

Synthesis, characterization and swelling behavior of guar gum-g-poly (methyl methacrylate) superabsorbent nanocomposite

Abstract

Novel guar gum-g-poly (methyl methacrylate) superabsorbent nanocomposite was synthesized by simultaneous free radical graft copolymerization reaction of guar gum (GG) and methyl methacrylate (MMA) using boric acid as a cross linking agent and hydrogen peroxide as an initiator in aqueous solution. The effect of factors such as initiator concentration, monomer concentration, cross-linker concentration, salt concentration, pH and temperature on swelling was investigated. Water absorption capacity of composite was investigated in distilled water as a function of percentage swelling and found to be 3000%. The morphological study of composite was carried out by SEM and TGA was used to study thermal stability. The grafting of MMA on guar gum was confirmed by FTIR. The composite was also characterized by XRD to study its crystallinity.

Keywords: Superabsorbent, guar gum, graft copolymerization, swelling, methyl methacrylate

1. Introduction

Superabsorbent polymers are moderately cross-linked hydrophilic network materials that can absorb and retain large quantities of aqueous fluids while preserving their shapes (1). Because of the unique characteristics they are extensively applied in various fields such as agriculture and horticulture (2, 3), hygienic products as disposable diapers and feminine napkins (4), wastewater treatment (5,6,7), bio-medical area as antibacterial materials (8) and drug delivery (9,10). However the traditional superabsorbents are mainly based on fully organic petroleum based polymers with relatively higher production cost and poor environmental friendly properties (11). Thus new types of cost-efficient and eco-friendly superabsorbents derived from naturally available raw materials have long been desired.

The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilize in agricultural materials, and are typed by the hydrolysed corn starch-g-poly (acrylonitrile), H-SPAN (12). Presently, natural macromolecules such as starch (13,14), cellulose (15), chitosan (16,17), gelatin (18), alginate (19) etc and their derivatives have been used as polymer matrix for preparing superabsorbents and the resulting materials also exhibited ameliorative properties.

GG is a hydrophilic, nonionic polysaccharide extracted from the endospermic seed of the plant *Cyamopsis tetragonolobus*. It consists of a linear backbone of - (1-4)-linked D-mannose units and is solubilised by the presence of randomly attached-(1-6) - linked galactose units as side chains. GG and its derivatives form valuable ingredients for foods, cosmetics and pharmaceuticals (20). GG has better reactivity and can be facilely modified by grafting vinyl monomers onto its backbone to derive new materials with improved structure and performance (21). The structure of guar gum is shown in Figure 1.

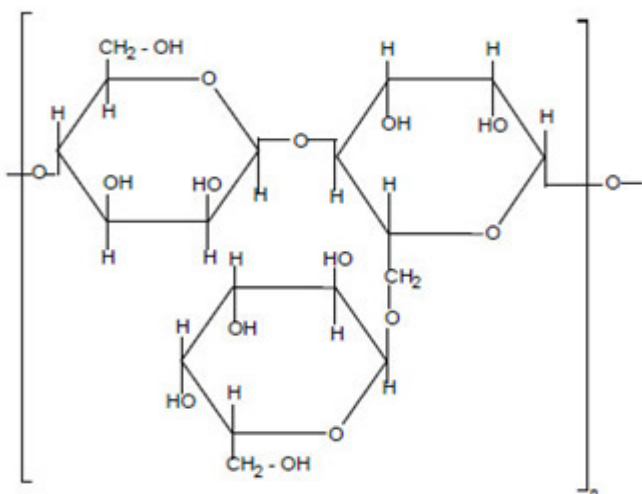


Fig.1 Structure of guar gum

2. Experimental

2.1 Materials

Guar gum (GG, Shri Ram Gum Industries Basni, Jodhpur), Methyl methacrylate (MMA stabilised for synthesis, Merck), Boric acid (H_3BO_3 , Qualigens Fine Chemicals), Acetone (Fischer Scientific, Qualigens), Hydrogen peroxide (H_2O_2 , Emplura 30% w/v) and Ethanol (C_2H_5OH , Emsure) All of these are used without further purification

2.2 Synthesis of guar gum-g-PMMA superabsorbent nanocomposites

GG (0.8g) was added in 50 mL of distilled water in a round-bottomed flask equipped with stirrer and thermostated water bath. The above solution was stirred for one hour. The monomer MMA (6mL/100mL) was added in above guar gum slurry and mixture was stirred for half an hour. Then required volume of initiator hydrogen peroxide (1mL/10mL) was added to generate radicals. The aqueous solution of cross-linker boric acid (0.1g/10 mL) was added in the mixture. The reaction mixture was continuously stirred and heated to 60°C for about 3 hours. After that it was precipitated using excess of acetone and kept overnight. Then it was washed several times with mixture of distilled water and ethanol (60:40) to remove homopolymer and unreacted mass. The grafted product was dried in oven at 80°C. Finally, the dried resulting product was pulverized into powder.

2.3 Absorbency or Swelling Measurement

Absorbency of superabsorbent composite is measured by the free swelling method and calculated in terms of percentage swelling. A 0.1 g of dry sample was immersed in distilled water at room temperature for 24 h to reach swelling equilibrium. The swollen gel was taken out, dried between folds of filter paper (blotting) and weighed. After weighing the swollen samples, the equilibrium water absorbency of the superabsorbent was calculated using Eq. (1)

$$\% \text{ Swelling} = \frac{W_2 - W_1}{W_1} \times 100 \quad \dots\dots\dots (1)$$

% Swelling is the equilibrium water absorbency of sample which are the averages of three measurements.

W_1 and W_2 are the weight of the dry sample and water swollen sample respectively.

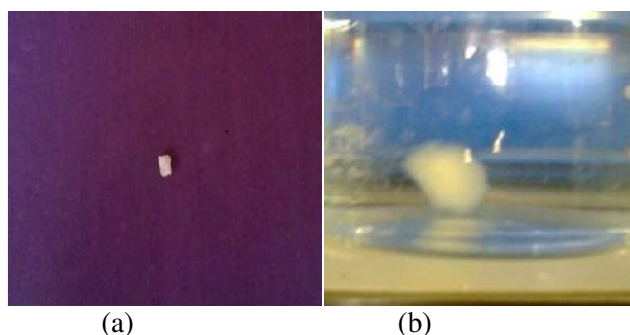


Fig.2 (a) Dry composite (b) Swollen composite

3. Results and discussion

3.1 SEM analysis

Scanning electron microscopy was used for analyzing surface morphology of prepared composite. SEM observations revealed that prepared superabsorbent composite has an uneven and coarse surface. It has porous and broad network structure. These observations are in good agreement with our water absorbency observations.

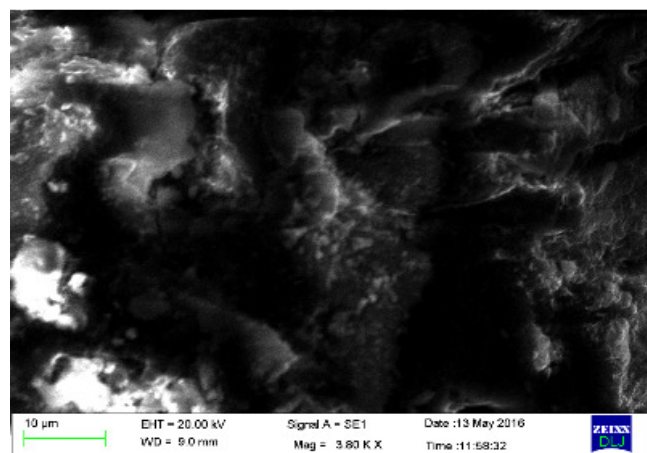


Fig. 3 SEM micrograph of guar gum grafted PMMA composite.

3.2 FTIR analysis

To study the functional groups and bonds characteristic of prepared superabsorbent, FTIR was carried out on sample made by pelleting with KBr. FTIR spectra was collected in a Agilent Cray 600 series spectrophotometer in the range $4000\text{--}400\text{ cm}^{-1}$. The FTIR spectrum for native guar gum showed broad

band in a region of 3324 cm^{-1} were attributed to stretching vibration of O–H bond that exhibited the presence of large number of free hydroxyl groups in the guar backbone. The finger printing region of guar gum consists of characteristic peaks from 862 to 1145 cm^{-1} designated to the C–O bond stretch. The bands at 1636 cm^{-1} and 1376 cm^{-1} are due to bending vibration of OH and CH_2 respectively. The sharp band at 2926 cm^{-1} was due to CH_2 group stretching [22]. The spectra of guar gum grafted PMMA composite exhibited a broad peak at 3453.8 cm^{-1} which indicates stretching vibration of the OH group, a smaller peak at 2925 cm^{-1} is attributed to C–H stretching vibrations. The absorption band at 1720 cm^{-1} is due to C=O stretching vibrations. There is a distinct absorption band from 1250 cm^{-1} to 1152 cm^{-1} which can be attributed to C–O–C stretching vibrations. The band at 1426 cm^{-1} can be attributed to bending vibration of C–H bonds of $-\text{CH}_3$ group. The peak at 1025.7 cm^{-1} is due to coupling of C–O stretching and O–H ‘in plane’ bending vibrations. The presence of the characteristic peaks clearly proves that PMMA has been successfully grafted onto the guar gum.

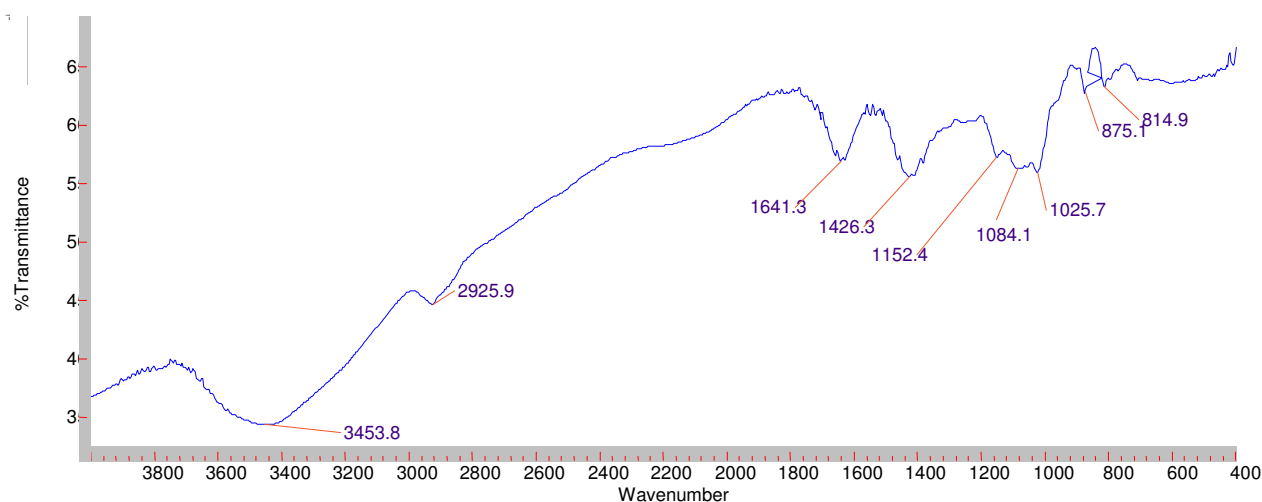


Fig.4 FTIR spectra of guar gum grafted PMMA composite

3.3 XRD Analysis

X-ray diffraction (XRD) is a powerful non destructive technique for characterizing crystalline materials. X-ray diffraction (XRD) pattern was obtained with Philips X’pert pyrosystem Cu $\text{K}\alpha$ radiation ($\lambda=1.54$ angstrom and $\theta = 0-80^\circ$) at room temperature. Crude guar gum was largely amorphous and two peaks were observed at the scattering angle (2θ) at 17.5° and 20.4° [23]. The grafted composite showed two peaks at scattering angle (2θ) at 30° and 50.9° . This shows the development of crystallinity in superabsorbent composite. The average crystallite size was calculated using Scherrer equation and found to be 36.7 nm .

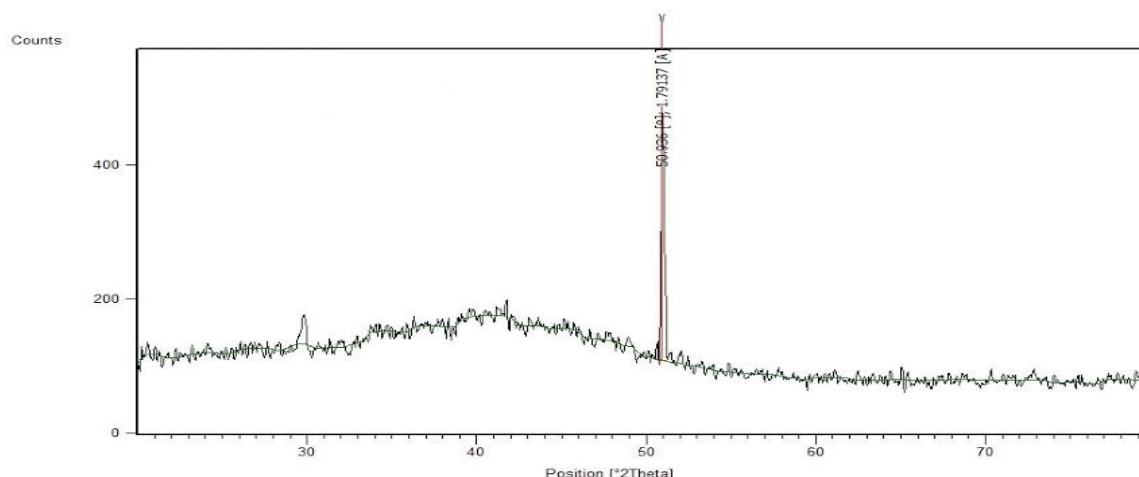


Fig.5 XRD pattern of guar gum grafted PMMA composite

3.4 TGA Analysis

Figure 6 shows the thermogram of GG-g-PMMA composite. From the figure it can be seen that there is no appreciable weight loss at 100°C. The onset of thermal degradation occurs at 261°C with a weight loss of 14% which is the result of desorption of water. The composite shows 71% weight loss at 335°C. There is about 84 % weight loss at 550°C. At 881°C composite loses 87% of its weight whereas guar gum loses almost all its weight at 600°C [24]. This shows the better thermal stability of grafted composite.

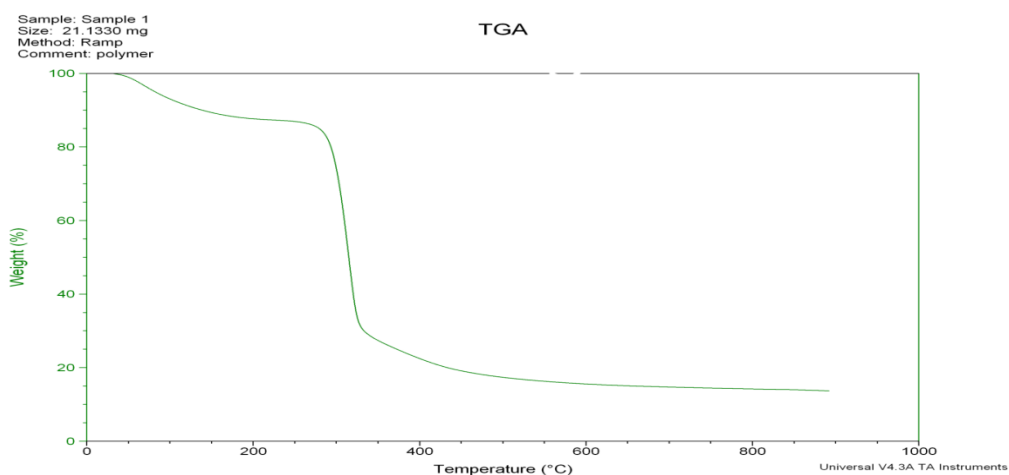


Fig.6 TGA curve of GG-g- PMMA composite

3.5 Effect of reaction parameters

3.5.1 Effect of monomer concentration

The influence of monomer (methyl methacrylate) concentration has been studied by synthesizing series of composites with varied volume of methyl methacrylate. The effect of monomer concentration on water

absorbency is shown in figure 7. It is clear from the figure that initially water absorbency increases by increasing monomer concentration and reaches maximum at 6 % (v/v) and thereafter it reduces. Copolymerization between MMA and guar gum increases the percentage swelling thereafter it decreases due to formation of homopolymer of MMA.

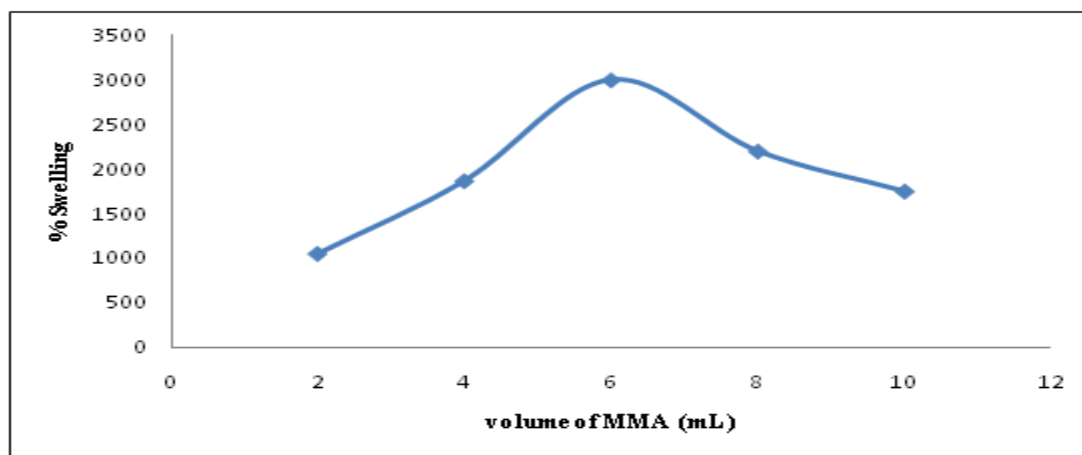


Fig.7 Effect of monomer concentration on percentage swelling

3.5.2 Effect of initiator concentration

Initiator has greater influence on rate of polymerization as it involves in initiating free radicals. Figure 8 depicts that continuous increase in water absorbency is observed till an optimum volume of 1mL which indicates that initiation of free radicals increases the polymerization which in turn increases absorbency and decreases with further increase in content of initiator. At higher levels of initiator concentration, grafting is unfavourable and this behaviour is attributed to the formation of excess number of free radical sites leading to shorter polymer chains. The molecular weight in free radical polymerization will decrease with an increase of initiator concentration. With the decrease of molecular weight, the relative amount of polymer chain ends increases. The polymer chain ends do not contribute to water absorbency [22, 25]. Therefore, the increase of initiator content is responsible for decrease in water absorbency.

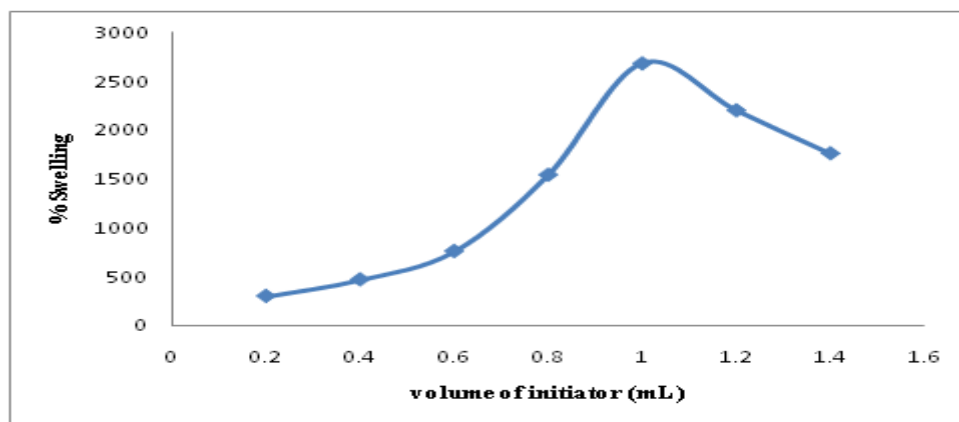


Fig.8 Effect of initiator concentration on percentage swelling

3.5.3 Effect of cross-linker content

Crosslinking density is an extremely important swelling control element. Relatively small changes can play a major role in modifying the properties of superabsorbent polymers. In our study the water absorbency decreases with increase of cross-linker content from 0.1 to 1.2 wt%. When the crosslinker content is more than 0.1 wt%, the absorbency of superabsorbent composite decreases because of an increase of soluble content. On the other hand, a higher crosslinker content results in generation of more crosslink points, which in turn causes the formation of an additional network i.e. intense cross linked structure and decreases the space left for water to enter [25]. The results are in conformity with Flory's network theory [26] and similar observations were previously reported by others [27, 28].

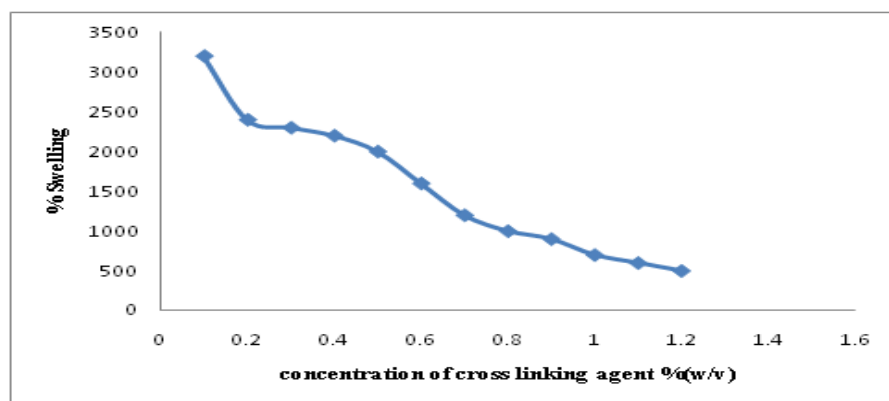


Fig.9 Effect of crosslinker concentration on percentage swelling

3.5.4 Effect of guar gum content

The effect of GG content on water absorbency of the superabsorbents is shown in Figure 10. The water absorbency increased with increasing the amount of GG from 0.2 to 1.6 wt %. When the amount of GG was low, the homopolymer content increases which cannot contribute to water absorbency. The homopolymer content decreased with the increase of GG content at a fixed cross-linking density [29].

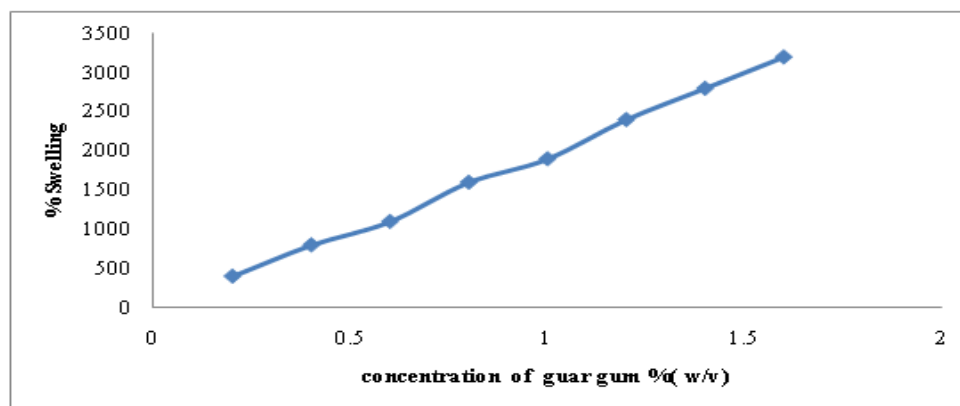


Fig.10 Effect of guar gum concentration on percentage swelling

3.5.5 Effect of reaction temperature

Figure 11 shows that percentage swelling of superabsorbent composite increase as the reaction temperature increases from 30 to 60°C and decreases with further increase in reaction temperature. When

the reaction temperature is decreased, the rate of polymerization also decreases, which results in the enhancement of cross-linking efficiency [28]. At the same crosslinker content, the water absorbency decreases with increase of cross linking efficiency according to Flory's network theory [26]. With the increase of reaction temperature, the polymerization reaction rate increases and the molecular weight decreases, so the water absorbency is also decreased.

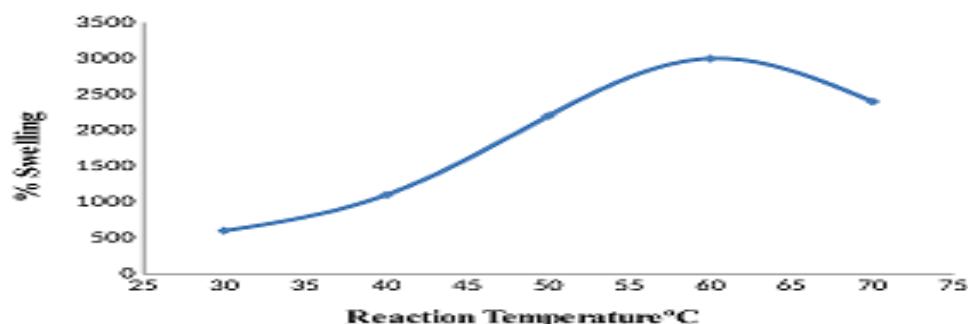


Fig.11 Effect of reaction temperature on percentage swelling

3.5.6 Effect of saline concentration on percentage swelling

The effect of NaCl and CaCl₂ concentration on percentage swelling was studied. The percentage swelling is less than in distilled water. Different concentration of NaCl and CaCl₂ solutions were prepared in order to study effect of ion charge and ion concentration on water absorption [30]. The water absorption decreases with increasing the ionic strength of saline solution as cited in Flory equation [26]. This can be attributed to change in osmotic pressure in the environment. The same reason results in the decrease in swelling as the concentration of salt is increased. At low salt concentration the swelling rate of composite is faster than at higher concentrations. The factors that caused the water absorption in the polymer included the osmotic pressure difference between the interior and exterior of polymer. The increasing osmotic pressure with increase of salt concentration led to decrease in osmotic pressure difference between the interior and exterior of the superabsorbent polymer [31]. In addition multivalent cations (Ca²⁺) can neutralize several charges inside the gel by complex formation with carboxylate groups, leading to increased ionic crosslinking degree and consequently loss of swelling [32]. The effect of cation charge and its concentration on swelling is shown in figure 12.

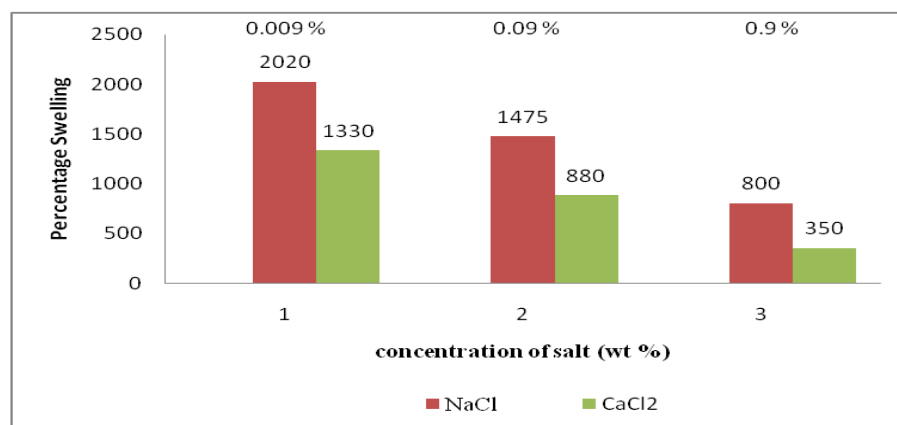


Fig.12 Effect of salt concentration on percentage swelling

3.5.7 Effect of pH

The percentage swelling of superabsorbent composite was studied at various pH values between 2.0 and 13.0 at room temperature. To prepare pH media, the stock NaOH (pH 13.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pH respectively. Under acidic pH, most of carboxylate groups are protonated, thus the main anion-anion repulsive forces are eliminated and as a result swelling capacity values are considerably lower. The swelling loss in highly basic solutions can be attributed to charge screening effect of excess Na^+ in swelling media, which in turn shields the carboxylate anions and prevents effective anion-anion repulsion [33]. In our study the prepared composite showed maximum percentage swelling (2560 %) at pH 9 as shown in figure 13.

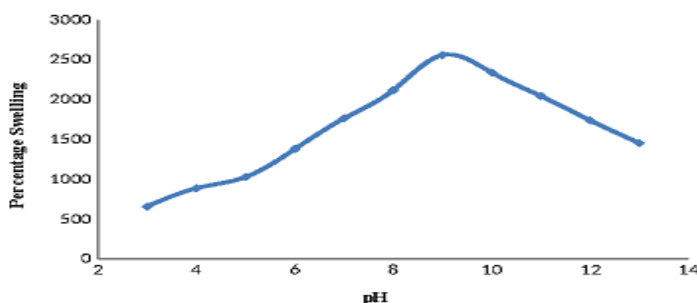


Fig.13 Effect of pH on percentage swelling

4. Conclusion

Novel superabsorbent composites of poly (methylmethacrylate)/guar gum were prepared in an aqueous solution by graft copolymerization reaction of methyl methacrylate on guar gum using boric acid as a crosslinker and hydrogen peroxide as an initiator. The composites were characterized by SEM, FTIR, TGA and XRD. The effects of initial monomer concentration, reaction temperature, amount of crosslinker, initiator concentration and guar gum concentration on water absorbency were investigated. Under our experimental conditions, prepared superabsorbent composites has water absorbency of 3000% which has composition of 1% (w/v) crosslinker, 6% (v/v) of methylmethacrylate, 1.6 % (w/v) of guar

gum, 10 % (v/v) of initiator and reaction temperature of 60°C. The effect of salt concentration and pH has also been studied. The prepared superabsorbent composite can be used in various applications like agriculture, horticulture, removal of toxic dyes, oil spill cleaning etc.

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