel is environmental friendly in nature [20-25].

#### TGA of NCH

The thermal decay of Guar gum-g-P(HEMA-co-AM) and Guar gum-g-P(HEMA-co-AM)/nano-CaO were considered by TGA analysis (Fig. 4). The early decay of samples are due to the existence of little moisture in the experimental samples but, wetness is found to be less in the NCH which might be due to the increasing of hydrophilicity. Later, the decay of graft copolymer at temperature  $180^\circ\text{C}$  and that of the NCH at  $258^\circ\text{C}$  is clarified as per the information that the thermal decay at higher temperature of the NCH might be ascribed to the incorporation of the copolymer into the structures of sheets of the nano-CaO. Due to strong interaction of nano-CaO with the other composite materials, it can resist at higher temperature. This is an added advantage for this nanohydrogel that at higher temperature it resist biodegradation because the calcium oxide is thermally stable and highly resistant to biodegradation [26, 27].

#### Absorbency or swelling measurement

##### Formula

$$\% \text{ of Water absorption} = \frac{(W_1 - W_2)}{W_2} \times 100$$

% of swelling or % of water absorption is the equilibrium water absorbency of sample which are the means of three measurements.  $W_1$  and  $W_2$  are the weight of the dry and dehydrated sample and water swollen sample respectively [28].

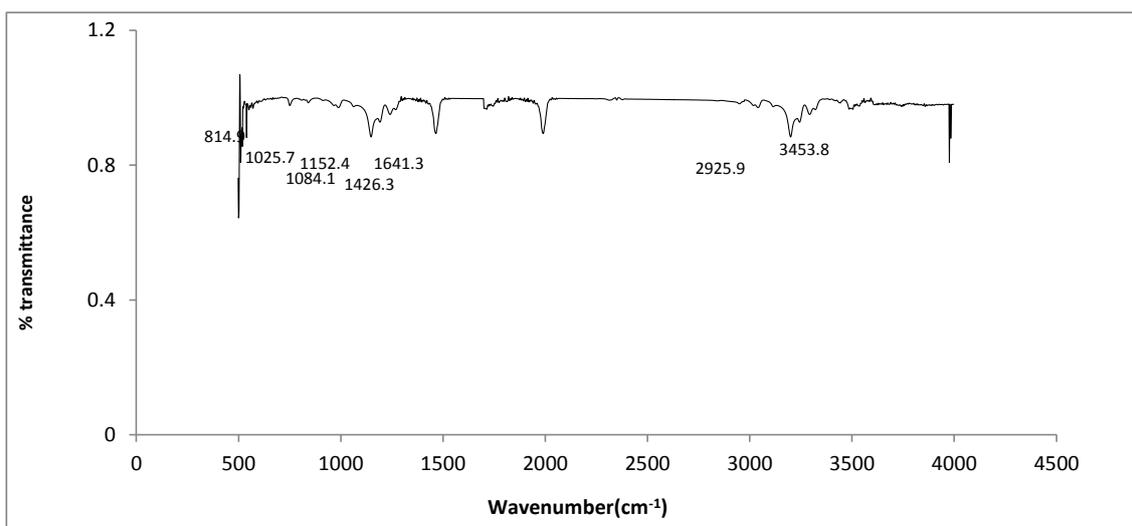


Fig. 2. FTIR spectra of guar gum-g-P(HEMA-co-AM)/nano-CaO NCH. AM, acrylamide; HEMA, 2-hydroxyethyl methacrylate; NCH, nanocomposite hydrogel.

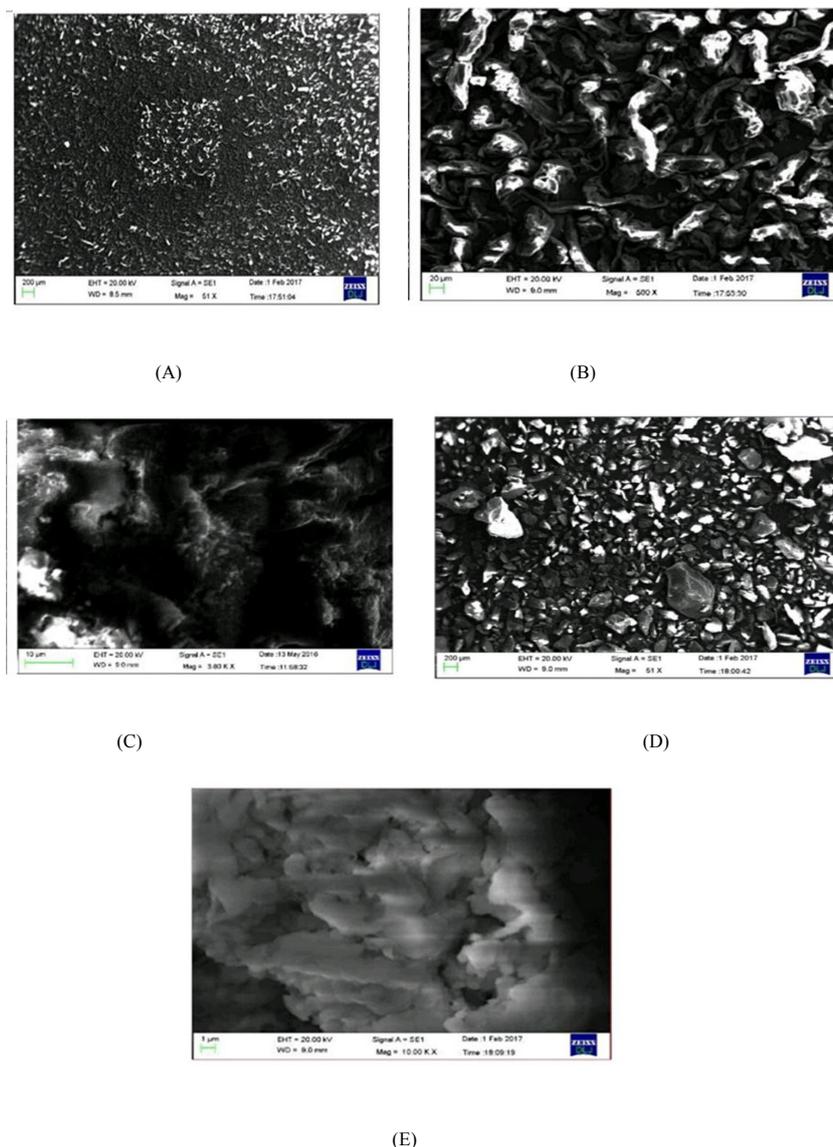


Fig. 3. FESEM of (a) Guar gum (Mag=51 $\times$ ), (b) Guar gum (Mag=500 $\times$ ), (c) Guar gum-g-P (HEMA-co-AM), (d) Guar gum-g-P(HEMA-co-AM)/nano-CaO-NCH and (e) After biodegradation of guar gum-g-P(HEMA-co-AM)/nano-CaO-NCH. AM, acrylamide; FESEM, field emission scanning electron microscope; HEMA, 2-hydroxyethyl methacrylate; NCH, nanocomposite hydrogel.

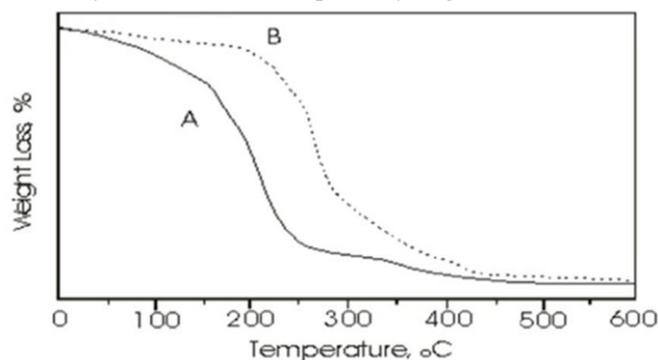


Fig. 4. TGA thermograms of (a) guar gum-g-P(HEMA-co-AM) and (b) guar gum-g-P(HEMA-co-AM)/nano-CaO NCH. AM, acrylamide; HEMA, 2-hydroxyethyl methacrylate; NCH, nanocomposite hydrogel; TGA, thermogravimetric analysis.

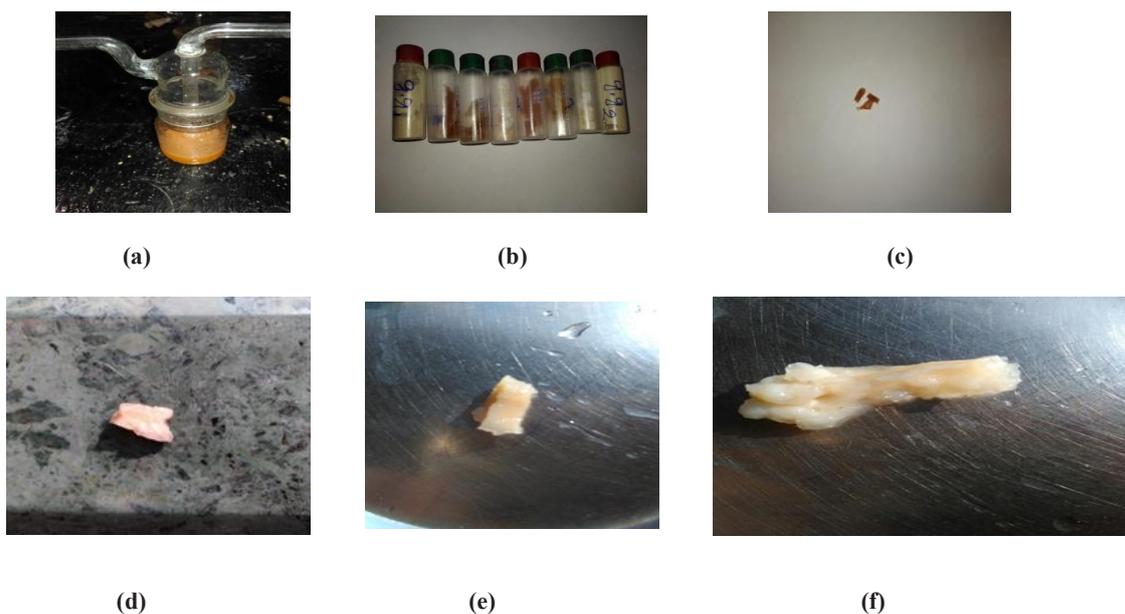


Fig. 5. Different stages of polymer nanocomposite with its swelling form.

Initiator has greater effect on the rate of polymerization because it generates the free radicals and initiates the reaction. The effect of initiator concentration was studied by changing initiator concentrations, the constant dynamic growth in water absorbency is noticed till an optimal volume which specifies that initiation of free radicals rises in the polymerization processes which in turn increases absorbency and then decreases. The consequence of polymer on water absorbency was shown in Fig. 6. It is clear

from the figure that initially water absorbency increases by increasing polymer concentration and subsequently it reduces. Co-polymerization between HEMA and AM, Guar gum with CaO NCH increases the percentage swelling and then decreases. The effect of Guar gum grafted copolymer on water absorbency of the synthesised superabsorbent Nano composites are also shown in Fig. 6. It was found that the water absorbency increased with increasing the amount of Guar gum [29, 30].

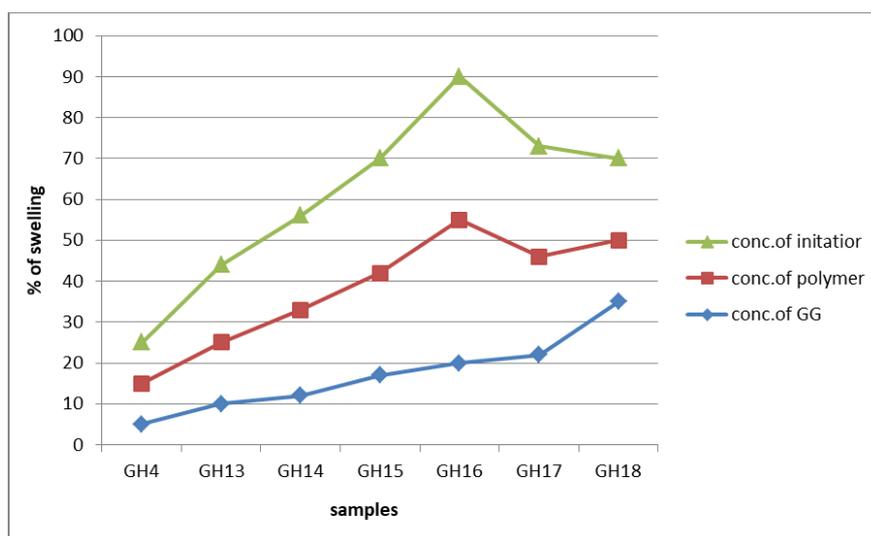


Fig. 6. Effect of concentration of initiator, polymer and guar gum on swelling capacity of superabsorbent composite.

## Conclusion

Novel superabsorbent Nano composite Guar gum-g-P(HEMA-co- AM) /nano-CaO-NCH was synthesized by using guar gum, HEMA, AM with egg shell powder by free radical graft copolymerization reaction process in the inert N<sub>2</sub> atmosphere. The prepared material was found to be excellent superabsorbent along with biodegradable property and considered as an environmental friendly novel materials. The composite exhibits hydrophilic–hydrophobic interactions. The composite was characterized by FESEM, FTIR, TGA and XRD. The properties of monomer concentration, reaction temperature, initiator concentration and guar gum concentration on water absorbency were examined. Under our investigational conditions superabsorbent composites has water absorbency of 1000% which has composition of 1% (w/v) HEMA 5% (v/v) of AM 1.4% (w/v) of guar gum, 10% (v/v) of initiator and reaction temperature of 60-80°C. The prepared superabsorbent compound can be required and used in various applications like agriculture, horticulture, removal of toxic dyes, oil spill cleaning etc. The biodegradability is maximum at 6 months and observed in our GH16 sample.

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