Complex Catalyzed Microwave Assisted Green Synthesis of Guargum-g-P (MMA-co-AM)/ MMT Nanocomposite Superabsorbent

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Abstract: ***Microwave assisted synthesis of a copolymer of vast application is being presented in recent communication. In the study, Guargum-g-P(MMA-co-AM)/montmorillonite nanocomposite superabsorbent has been prepared by microwave method. The electromagnetic energy was generated by magnet at 2.45GHz .The power has been adjusted between 10W & 700W in a microwave continuously. The temperature of the reaction vessel has been kept in control with an IR temperature pickup. Graft copolymerization of guargum (GG) with two monomers such as MMA (hydrophobic) and AM (hydrophilic) under the influence of microwave irradiation in presence of cobalt (III) complex as catalyst and ammonium persulfate as initiator with and without additive MMT has been studied. The maximum grafting obtained under MW irradiation method has been found to be 91.5% in 180s. The yield of guargum-grafted-P(MMA-co-AM) copolymer and guargum-grafted- P(MMA-co-AM) / MMT nanocomposite have been characterized by using IR, XRD,SEM and their properties like superabsorbency and biodegradability, etc are evaluated for their better commercialisation and industrialisation as well.***

Keywords: Guargum, Graft copolymerization, Microwave assisted synthesis, Superabsorbent

1. Introduction

The use of microwave (MW) irradiation is one of the best methods to conduct the preparation of polymers and nanocomposites. Due to the homogeneity, high efficiency and low energy consumption of microwave irradiation, microwave-assisted chemical synthesis has attracted wide attention and microwave assisted heating increases the rate of polymerization rapidly and improve the properties of the products. We found better quality and quantity of products in presence of transition metal chelating complex in MW irradiation [1]. Microwave heating is ideal for rapid transformation and do not require extensive heating. Microwave assisted synthesis can be faster than those of conventional heating method which results less energy consumption [2]. Microwave assisted transition metal complex catalyse emulsion polymerization has greater advantages of rapid reaction, high percentage of the products in very less energy consumption. The reactions are completed in few minutes instead of hours [3, 4]. The non-conventional emulsifier-free- emulsion polymerization i.e microwave-assisted synthesis has been chosen for polymerization process throughout the research work to prepare required polymer nanocomposite, because it is both time and energy saving process [5]. The emulsion polymerization is a unique process which controls the chain initiation, propagation, chain transfer and chain termination easily [6].

Guargum is a hydrophilic and non- ionic edible carbohydrate polymer having high molecular weight which swells in cold water. It is very cheap, easily available and non–toxic polysaccharide. So it is widely used in many industrial fields and chemical laboratories. It consists of a straight chain of mannose units which act as highly efficient water thickening stabilizing, binding and emulsifying agents. Guargum based materials modified by grafting cross linking irradiation are attractive [7, 8]. An improved moisture retention capacity for MMA-co-AM grafted guargum nanocomposite superabsorbent has been synthesized [9, 10]. Microwave assisted grafting is a convenient method with rapid reaction rates and higher yields. Superabsorbent polymers are moderately cross- linked hydrophilic network that can absorb and retain large quantities of aqueous fluids retaining their shapes [11]. Because of the unique characteristics they are broadly used such as hygienic products as disposable diapers and feminine napkins, gardening in desert areas [12, 13]. Thus new types of cost efficient and green synthesized eco-friendly superabsorbents derived from naturally available raw materials have long been desired.

In this paper, we have tried to synthesize nanocomposite superabsorbent by microwave irradiation technique through graft copolymerization of two monomers such as methyl methaacrylate (MMA) and acrylamide (AM) onto the chain of guargum with nanofiller MMT to furnish the superabsorbent polymer nanocomposites [14]. We have to study the different characteristics of the so prepared nanocomposite superabsorbent by swelling behaviour and biodegradability which have wide range application on elements of the environments and will have positive effect in green revolution [15].

2. Experimental

2.1 Materials

Monomers such as acrylamide and methyl methacrylate were purchased from Himedia, Mumbai, India and were purified as per the standard procedure done by us earlier[16,17]. All other ingradients such as the ammonium persulfate, guargum were purchased from E. Merck, India. Unmodified MMT was purchased from Nanocor company

(USA). Orthophosphoric acid and methanol was purchased from Qualigen India Ltd.

2.2 Preparation of Hexamine Cobalt (III) Cloride [Co (NH$_3$)$_6$]Cl$_3$

It was prepared by the method available in the literature. 240gm (1 mol) of Cobalt (III) Chloride hexahydrate and 160gm (1 mol) of ammonium chloride were added to 200ml of water. The mixture was shaken until most of the salts had dissolved. Then 4gm of activated decolorized charcoal and 50ml concentrated ammonia solution were added. Air was bubbled through the mixture vigorously for about 4h until the red solution becomes yellowish brown. The crystals and carbon were filtered. Then about 15-30 ml of conc. HCl was added. 1500 ml of water and sufficient acid was used to give the entire mixture an acidic reaction. The mixture was heated on a hot plate to get complete solution and as filtered in hot condition. The hexamine cobalt (III) chloride was precipitated by adding 400 ml of conc. HCl and cooled at 0^{0}C. At last the precipitate was filtered and washed with first 65% and then 95% alcohol then it was dried in oven.

2.3 Preparation of Guargum-g-P(MMA-co-AM) Co-polymer

In various reaction vessels, desired quantities of methyl methacrylate, acrylamide, guargum, Cobalt (III) chloride complex and deionised water were taken and stirred at 200 rpm in an inert atmosphere with 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^{0}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 co-polymer was washed in benzene and then deionised water for thrice to remove excess water soluble substances present. The co-polymer was dried in air till a constant mass was obtained. Similarly a number of samples were prepared by microwave irradiation .Finally it was dried in an oven at 80^{0}c for 3-4 h. The dried product was pulverised into powder and weighed in an electronic weighing machine. Percentage of conversion of co-polymer is calculated by using following formula.

Percentage of Conversion = (W – Wo)/ Wo × 100
Where W= Wt. of Guargum-g-P(MMA-co-AM)
Wo = Wt. of Guargum

2.4 Preparation of [Guargum-g-P(MMA-co-AM)]/MMT nanocomposite

In various reaction vessels, desired quantities of methyl methacrylate, acrylamide, guargum, MMT, Cobalt (III) chloride complex and deionised water were taken and stirred at 200 rpm in an inert atmosphere with nitrogen gas for 15 min. Other procedures are similar as above described for the preparation of the co-polymer and the nanocomposite samples were prepared..Effect of variation of concentration of Guargum, MMA, AM, APS and MMT with respect to time in second were given in table 1 by microwave irradiation method. The percentage of conversion is calculated by using above formula also.

Table 1: Effect of variation of concentration of Guargum, MMA, AM, MMT, APS with time by microwave heating

Sample Code	Guargum amount (in gm)	[MMA] mole.dm^{-3}	[AM] mole.dm^{-3}	[APS] mole.dm^{-3}	[Co (III) complex] mole .dm^{-3}	[MMT] mole. dm^{-3}	Time in sec	% of conversion
GH$_1$	0.2	0.6	0.8	2.0	0.2		180	81.2
GH$_2$	**0.4**	**0.6**	**0.8**	**2.0**	**0.2**		**180**	**90.5**
GH$_3$	0.6	0.6	0.8	2.0	0.2		180	89.8
GH$_4$	0.8	0.6	0.8	2.0	0.2		180	87.8
GH$_5$	0.4	0.2	0.8	2.0	0.2		180	80.3
GH$_6$	0.4	0.4	0.8	2.0	0.2		180	78.9
GH$_7$	0.4	0.8	0.8	2.0	0.2		180	77.8
GH$_8$	0.4	0.6	0.2	2.0	0.2		180	74.9
GH$_9$	0.4	0.6	0.4	2.0	0.2		180	75.3
GH$_{10}$	0.4	0.6	0.6	2.0	0.2		180	75.2
GH$_{11}$	0.4	0.6	1.0	2.0	0.2		180	74.6
GH$_{12}$	0.4	0.6	0.8	0.5	0.2		180	75.9
GH$_{13}$	0.4	0.6	0.8	1.0	0.2		180	74.8
GH$_{14}$	0.4	0.6	0.8	1.5	0.2		180	74.3
GH$_{15}$	0.4	0.6	0.8	2.5	0.2		180	79.6
GH$_{16}$	0.4	0.6	0.8	2.0	0.2	1.25	180	86.5
GH$_{17}$	0.4	0.6	0.8	2.0	0.2	2.5	180	87.4
GH$_{18}$	**0.4**	**0.6**	**0.8**	**2.0**	**0.2**	**5.0**	**180**	**91.5**
GH$_{19}$	0.4	0.6	0.8	2.0	0.2	10.0	180	86.9
GH$_{20}$	0.4	0.6	0.8	2.0	0.2	5.0	120	85.2
GH$_{21}$	0.4	0.6	0.8	2.0	0.2	5.0	150	86.4
GH$_{22}$	0.4	0.6	0.8	2.0	0.2	5.0	210	87.1

GH$_{1-15}$ = Guargum-g-P(MMA-co-AM) copolymer, GH$_{16-22}$ = Guargum-g-P(MMA-co-AM)/MMT nanocomposite

3. Characterization

3.1 FTIR Spectroscopy

The FTIR spectra were used to analyse composition of the samples that gave information about grafting behaviour and functional groups present in the composite structure in the range of 400 - 4000 cm^{-1} by a Perkin Elmer Paragon 500 FTIR (Boston, MA) Spectrophotometer using KBr pellets to prepare the samples.

3.2 X-ray diffraction (XRD)

XRD monitoring diffraction was performed on Philips PW-1847 X-ray crystallographic (Utah, Saltlake city) unit equipped with a Guinier focusing camera CuK_2 radiation.

3.3 Scanning Electron Microscopy (SEM)

The morphological characteristics of neat guargum, copolymer and composite were observed by using scanning electron microscope (Hitachi S4800, Japan)

4. Property Study

4.1 Water absorbency

1g of the sample was immersed in water at room temperature until equilibrium was reached. The water absorption was determined by weighing the swollen sample after it had been allowed to drain on a sieve for 10 min. The water absorbency [18] Q was calculated using the following equation:

$Q = (m - m_{o)/}m_o \times 100$

Where m and m_o are the weight of the swollen sample by water and weight of the absorbent respectively

4.2 Biodegradation

Biodegradation was done in sludge water. The activated sludge water was collected from septic tank receiving toilet and domestic waste water. The sludge water was collected [18] in a polypropylene container, which was filled completely and then closed perfectly. Then the waste water 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 ± 2^0C). Duplicate samples were removed at time intervals for biodegradation study through weight loss. Vessels containing polymer sample without sludge water were treated as control.

5. Result and discussion

5.1 FTIR Spectroscopy

FTIR spectrograms of neat guargum Fig 1 A shows characteristic bands at 3430 and 2945 cm^{-1} for -OH stretching vibrations and –C-H stretching of guargum. Similarly the bands at 1468 and 1098 cm^{-1} corresponds to -C-H and –O-H bending vibrations [19]. The spectrum of PMMA indicates the peak at 3310 cm^{-1} due to – C- H stretching and 1745 cm^{-1} due to presence of ester group. For PAM (Fig 1 C) the peaks are obtained at 3401, 1649 and 1600 cm^{-1} group which indicate the –N-H stretching, the -CO- stretching and –N-H bending of amide group respectively. In addition to that –C-N stretching band at 1390 cm^{-1} and a weak band at 599 cm^{-1} for –N-H out of plane bending frequency is observed [16]. It is observed that all most all the peaks of PMMA, PAM and guargum are found in guargum grafted copolymer and composite, but two new peaks at 514 and 517 cm^{-1} are observed in nanocomposite guargum-g-P(MMA-co-AM)/MMT. These two peaks are due to Al-O stretching and Si-O bending of MMT. Similar results were reported in literature [20,21].

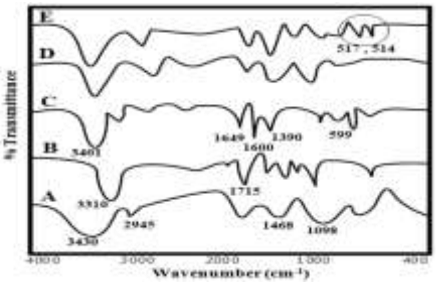

Figure 1: FTIR Spectra of (A) guargum, (B) PMMA, (C) PAM, (D) Guargum-g-P(MMA-co-AM) copolymer (GH_2) , and (D) Guargum-g-P(MMA-co-AM)/MMT nanocomposite (GH_{18})

5.2 X-ray diffraction

XR diffractogram of guargum Fig 2(A) shows a sharp peak at 18.4 and 41.2 degree. For PMMA sharp peaks are observed at 15 degree and 38 degree. Similarly one peak is observed at 30^o for PAM shown in Fig 2 C. It is shown that there are no sharp peaks obtained for synthesized composite. It is concluded that the composite is amorphous in nature and in nano order.

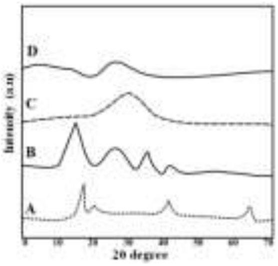

Figure 2: XR diffractograms of (A) Guargum, (B) PMMA, (C) PAM, (D) Nanocomposite Guargum-g-P(MMA-co-PAM)/MMT (GH_{18})

5.3 Scanning Electron Microscopy

SEM analysis was carried out for morphological study of composite (Fig 3 A), grafted copolymer (Fig 3 B) and guargum (Fig 3 C). Figure 3 A shows that prepared superabsorbent composite has an uneven and coarse surface. It has porous and broad network structure. These observations are in good agreement with more water-absorbency observations.

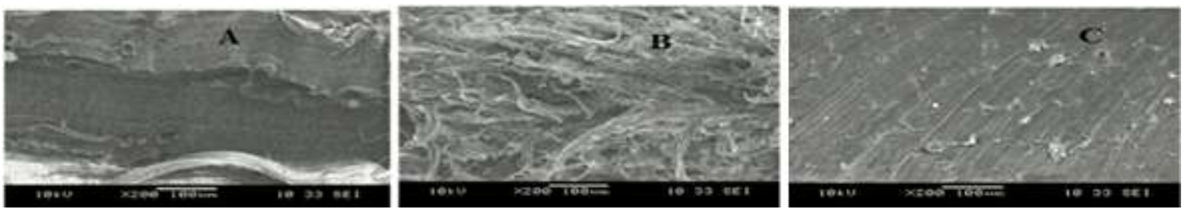

Figure 3: SEM of (C) Guargum, (B) Guargum-g-P(MMA-co-AM) copolymer (GH_2) and (A) Guargum-g-P(MMA-co-AM)/MMT nanocomposite (GH_{18})

5.4 Water absorbency or Swelling behaviour

Water absorption capacity of different samples is illustrated in the Figure 4. From the figure it was found that the composite coded with GH_{18} shows maximum water absorbency in 36h. So it is concluded that the prepared nanocomposite is a good superabsorbent. Superabsorbency is increased due to addition of MMT.

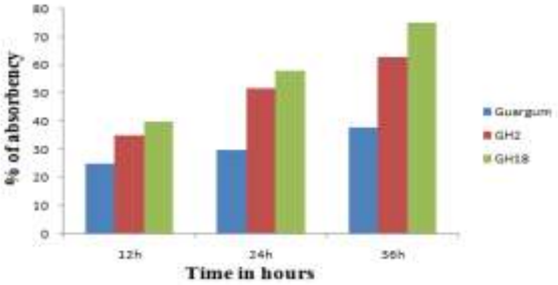

Figure 4: Water absorbency of Guargum, Guargum-g-P(MMA-co-AM) copolymer (GH_2) and Guargum-g-P(MMA-co- AM)/ MMT nanocomposite (GH_{18}) in 12h, 24h and 36h

5.5 Biodegradability

The biodegradation of different samples are given in Figure 5. In six months time all samples show satisfactory results, but nanocomposite GH_{18} is more biodegradable as compared to others. It is due to hydrophilic nature of PAM and MMT and also excellent property in pore size of nanocomposite which opened a good environment for growth of microorganism those are responsible for biodegradation. So the synthesized composite is green composite.

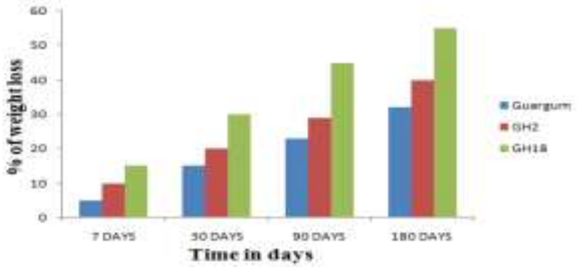

Figure 5: Biodegradation of Guargum, Guargum-g-P(MMA-co-AM) copolymer (GH_2) and Guargum-g-P(MMA-co-AM)/MMT nanocomposite (GH_{18}) in sludge water.

6. Conclusion

Guargum based composites were synthesized using microwave technique from methyl methacrylate and acrylamide as monomer and montmorillonite as a nanofiller. In this research work we use ammonium persulfate as initiator and hexaminecobalt(III) chloride as catalyst. The resulting composites were characterized by FTIR, XRD and their morphology by SEM. The observed IR peaks indicate the inclusion of MMT in the guargum copolymer P(MMA-co-AM) forming composite. XRD reveals that the synthesized composite is a nanocomposite. Water absorbency and biodegradation test confirmed that the prepared composite Guargum-g-P(MMA-co-AM)/MMT is a green composite and is an eco-friendly superabsorbent and can be used as soil conditioner as well as superabsorbent in the dried land for green vegetation.

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