

Gentamicin-Loaded Poly(acrylic acid)-Grafted Cotton Fibers, Part 1: Synthesis, Characterization, and Preliminary Drug Release Study

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ABSTRACT: This study describes preparation of poly(acrylic acid)-grafted cotton fibers and release of antibiotic drug gentamicin sulfate from them under physiological conditions. Poly(acrylic acid) has been grafted onto cellulose backbone of cotton fibers via Ce(IV)-initiated polymerization in aqueous medium. The conditions obtained for optimum grafting were as follows: initiation time 30 min; initiation temperature 37°C; monomer concentration 27.8 mM; grafting temperature 30°C; nitric acid (catalyst) concentration 0.1M. The grafted fibers were characterized

by FTIR, TGA, and SEM analysis. The antibiotic drug gentamicin sulfate (GS) was loaded into the grafted fibers by equilibration method and release was studied under physiological conditions. The kinetic release data was interpreted by first-order kinetic model. Finally, drug-loaded fibers showed fair antibacterial action against *Escherichia coli*. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 366–374, 2011

Key words: grafting; cotton; polymerization; drug release

INTRODUCTION

Recently there has been growing interest to develop antimicrobial fibers that could be used in a number of biomedical applications such as personal care products, military and biodefence protective suits and coatings, burn and wound dressings, etc.^{1–4} These antimicrobial fibers are usually made from natural and biodegradable polymers such as gelatin,⁵ sodium alginate,^{6–7} cellulose,^{8–9} chitosan¹⁰ as well as from synthetic polymers such as polylactide,^{11–12} etc. Of these, cellulose has been the most frequently used biopolymer in antibacterial dressing materials due to its biocompatibility, nontoxicity, easy availability and above all, low cost.¹³ In addition, the fair susceptibility of cellulose towards chemical modifications to attach or incorporate any desired functionality is an extraordinary plus point that makes it most acceptable to be used in biomedical applications, particularly in wound and burn dressings.¹⁴ Finally, fair mechanical strength, sweat absorptivity, feeling like human skin and comfort are also additional features that can not be overlooked.

In recent past, the cationic antibiotic drug gentamicin sulfate has been frequently used in wound

dressing materials. For example, Campos et al.¹⁵ have prepared chitosan crosslinked film and investigated it for controlled release of gentamicin while covering and protecting the wound. *In vitro* gentamicin release from the crosslinked films, at physiological conditions of pH and temperature, was studied for 2 weeks. The effect of initial drug concentration and crosslinking ratio on the kinetics of drug release was also studied. Similarly, Simovic et al.¹⁶ developed a mathematical model to estimate the release of gentamicin sulfate from chitosan hydrogel, using Franz diffusion technique. The diffusive transport of drug through three connected compartments, that is chitosan hydrogel, membrane, and solution, was considered by using Fick's second law. The value of diffusion coefficient of drug was considered for every initial drug concentration. In a study by Zilberman et al.,¹⁷ gentamicin-eluting bioresorbable core/shell fiber structures were developed using a technique involving freeze drying of inverted emulsions. These structures were composed of a polyglyconate core and a porous poly(D,L-lactic-co-glycolic acid) (PDLGA) shell loaded with the antibiotic agent gentamicin sulfate. The investigation was focused on effect of the emulsion's composition (formulation) on the fibers, and on bacterial inhibition. The release profiles exhibited an initial burst effect followed by a decrease in release rate.

In the present work, a cationic antibacterial drug Gentamicin sulfate (GS) has been loaded into poly(acrylic acid)-grafted cotton cellulose fibers to

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develop a wound dressing material that could release the active ingredient and target it at the wound. As these fibers contain exchangeable or free H^+ ions in their grafted network, the cationic antibiotic drug gentamicin sulfate can conveniently be loaded into these fibers. In addition, amount of polyacrylic acid grafted onto cotton cellulose fibers can also act as one of the rate controlling parameters. This drug has been frequently used as an effective antibacterial agent in wound dressings. Gentamicin is a broad-spectrum antibiotic that is active against both gram-positive and gram-negative bacteria. It functions by inhibiting DNA gyrase, a Type II topoisomerase, and topoisomerase IV enzyme necessary to separate bacterial DNA, thereby inhibiting cell-division drug-load.¹⁷

EXPERIMENTAL

Materials

Cotton fibers were purchased from a local textile mill (Indore, India) and were used as received with no chemical treatment. The monomer acrylic acid (AAc), crosslinker *N,N*-methylene bisacrylamide (MB), initiator ceric ammonium nitrate (CAN) were purchased from Hi Media Chemicals, Mumbai, India, and were analytical grade. The antibiotic drug Gentamicin sulfate (GS; molar mass 575.67, Batch no. NPH-10073, Piramal Healthcare, India) was purchased from a local medical store. Double distilled water was used throughout the experiments.

Preparation of polyacrylic acid-g-cotton fibers (PAAc-g-CF)

All procedures, from solution preparation to the graft copolymerization were carried out at room temperature. Both the initiator (CAN) and monomer/crosslinker were dissolved in 0.1M HNO_3 and bubbled with N_2 .

Prewighed cotton fibers were placed in 25 mL of 20 mM CAN solution for 30 min, blotted with tissue paper to remove extra CAN, and then immersed in 25 mL of a solution containing preweighed quantities of monomer AAc and crosslinker MB. After the grafting reaction was over, each substrate was equilibrated in distilled water to remove unreacted salts. Finally, the grafted fibers were put in 50% methanol solution to remove any homopolymer formed¹⁸ and placed in a dust free chamber at 40°C until the fibers were completely dry. The percent grafting (PG) was calculated using the following expression:

$$\text{Percent grafting} = (\text{PG}) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o and W_g are the fiber weights before and after graft copolymerization respectively. To check

the reproducibility of the results obtained, experiments were carried out in triplicate and the average values have been reported in data.

Preparation of gentamycin sulfate loaded grafted cellulose (GSLG) fibers

The incorporation of model drug gentamicin sulfate into grafted fibers was carried out using the method of equilibration.¹⁹ A preweighed quantity of grafted fibers was placed in 25 mL of drug solution (w/v) for a period of 24 h to attain equilibration. Finally, the fibers were taken out, washed superficially with water to remove loosely-bound surface drug, and then allowed to dry in a dust-free chamber at 40°C till the fibers attained constant weight. The quantity of drug present per gram of fibers was calculated using the expression:

$$\begin{aligned} &\text{Amount of drug (mg g}^{-1} \text{ fibers)} \\ &= \frac{(\text{Final weight of fibers} - \text{Initial weight of fibers})}{\text{Initial weight of fibers}} \end{aligned} \quad (2)$$

For example, the fibers with percent grafting of 31.8% were found to contain 65 mg of drug per gram of fibers. These fibers were used for the purpose of release study and shall be designated as GSLGF (65) where the number in parenthesis denotes the amount of drug (in mg) present per gram of fibers.

Characterization of fibers

FT-IR spectral analysis

The Fourier Transform-Infrared (FTIR) spectra of plain and grafted fibers were recorded with an FT-IR spectrophotometer (Shimadzu, 8400 S Columbia) using KBr. For this, fibers were cut into a number of small pieces and mixed with KBr. The scans recorded were the average of 100 scans and the spectral range was 400 to 4000 cm^{-1} .

Thermogravimetric analysis of fibers

Thermogravimetric analysis (TGA) of fibers was performed using a thermogravimetric analyzer (Mettler, Teledo TGA/SDTA 851, Switzerland). A definite quantity of fibers were placed in a ceramic crucible and analyzed over the temperature range of 30 to 600°C at the heating rate of 10°C min^{-1} , under the flow of N_2 gas at the rate of 30 mL min^{-1} . The initial weight of plain and grafted fibers was 15.12 and 40.20 mg, respectively.

SEM analysis of fibers

The surface morphology of cotton fibers and grafted cotton fibers was studied using Hitachi S-4700 (New

Jersey) scanning electron microscope (SEM) operating at an acceleration voltage of 15 kv. All samples were dried in vacuum at room temperature and coated with gold before scanning. Surface morphologies were imaged at different magnifications.

In vitro drug release study

The preweighed drug loaded fibers were placed in 20 mL of release medium (i.e., physiological fluid) at 37°C. After definite time intervals, fibers were transferred into fresh release medium, and the amount of drug released was determined spectrophotometrically at 255 nm. The quantity of drug was calculated using Lambert-Beer's plot obtained for drug solutions of known concentrations.

Microbial experimentation

To measure the activity of drug-loaded fibers in quantitative manner, approximately 10^8 colony forming units (CFU) of *Escherichia coli* were cultured on a nutrient agar plate supplemented with drug-loaded fibers that were placed at the center of the plates. The plates were examined for a possible clear zone around the fibers after incubation at 37°C for 24 h. The plate, supplemented with plain fibers, was used as control set.

RESULTS AND DISCUSSION

Preparation of poly(acrylic acid)-grafted fibers (PAGF)

The Ce (IV) ion method has gained considerable importance in the graft polymerization reactions, due to its ease of application and its fair grafting efficiency.²⁰ Cerium (IV) has been reported to oxidize cellulose to produce cellulose macroradicals. Moreover, free-radicals are also produced by the action of catalyst HNO₃ on cerium (IV). These free radicals act upon the double bond of vinyl monomer acrylic acid to initiate the chain formation. The termination of growing grafted chains occurs via reaction with initiator, coupling, recombination, and disproportionation.²¹

Effect of initiation time on PG

The initiation time plays a significant role in affecting the extent of grafting. In a series of experiments, preweighed cotton fibers were put in 20 mM CAN solutions for different time durations and then transferred for a period of 1 h into the reaction mixture which contained 27.8 mM of AAc and 0.123 mM of crosslinker MB at 30°C. The results, as shown in Figure 1, indicate that PG initially increases with the initiation time, attains an optimum value of 87.6 for the initiation time of 30 min and then it levels off.

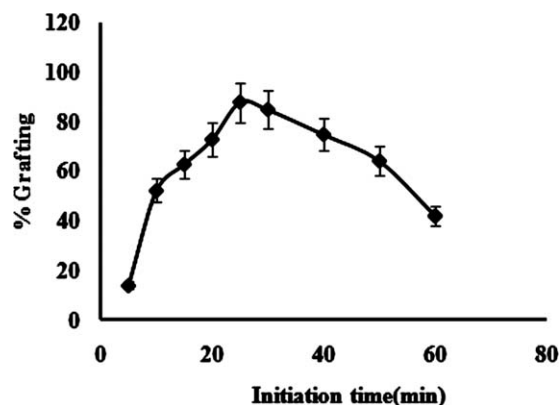


Figure 1 Effect of initiation time on percent grafting.

The results observed may be attributed to the fact that with the increase in initiation time, more and more free radicals are generated on cellulosic backbone, thus resulting in increase in percent grafting. However, when the initiation time is increased beyond 30 min, the number of free radicals generated along cellulosic chains does not increase any more as it has already attained a saturation value and hence the percent grafting levels off. Similar results have also been reported by Khullar et al.²⁴ for grafting of acrylonitrile onto cellulosic material derived from bamboo. According to them the observed decrease in percent grafting could also be attributed to the decay of free radical activity of Ce(IV) oxidized cellulose resulting from the free radical termination by charge transfer. Therefore, an initiation time of 30 min appears to be sufficient for optimum grafting.

Effect of initiation temperature on PG

The temperature at which initiation process occurs is also one of the significant parameters which affect percent grafting. In a series of experiments, cotton fibers were placed in 20 mM CAN solutions for 30 min at different temperatures and subsequently transferred into polymerization solution, which was premaintained at 30°C. The results, as shown in Figure 2, indicate an interesting trend. The percent grafting increases with initiation temperature, attains an optimum value at 37°C, and then begins to decrease with further increase in temperature. The results may be explained as follows: when temperature is below 37°C, the number of active sites generated along the cellulosic backbone may not be enough, thus resulting in less percent grafting. Likewise, when the initiation temperature is sufficiently high, i.e., above 37°C, a decrease in percent grafting is noticed which may simply be attributed to a faster recombination of free radicals, thus finally yielding fewer numbers of active sites available along the cellulosic macromolecular chains for grafting reaction.

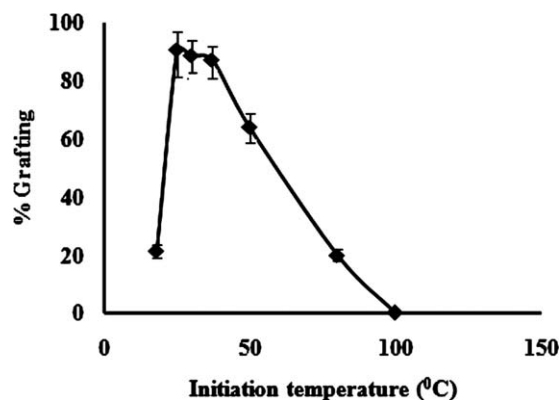


Figure 2 Effect of initiation temperature on percent grafting.

to take place. Almost similar results have also been reported elsewhere.²⁵

Effect of HNO₃ concentration on PG

The effect of variation in concentration of catalyst (i.e., HNO₃) on the percent grafting was also investigated. Preweighed cotton fibers were placed for 30 min in 20 mM CAN solutions, prepared in HNO₃ solutions of varying concentrations, in the range of 0.02 to 0.25M at 37°C. After removal from catalyst solutions, they were put in reaction mixtures at 30°C for polymerization to occur. The results have been shown in the Figure 3. It is clear that percent grafting increases with the increase in HNO₃ concentration upto 0.1M and then it begins to decrease with further increase in HNO₃ concentration.

The plausible explanation of such behavior is that HNO₃, in the polymer grafting reaction 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 the unfolding of cellulosic chains and improvement of the monomer accessibility. However, when the concentration of HNO₃ is increased beyond 0.1M, it

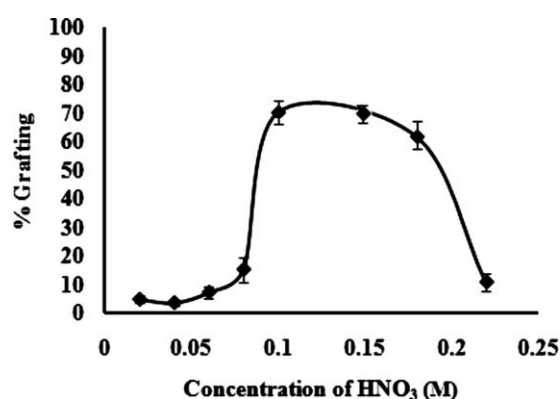


Figure 3 Effect of catalyst (i.e., HNO₃) concentration on percent grafting.

may be sufficient to cause the partial degradation of cellulose chains as well as of graft chains. In addition, the fall in PG may also be attributed to the enhanced coagulation of colloidal homopolymer, which might have been formed due to presence of a trace amount of unremoved Ce(IV) in the solution and in the fiber structure at lower pH. This results in retardation in diffusivity of monomer molecules from solution phase into the fiber phase.²⁷ Therefore percent grafting is observed to decrease beyond 0.10M concentration of HNO₃.

Effect of reaction temperature on percent grafting

The percent grafting was determined at different reaction temperatures, in the range of 5 to 60°C under identical conditions. The results, as shown in Figure 4, reveal that the optimum percent grafting is obtained at around 30°C and it decreases on either sides along the temperature axis. This may be attributed to the fact that with the increase in temperature the percent grafting is enhanced due to faster diffusion of monomer molecules towards the active grafting sites generated along the cellulose chains in the fibers. In addition, reduced viscosity of the reaction medium also favors faster diffusion of monomer molecules. However, as the temperature is increased beyond 30°C, the percent grafting begins to decrease. This may probably be due to faster recombination of growing chains and enhancement in formation of homopolymer.

We also investigated effect of monomer concentration on percent grafting. The optimum acrylic acid concentration was found to be around 27.8 mM (data not shown).

Characterization of fibers

FT-IR analysis of fibers

The FT-IR spectra of cellulosic fibers and polyacrylic acid-grafted-cellulosic fiber are shown in Figure 5.

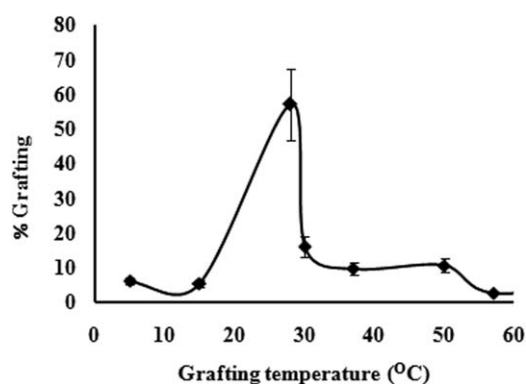


Figure 4 Effect of grafting temperature on percent grafting.

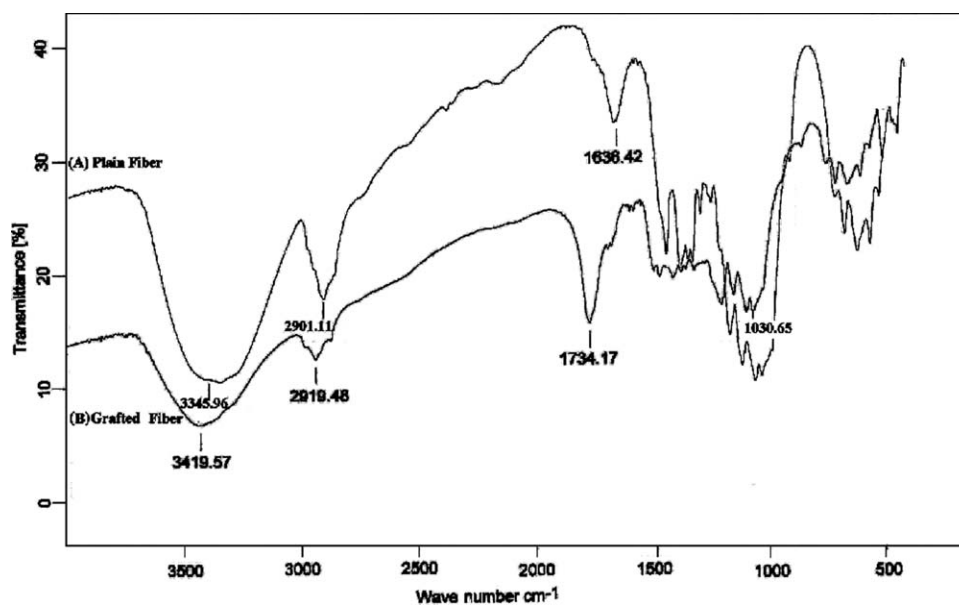


Figure 5 FT-IR spectral analysis of (A) plain fibers and (B) grafted fibers.

The grafted sample shows a broad band at 3400 to 3600 cm^{-1} which may be attributed to sum of contributions from hydrogen bonded —OH stretching of cellulose as well as hydrogen bonded ν_{OH} from carboxylic groups of polyacrylic acid and ν_{NH} from amide groups of crosslinker MB. In addition, the grafted sample also contains typical signals of cellulose backbone (ν_{CH} 1431 cm^{-1} , ν_{COC} 1059 cm^{-1} , $\nu_{\beta\text{ linkage}}$ 890 cm^{-1}). However, the grafted sample exhibits a sharp peak at 1734 cm^{-1} attributable to —C=O stretching vibrations from carboxylic groups of PAAC. Moreover, there is also a sharp peak observed at 1030 cm^{-1} for —C—CHO stretching, thus confirming the formation of aldehydic group in cellulose network during grafting by CAN initiator. It is to be noted that the percent transmittance, observed in spectra, is quite low. This could probably be due to the fact that greater quantity of polymer was taken in sample preparation for FT-IR spectral analysis.

Thermogravimetric analysis of fibers

The results of thermogravimetric analysis of plain and grafted cellulose fibers are shown in Figure 6(A,B), respectively. It can be seen that plain cellulose fibers begin to decompose at 270°C (i.e., $T_{\text{id}} = 270^\circ\text{C}$) and the decomposition process is quite rapid in the temperature range of 300 to 400°C through the formation of levoglucosan and other volatile compounds.²² On the other hand, the polyacrylic-cellulose fibers exhibit initial decomposition temperature of 180°C . The thermogram shows biphasic decomposition process. The first phase of effective decomposition occurs in the range of 230 to 300°C which is attributed to dehydration and decarboxyl-

ation of carboxylic groups of polyacrylic acid graft chains.²³ The second phase degradation then begins as the temperature is raised beyond 330°C . The earlier decomposition temperature of grafted fibers and their biphasic thermogram are also indicative of polymer grafting onto cellulosic backbone. The overall weight loss suffered by plain and grafted fibers was about 80 and 96% , respectively.

SEM analysis of fibers

The grafting of a polymer onto fibers usually results in change in surface morphology of the resulting fibers which can conveniently be observed using scanning electron microscopy (SEM) analysis. Figure 7 shows a comparative depiction of surface morphology of plain and polyacrylic acid grafted fibers at various magnifications. Figure 7(A,B) are images of plain and grafted fibers respectively, obtained

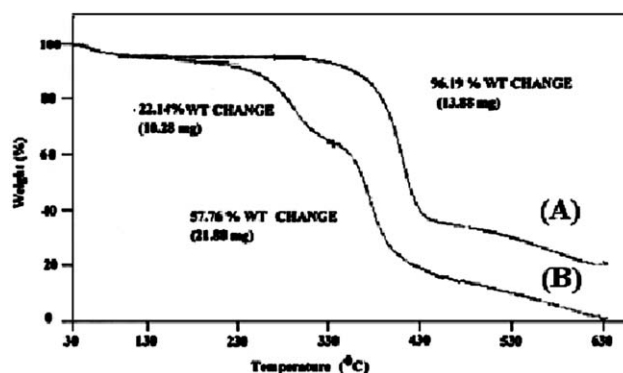


Figure 6 Thermogravimetric analysis of (A) plain fibers and (B) grafted fiber.

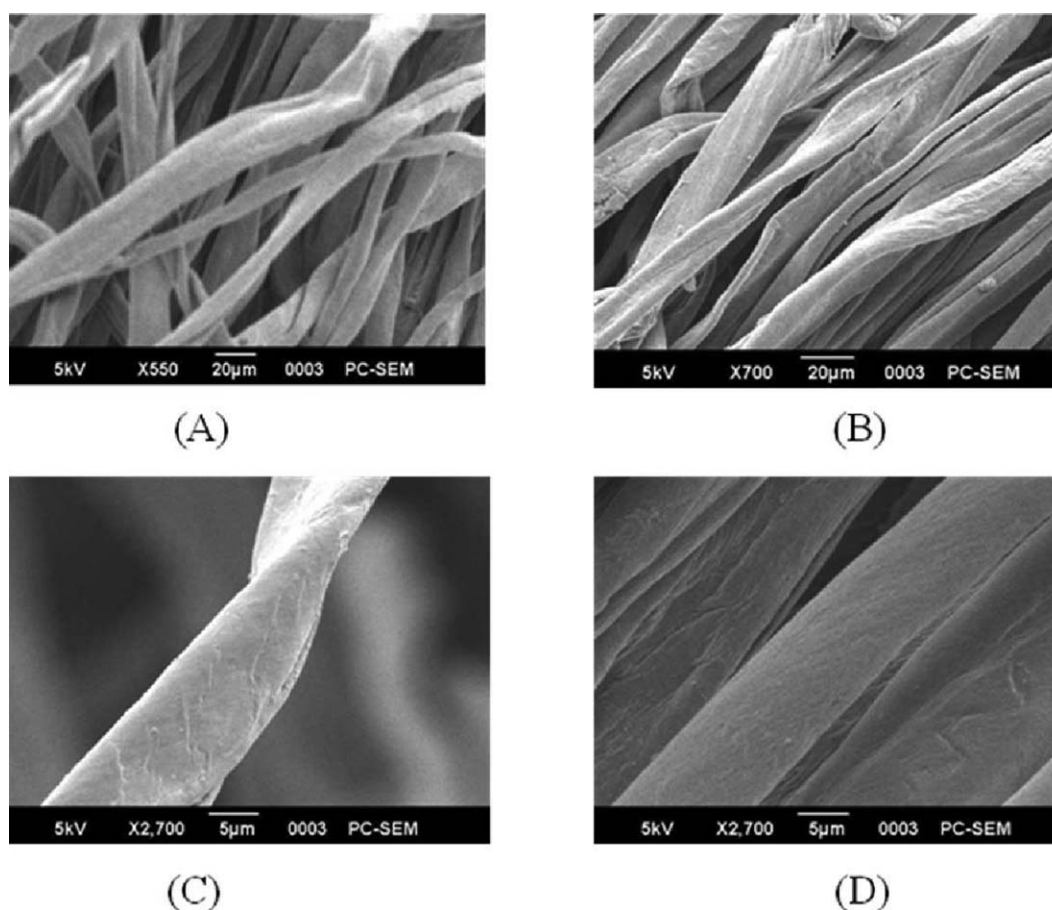


Figure 7 SEM analysis of (A) plain fibers (bar scale 20 μm), (B) grafted fibers (bar scale 20 μm) and (C) plain fibers (bar scale 5 μm), (D) grafted fibers (bar scale 5 μm),

with 300 \times magnifications and bar scale of 50 μm . In addition, Figure 7(C,D) also show surface images of plain and grafted fibers obtained at 550 \times and 600 \times magnifications, respectively, with bar scale of 20 μm . It is quite clear that the surface has not only become quite rough due to formation of polymer but there is also an appreciable increase in thickness of fibers.

Loading of drug into grafted fibers

Gentamycin sulfate (GS) is a water soluble drug with a fair solubility of about 50 mg/mL water.²⁷ In aqueous medium it is present in the form of cation.

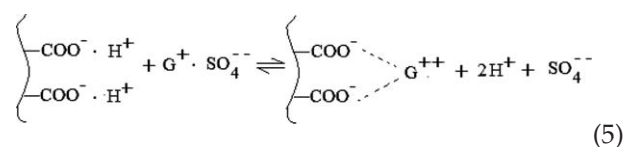


The poly(acrylic acid)-grafted-fibers have carboxylic groups attached along the polyacrylic acid grafted chains with free or counter H^+ ions.



When grafted fibers are placed in aqueous drug solution, there occurs ion-exchange process between counter H^+ ions attached along the fibers and G^{++}

ions present in the aqueous solution, as shown below:



Therefore, the drug is loaded into grafted fibers via ion-exchange mechanism.

Release of GS from grafted fibers

While investigating the release of drug, it should be noted that body fluid has complex composition and therefore choice of release medium is important. In a study of the composition of serum fluid, formed after auxiliary dissection, Bonnema et al.²⁸ found that on the first postoperative day, the drainage fluid contained blood contents and a high concentration of creatine phosphokinase. After day one, it changed to a peripheral lymph-like fluid that contained different cells and more protein. Trengrov et al.²⁹ found that wound fluid, collected from leg ulcer, contained 0.6 to 5.9 mM/L glucose and 25 to

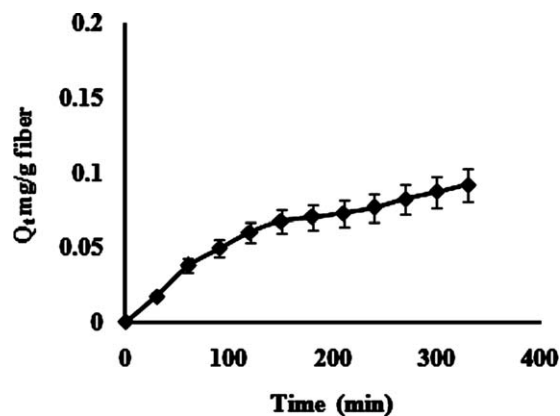


Figure 8 Dynamic release of drug GS from GSLGC (65) fibers in the physiological fluid at 37°C.

61 g/L protein. Similarly, Fraohm et al.³⁰ analyzed the fluid from a post operative wound, and found that wound fluid contained fragments of peptide. Thus, looking to variation in various wound fluid compositions, we decided to carry out our *in vitro* release study in the physiological fluid (PF), as suggested by British Pharmacopoeia, which contained 142 mM of NaCl and 2.5 mM of CaCl₂. The results of release experiments, carried out with GSLGC (65) fibers, in physiological fluid at 37°C are shown in the Figure 8. Drug release from simple swellable systems may be described by the well-known power law expression³¹

$$\frac{Q_t}{Q_\infty} = k_t^n, \quad \text{for } 0 < \frac{Q_t}{Q_\infty} < 0.60 \quad (6)$$

The log-log form of eq. (6) was used to calculate drug diffusion exponent “*n*,” which was calculated using slope of the linear plot obtained between $\ln Q_t/Q_\infty$ and $\ln t$ (Fig. 9). The value of diffusion exponent “*n*” was found to be 0.645. According to Ritger and Peppas,³² the criteria of release kinetics from swellable systems, i.e., zero-order, anomalous

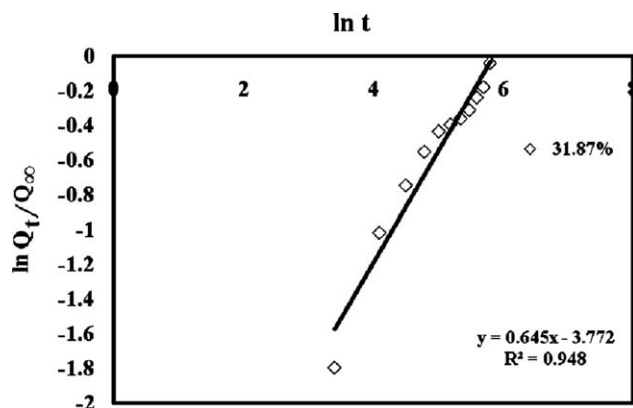
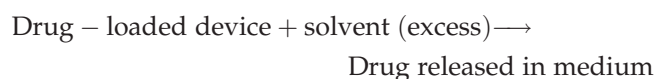


Figure 9 $\ln Q_t/Q_\infty$ versus $\ln t$ plot for determination of release exponent *n*.

kinetics and Fickian release are represented by $0.89 < n < 1.0$, $0.45 < n < 0.89$, and $n = 0.45$, respectively. In the light of this, the value obtained in present study i.e., ($n = 0.645$) indicates that drug is released from the grafted polymer network in a chain-relaxation controlled manner. This can be attributed to the fact that at the experimental pH 7.4, the ionization of carboxylic groups cause relaxation of grafted polymeric chains due to electrostatic repulsion among similarly charged $-\text{COO}^-$ groups. These groups are produced owing to ionization of $-\text{COOH}$ groups of polyacrylic acid grafted chains as the pH of release medium is above the pK_a value of poly(acrylic acid),³³ i.e., pK_a 5.2. Therefore, mutual repulsion causes polymeric chains to unfold, thus causing an increase in the mesh size of network. Hence, drug is released under chain-relaxation controlled mechanism. Here it is noteworthy that in this study *in vitro* drug release experiment has been carried out under sink conditions for which the above power-law expression is applicable. However, in a wound the volume of fluid is not so large as to maintain sink conditions and therefore conclusions drawn using eq. (9) may not be significantly applicable on *in vivo* conditions.

Fitting of kinetic model

The release of a bioactive material from a drug-loaded device can be represented as³⁴



If Q_0 is the initial amount of drug present in the device and Q_t is the amount of drug released in time t , then for the first-order kinetic model we can write:

$$-\ln \left(\frac{1 - Q_t}{Q_0} \right) = k_1 t \quad (7)$$

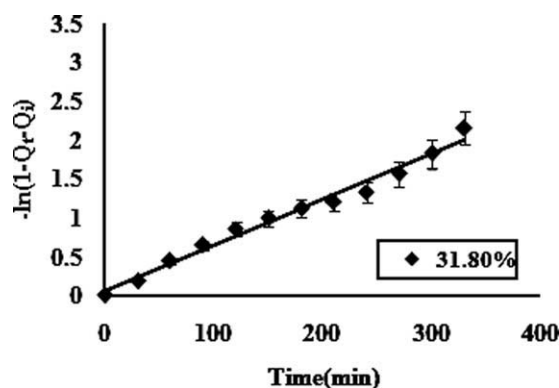


Figure 10 First-order kinetic plot for release of gentamicin under physiological conditions.

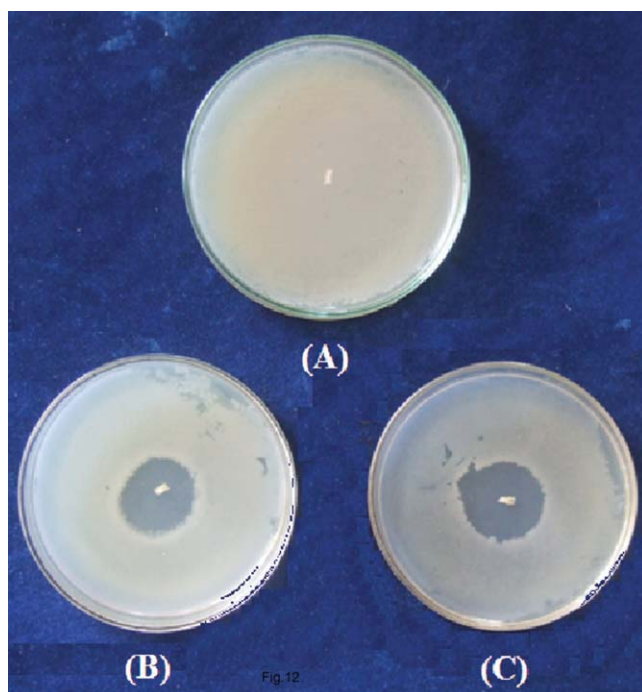


Figure 11 “Zone of inhibition” appearing in the petri-plates supplemented with (A) plain (B) GSLGC (2), and (C) GSLGC (4) fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, a linear plot, obtained between $-\ln(1 - Q_t/Q_0)$ and t confirms the fitness of first order kinetic model on release data. The kinetic release data, as shown in Figure 8, was applied on eq. (7) and a linear plot with a fair regression value of 0.9800 was obtained between $-\ln(1 - Q_t/Q_0)$ and t as displayed in Figure 10. This confirmed the suitability of first-order kinetic model in this study. The value of first order rate constant was found to be $6.1 \times 10^{-3} \text{ min}^{-1}$.

Antibacterial study

To test the antimicrobial efficiency of the drug-loaded fibers, we prepared two such fiber samples by equilibrating 31.8% grafted fibers in 2 and 4% (w/v) drug solutions, and designated them as GSLGC (2) and GSLGC (4), respectively. The results of the antibacterial test conducted with these fiber samples have been shown in the Figure 11. It can be seen that Petridish, supplemented with plain fibers [Fig. 11(A)] exhibits a dense population of bacterial cells while Petridishes, supplemented with grafted fiber samples GSLGC (2) and GSLGC (4) show clear zones of inhibition around the bunch of fibers placed in the center [Fig. 11(B,C), respectively].

The observed finding may be attributed to the release of drug molecules from the drug-loaded grafted fibers. The radii of inhibition-zones were found to be 20 and 24 mm, respectively.

CONCLUSIONS

From the above study it may be concluded that cotton cellulose fibers can be grafted with polyacrylic acid chains under moderate conditions in aqueous medium. The cationic drug gentamycin sulfate is fairly loaded into grafted fibers through ion-exchange mechanism. The kinetic drug release data, obtained at 37°C in the physiological fluid, demonstrated first-order release kinetics. The second part of the work is currently under study which includes detailed investigation of rate controlling parameters such as degree of crosslinking of grafted polymer network, amount of polyacrylic acid grafted onto fibers, quantity of drug that is loaded into fibers, etc. Attempts shall also be made to obtain “zero-order” release from the fibers which is most desirable in the case of drug-delivery applications.

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