Development of Cotton Fabric with Antibacterial Properties: Part I: Preparation of Poly(acrylamide-co-itaconic acid) grafted Cotton Fabric and its Water Uptake Analysis

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Development of Cotton Fabric with Antibacterial Properties: Part I: Preparation of Poly(acrylamide-co-itaconic acid) grafted Cotton Fabric and its Water Uptake Analysis

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Graft co-polymerization of monomers acrylamide (AAm) and itaconic acid (IA) on to cotton fabric has been carried out in aqueous medium using ceric ammonium nitrate as initiator under the catalytic activity of nitric acid. The cotton fabric was optimally initiated in 20 mM aqueous solution of initiator for 15 min, followed by its immersion in aqueous solution containing of monomers AAm and IA, and cross-linker N,N′-methylene bisacrylamide (MB)at 30°C. To obtain optimum conditions, the percent grafting was investigated as a function of concentration of the monomers, the cross-linker and the initiator, reaction temperature and time of immersion for initiation. The grafted cotton fabric was also investigated for its water uptake behavior.

Keywords: cotton fabric; grafting; itaconic acid; hydrogel; antibacterial activity

1 Introduction

With the growing public health awareness of disease transmission, cross-infection and malodorous caused by microorganisms, the use of antimicrobial materials has increased in many application areas, especially as protective clothing for medical persons and warfare or defense people, sportswear, underwear and other health related products (1). Depending on the applications, materials can be fabricated by making them monolithic to be impermeable to challenging microorganisms by controlling microporous pore sizes or applying a layer of coating to restrict the penetration of pathogens and viruses (2, 3). Antimicrobial materials can be chemically engineered by adding functional antimicrobial agents onto the surface or within the matrix to either kill or inhibit growth of microorganisms. Due to the developing resistance of bacteria against bactericides and antibodies, and due to irritant and toxic nature of some antimicrobial agents, the biomaterial scientists have focused their research on nano-sized metal particles such as silver, titanium dioxide, zinc oxide etc. (4–6). With the use of nano-sized particles, the number of particles per unit area is increased, and thus anti-bacterial effect can be maximized. It is well known that silver nanoparticles are highly toxic to microorganisms (7), showing strong biocidal effects on as many as 16 species of bacteria including *E. Coli* and *S. Epidermis* (8). Silver-based antimicrobial agents have been introduced in many ways such as doping silver onto the host material (9), compositing it with other compounds (10), applying it as stable emulsion (11), etc.

Most recently, we have developed a novel strategy to synthesize silver nanoparticles within the swollen poly (acrylamide-co-acrylic acid) hydrogels and studied its antimicrobial activity against E. *Coli* (12). In a continuous attempt to apply this facile method for the development of anti-microbial cotton fabric, we hereby report a detailed investigation of graft co-polymerization of monomers acrylamide and itaconic acid onto cotton fabric and water uptake analysis of resulting grafted fabric. In the next part, we shall introduce silver nanoparticles into a swollen grafted copolymer layer beneath the fabric by using the same novel approach which involves entrapment of Ag^+ ions into the swollen network followed by citrate reduction. Finally, the silver nanoparticles containing cotton fabric, so produced will be investigated for its antimicrobial activity.

Here it is worth mentioning that monomer acrylamide is a well known neurotoxin with good transdermal permeation and therefore, due care must be taken to remove unreacted acrylamide molecules from the grafted product. As far as skin permeation of polyacrylamide is concerned, it cannot permeate through skin due to large molecular weight. It has

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also been used as a filling material by surgeons for the treatment of depressions and wrinkles of the glabella, malar and upper lip region, lip augmentation, augmentation namma-plasty, phalloplasty, atrophy or paralysis of the vocal cords (13). The purpose of taking itaconic acid as one of the monomers is not only to impart pH-sensitive water absorbent behavior to the fabric owing to ionization of its -COOH groups above its pKa values, but also to incorporate more and more Ag^+ ions into the swollen grafted copolymer layer through ion exchange process between Ag^+ ions present in external solution and H^+ ions present in the swollen gel phase. In addition, it has also been reported that the presence of itaconic acid also enhances wrinkle resistance of the fabric (14). The structure of monomer acrylamide and dissociated forms of co-monomer itaconic acid are shown below:

Acrylamide

N, N' methylene bisacrylamide

Itaconic acid
at $pK_1 = 3.85$

Itaconic acid
at $pK_2 = 5.44$
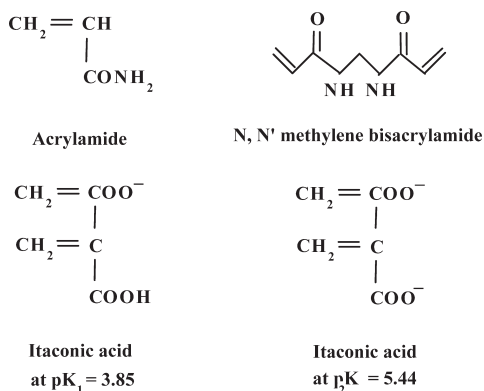
2 Experimental

2.1 Materials

The monomers acrylamide (AAm) and itaconic acid (IA), crosslinker N,N′-methylene bisacylamide (MB) and initiator ceric ammonium nitrate (CAN) were obtained from Hi Media, Mumbai, India. The catalyst nitric acid (HNO_3) and other salts were also analytical grade and received from Research Lab, Pune, India. The cotton fabric weighing $137 \, g/m^2$, was purchased from a local merchant and used after equilibrating in distilled water for a period of 24 h. The monomer AAm was recrystallized in methanol to remove the inhibitor. The doubly distilled water was used throughout the investigation.

2.2 Grafting Procedure

All procedures, from solution preparation to the graft co-polymerization were performed at room temperature. Both, the initiator (CAN), and monomer/crosslinker were dissolved in 0.1M HNO_3, and bubbled with N_2. Unless otherwise stated, a pre-weighed cotton piece was put in 10 ml of 20 mM CAN for15 min, blotted with tissue paper to remove extra CAN,

and then immersed in 20 ml of solution, containing pre-determined quantities of monomers AAm, IA and the cross-linker MB. After graft polymerization reaction, each substrate was equilibrated in distilled water to remove unreacted salts. Finally, the grafted fabric was put in acetone to remove the formed homopolymer (15) and also to remove water from grafted fabric and then dried at 40°C in a dust-free chamber till the fabric was completely dry.

The percent grafting (G) was calculated using the expression:

$$\%\text{Grafting}(G) = \frac{W_g - W_o}{W_o} \times 100$$

where w_o and w_g are the sample weights before and after graft co-polymerization, respectively.

2.3 Water Uptake Analysis

Completely dry pre-weighed grafted cotton fabric was placed in 250 ml of a phosphate buffer solution of pH 7.4 and its mass was measured at different time–intervals till the fabric attained constant weight. The percent equilibrium mass swelling ($\%M_s$) was calculated using the following formula (16):
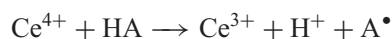
$$\%M_s = \frac{\text{Swollen Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

All the experiment were carried out with five samples and average values have been reported in the data.

3 Results and Discussion

3.1 Tentative Mechanism of Grafting

In the presence of an acid used, HNO_3 (HA), primary radical species formation occurs as a result of the action of acid on Ce(IV):

$$Ce^{4+} + HA \longrightarrow Ce^{3+} + H^+ + A^\bullet$$

Once the free-radical species ($A^\bullet$) are formed, they produce cellulose macroradicals via direct abstraction of hydrogen atom cellulose molecules.

$$Cell - OH + A^\bullet \longrightarrow Cell - O^\bullet + HA$$
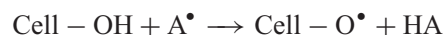
where $Cell - OH$ represents cellulose molecule. Cellulose macroradicals may also be formed by direct attack of Ce^{4+} ions on cellulose molecule via H abstraction.

$$Cell - OH + Ce^{4+} \longrightarrow Cell - O^\bullet + Ce^{3+} + H^+$$
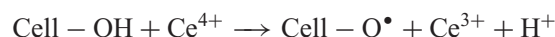
These cellulose macroradicals, so produced, combine with monomers AAm and IA to induce graft-copolymerization.

3.2 Selection of Grafting Procedure

In order to decide the method of carrying out graft-copolymerization onto cotton, we followed two approaches. In the first one, the cotton fabric was put in the aqueous solution containing pre-calculated quantities of monomers AAm and IA, initiator CAN and crosslinker MB for a period of 8 h at room temperature. A marginal increase in the weight of the fabric was observed thus suggesting that homopolymer was predominantly formed. This indicated that the extent of grafting on cellulose present in cotton fabric was almost nil. Hence, we adopted another two-step approach which involved immersion of cotton fabric in CAN initiator solution for a definite time followed by its transfer into another solution containing definite amounts of monomers AAm and IA, and crosslinker MB. After 3 h, we observed an appreciable increase in the weight of the fabric thus suggesting the formation of graft co-polymer onto cellulose backbone. So, we decided to follow this two-step approach for further studies. In this two-step process we found one more significant result. If the excess CAN solution, retained on the fabric surface, was not removed properly before transferring the CAN-treated fabric into monomer/crosslinker solution, then the grafting onto fabric was hindered greatly. An appreciable quantity of co-polymer was formed in the solution and sometimes even whole solution was polymerized and converted into hydrogel. This may simply be attributed to the fact that excess CAN diffuses into the reaction mixture and induces both complexation with vinyl monomer as well as homopolymerization (17, 18). On the contrary, a noticeable quantity of graft copolymer formed onto the fabric only when excess CAN was removed almost completely from the fabric surface by blotting of the initiator–saturated fabric before introducing it into solution containing monomer and crosslinker. In this case, the reaction mixture did not show any sign of appearance of turbidity thus indicating almost no homopolymerization. Therefore, it was concluded that the whole study shall be performed by removing excess CAN in this two-step process.

3.3 Effect of Initiation Time

The effect of time of immersion of fabric in the CAN solution on percent grafting was studied by dipping pre-weighed fabric in 20 mM CAN solution for different time-periods follow by their transfer into 20 ml of reaction mixture, containing 2 M of AAm, 40 mM of MB and 0.05 mM of IA, for a total period of 3 h at 30°C. The results, as depicted in Figure 1 clearly indicate that an initiaton time of 15 min appears to be the optimum for maximum grafting of nearly 198%. It is clear that an immersion time of less than 15 min is not sufficient for complete formation of free radicals along the cellulose chains in the cotton fabric. Moreover, when the fabric is put in CAN solution for a relatively longer time (i.e., more than 15 min), there is slight decrease in the percent grafting which, might probably be due to the
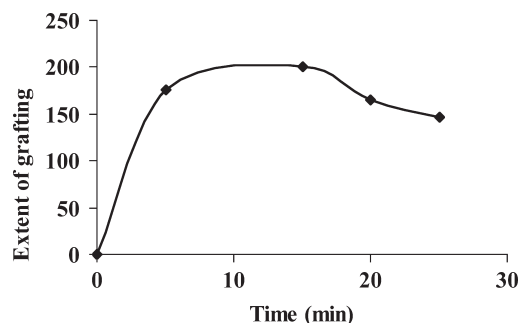

Fig. 1. Effect of initiation time on percent grafting.

over saturation of fabric with CAN solution and so a little trace of CAN might have been left in the fabric pores even after blotting with tissue paper. This extra unremoved Ce(IV) may hinder the graft-polymerization process as discussed earlier, thus finally causing a slight decrease in the percent grafting. Here should be noted that in the present study we have just attempted to obtain conditions under which optimum grafting can be achieved. However, such a higher degree of grafting may cause adverse effect on the basic properties of the fabric. So a balance between these two must be maintained.

3.4 Effect of CAN Concentration

In order to investigate the effect of CAN concentration on the percent grafting onto the fabric, pre-weighed pieces of dry fabric were put in at CAN solutions of different concentrations, in the range 7.5 mM to 60 mM, for a period of 15 min followed by their transfer into (monomer + crosslinker) solution for 3 h at 30°C. The results, as depicted in the Figure 2, clearly indicate that for 15 to 20 mM CAN concentration maximum grafting is observed while it decreases below 15 mM and after 20 mM. The observed finding may be explained as follows: When CAN concentration is below 15 mM, it may not be sufficient for generation of maximum number of free-radicals along the cellulose chains, thus resulting in insufficient grafting. Now, with a further increase in the CAN concentration, percent grafting increases as more and more radicals are formed.
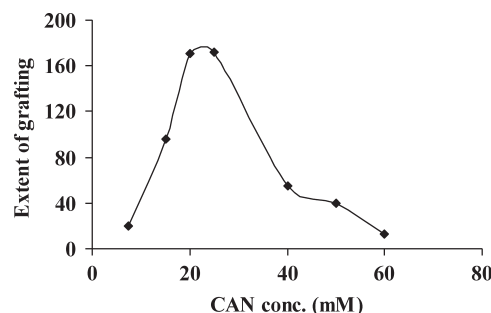

Fig. 2. Effect of initiator concentration on percent grafting.

However, when the CAN concentration is increased beyond 20 mM, a continuous decrease in the % grafting is observed. This may be attributed to the presence of some traces of un-removed CAN solution of higher concentrations within the pores of cellulosic fiber network. The higher concentration of unremoved Ce(IV) inhibits the hydrogel formation within the fabric through complexation with invading monomer molecules as well as inducing co-polymerization in the solution phase. Moreover, beside initiation Ce(IV) is also reported to participate in the termination of graft chains (19). So, it is logical to establish the fact that when Ce(IV) concentration is sufficiently higher, the free radicals speed up the termination step, thus causing a decrease in the graft yield. Therefore it appears that a CAN concentration of 20 mM is sufficient for optimum grafting onto the fabric.

3.5   Effect of AAm and MB Concentration

The increase in concentration of AAm in the feed mixture (or reaction mixture) results in an increase in the percent grafting as shown in Figure 3. This may be explained on the basis of the fact that with the increase in AAm concentration, the number of monomer molecules approaching the reactive sites in the fabric network also increases. In other words, the availability of monomer (AAm) molecules in the vicinity of the immobilized cellulose macroradicals increases thus causing an increase in percent grafting. Similar results have also been reported for grafting of methylacrylonitrile onto sulfonated jute-cotton (20).

N,N′-methylene bisacrylamide (MB) is a bifunctional molecule which is used for crosslinking of the polymeric chains in a hydrogel system. As it participates in the polymerization process, it is not unfair to treat it as bifunctional monomer. When its concentration was varied in the range 0 to 0.08 mM, the percent grafting was observed to increase from 55.0 to 171.4 (Figure 3) thus indicating that its role in
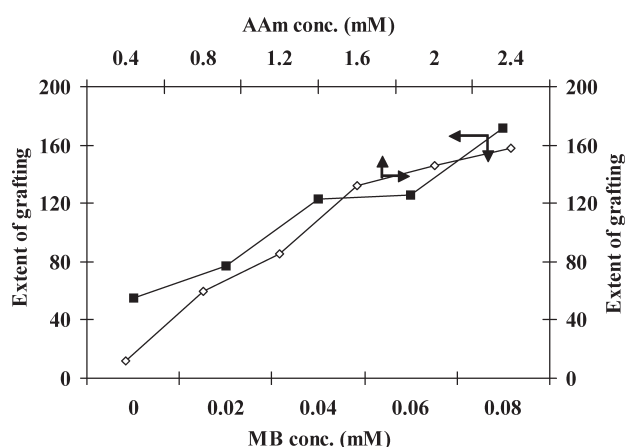
the grafting process is to attach more and more growing macromolecular chains through its bifunctional reactive sites.

3.6   Effect of Catalyst

The effect of catalyst, i.e., HNO_3 concentration on the percent graft yield is depicted in Figure 4. It is clear that % grafting increases with the increase in HNO_3 concentration up to 200 mM and then it begins to decrease with a further increase in catalyst concentration. The plausible explanation of such behavior is that HNO_3, in the grafting medium, assists the grafting, both by causing inter and intracrystalline swelling of the substrate and by acting as a catalyst in the hydrolysis of cellulose, leading to unfolding of the chains and improvement of the monomer accessibility. On the other hand, when the concentration of acid increases beyond 200 mM, it may become sufficient to cause the degradation of backbone chains of cellulose as well as of the graft chains. In addition, the fall in the graft yield may also be attributed to the enhanced coagulation of collidal homopolymer which might have been formed due to the presence of a trace amount of unblotted Ce(IV) in the solution and in the fiber structure at lower pH. This may retard the diffusion of monomer molecules into the fiber phase (21). Therefore, the percent grafting is observed to decrease when catalyst concentration exceeds beyond 200 mM.

3.7   Effect of Reaction Temperature

Figure 5 describes the effect of increase in the temperature of the monomer/crosslinker solution (i.e., second step) on the percent grafting. It is clear that as the temperature is raised beyond 20°C, the percent grafting increase sharply and finally it attains the limiting value when the temperature of the reaction mixture is nearly 45°C. This can be explained well on the basis of the fact that increase in temperature causes faster diffusion of monomer molecules towards active grafting sites present on the cotton cellulose. In addition, an increase in temperature is also accompanied by an increase in rate of propagation. However, when the temperature is raised to 45°C, the enhanced degradation of cellulose chain by acid catalyst may stop the further increase in
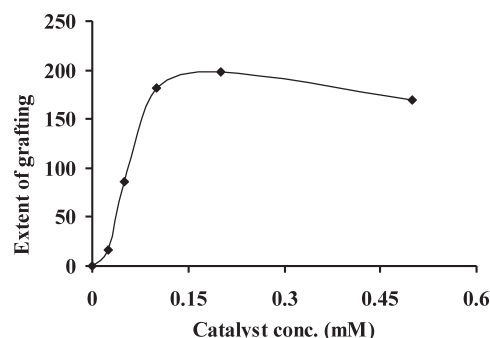

Fig. 3. Effect of concentrations of monomer acrylamide and crosslinker MB on percent grafting.

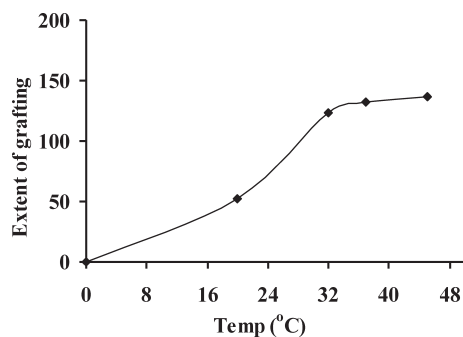**Fig. 4.** Effect of catalyst concentration on percent grafting.

Fig. 5. Effect of temperature on percent grafting.

percent grafting. This argument is further supported by our observation that when grafting was carried out at 50°C, the fabric suffered a great weight loss, became brittle and was torn into small pieces thus indicating breakdown of cellulosic chains by HNO_3 at high temperature. Finally, at higher temperature, the possibility of recombination of free radicals generated on the cellulose backbone should also be considered. Therefore 30 to 45°C appears to be the suitable temperature range for optimum grafting.

3.8 Effect of IA Content

As observed previously, the increase in concentration of monomer AAm resulted in an increase in percent grafting onto the cotton fabric. However, when the concentration of other monomer IA, was increased in the range to 0.0 to 0.38 mM, the grafting trend was just the opposite. The percent grafting was found to decrease appreciably with the increase in the IA content as shown in Figure 6. The results may possibly be explained on the basis of the fact that:

(a) as the reactivity of IA is very low as compared to that of other monomer AAm, the increasing concentration of IA overall decreases the rate of propagation, thus ultimately lowering the percent grafting;

(b) It is a well established fact that some portion of IA is involved in the esterification of cellulose without participating in polymerization (22). With the increase in
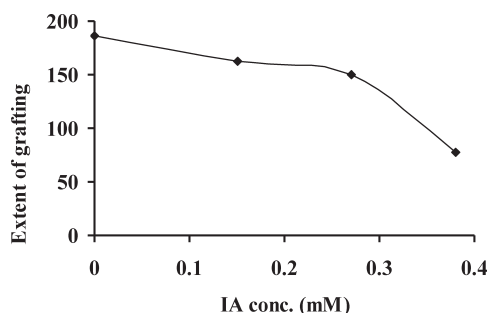

Fig. 6. Effect of IA monomer concentrations on percent grafting.

concentration of itaconic acid, more and more IA molecules penetrate into bulk of the cotton fibers thus participating in esterification. Here, it is worth mentioning that an IA monomer has two carboxylic acid groups, only one of which is able to esterify cellulose because formation of a five membered cyclic anhydride intermediate is necessary for esterification as shown below (23).
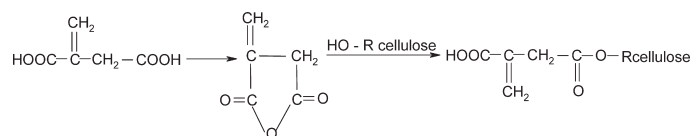
Therefore consumption of itaconic acid in esterification of cellulose causes an overall decrease in the percent grafting. Although the esterification has been observed to take place significantly at as high temperature as 140–200°C, therefore, the extent of esterification reaction at 30° should almost be negligible. Therefore, the low reactivity of IA as mentioned above appears to be the major cause of observed decrease in extent of grafting. Hence, finally it may be concluded that the monomers, AAm and IA show opposite grafting trend when their concentrations are increased in the feed mixture.

3.9 Water Uptake Analysis

A crystal clear photograph, of plain fabric, grafted fabric in dry and swollen state recorded with optical microscope is depicted in the Figure 7.

The fine cellulosic fiber network is clearly seen in the plain fabric (Figure 7A). When the copolymer is grafted on the fabric, the fiber network is almost covered by the co-polymeric graft chains as seen in the Figure 7(B). Finally, when the grafted fabric is put in the phosphate buffer of pH 7.4, the grafted polymeric chains absorb water and the fabric becomes hydrated as shown in Figure 7(C).

The swelling behavior of a hydrogel depends up to a number of factors such as crosslink density, composition of monomers in the feed mixture, nature of monomers (i.e. ionic or non ionic), size of hydrogel sample, its porosity etc. (24). However, its simple correlation with extent of grafting is rather difficult to establish. To illustrate our point, we studied swelling behavior of grafted hydrogels prepared with different concentration of IA and compared the swelling data with that of grafted gels prepared with different concentrations of crosslinker MB. The results, as depicted in the Figure 8(A) and (B) clearly reveal some interesting facts. For the grafted gels containing varying amounts of IA, water uptake varies directly with percent grafting. The percent mass swelling increases from 205 to 325 as the percent grafting increases from 77 to 186. On the other hand, for the grafted gels containing increasing concentrations of crosslinker, the percent swelling has inverse relation with the percent grafting. As shown in the Figure 8 (B), with the increase in percent grafting from 55 to 126, the percent mass swelling decreases from 476 to nearly 250.
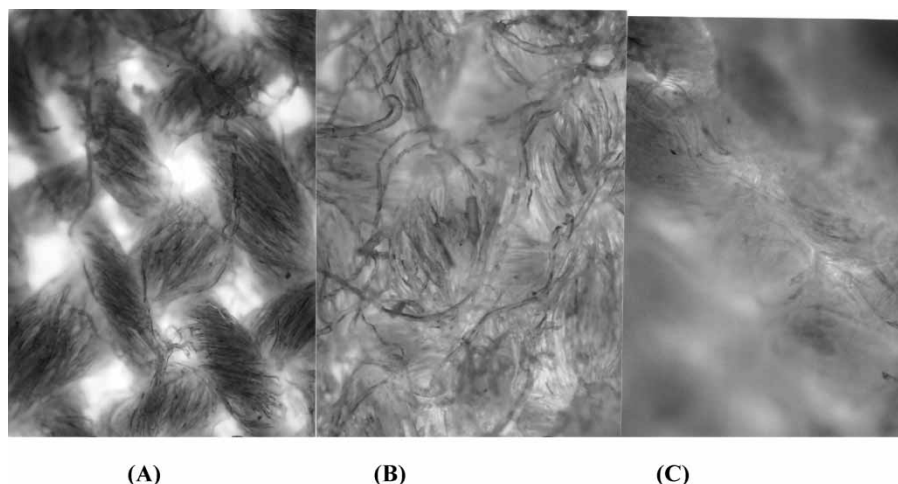
Fig. 7. Optical microscope of (A) plain cotton fabric (B) grafted fabric and (C) hydrated fabric.

These two opposite trends may be explained on the basis of the nature of the repeat units involved in the grafting process.

In the case of, fabrics grafted with hydrogels having increasing amounts of IA, the decrease in percent grafting implies the decrease in the amounts of monomer AAm and IA present in the grafted fabric. This directly results in less water uptake because both of the monomers are hydrophilic in nature and the later one is also ionic. Therefore, smaller the extent of grafting, smaller the contents of AAm and IA is the grafted product and so the degree of swelling will be lower. On the other hand, for the fabrics grafted with gels, increasing amounts of crosslinker, the water uptake is observed to decrease with the extent of grafting. The reason is that with the increase in percent grafting, the amount of crosslinker also increases within the grafted fabric. The increasing content of crosslinker implies to the increasing degree of crosslinking within the grafted polymer network. As a result, the free space available for accommodation of water molecules decreases. Moreover, with the increase in degree of crosslinking, the grafted gel becomes more rigid. This finally causes a decrease in water uptake. In this way, the two grafted products show opposite swelling trends.
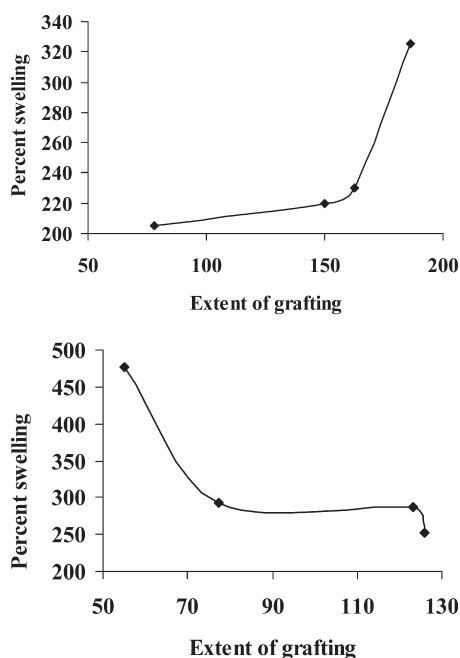
4   Conclusions

From the above study, it is concluded that grafting of poly(-acrylamide-co-itaconic acid) onto cotton cellulose fabric depends upon a number of parameters such as concentration of catalyst, amount of crosslinker, amount of monomers, initiator concentration, initiation time, and reaction temperature. Moreover, the swelling of resulted grafted cotton fabric depends on the nature of repeat unit and their concentrations in the grafted product.

In the next part, a detailed investigation of entrapment of silver nanoparticles into grafted fabric will be carried out and the resulting fabric shall also be tested for its antimicrobial activity.

Fig. 8. Equilibrium water uptake as a function of percent grafting for cotton fabric grafted with different concentrations of (A) IA and (B) crosslinker MB.

5   Acknowledgement

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