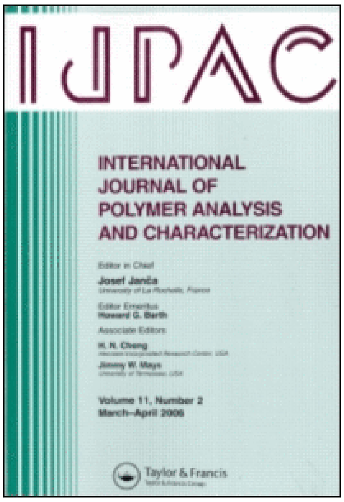

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Synthesis, Characterization, and Swelling Studies of Gum Arabic-Grafted Methacrylic Acid Polymeric Network

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SYNTHESIS, CHARACTERIZATION, AND SWELLING STUDIES OF GUM ARABIC–GRAFTED METHACRYLIC ACID POLYMERIC NETWORK

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Gum arabic–based copolymer has been synthesized by free radical polymerization of methacrylic acid (MAA) onto gum arabic in the presence of potassium persulfate (KPS). Hexamethylene tetramine (HMTA) was used to give the copolymer a three-dimensional cross-linked structure. The reaction has been carried out under vacuum in order to prevent hindrance caused by air in the reaction. Various reaction parameters like reaction time, temperature, pH, KPS concentration, MAA concentration, HMTA concentration, vacuum, and amount of solvent have been optimized to achieve maximum percentage grafting. The characterization was carried out using FT-IR, SEM, and TGA/DTA/DTG techniques, which confirmed the grafting of MAA onto gum arabic. Various swelling studies have been carried out with the copolymer at room temperature, at elevated temperatures, in different salt solutions, and in different pH media. The results showed that MAA concentration, temperature, and pH affect the percentage swelling of graft copolymer to a reasonable extent. The copolymer swelled in different salt solutions but to a lesser extent than in distilled water.

***Keywords*:** Grafting; Gum arabic; Methacrylic acid; Polymeric network; Swelling behavior

INTRODUCTION

Natural polymers like cellulose, dextrin, chitosan, psyllium, guar gum, and gum arabic have been of great importance in their raw form in the past. But from the commercial point of view they faced many drawbacks including instability and difficulty in processing. Grafting of these natural polymers[1–5] with different vinyl monomers such as acrylonitrile, acrylic acid, methacrylic acid, methyl methacrylate, and acrylamide has been of great interest for researchers as grafting improves the properties of natural polymers without causing any drastic change in their basic

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properties and thus expands their area of applicability.[6–10] Grafted polymers find applications in various fields ranging from food additives to agriculture and the biomedical sector.[11,12] In addition to this, grafting induces stimuli responsiveness in most of these polymeric materials so they respond to a large number of external factors like pH, temperature, ionic strength, and electric field, which is further helpful in utilizing these materials for wider scale applications.[13–20]

The present research deals with the synthesis of a gum arabic and methacrylic acid (MAA)–based polymeric network, using potassium persulfate (KPS) as initiator and hexamethylene tetramine (HMTA) as cross-linker. Gum arabic is one of the most useful plant gums; it is extracted as an amorphous extrudate from the stem of *Acacia arabica*, found in tropical and subtropical areas of the world. Gum arabic is a highly branched polysaccharide consisting of ß-(1→3) galactose backbone (36–42%) having linked branches of arabinose (24–29%) and rhamnose (12–14%) with glucuronic acid (16–17%) as terminating units.[21] It is available in the form of round lumps, granules, thin flakes, and powder, all of which may be white or slightly yellowish in color. It is a natural polysaccharide of commercial importance that finds applications in confectionery, flavorings, beverages, pharmaceuticals, cosmetics, and inks due to its extraordinary adhesive, suspending, stabilizing, and emulsifying properties. Grafting and network formation of gum arabic with different monomers and cross-linkers under variable synthetic conditions constitute an important method to develop a range of polymers with improved properties and applications.[22]

Since not much research has been done on gum arabic, it was thought worthwhile to work on this polysaccharide and synthesize its polymeric hydrogels. The synthesis was carried out by free radical polymerization using the KPS-HMTA system. The resultant candidate polymer was further characterized using FT-IR, SEM, and TGA/DTA/DTG techniques and finally evaluated for its swelling behavior under different conditions.

EXPERIMENTAL SECTION

Materials and Methods

Gum arabic, methacrylic acid, potassium persulfate, and hexamethylene tetramine (all from Merck Pvt. Ltd.) were used as received. Deionized water was used as solvent throughout the experiments. Weighing was done on an electronic balance (Libror AEG-220, Shimadzu). Fourier transform-infrared (FT-IR) spectra of the gels were recorded in KBr pellets using a PerkinElmer spectrophotometer. Scanning electron micrographs (SEM) of the samples were taken on a JEOL Steroscan 150 Microscope. Thermogravimetric analysis/differential thermal analysis/differential thermogravimetric (TGA/DTA/DTG) studies were carried out on a PerkinElmer Pyris Diamond thermal analyzer in air at a heating rate of 10°C/min.

Synthesis of Sample

Gum arabic (1.0 g) was taken in a beaker and 15 mL of deionized water was added. The mixture was stirred thoroughly to obtain homogeneity. This was followed by addition of a known amount of MAA ($1.59\,\mathrm{mol L^{-1}}$) and KPS ($3.69 \times 10^{-2}\,\mathrm{mol L^{-1}}$). The reaction was carried out at 60°C for 240 min. All the reaction parameters, like initiator concentration, amount of solvent, reaction time, reaction temperature, vacuum, and pH of the reaction medium, were optimized to achieve the maximum percentage grafting (P_g) (see Table I) before proceeding to the final synthesis by using the following equation:[23]

$$\%Grafting\ (P_g) = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_o are the weights of grafted and ungrafted samples, respectively.

Table I. Optimized parameters for the synthesis of Ga-cl-poly(MAA)

Sample no.	[KPS] × 10^{-2} (molL^{-1})	Vacuum (mm Hg)	Time (min)	Solvent (ml)	Temp (°C)	pH	[MAA] (molL^{-1})	[HMTA] × 10^{-2} (molL^{-1})	P_g	P_s
1	1.23	450	180	15	60	7	0.795	—	83.2	—
2	2.46	450	180	15	60	7	0.795	—	112.4	—
3	3.69	450	180	15	60	7	0.795	—	123.2	—
4	4.92	450	180	15	60	7	0.795	—	98.5	—
5	6.15	450	180	15	60	7	0.795	—	68.7	—
6	3.69	150	180	15	60	7	0.795	—	143.6	—
7	3.69	250	180	15	60	7	0.795	—	169.4	—
8	3.69	350	180	15	60	7	0.795	—	135.3	—
9	3.69	450	180	15	60	7	0.795	—	123.2	—
10	3.69	550	180	15	60	7	0.795	—	116.8	—
11	3.69	250	120	15	60	7	0.795	—	69.3	—
12	3.69	250	180	15	60	7	0.795	—	169.4	—
13	3.69	250	240	15	60	7	0.795	—	189.3	—
14	3.69	250	300	15	60	7	0.795	—	96.3	—
15	3.69	250	360	15	60	7	0.795	—	85.2	—
16	3.69	250	240	5	60	7	0.795	—	15.1	—
17	3.69	250	240	10	60	7	0.795	—	72.2	—
18	3.69	250	240	15	60	7	0.795	—	189.3	—
19	3.69	250	240	20	60	7	0.795	—	63.2	—
20	3.69	250	240	25	60	7	0.795	—	07.9	—
21	3.69	250	240	15	40	7	0.795	—	15.9	—
22	3.69	250	240	15	50	7	0.795	—	65.9	—
23	3.69	250	240	15	60	7	0.795	—	189.3	—
24	3.69	250	240	15	70	7	0.795	—	98.9	—
25	3.69	250	240	15	80	7	0.795	—	23.4	—
26	3.69	250	240	15	60	3	0.795	—	112.2	—
27	3.69	250	240	15	60	5	0.795	—	132.2	—
28	3.69	250	240	15	60	7	0.795	—	189.3	—
29	3.69	250	240	15	60	9	0.795	—	122.1	—
30	3.69	250	240	15	60	11	0.795	—	111.4	—
31	3.69	250	240	15	60	7	0.795	2.377	—	1027.1
32	3.69	250	240	15	60	7	1.192	2.377	—	1487.3
33	3.69	250	240	15	60	7	1.590	2.377	—	1990.2
34	3.69	250	240	15	60	7	1.943	2.377	—	1328.9
35	3.69	250	240	15	60	7	2.385	2.377	—	923.3
36	3.69	250	240	15	60	7	0.795	1.590	—	1810.3
37	3.69	250	240	15	60	7	0.795	2.377	—	1990.2
38	3.69	250	240	15	60	7	0.795	4.755	—	2111.5
39	3.69	250	240	15	60	7	0.795	7.132		1458.0
40	3.69	250	240	15	60	7	0.795	9.510		1022.5

The product so obtained was gum arabic-g-poly(methacrylic acid) [Ga-g-poly (MAA)]. Cross-linking of Ga-g-poly(MAA) was carried out using HMTA. Optimization of MAA and HMTA concentration was carried out as a function of percentage swelling (P_s) in deionized water using the following equation:[24]

$$\%Swelling\ (P_s) = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of swollen and dry samples, respectively.

The final cross-linked product, Ga-cl-poly(MAA) (Figure 1), was used for swelling studies.

Effect of Monomer Concentration on Swelling Capacity

To study the effect of MAA concentration on the percentage swelling, the molar concentration of MAA was varied from 0.795 to 2.385 $molL^{-1}$. A 100 mg amount of each sample was taken and immersed in deionized water for 24 h, and percentage swelling was calculated using the above equation.

Swelling Behavior of Synthesized Polymer

Swelling study was carried out at room temperature for 24 h. The readings were taken after a time interval of 4 h. Thereafter, swelling studies were carried out in a temperature range of 15–55°C. Further, the optimized temperature (45°C) was selected for swelling studies in different pH media (0.5 N HCl, deionized water, and 0.5 N NaOH). The samples were kept in the solution for 24 h, and then the percentage swelling was calculated using the previous equation.

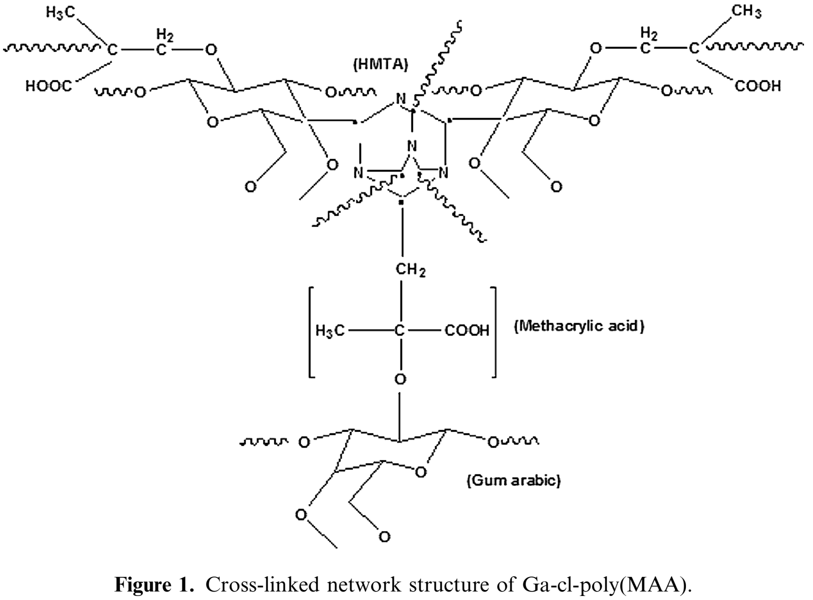

Figure 1. Cross-linked network structure of Ga-cl-poly(MAA).

Swelling Studies in Salt Solution

The synthesized polymer was studied for its salt-resistant behavior by taking different salts like NaCl, $MgCl_2$, and $FeCl_3$ of varying concentrations (1%, 5%, 10%, 15%, and 20%). A 100 mg amount of sample was immersed in each solution for 24 h at room temperature. The swollen samples were taken out of the respective salt solutions after 24 h. Samples were wiped gently and weighed to get the percentage swelling using the P_s equation.

RESULTS AND DISCUSSION

Scheme of Polymerization

The –OH groups present on the backbone polymer act as the active site for the graft copolymerization of poly(MAA) onto it. The mechanism for this is discussed below:[25]

Initiation

$$\begin{gathered}
{}^-O_3S\text{-}O\text{-}O\text{-}SO_3{}^- \longrightarrow 2SO_4^{-*} \\
SO_4^{-*} + H_2O \longrightarrow HSO_4^- + {}^*OH \\
Ga\text{-}OH + SO_4^{-*} \longrightarrow Ga\text{-}O^* + HSO_4^- \\
Ga\text{-}OH + {}^*OH \longrightarrow Ga\text{-}O^* + H_2O \\
M + {}^*OH \longrightarrow {}^*M\text{-}OH \\
M + SO_4^{-*} \longrightarrow {}^*M\text{-}SO_4^-
\end{gathered}$$

Propagation

$$\begin{gathered}
Ga\text{-}OH + {}^*M\text{-}OH \longrightarrow Ga\text{-}O\text{-}M^* + H \\
Ga\text{-}O\text{-}M^* + nM \longrightarrow Ga\text{-}O\text{-}(M)_n\text{-}M^* \\
Ga\text{-}O^* + nM \longrightarrow Ga\text{-}O\text{-}(M)_{n-1}M^* \\
{}^*M\text{-}OH + nM \longrightarrow HO\text{-}(M)_n\text{-}M^*
\end{gathered}$$

Termination

$$\begin{gathered}
Ga\text{-}O\text{-}(M)_n\text{-}M^* +{}^* M\text{-}(M)_n\text{-}O\text{-}Ga \\
\rightarrow Ga\text{-}O\text{-}(M)_n\text{-}M_2\text{-}(M)_n\text{-}O\text{-}Ga \text{ (Graft copolymer)}
\end{gathered}$$

$$\begin{gathered}
Ga\text{-}O\text{-}(M)_{n-1}M^* + M^*\text{-}(M)_{n-1}\text{-}O\text{-}Ga \rightarrow \\
Ga\text{-}O\text{-}(M)_{n-1}\text{-}M_2\text{-}(M)_{n-1}\text{-}O\text{-}Ga \text{ (Graft copolymer)}
\end{gathered}$$

$$\begin{gathered}
Ga\text{-}O\text{-}(M)_n\text{-}M^* + {}^*OH \longrightarrow Ga\text{-}O\text{-}(M)_{n+1}\text{-}OH \\
HO\text{-}(M)_{n-}M^* +{}^* M\text{-}(M)_n\text{-}OH \longrightarrow HO\text{-}(M)_n\text{-}M_2\text{-}(M)_n\text{-}OH \\
\text{(Homopolymer)}
\end{gathered}$$

M^* = monomer free radical; $Ga\text{-}O^*$ = backbone free radical

Formation of SO_4^{-*} takes place as a result of persulfate dissociation, which further reacts with water to give $^*OH$. The generated SO_4^{-*} attacks gum arabic, thereby resulting in the formation of a free radical site on the backbone. $^*OH$ attacks the backbone polymer and the monomer (MAA), leading to the generation of free radical sites on both of them. These two generated free radicals react with each other, resulting in the formation of graft copolymer and propagation of graft copolymerization reaction. However, the termination of the reaction takes place either by reaction between $^*OH$ and a free radical or by the reaction between two activated chains.

FT-IR Spectroscopy

IR spectrum of backbone polymer exhibited broad peaks at 3365.2 cm^{-1} (O-H stretching of carbohydrates), 2939.1 cm^{-1} (CH_2 asymmetric stretching), 1424.3 cm^{-1} (CH, CH_2, and OH in-plane bending in carbohydrates), 1149.8 cm^{-1} (C-O stretching region as complex bands, resulting from C-O and C-O-C stretching vibrations), and 603.7 cm^{-1} (pyranose rings), whereas IR spectrum of Ga-cl-poly(MAA) showed peaks at 1725.0 cm^{-1} and 1631.1 cm^{-1} (C=O stretching in acids) in addition to peaks obtained with gum arabic, clearly showing the incorporation of MAA molecules onto the polymeric backbone.

Scanning Electron Microscopic Studies of the Gels

SEM studies were conducted by gold plating the hydrogels in order to facilitate their conducting impact. Microscopic beam was used to synchronize the scanning for the maintenance of small size over large distance relative to the specimen. Highly resolved three-dimensional appearances with great depth of field were obtained. SEM studies clearly differentiate the morphological differences on the surface of gum arabic, which was homogeneous, and Ga-cl-poly(MAA), having uneven and cross-linked structure, as shown in Figures 2 and 3.

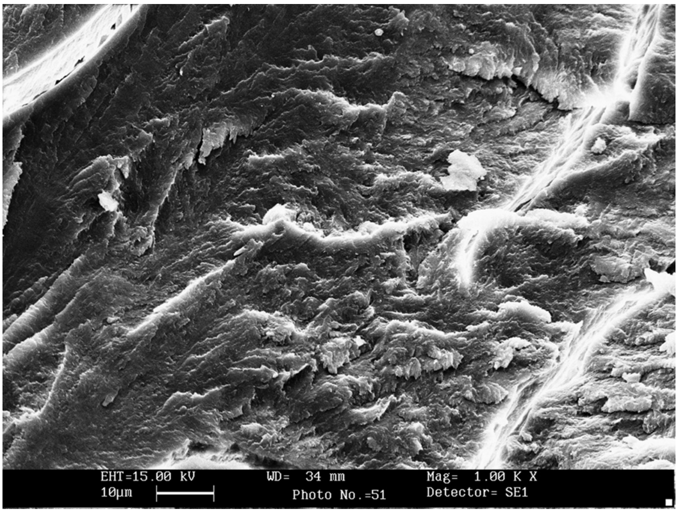

Figure 2. SEM of gum arabic.

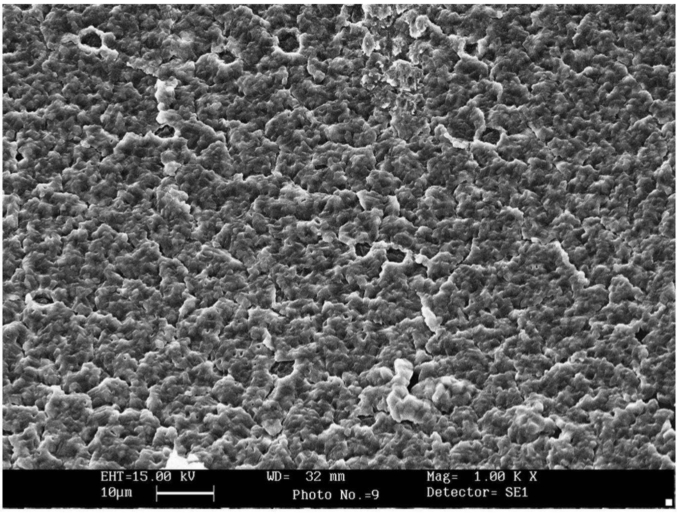

Figure 3. SEM of Ga-cl-poly(MAA).

Thermal Behavior of Gels

TGA/DTA and DTG studies of gum arabic and synthesized polymer were performed as a function of percent weight loss versus temperature. A 10.0 mg amount of the backbone and synthesized sample was taken in a silica crucible to carry out the thermal analysis with temperatures ranging from 50° to 800°C. The heating rate of the sample was 10°C/min. The combustion of the sample continued for 80 min, and the results, weight loss (%) versus temperature (°C) in the case of TGA, DTA signal (μV) versus temperature (°C) in the case of DTA, and rate of weight loss (mg/min) versus temperature (°C) in the case of DTG, were compiled automatically by the software.

Figures 4 and 5 show that gum arabic has initial decomposition temperature (IDT) at 227°C and final decomposition temperature (FDT) at 517°C, whereas for Ga-cl-poly(MAA), IDT and FDT were found to be 199°C and 485°C, respectively. The decrease in IDT and FDT of the synthesized polymer could be due to the fact that upon grafting, the basic structure of the backbone polymer got disturbed, therefore the resultant Ga-cl-poly(MAA) suffered from less thermal stability. However, in both cases, two-stage decomposition has been observed. First-stage decomposition takes place from 227° to 296°C in the case of gum arabic with a weight loss of 4.12 mg and from 199° to 411°C in the case of Ga-cl-poly(MAA) with a weight loss of 5.58 mg; second-stage decomposition takes place from 296° to 517°C in the case of gum arabic with a weight loss of 3.98 mg and from 411° to 485°C in the case of Ga-cl-poly(MAA) with a weight loss of 2.58 mg. The thermograms obtained from DTA reveal that gum arabic has three exothermic peaks at 292°C (30 μV), 470°C (131 μV), and 513°C (212 μV). On the other hand, Ga-cl-poly(MAA) showed exothermic peaks at 224°C (9 μV), 367°C (42 μV), and 484°C (243 μV). It shows that exothermic combustion of Ga-cl-poly(MAA) persists at lower temperature.

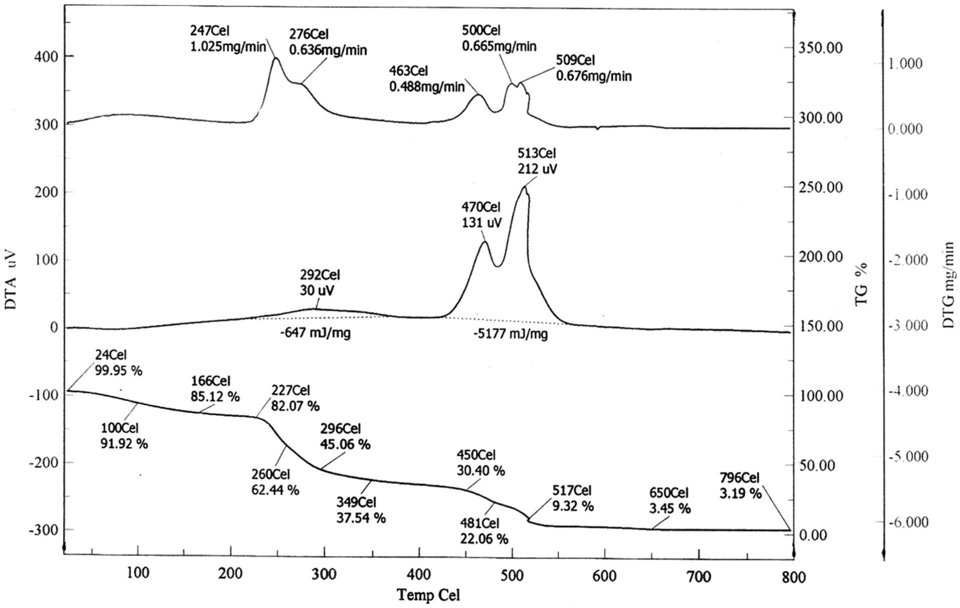

Figure 4. TGA/DTA/DTG of gum arabic.

Further, from DTG studies, it is revealed that weight loss rate of 1.025 mg/min and 0.636 mg/min has been obtained at a temperature range of 227°–296°C of TGA, whereas, in the temperature range of 296°–517°C of TGA, weight loss of

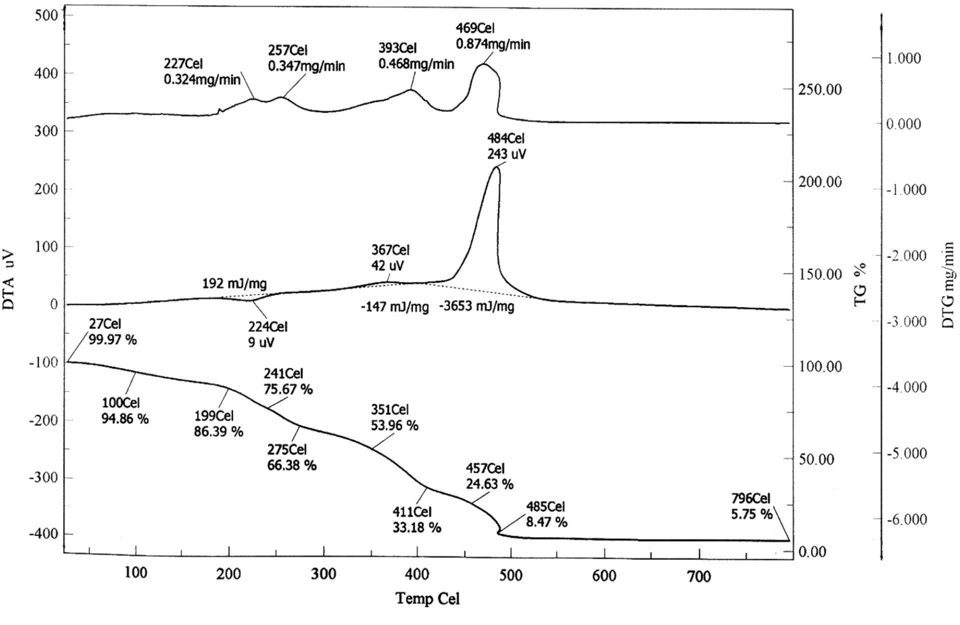

Figure 5. TGA/DTA/DTG of Ga-cl-poly(MAA).

0.488 mg/min at 463°C, 0.665 mg/min at 500°C, and 0.676 mg/min at 509°C has been observed. On the other hand, DTG studies of Ga-cl-poly(MAA) reveal that initially there was negligible weight loss rate, which gradually increased from 227° to 469°C (0.324 mg/min at 227°C, 0.347 mg/min at 257°C, 0.468 mg/min at 393°C, and 0.874 mg/min at 469°C). The above results clearly show that Ga-cl-poly(MAA) is thermally less stable than the backbone polymer because GA-cl-poly(MAA) underwent morphological changes during grafting that disturbed its basic structure.

Effect of MAA Concentration on Swelling Capacity

It was observed that with increase in MAA molar concentration, there was an increase in percentage swelling (Figure 6), and P_s of 1990.2% was observed with 1.590 $molL^{-1}$ of MAA concentration. Further increase in MAA molar concentration resulted in decreased P_s. The initial increase in P_s could be due to increase in number of active sites with increase in grafting. However, after reaching the optimum concentration of 1.590 $molL^{-1}$, further increase in monomer concentration resulted in more networking, and therefore resulted in decreased P_s with more compactness of the candidate polymer.[25]

Swelling Study at Room Temperature

As is evident from Figure 7 that percentage swelling increased with increase in time at room temperature and maximum swelling (2111.5%) was found after a time interval of 24 h. However, it was found that the swelling increased rapidly up to 12 h and after that the increase was very gradual and became almost constant while approaching the 24 h time interval. This is due to the fact that with increase in time interval, the porous network of the polymer became saturated with water molecules with no more room for further accommodation.[26]

Temperature Sensitivity of Graft Copolymer

Swelling temperature was varied from 15° to 55°C. It was observed that with increase in temperature, P_s was found to increase up to 45°C (2940.2%). However,

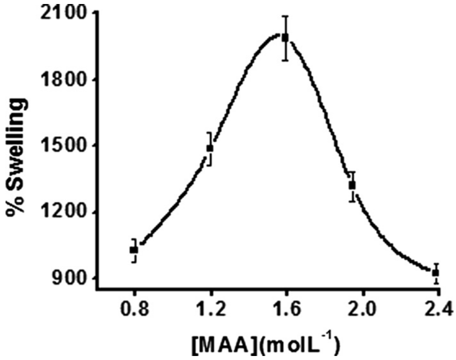

Figure 6. Effect of monomer concentration on percentage swelling.

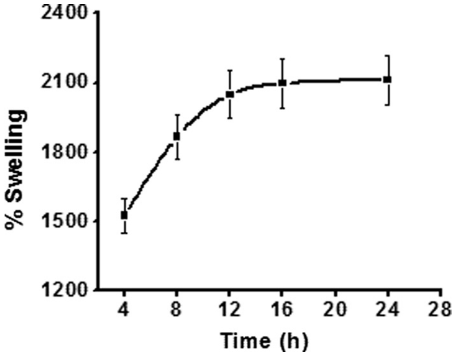

Figure 7. Percentage swelling at room temperature.

further increase in temperature resulted in decreased P_s (Figure 8). The decrease in P_s beyond optimum temperature is due to the fact that with increase in temperature, the elasticity of the polymeric matrix increases, but after reaching optimum temperature, the matrix starts collapsing, leading to desorption with further increase in temperature.[27] At low temperature, the hydrophilic groups of the hydrogels form hydrogen bonds with water molecules. These bonds act cooperatively to form a stable shell of hydration around the hydrophobic groups, resulting in greater water uptake and producing a larger swelling ratio. But with increase in external temperature, the associative interactions among the hydrophobic groups release the entrapped water molecules from the hydrogel networks, thereby resulting in decreased P_s.[28]

pH-Dependent Swelling of Graft Copolymer

The synthesized copolymer was placed in three different media, acidic (0.5 N HCl solution), neutral (deionized water), and alkaline (0.5 N NaOH), and it was found that the copolymer swells to a greater extent in neutral medium, followed by alkaline medium and acidic medium (Figure 9). Under acidic condition, anionic carboxylate groups of the copolymer are protonated, resulting in vanishing of

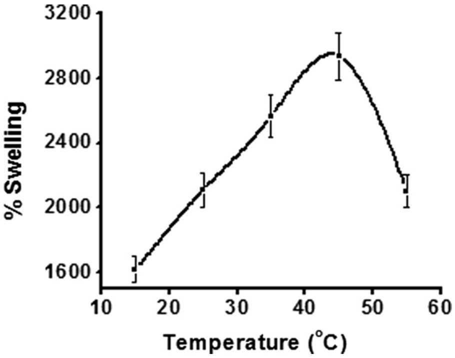

Figure 8. Effect of temperature on percentage swelling.

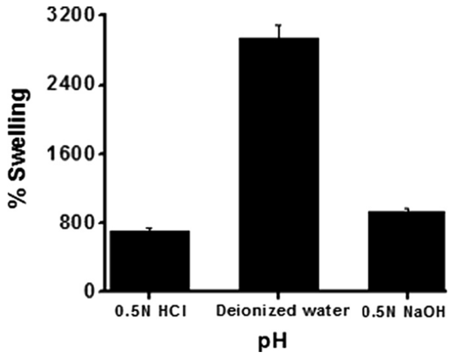

Figure 9. Effect of pH on percentage swelling.

electrostatic repulsive forces in the network, which is ultimately responsible for swelling, while under basic conditions, the repulsive anion-anion forces are functioning, but a screening effect of the counterions (Na^+) hinders the swelling and opposes its further increase.[29]

Swelling in Salt Solution

The swelling of synthesized polymer appreciably decreases in saline solutions as compared to the values obtained in distilled water. This phenomenon is observed in the swelling of all ionic hydrogels and is explained by charge screening effect of additional cations causing non-perfect anion-anion electrostatic repulsion, leading to decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution.[30] Further, it was observed that with increase in salt concentration, the percentage swelling decreases. The percentage swelling of synthesized polymer in various salt solutions followed the trend: $NaCl > MgCl_2 > FeCl_3$, which is quite evident from the increasing charge of the cations of the salt ($Na^+ > Mg^{2+} > Fe^{3+}$) as ionic cross-linking takes place between the multivalent cations of the salts and carboxylate groups of the polymer, leading to decreased swelling (Figure 10).[22]

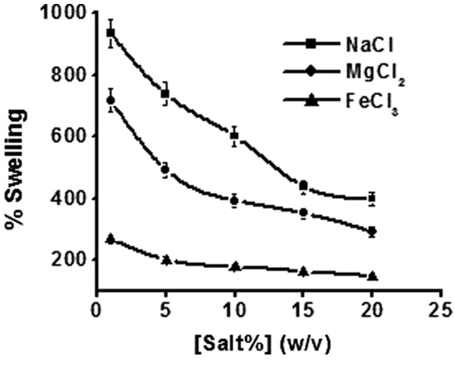

Figure 10. Effect of salt concentration on percentage swelling.

CONCLUSIONS

Grafting has been done successfully onto the gum arabic backbone using KPS-HMTA system. Results of different swelling studies showed that the copolymer swelled more in distilled water than in acidic and basic media. Monomer concentration was found to affect the percentage swelling of the polymer. It also showed salt-resistant swelling behavior in different salt solutions and sensitivity towards temperature by swelling maximum at a particular temperature. Thus, we conclude that the copolymer is pH as well as temperature sensitive and can be efficiently utilized as a drug delivery device. Since the copolymer also showed salt-resistant swelling, it can be used in the water treatment industry.

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