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## Green Synthesis and Characterization of GG-G-P (MMA-Co-AN)/MMT Nanocomposite Superabsorbent Using Microwave Irradiation



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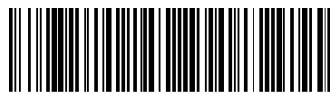
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### ABSTRACT

Complex catalyzed nanocomposites superabsorbent has been synthesized using guar gum, acrylonitrile, methyl methacrylate by graft copolymerization reaction in presence of ammonium persulphate (APS) as an initiator, hexamine Co(III) chloride complex and MMT as nanofiller *via* microwave irradiation technique. Fourier transform infrared spectroscopy (FTIR) analysis was carried out to confirm chemical structure of the composite formed *via* grafting and Scanning Electron Microscope (SEM) was used for morphological study. The composite was also characterized by X-ray diffraction (XRD) to study its crystalline nature. Thermo Gravimetric Analysis (TGA) curves reveal that the composite is thermally more stable than the guar gum and the monomers. The water absorption capacity of the superabsorbent was measured as a function of percentage swelling. Further, XRD diffractograms suggested the exfoliation of the nanoclay MMT in guar gum grafted methyl methacrylate and acrylonitrile. The effect of nanoclay on the swelling characteristics of the nanocomposite has been examined.

## INTRODUCTION

Most of the gums like Arabic gum, Acacia gum, Guar gum (GG) etc. are abundantly available and are commonly used as thickening, stabilizing, binding and emulsifying agents. These are mainly classified based on their ionic nature and origin. GG is a plant based hydrophilic, nonionic and an edible polysaccharide which is extracted from *Cyamopsis tetragonoloba* [1]. It mainly consists of galactomannans with (1, 4)-linked-B-D-mannopyranose units [2]. It is a high molecular weight carbohydrate polymer which swells in cold water. Hence, it is widely used as a thickener emulsifier in food, cosmetics and pharmaceutical industries. Gum based materials modified by grafting crosslinking irradiation are attractive for agricultural applications [3]. An improved moisture retention capacity for acrylic-acid-aniline grafted gum hydrogels has been synthesized [4]. Similar observations that have been made for grafted gum exhibited both water retention as well as dye removal properties [5]. Grafted gums with electrical conductivity applications have also been synthesized [6]. Similar usage of GG for sensor based applications has been developed [7]. Various researchers have also used gums for drug delivery applications such as for antibiotics. Interpenetrating networks for controlled release of amoxicillin trihydrate exhibited Fickian diffusion characteristics [8, 9]. GG showed potential for tablet coating, carriers for drug release [10]. GG (fig. 1) has better reactivity and can be facilely modified by grafting vinyl monomers onto its backbone to derive new materials with improved structure and performance [11].

Superabsorbent can absorb and retain huge volumes of aqueous fluids even under some pressure compared with traditional absorbents (i.e. cotton, sponge, colloid silica ) therefore it found extensive application in various fields including hygienic products, agriculture and horticulture, wastewater treatment and drug delivery system, etc.[12]. Currently, most of the superabsorbent used in practice is mainly petroleum-based synthetic polymers with high production cost and poor environmentally friendly characteristics, and thus the study and development of natural polymer-based superabsorbents has become subject of great interest due to their commercial and environmental advantages [13]. Presently, many natural polysaccharides such as starch [14], cellulose [15], chitosan [16] and alginate [17], etc. and their derivatives have been used to prepare new type of superabsorbents. Because of their exceptional properties, i.e., biocompatibility, biodegradability, renewability and nontoxicity, polysaccharides are the main part of the natural based superabsorbent composites. Graft copolymerization of vinyl monomers onto polysaccharides is an efficient route for the

preparation of superabsorbent. Vinyl graft copolymerization onto polysaccharides and proteins is a well-known method for synthesis of natural-based superabsorbent composite [18]. In this research work, we have tried to prepare nano superabsorbent which can be used in various fields.

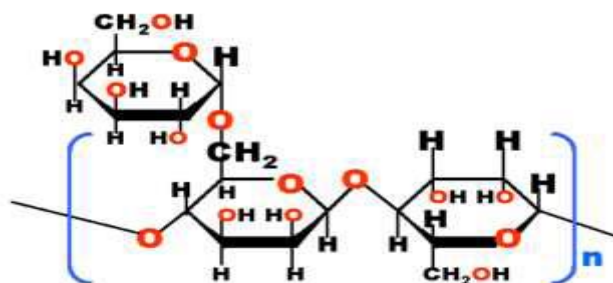


Figure 1: Structure of guar gum (GG)

## MATERIALS AND METHODS

### Materials

Monomer such as acrylonitrile and methyl methacrylate were purchased from Himedia, Mumbai, India and were purified as per the standard procedure done by us earlier [19]. All other chemicals such as the ammonium persulfate, guar gum were purchased from E. Murk, India. Unmodified MMT was purchased from Nanomer company (USA). Orthophosphoric acid and methanol was purchased from Qualigen India Ltd.

### Preparation of Hexamine Cobalt (III) chloride $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$

It was prepared by the method available in the literature and its preparation was done by us earlier [20] and it is used as catalyst in this research work.

### Preparation of GG-g-P (MMA-co-AN) copolymer

In various reaction vessels, desired quantities of methyl methacrylate, acrylonitrile, guar gum, Cobalt (III) chloride complex and deionized water were taken and stirred at 200 rpm in an inert atmosphere by passing nitrogen gas for 15 min. Then the reaction vessels were sealed with rubber septums. The reaction vessels were kept in a constant temperature bath. Then required amount of initiator ammonium persulfate was injected carefully into the reaction vessels and heated under 700W microwave irradiation constantly. After attaining 70°C, the

microwave power was reduced to 40W. The duration of polymerization was continued for 120s – 210s. Then the reaction was ceased and the vessel was cooled under ice water. The grafted copolymer was washed in benzene and then deionized water for thrice to remove excess water soluble substances present. The copolymer was dried in air till a constant mass was obtained. Similarly, a number of samples were prepared by microwave irradiation. Interaction of methyl methacrylate and acrylonitrile is given in Figure 2. Finally, it was dried in an oven at 80°C for 3-4 h. The dried product was pulverised into powder and kept in plastic bag for characterization.

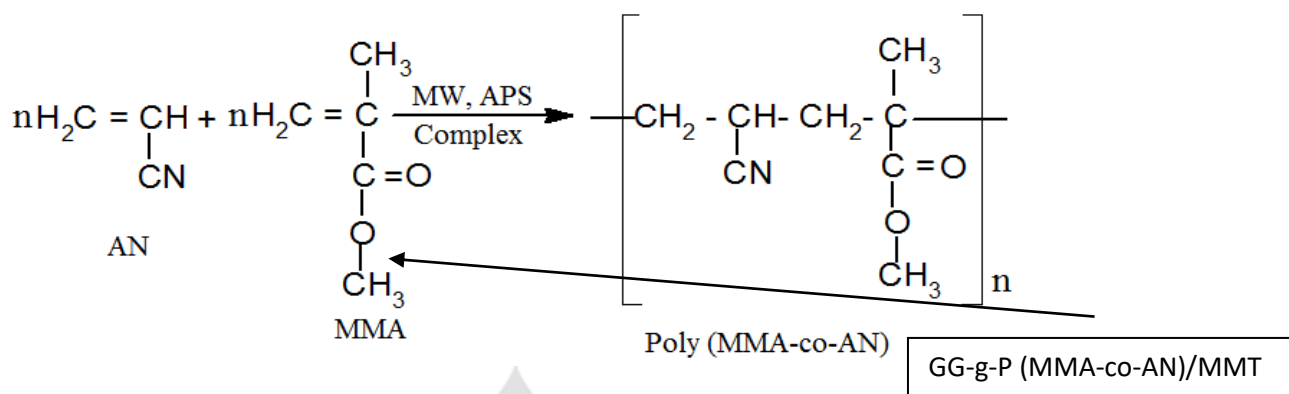
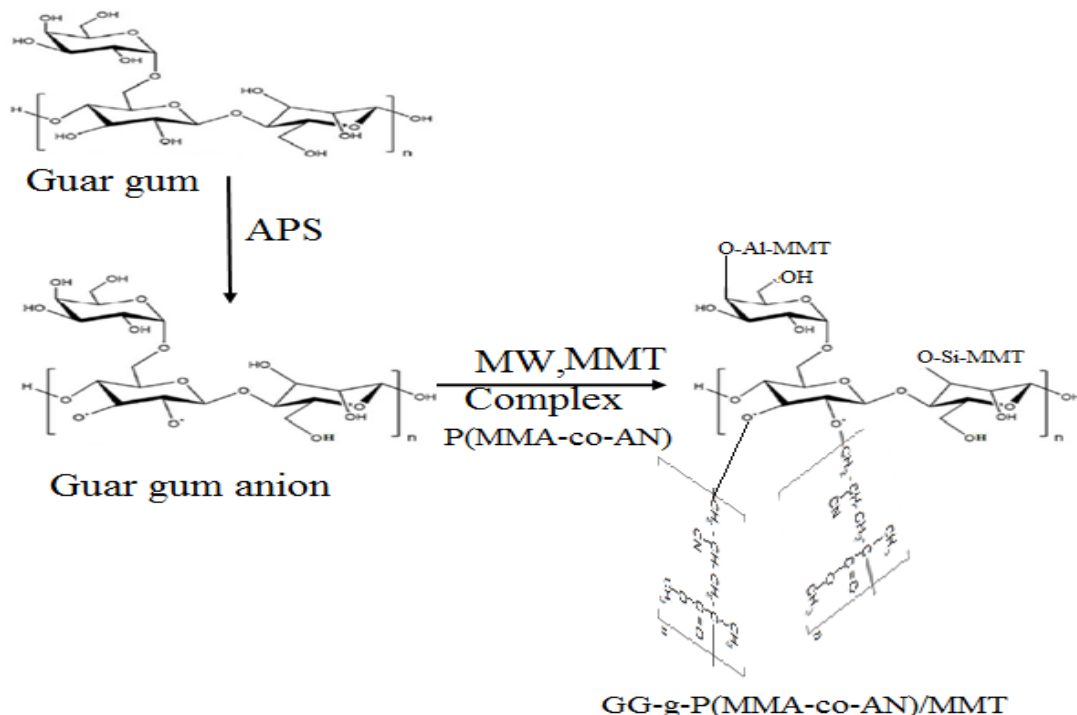


Figure 2 Scheme of formation of Copolymer P (MMA-co-AN)

### Preparation of GG-g-P (MMA-co-AN)/MMT nanocomposite

In various reaction vessels, desired quantities of methyl methacrylate, acrylonitrile, guar gum, MMT, Cobalt (III) chloride complex and deionized water were taken and stirred at 200 rpm in an inert atmosphere of nitrogen gas for 15 min. Other procedures were similar as above described for the preparation of the copolymer and the nanocomposite samples were prepared which is shown in Figure 3 and the samples were stored in oven for characterization.



**Figure 3 Scheme of formation of Nanocomposite GG-g-P (MMA-co-AN)/MMT**

## Characterization

### Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis of pure guar gum, pure MMA, AN, guar gum grafted copolymer and the composite were carried out using FTIR spectrophotometer (Perkin-Elmer spectrum 1000) between 400 and 4000  $\text{cm}^{-1}$ . The samples were coated on a potassium bromide (KBr) plate and dried in a vacuum oven at 120°C before it was tested.

### X-Ray Diffraction Studies (XRD)

XRD measurements for the composites have been performed using advanced diffractometer (analytical, XPERT-PRO) equipped with Cu-K $\alpha$  radiation source ( $\lambda = 0.154 \text{ nm}$ ). The diffraction data were collected in the range of  $2\theta = 3^\circ - 60^\circ$  using a fixed time mode with a step interval of 0.05°.

### **Thermogravimetric Analysis (TGA)**

The TGA of guar gum, monomer and grafted guar gum nanocomposite were carried out by using Perkin-Elmer Pyris Diamond 6000 analyzer in an atmosphere of nitrogen. The sample was subjected to a heating rate of 10°C /min in a heating range of 20°C - 900°C.

### **Scanning Electron Microscope (SEM)**

The morphological characterization of the specimen was carried out using a SEM (JEOL, JSM-840A microscope). The specimens were gold sputtered prior to microscopy.

### **Water Absorbency**

Absorbency of superabsorbent polymer composite is measured by the free swelling method and calculated in terms of percentage swelling. 0.1 g of dry sample was immersed in distilled water at room temperature for 12 hours to reach swelling equilibrium. The swollen composite was taken out, dried between folds of filter paper (blotting method) and weighed. After weighing the swollen samples, the equilibrium water absorbency of the superabsorbent was calculated using Eq. (1)

$$\text{Percentage Swelling} = \frac{w_2 - w_1}{w_1} \times 100 \quad \text{-----} \quad (1)$$

$w_1$  = Weight of the dry sample

$w_2$  = Weight of water swollen sample

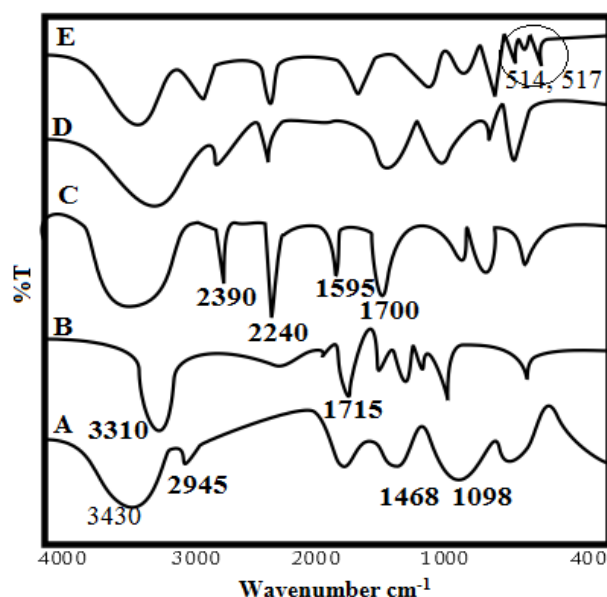
### **Biodegradability**

#### **Degradation by sludge water**

The activated sludge water was collected from septic tank receiving toilet and domestic wastewater. The sludge water was collected in a polypropylene container, which was filled completely and then closed perfectly. Then the wastewater was transferred to the lab immediately. After settling for 1h the total solid concentration was increased to 5000 mg/l. Then activated sludge water and sample (0.2g) were incubated together in a sterilized vessel at room temperature ( $28 \pm 2^\circ\text{C}$ ). Immersed samples were removed at time intervals for biodegradation study through weight loss. Vessels containing polymer sample without sludge water were treated as control.

## RESULTS AND DISCUSSION

### IR Spectra



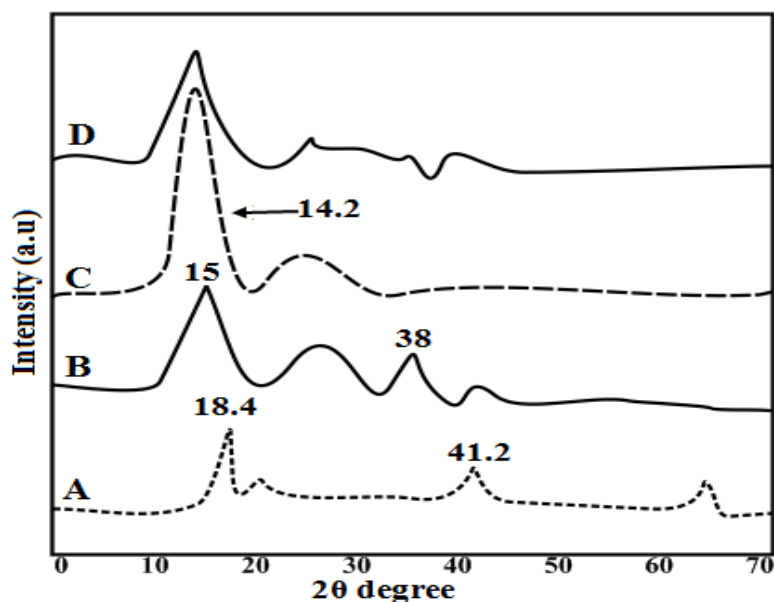
**Figure 4 FTIR Spectra of Guar gum (A), PMMA (B), PAN (C), GG-g-P(MMA-co-AN) copolymer (D), and GG-g-P(MMA-co-AN)/MMT composite (E)**

FTIR spectrograms of neat GG Fig 4 (A) shows characteristic bands at 3430 and 2945  $\text{cm}^{-1}$  for -OH stretching vibrations and -C-H stretching of GG. The bands at 1468 and 1098  $\text{cm}^{-1}$  corresponds to -C-H and -O-H bending vibrations [20]. The spectra of grafted copolymer and composite showed the existence of a moderate peak at 2240  $\text{cm}^{-1}$  in Figure 4 (D) and (E) which is an evidence of grafting and this peak is due to stretching vibration of nitrile group. There is also a small characteristic peak at 2390  $\text{cm}^{-1}$  which is a peak for cyanide group. It is observed that all most all the peaks of polymethyl methacrylate, polyacrylonitrile and GG are found in GG grafted copolymer and composite, but two new peaks at 514 and 517  $\text{cm}^{-1}$  are observed in nanocomposite GG-g-P(MMA-co-PAN)/MMT. These two peaks are due to Al-O stretching and Si-O bending of MMT. Similar results were reported in literature [21].

### XRD

XRD diffractogram of GG Fig 5 (A) shows a sharp peak at 18.4 and 41.2°. For PMMA sharp peaks are observed at 15° and 38°. One peak is observed at 14.2° for PAN shown in Fig 5 (C). It is shown that there are no sharp peaks obtained for synthesized composite Fig 5 (D) and a small peak is observed at 14.2° which indicates the presence of nitrile group in the composite.

It is concluded that the composite is amorphous in nature and is in nano order. Further, the XRD patterns suggest that the hydrophobic PAN is inserted into the galleries of the hydrophilic silicate through polymerization and the disordered insertion of the polymer into hydrophilic silicate layers made the nanocomposite hydrophilic in nature which is confirmed by percentage of swelling.

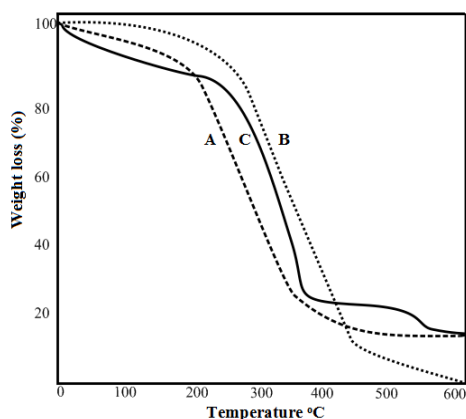


**Figure 5 XRD of Guar gum (A), PMMA (B), PAN (C) and GG-g-P(MMA-co-AN)/MMT (D)**

### TGA

TGA curves of guar gum, PMMA and GG-g-P (MMA-co-AN)/MMT nanocomposite are shown in Figure 6. TGA of guar gum Fig 6 (A) shows weight loss in two stages. The onset of thermal degradation occurs at 250°C with weight loss of 15% which is due to presence of moisture in sample. The second stage is degradation stage which occurs at 325°C with weight loss of 73%. In TGA curve of the nanocomposite Fig 6 (C), 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. TGA curve of PMMA Fig 6 (B) shows weight loss of 20% at 337°C. PMMA shows about 100% weight loss at 425°C. This shows the better thermal stability of the grafted nanocomposite.

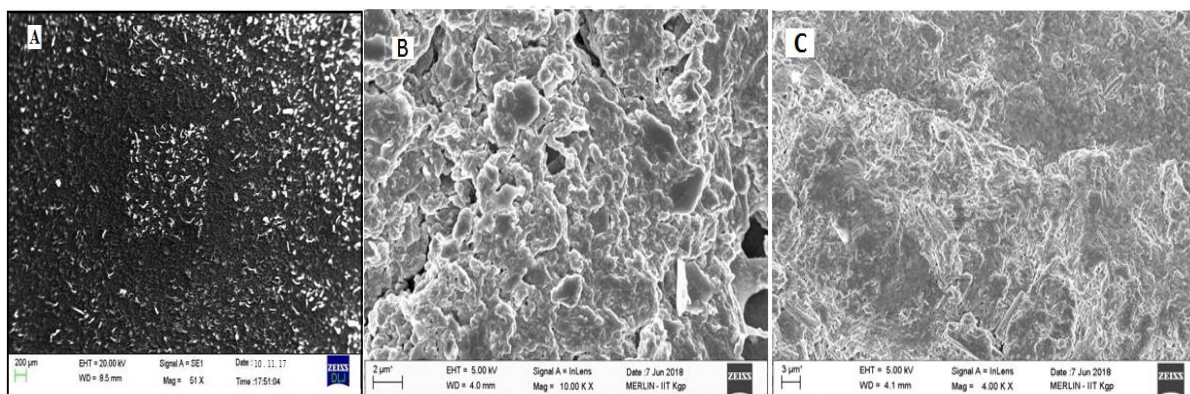




**Figure 6 TGA curve of Guar gum (A), PMMA (B) and GG-g-P(MMA-co-AN)/MMT Nanocomposite**

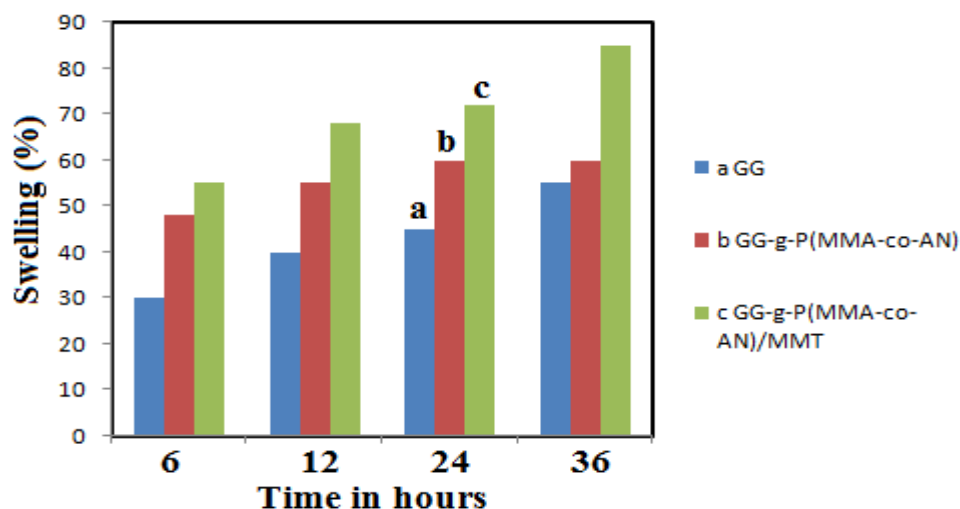
### SEM

SEM was used for analyzing surface morphology of the prepared composite. Fig. 7 shows SEM micrographs of guar gum and prepared superabsorbent composite at different magnifications. SEM observation reveals that the prepared superabsorbent composite has an uneven and coarse surface. It is clear from figure that the composite has more rougher and porous structure as compared to guar gum. These observations are in good agreement with our percentage of swelling observations.



**Figure 7 SEM micrograph of Guar gum (A), GG-g-P(MMA-co-AN) copolymer(B), GG-g-P(MMA-co-AN)/MMT (C)**

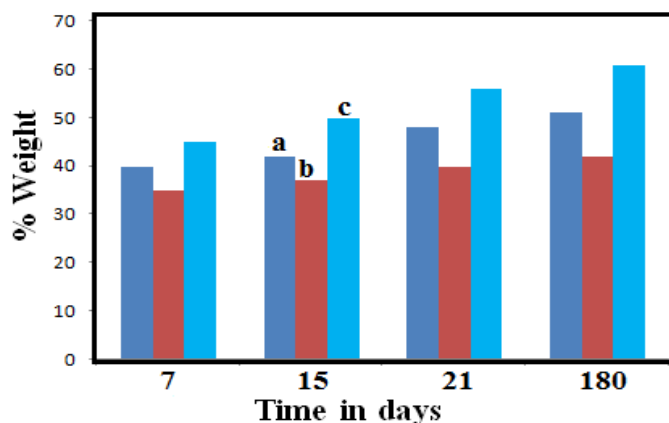
### Water Absorbency



**Figure 8 Percentage swelling of guar gum (a), GG-g-P(MMA-co-AN) copolymer (b) and GG-g-P(MMA-co-AN)/MMT composite (c)**

Water absorbency was determined for 36 h and it is expressed as the function of percentage swelling in fig. 8. It is observed that the water absorbency is more for the composite though there is a hydrophobic monomer in the composite (Fig.8). Reason is that the hydrophobic monomers are inserted into the galleries of the hydrophilic silicate through polymerization and the disordered insertion of the polymer into the hydrophilic silicate layers made the nanocomposite hydrophilic in nature.

### Biodegradability



**Figure 9 Biodegradation of GG (a), GG-g-P(MMA-co-AN) copolymer (b) and GG-g-P(MMA-co-AN)/MMT nanocomposite (c)**

Biodegradability in function of weight loss of GG, Copolymer GG-g-P(MMA-co-AN) and nanocomposite GG-g-P(MMA-co-AN)/MMT were given in figure 9. In 180 days all samples show satisfactory results, but GG-g-P(MMA-co-AN)/MMT is more degradable as compared to others. It is due to hydrophilic nature of nanocomposite or high water content in the nanocomposite which facilitates the growth of micro-organisms rapidly and is responsible for enhancing the biodegradation which is leading to weight loss. It is interesting that the biodegradation of copolymer is lesser than the others in each case. It is due to hydrophobic nature of P(MMA-co-AN) which does not open the room for growing the micro-organism and is responsible for lesser biodegradation.

## CONCLUSION

Novel guar gum-g-poly (MMA-co-AM)/MMT superabsorbent composite was synthesized in aqueous solution using APS as an initiator and Co(III) chloride complex as catalyst in the graft copolymerization reaction. FTIR confirmed grafting between methyl methacrylate, acrylonitrile and guar gum. SEM analysis showed that the composite has rough and porous surface. XRD curves indicate that the composite is nanocomposite. TGA studies reveal that the nanocomposite is thermally stable. The water absorbency of the nanocomposite was increased using MMT as nanofiller. The composite shows maximum percentage swelling in distilled water and maximum biodegradability also. So it is a good green composite and it can be used for vegetation in dried land and also soil conditioner.

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