PREPARATION AND CHARACTERIZATION OF ANTIMICROBIAL ABSORBENT LAYER FOR BABY DIAPER

A Major Project Dissertation submitted in partial fulfillment of the requirement for degree of

Master of Technology
In
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Submitted by

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CERTIFICATE

This is to certify that this is a bonafide record of project work based on topic **“Preparation and Characterization of Antimicrobial Absorbent Layer for Baby Diaper”** is submitted by **Priyadarshan Sahoo** (M-Tech - 2K12/PTE/12). This project was carried under my supervision in year 2013-14 and being submitted towards partial fulfillment of the requirement for the award of Master of Technology in Polymer Technology in Delhi Technological University.

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Abstract

This project report is focused on the preparation and characterization of absorbent layer of baby diapers using bamboo fabric grafted with hydrogel. Graft copolymerization of acrylic acid (AA) hydrogel onto bamboo rayon fabric is carried out using potassium persulphate (KPS) as a free radical initiator in the presence of methylenebisacrylamide (MBA) as a cross-linker. The effects of reaction variables, such as concentration of MBA and KPS are optimized on the basis of water and synthetic urine absorbance capacity.

Further, hydrogel layer is treated with sodium hydroxide to generate sodium polyacrylate. The swelling kinetics of sodium polyacrylate grafted hydrogel bamboo fabric is studied in pure water and synthetic urine. It is observed that sodium polyacrylate grafted hydrogel layer show less Fickian diffusion.

The grafting of acrylic acid hydrogel layer on the bamboo fabric is confirmed by FTIR spectroscopy. SEM micrograph shows a surface deposition of acrylic acid onto the bamboo fabric. Further the absorbent layer is modified by Silver Nitrate solution to give it bacterial resistance. The absorbent layer shows excellent antibacterial activity against Gram positive (*S. aureus*) and Gram negative (*E. coli*) bacteria.

TABLE OF CONTENTS

	CONTENTS	PAGE NO.
	Certificate	i
	Acknowledgement	ii
	Abstract	iii
	Contents	iv
	List of Figures	vii
	List of Tables	ix
Chapter 1	**Introduction and objectives**	1
	1.1 Introduction	1
	1.2. Objectives	5
Chapter 2	**Literature review**	6
	2.1. Bamboo tree and cultivation in India	6
	2.2. Chemical composition of bamboo	7
	2.3. Uses of bamboo	8
	2.4. Manufacturing process of bamboo fibre	9
	2.5. Grafting	11
	2.6. Cellulose grafting	12
	2.7. Grafting of bamboo fibres	15
	2.8. Diaper & its uses	17
	2.9. Structure of a baby diaper	18
	2.10. Construction of the absorbent core	20
	2.11. Principle of absorption	21

	2.12. Theoretical swelling of hydrogel	22
	2.13. Kinetics of hydrogel swelling	22
	2.14. Existing diaper problem	24
Chapter 3	**Materials & methods**	26
	3.1. Materials	26
	3.2. Methods	26
	3.2.1. Grafting of bamboo fabric with Acrylic acid	26
	3.2.2. Preparation of antimicrobial absorbent layer	27
	3.2.3. Determination of mass swelling ($S_{m,}$ %)	27
	3.2.4. Measurement of hydrophilic group	28
	3.2.5. Characterizations of NaAA grafted bamboo rayon fabric	29
	3.2.5.1. Fourier transform infrared spectroscopy (FTIR)	29
	3.2.5.2. Energy dispersive X-ray spectroscopy (EDXS)	29
	3.2.5.3. Scanning electron microscopy (SEM)	29
	3.2.6. Antibacterial testing	29
Chapter 4	**Results and Discussion**	31
	4.1. Study on grafting percentage	37
	4.2. Optimization based on swelling	39
	4.2.1. Mass swelling in water	39
	4.2.2. Mass swelling in synthetic urine	43
	4.3. Study on swelling kinetics	47
	4.4. Analysis of –COOH Group in the optimized sample	58

	4.5. Determination of silver ion on hydrogel	58
	4.6. Structural analysis through FTIR	60
	4.7. Morphological analysis	61
	4.8. Antibacterial testing	62
Chapter 5	**Conclusions and future scope**	64
	5.1. Conclusions	64
	5.2. Future scope	65
	References	66

LIST OF FIGURES

Figure	Page No.
Figure 1: Effect of initiator (KPS) and crosslinker (MBA) concentration on grafting (%)	38
Figure 2: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 0.5% KPS and three different concentration of MBA.	41
Figure 3: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 1.00% KPS and three different concentration of MBA.	41
Figure 4: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 2.00% KPS and three different concentration of MBA.	42
Figure 5: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 3.00% KPS and three different concentration of MBA.	42
Figure 6: Mass of Synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 0.05% KPS and three different concentration of MBA.	45
Figure 7: Mass of Synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 1.00% KPS and three different concentration of MBA.	45
Figure 8: Mass of Synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 2.00% KPS and three different concentration of MBA.	46
Figure 9: Mass of Synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 3.00% KPS and three different concentration of MBA.	46
Figure 10: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 0.5% KPS and three different concentration of MBA.	49
Figure 11: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 1.0% KPS and three different concentration of MBA.	50
Figure 12: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 2.0% KPS and three different concentration of	51

MBA.	
Figure 13: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 3.0% KPS and three different concentration of MBA.	52
Figure 14: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 0.5% KPS and three different concentration of MBA.	53
Figure 15: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 1.0% KPS and three different concentration of MBA.	54
Figure 16: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 2.0% KPS and three different concentration of MBA.	55
Figure 17: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 3.0% KPS and three different concentration of MBA.	56
Figure 18: Swelling mechanism analysis of optimized NaAA grafted bamboo rayon	57
Figure 19: FTIR Spectra of plain bamboo rayon fabric and NaAA grafted bamboo rayon fabric	60
Figure 20: SEM micrographs for (a) & (c) parent bamboo fabric and (c) & (d) NaAA grafted bamboo fabric	61
Figure 21: Zone of inhibition (a) *S. Aureus* treated (b) *E. Coli* treated (1) plain bamboo rayon fabric (2) NaAA grafted bamboo rayon fabric (3) silver modified NaAA grafted bamboo rayon fabric.	62

LIST OF TABLES

Tables	Page No.
Table 1: Effect of initiator (KPS) and crosslinker (MBA) concentration on grafting (%)	38
Table 2: Swelling (%) of NaAA grafted bamboo rayon fabric in water	40
Table 3: Swelling (%) of NaAA grafted bamboo rayon fabric in synthetic urine	44
Table 4: Swelling constant (K) and diffusion exponent (n) for sample of 0.5% KPS and three different concentration of MBA in water	49
Table 5: Swelling constant (K) and diffusion exponent (n) for sample of 1.0% KPS and three different concentration of MBA in water	50
Table 6: Swelling constant (K) and diffusion exponent (n) for sample of 2.0% KPS and three different concentration of MBA in water	51
Table 7: Swelling constant (K) and diffusion exponent (n) for sample of 3.0% KPS and three different concentration of MBA in water	52
Table 8: Swelling constant (K) and diffusion exponent (n) for sample of 0.5% KPS and three different concentration of MBA in synthetic urine	53
Table 9: Swelling constant (K) and diffusion exponent (n) for sample of 1.0% KPS and three different concentration of MBA in synthetic urine	54
Table 10: Swelling constant (K) and diffusion exponent (n) for sample of 2.0% KPS and three different concentration of MBA in synthetic urine	55
Table 11: Swelling constant (K) and diffusion exponent (n) for sample of 3.0% KPS and three different concentration of MBA in synthetic urine	56
Table 12: Swelling constant (K) and diffusion exponent (n) for optimized NaAA grafted bamboo rayon	57
Table 13: Elemental Analysis (wt.%) of parent and silver treated sample	59
Table 14: Zone of inhibition for sample treated with *E. coli*	63
Table 15: Zone of inhibition for sample treated with *S. aureus*	63

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1. Introduction

Bamboo belongs to the *Poaceae* family, a subfamily of *Bambusoideae* and includes the largest member of grass family. There are more than 1,450 species of bamboo, of which only around 50 species are routinely cultivated in the tropical and sub-tropical region of the world. India is the IInd highest producer of bamboo in the world and 45% of total production of bamboo of the country is being utilized in paper industries [1, 2]. The Department of Agriculture & Cooperation, Ministry of Agriculture (Govt. of India) had launched a Centrally Sponsored Scheme of “National Bamboo Mission” to increase the cultivation of bamboo trees in 26 states [3]. The main component of bamboo is cellulose (about 57 - 63%) with a α-cellulose content of 36 - 41%, lignin (22 - 26%), penthosans (16 - 21%) and minor constituents like resins, tannins, waxes and inorganic salts [4, 5]. The one responsible for bamboo’s antibacterial properties is 2, 6-bimethoxy-p-benzoquinone, called ‘Bamboo kun’ [6, 7].

There are two main manufacturing processes used to make fibres from bamboo viz. chemical processing and mechanical processing. In the mechanical process, the woody parts of the bamboo plant are crushed and then natural enzymes are used to break the bamboo walls into a soft mass so that the natural fibres can be mechanically combed out and spun into yarn [8-10]. The chemical process to make bamboo fibre and yarn essentially follows the rayon/viscose manufacturing process. Such kind of manufacturing process for regenerated bamboo fibre resembles that of viscose rayon fibre; consequently, regenerated bamboo fibre is also called bamboo viscose [11-13].

Bamboo is the fastest growing plant in the world - some species grow even one meter per day. Furthermore bamboo tolerates poor soils, which makes it useful for planting on degraded land [2, 4]. It has a great ability to reduce greenhouse gases, absorbing five times more CO_2 than an equivalent stand of trees and producing 35% more oxygen. It checks soil erosion.

Graft copolymerization is a commonly used method for the modification of surfaces of polymers [14-16], and it is an important tool in order to modify the physical or chemical properties of polymers. During grafting, the side chains are covalently bonded to the main polymer backbone or substrate to form a copolymer with branched structure. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting. Chemical means the grafting can proceed along two major paths, viz. free radical and ionic [15, 16].

Cellulose is a naturally occurring polymer consists of a linear polysaccharide with long chains which consists of β-D-glucopyranose units joined by β-1,4 glycosidic linkages []. In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups [4]. There are number of techniques of grafting onto cellulose claimed through the research, which includes chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting. Even though grafting of cellulose has been investigated the larger extent, the research on the bamboo fibre grafting is explored in a limited extent.

Wang *et al.* [31] studied the grafting of bamboo fibre using methacryloyloxyethyl tri-methyl ammonium chloride (DMC) as monomer and ammonium ceric nitrate (CAN) as initiator. Xu *et al*. [32] prepared super absorbent resin based on the graft copolymerization of bamboo pulp cellulose and monomer acrylamide. Khullar *et al.* [33] grafted acrylonitrile onto the cellulose isolated from bamboo (Dendrocalamus strictus) in heterogeneous medium using ceric ammonium nitrate and studied the effect of process parameters on extent of grafting and grafting efficiency. Liu *et al.* [34] prepared the graft copolymerization of methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) onto bamboo fibre using Ce^{4+} as initiator.

Superabsorbent disposable baby diapers are sophisticated, well-engineered products that provide many benefits including convenience, comfort, exceptional leakage protection, improved hygiene and skin care benefits compared with cloth diapers. The modern superabsorbent disposable diaper consists of three basic functional product zones [36, 37]. The top sheet is the layer in direct contact with the baby’s skin. It consists of a soft nonwoven synthetic sheet, composed of polypropylene/polyethylene, either alone or as a blend, which allows liquids to pass through while remaining relatively dry and soft. The middle sheet consists of two layer i.e. acquisition/distribution layer and absorbent core [37, 38]. The acquisition/distribution layer is usually composed of a modified cellulose patch and a polyester-based layer sandwiched between the top sheet and the core, which is not in direct contact with the skin. The absorbent core is the inner-most layer of the diaper. It typically consists of a blend of polyacrylate granules blended with fluff cellulose pulp (bleached by an elemental chlorine-free process) and encapsulated by either a cellulose or polypropylene nonwoven layer. The back sheet is the water-resistant outer layer of the diaper, typically made of a polyethylene film laminated with a soft textured, cloth-like polypropylene [37-40].

Disposable baby diaper generally used hydrogel as superabsorbent polymer. This superabsorbent polymer (sodium polyacrylate) is either dispersed or blended with fluff cellulose pulp. The polymer may not be uniformly dispersed or blended throughout the cellulosic pulp. The sodium polyacrylate hold more liquid but this create a breeding ground for bacteria causing a bacterial illness called toxic shock syndrome. To overcome these difficulties an attempt has been made to construct antimicrobial absorbent layer for baby diaper [52, 53].

In the present work, absorbent layer of baby diaper is prepared using bamboo fabric grafted with sodium polyacrylate hydrogel. The hydrogel layer is loaded with silver ion. The developed layer is characterized for swelling, structural and antimicrobial properties for baby diaper application.

1.2. Objectives

a. To prepare the absorbent layer by grafting acrylic acid onto the bamboo rayon fabric.

b. To prepare the antimicrobial absorbent layer.

c. To study the swelling behaviour and swelling kinetics of absorbent layer in water and synthetic urine.

d. Characterization of absorbent layer for its structural and antimicrobial properties.

CHAPTER 2

LITERATURE REVIEW

2.1. Bamboo tree and cultivation in India

Bamboo is an ancient woody grass widely distributed in tropical, subtropical and mild temperate zones. Traditionally seen as the “poor man’s tree”, in recent years bamboo has risen to a high-tech, industrial raw material and substitute for wood [1, 2]. Bamboo belongs to the *Poaceae* family, a subfamily of *Bambusoideae* and includes the largest member of grass family. There are more than 70 genera of bamboo divided into about 1,450 species, of which only around 50 species are routinely cultivated throughout the world [1, 3].

Bamboo tree can grow in very hard conditions without requiring any pesticides and herbicides. Bamboo is the fastest growing plant in the world - some species grow even one meter per day. Furthermore bamboo tolerates poor soils, which makes it useful for planting on degraded land [2, 4]. It has a great ability to reduce greenhouse gases, absorbing five times more CO_2 than an equivalent stand of trees and producing 35% more oxygen. Bamboo is giving economic security and employment opportunity to unemployed people. Bamboo shoots are also a nutrient food items in different forms and this plants have enumerable utilities in our day to day life. Identification of bamboos and there suitability to a particular locality is very important for successful cultivation [3, 5].

India is the 2nd highest producer of bamboo in the world and 45% of total production of bamboo of the Country is being utilized in paper industries. The Department of Agriculture & Cooperation, Ministry of Agriculture (Govt. of India) had launched a Centrally Sponsored Scheme of "National Bamboo Mission", during the Xth Plan with effect from 2006-07, covering twenty-seven (27) States of the country [2, 3]. The Mission's objectives are to promote the growth of the bamboo sector through an area-based regionally differentiated strategy, to increase the coverage of area under bamboo in potential areas, with suitable species to enhance yields; to promote marketing of bamboo and bamboo based handicrafts, to promote, develop and disseminate technologies through a seamless blend of traditional wisdom and modern scientific knowledge, to generate employment opportunities for skilled and unskilled persons, especially unemployed youths [6, 7].

2.2. Chemical composition of bamboo

The chemical structure of bamboo fibres is similar to that of wood. The main component is cellulose (about 57 - 63%) with a α-cellulose content of 36 - 41%, lignins (22 - 26%), pentosan (16 - 21%) and minor constituents like resins, tannins, waxes and inorganic salts[5, 6]. Compared with wood, however, bamboo has higher alkaline extractives, ash and silica contents [6, 7]. Alpha-cellulose, lignin, extractives, pentosan, ash and silica content increased with increasing age of bamboo.

The presence of large amounts of starch makes bamboo highly susceptible to attack by staining fungi and powder-post beetles. The most significant components in the bamboo's chemical constitution are those providing its extraordinary fungal and bacterial resistance. The one responsible for bamboo's antibacterial properties is 2, 6-bimethoxy-p-benzoquinone, called 'Bamboo kun' [6]. The highly distinctive fungal resistance occurs due to a protein-dendrocin [7, 8].

2.3. Uses of bamboo

Bamboo can be used in a variety of ways ranging from little processed culm based products to newly developed industrial products as a substitute for traditional hardwoods. Another dimension to the rapidly growing bamboo market is the wide range of uses from low-cost products such as cheap housing (such as the growing use of bamboo based disaster relief housing) to high-end products such as parquet flooring and decking. [9, 10]

Bamboo culms are widely used as a construction material due to its low cost of production and its strength: Scaffolding, Bridges, Housing material, Reinforced concrete, Pipes [6, 3]. Several bamboo-producing countries, such as China and India use bamboo in pulp and paper. Bamboo paper has practically the same quality as paper made from wood. Its brightness and optical properties remain stable, while those of paper made from wood may deteriorate over time. Also bamboo used in construction of household furniture and flooring. Bamboo flooring has certain advantages over wooden floors due to its smoothness, brightness, stability, high resistance, insulation qualities and flexibility. Through pyrolysis, bamboo can be converted into three valuable products: bamboo charcoal, oil and gas. Bamboo charcoal is an excellent fuel for cooking and barbequing. Activated bamboo charcoal can be used for cleaning the environment, absorbing excess moisture and producing medicines. The absorption capacity of bamboo charcoal is six times that of wood charcoal of the same weight [9, 10].

Bamboo clothing is a relatively new product, but is expected to grow rapidly due to the materials unique mechanical and environmental qualities. Bamboo fabrics are made from pure bamboo fibre yarns which have excellent wet permeability, moisture vapour transmission property, soft hand, better drape, easy dying and splendid colors. It is a newly founded, great prospective green fabric. Bamboo non-woven fabric made by pure bamboo pulp, used as sanitary napkin, masks, mattress, food packing bags due to its anti -bacteria nature [10].

2.4. Manufacturing process of bamboo fibre

There are two main manufacturing processes used to make fibres from bamboo viz. chemical processing and mechanical processing. Both methods engender negative impacts on the environment and human health, and there is room for improvement through closed-loop manufacturing strategies, more efficient equipment, and the use of more eco-friendly compounds to extract fibres [11].

In the mechanical process, the woody parts of the bamboo plant are crushed and then natural enzymes are used to break the bamboo walls into a soft mass so that the natural fibres can be mechanically combed out and spun into yarn. Since this process is more labour intensive and costly, this type of manufacturing process of bamboo fibre for clothing is rarely used. The bamboo fibre made using the mechanical process, which resembles ramie-like method, are generally named as “original”, “bio”, and “natural” bamboo fibres [12].

The chemical process to make bamboo fibre and yarn essentially follows the rayon/viscose manufacturing process. Such kind of manufacturing process for regenerated bamboo fibre resembles that of viscose rayon fibre; consequently, regenerated bamboo fibre is also called bamboo viscose [13].

Bamboo leaves and the soft, inner pith from a hard bamboo trunk are extracted and crushed. In the steeping process, the crushed bamboo cellulose is soaked in a solution of 15% to 20% sodium hydroxide at a temperature of between 20 °C and 25 °C for one to three hours to form alkali cellulose. The bamboo alkali cellulose is pressed to remove excess sodium hydroxide solution. The alkali cellulose is shredded by a grinder to increase the surface area and make the cellulose easier to process. The shredded alkali cellulose is left to dry for 24 hours to be in contact with the oxygen of the ambient air. During this process, the alkali cellulose is partially oxidized and degraded to a lower molecular weight due to high alkalinity. This degradation is controlled to produce chain lengths short enough to produce correct viscosities in the spinning solution. In the next stage of sulphurization, carbon di-sulphide is added to the bamboo alkali cellulose to sulphurize the compound, causing it to jell. The remaining carbon disulphide from the sulphurization is removed by evaporation due to decompression and cellulose sodium xanthogenate is the result. In the dissolving step, a diluted solution of sodium hydroxide is added to the cellulose sodium xanthogenate, dissolving it to create a viscose solution consisting of about 5% sodium hydroxide and 7% to 15% bamboo fibre cellulose. After subsequent ripening, filtering and degassing, the viscose bamboo cellulose is forced through spinneret nozzles into a large container of diluted sulphuric acid solution which hardens the viscose bamboo cellulose sodium xanthate and reconverts it into cellulose bamboo fibre threads which are spun into bamboo fibre yarns.

The Problem with the Viscose Rayon Process is that the solvent used for this process is carbon disulphide, a toxic chemical that is a known human reproductive hazard. It can endanger factory workers and pollute the environment via air emissions and wastewater. The recovery of this solvent in most viscose factories is around 50%, which means that the other half goes into the environment. Other potentially hazardous chemicals are also used in the viscose process, including sodium hydroxide and sulphuric acid [7].

2.5. Grafting

Graft copolymerization is a commonly used method for the modification of surfaces of polymers, and it is an important tool in order to modify the physical or chemical properties of polymers. During grafting, the side chains are covalently bonded to the main polymer backbone or substrate to form a copolymer with branched structure. Graft copolymers have many different and useful properties different from those which each have alone. Grafting methods can be classified mainly according to grafting medium and the type of initiation mechanisms. Grafting can be performed in a homogeneous or in a heterogeneous medium [15].

Considerable work has been done on techniques of graft co-polymerization of different monomers on polymeric backbones. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting. Chemical means the grafting can proceed along two major paths, viz. free radical and ionic. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical mechanism, grafting in the melt and atom transfer radical polymerization (ATRP) are also interesting techniques to carry out grafting [16].

2.6. Cellulose grafting

Cellulose is a naturally occurring polymer, and it is the most abundant and renewable polymer in the world. In addition, it is one of the most promising raw materials due to its abundance, easy availability, and low cost. It is a linear polysaccharide with long chains, which consists of β-D-glucopyranose units joined by β-1, 4 glycoside linkages. In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups [15].

The graft copolymerization of various monomers onto cellulose and cellulose derivatives have been carried out by different methods that can be generally classified into three major groups: Free radical polymerization, Ionic and ring opening polymerization and Living radical polymerization. There are number of techniques of grafting claimed through the research which includes chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting.

Chemical initiated grafting

Chemical initiated grafting can proceed through two major paths, viz. free radical and ionic. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical mechanism, grafting in the melt and atom transfer radical polymerization (ATRP) are also interesting techniques to carry out grafting.

Free-radical grafting

In the chemical process, free radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft co-polymers. An example of free radicals produced by an indirect method is the production through redox reaction, viz. Mn/H_2O_2, persulphates [16, 17]. Radical polymerization has received the greatest amount of attention among all of the polymerization methods. About 60% of all available polymers are still obtained by this method.

Mechanism of grafting using potassium persulphate as initiator

Initiation via the use of potassium persulfate involves the generation of the initiating species on the swollen cellulose substrate backbone. This is usually carried out by saturating the cellulose substrate with potassium persulfate (KPS).

$$\mathbf{S_2O_8^{(2-)} \longrightarrow 2SO_4^{-\cdot}}$$

There are different views regarding the activity of $SO_4^{-\cdot}$. Some authors reported that initially formed $SO_4^{-\cdot}$ reacts with water to form $OH^{\cdot}$, subsequently producing free radicals on the polymeric backbone:

$$\mathbf{SO_4^{-\cdot} + H_2O \longrightarrow HSO_4^{-} + OH^{\cdot}}$$

An alternate view is that $SO^{-}_{4}\cdot$ reacts directly with the polymeric backbone (e.g. cellulose) to produce the requisite radicals

$$\mathbf{SO_4^{-\cdot} + R_{polymer}\text{-}OH \longrightarrow HSO_4 + R_{polymer}\text{- }O.}$$

Ghosh and Das [18] modified cotton cellulose by grafting acrylic acid in the presence of potassium persulfate as free radical initiator. Suo *et al.* [19] applied this initiation technique for the graft copolymerization of acrylic acid and acrylamide monomers onto carboxy methyl cellulose, to make cellulose-based super absorbent polymers. Similarly, Aliouche *et al.* [20] synthesized cellulose substrates with improved absorption and retention via the graft copolymerization of acrylic acid and acrylonitrile using KPS as the initiator. The graft copolymerization of itaconic acid onto cellulose fibres using potassium persulfate has also been reported [21, 22].

Ionic Grafting

The grafting of cellulosic polymers using ionic grafting technique require the stringent reaction conditions (low temperature, highly pure reagents, inert atmosphere, anhydrous condition, etc.); hence reports regarding this method are relatively few in numbers compared to other techniques [23].

Radiation Induced Grafting of Cellulose

The cellulose grafting initiated using radiation like ultraviolet light especially high-energy radiation (gamma-rays from radioactive isotopes or electron beams) has received considerable attention over several decades. The irradiation of cellulose results in formation of radicals that can initiate grafting in the presence of vinyl and acrylic monomers [24, 25].

Enzymatic Grafting

The enzymatic grafting method is quite new. The principle involved is that an enzyme initiates the chemical/electrochemical grafting reaction. For example, tyrosinase is capable of converting phenol into reactive o-quinone, which undergoes subsequent non-enzymatic reaction with chitosan. Enzymatic grafting on a poly(dicarbazole-N-hydroxy succinimide) film was reported by Cosnier *et al.*, thionine and toluidine blue have been irreversibly bound to the poly(dicarbazole) backbone and the grafting of polyphenol oxidase (PPO) on polydicarbazole has been reported [25, 26].

Living Polymerization

The recent advent of controlled/living radical polymerization techniques (CRP) such as nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT) which are tolerant to moisture and compatible with a large range of functional groups has opened new prospects in this research area allowing to precisely tailor the properties of the polysaccharide-based hybrids by tuning the synthetic graft length, the chemical composition and the topology [28].

Grafting using Ionic Liquids (ILs)

Ionic liquids or ‘‘molten salts’’ are in general defined as liquid electrolytes composed entirely of ions. One of the most important features of ILs is their non-measurable vapor pressure. They are defined as ‘‘green’’ solvents mainly because of the absence of volatile organic compounds (VOC) emission. Also in terms of inhalation and vapour of the solvent, the risk is limited in comparison to other volatile organic solvents in spite of IL toxicity. Furthermore, ILs has other attractive properties, such as high chemical and thermal stability, non-flammability, as well as high ionic conductivity [29, 30].

2.7. Grafting of Bamboo Fibres

Even though grafting of cellulose has been investigated the larger extent, the research on the bamboo fibre grafting is explored in a limited extent.

Wang *et al.* [31] studied the grafting of bamboo fibre using methacryloyloxyethyl tri-methyl ammonium chloride (DMC) as monomer and ammonium ceric nitrate (CAN) as initiator and optimized the variables for getting the maximal pigment dyeing. Xu *et al.* [32] prepared super absorbent resin based on the graft copolymerization of bamboo pulp cellulose and monomer acrylamide. Khullar *et al*. [33] grafted acrylonitrile onto the cellulose isolated from bamboo (*Dendrocalamus strictus*) in heterogeneous medium using ceric ammonium nitrate and studied the effect of process parameters on extent of grafting and grafting efficiency. They found that graft copolymerization of acrylonitrile onto cellulosic material derived from bamboo (*Dendrocalamus strictus*) can be initiated effectively using ceric ammonium nitrate as an initiator.

Liu et al. [34] prepared the graft co-polymerizations of methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) onto bamboo fibre using Ce^{4+} as initiator. They found the remarkable decrease in tensile strength and initial modulus, increase in breaking elongation and flexibility, increase in acid and base resistance and increase in thermal stability of the grafted fibre. However, the moisture regain of the fibre decreased.

Lin *et al*. [35] studied the grafting of acrylonitrile onto bamboo (Melocanna baccifera) in the presence of ceric ammonium nitrate. The confirmation of formation of graft copolymer was detected by the nitrile group absorption at 2260 cm^{-1} in the IR spectrum. The grafting reaction was found to be depended strongly on the concentration of acrylonitrile. Grafting percentages evaluated by IR spectroscopy were found to be less reliable than those by the gravimetric method. The grafting retarded on bamboo since the graft chains were shortened greatly in the presence of lignin.

2.8. Diaper & its uses

A disposable, absorbent type-style diaper for bariatric incontinent users includes a non-woven top sheet, an absorbent core containing fluff and super absorbent polymer, a fluid-impervious back sheet (micro porous) that covers at minimal the absorbent core at its widest point, a non-woven back sheet layer that is glued to the fluid-impervious back sheet and the overlaying non-woven top sheet. The diaper will also contain standing leg-cuffs and elastomeric side panels (air-permeable) [36].

The super-absorbent (SAP) was first introduced into the diaper in 1982 by Unicharm in Japan, following its use in sanitary napkins. It is rather amazing that it took so long for this material to be finally used in a diaper when it had been discovered so many years before. It was in 1966 when Billy Gene Harper, who worked for Dow Chemical, and Carlyle Harmon, who worked for J&J, filed their patent for the superabsorbent polymer. Even when Victor Mills is recognized as the father of the diaper, Harper and Harmon really should deserve similar recognition [36, 37].

2.9. Structure of a baby diaper

The typical design elements and raw materials of today's typical superabsorbent disposable diaper are shown in the following figure [37, 38]

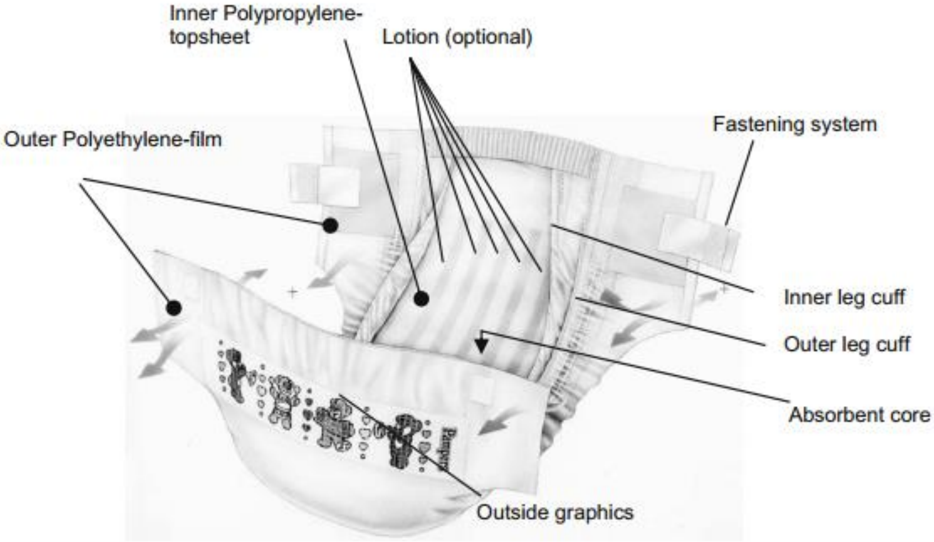


Figure: The structure of baby diaper [37]

The modern superabsorbent disposable baby diaper consists of three basic functional product zones, as described below.

Direct skin contact materials

- The top sheet is the layer in direct contact with the baby's skin. It consists of a soft nonwoven synthetic sheet, composed of polypropylene/polyethylene, either alone or as a blend, which allows liquids to pass through while remaining relatively dry and soft. The main function of this layer is to transfer urine and other liquids quickly to the layers beneath. In addition, the top sheet may carry a lotion to protect the skin from over hydration and irritation.

Indirect skin contact materials

- The acquisition/distribution layer is usually composed of a modified cellulose patch and a polyester-based layer sandwiched between the top sheet and the core, which is not in direct contact with the skin. Its main function is to facilitate the movement of liquid away from the baby and to distribute it more evenly across the entire diaper core for efficient and maximal absorbency.
- The absorbent core is the inner-most layer of the diaper. It typically consists of a blend of polyacrylate granules blended with fluff cellulose pulp (bleached by an elemental chlorine-free process) and encapsulated by either a cellulose or polypropylene nonwoven layer. The cellulose portion of the core functions to quickly absorb and transfer urine to the polyacrylate superabsorber. The superabsorber is able to absorb urine and to lock it within its polymeric structure to keep it away from baby’s skin, even under pressure as when a baby sits on a full diaper. [37, 38]

Back sheet and fastening system

- The back sheet is the water-resistant outer layer of the diaper, typically made of a polyethylene film laminated with a soft textured, cloth-like polypropylene. Its function is to prevent liquid from leaking out of the diaper into the outer clothing.
- Additional elements include features primarily designed to ensure a good fit to the diaper. Such design elements may include stretch side panels, fastening systems and tapes to improve fit, and leg cuffs to prevent leakage.

In some products, aesthetics such as colorants or scents may be added. The functional elements may vary depending on the style of diaper, the manufacturer, and consumer preference [36-39].

2.10. Construction of the absorbent core

Many aspects must be considered in the design of the polymer matrix in the diaper core. The absorption rate of the diaper must not be slower than the urination rate of the baby, otherwise leakage will occur. On the other hand, fast swelling of the polymer may or may not be desirable. In some diaper designs, fast swelling may cause the diaper to leak if the porosity and permeability of the composite is reduced. The absorption rate of superabsorbent polymers is affected by the maximum absorption capacity of the polymer and its particle size and shape. In addition, particle size, placement, and relative amounts play a large role in the optimization of absorption. When the superabsorbent swelling is delayed in the wetting region of some diaper designs, there is more time to distribute urine through the diaper. By distributing the liquid better throughout the diaper, there is less saturation of the core in the wetting region, so further wetness may be absorbed [36, 38].

Superabsorbent polymer is added to baby diapers in basically two ways: layered or blended. Japanese diaper manufacturers commonly adopt the layered application. In this method, powdered superabsorbent polymer first is scattered onto a layer of fluff pulp. The fluff is then folded, so that the polymer is located in a centralized layer in the absorbent structure. This structure is covered with a non-woven fabric layer. In the blended application, the superabsorbent polymer first is mixed homogeneously with the fluff pulp. Then the mixture is laid down to give the absorbent structure, which is subsequently covered with a non-woven fabric. The blended application of the SAP is representative of American diaper manufacturers.

The Polyacrylic acid contains an ionizable group on each repeat unit (-COOH). These polymer chains are then crosslinked at the –OH. [39] The mechanism of swelling of ionized, crosslinked polymer networks is based upon the concept of osmotic pressure. According to Flory, the polymer acts as a semipermeable membrane which does not allow charge substituents to exit the polymer into the surrounding solution. This is because the ionized monomeric units contain fixed charges which attract and fix ions from the outer solution. Therefore, a charge gradient is set up, in which the concentration of free ions is greater outside of the polymer. Therefore, the osmotic pressure exerted by the gradient causes the polymer chain to swell as further ions diffuse in [39, 40].

2.11. Principle of absorption

Superabsorbent polymers are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated ionic functional groups. Except for the molecular-sized chains that make up the network, this picture of a network is remarkably similar looking to the mass of cotton fibres. The difference is that cotton takes up water by convection – water is "sucked" up, wetting the dry fibres; SAPs work by diffusion on the molecular level, since their "fibres" are actually long chained molecules. [40]

Water diffuses into a particle of superabsorbent polymer when the concentration of water is initially lower in the interior of the particle. As water travels into the particle, it swells to accommodate the additional molecules. Because the polymer molecules are crosslinked, they do not dissolve in the absorbing liquid. Absorbency under load and stability of the gel against shear are important properties of superabsorbent polymers and relate strongly to diaper performance. Diaper leakage was closely correlated to the stability of gel to shearing. More rigid superabsorbent particles, created by increasing the crosslinking, allow for a higher gel modulus and help the particle withstand the shearing from the baby's weight. [40-43]

2.12. Theoretical swelling of hydrogel

During the past decades, modelling of polymeric networks swelling has been conducted on different scales, based on global macroscopic to microscopic theories. For instance, the global swelling ratio of polyelectrolyte gels is well explained through statistical theory. Based on this macroscopic theory, the equilibrium state is achieved by a minimum of the Gibbs free energy, ΔF. This theory is applied for chemical and also thermal stimulations [40, 41].

2.13. Kinetics of hydrogel swelling

Swelling is a continuous process of transition from un-solvated glassy or partially rubbery state to a relaxed rubbery region. It is well known that sorption processes for polymer-solvent systems frequently do not conform to the behavior expected from the classical theory of diffusion. Although penetrant sorption by rubbery polymers may be described by Fickian transport with a concentration dependent diffusion coefficient, this description usually is not successful for glassy polymers. The slow reorientation of polymer molecules can lead to a wide variety of anomalous effects for both permeation and sorption experiments, particularly when such experiments are conducted near or below the glass transition temperature (Tg). Based on the Bajpai classification, two basic categories may arise: first, is the Fickian or Case I transport, which appears when the Tg of polymer is well below the medium temperature. In this case, the polymer chains have a high mobility and the water penetrates easily in the rubbery network [41, 42].

The non-Fickian diffusion, which appears when the Tg of polymer is well above the experimental temperature. In this situation, the polymer chains are not adequately mobile to permit urgent penetration of water into the polymer core. Depending on the relative rates of chain relaxation and diffusion, they commonly classified the non Fickian diffusion to two subsections: "Case II transport" and "anomalous transport" [43, 44].

Sigmoidal experimental swelling curves are often taken to indicate non-Fickian behavior. Deviations from the fixed boundary Fickian behavior are usually attributed to some of the following phenomena: (i) variable surface concentration, (ii) a history dependent diffusion coefficient, (iii) stresses between parts of the gel swollen to different extents and (iv) polymer relaxation [45, 46].

A simple and useful empirical equation, so-called power law equation, is commonly used to determine the mechanism of diffusion in polymeric networks:

$$\frac{M_t}{M_\infty} = kt^n$$

The constants, k and n, are characteristics of the solvent-polymer system. The diffusional exponent, n, is dependent on the geometry of the device as well as the physical mechanism of solute uptake or drug release. Peppas *et al.* [48] were the first to give an introduction to the use and the limitations of these equations. By determining the diffusional exponent, n, one can gain information about the physical mechanism controlling solute uptake by or drug release from a particular device. For a film, $n = 0.5$ indicates Fickian diffusion, $n > 0.5$ indicates anomalous transport and $n = 1$ implies case II (relaxation-controlled) transport [47, 49].

For Fickian diffusion, the n values close to 0.5 or over 0.5 have been reported in the most published articles, while fewer articles have reported the case of $n < 0.5$. The Fickian diffusion, actually, refers to a situation where water penetration rate in the gels is less than the polymer chain relaxation rate. Nevertheless, when the water penetration rate is much below the polymer chain relaxation rate, it is possible to record the n values below 0.5 this situation is called less Fickian behavior [50, 51].

2.14. Existing diaper problem

Babies wear diapers almost the whole of twenty four hours a day. Diapers are really one of the basic requirements for babies. Using disposable diapers has many advantages but at the same time affects the baby’s health also. Disposable diaper has many chemicals in it which affects the health of the baby. Some disposable diapers are bleached with chlorine, resulting in traces of dioxins. According to the World Health Organization dioxins are persistent environmental pollutants. This can cause major health problem such as development delays, damaged immunity, hormone interference when they grow up and certain cancers [52]. The usually unmentioned truth to this disposable diaper health risk is that dioxin is present in a great deal of sanitary items such as tampons and upwards of 95% of human exposure is through food not diapers, tampons or other items containing trace amounts. [38, 53]

Disposable diapers contain sodium polyacrylate, is a type of super absorbent polymer used to make disposable diapers hold more liquid without leaking. Sodium polyacrylate was previous removed from tampons due to causing a bacterial illness called toxic shock syndrome. However toxic shock syndrome was caused by Sodium polyacrylate being placed within the body for extended time periods. This is because toxic shock could be prevented even in tampon use with regular replacement [52, 53].

Disposable diapers cause an increased occurrence of diaper rash in infants. Rates of diaper rash were found as follows with the different types of diapers cloth with plastic outer cover 60%, cellulose disposables 39%, and absorbent gel disposables 29%, absorbent gel disposables with breathable covers 13% [37].

Antimicrobial materials and bactericides in general are chemical compositions that are used to prevent microbiological contamination and deterioration of products, materials, and systems. Such antimicrobial materials and bactericides can also effectively Work for the removal or reduction of foul odours developed from disposable absorbent articles which has already absorbed body fluids [38, 53]. Based on the foregoing, there is a need for disposable absorbent articles, which have an effective odour and antimicrobial reduction function.

CHAPTER 3

MATERIALS & METHODS

3.1. Materials

Raw bamboo fabric is purchased from market. Acrylic Acid ($C_3H_4O_2$, M.W. 72.06), Potassium Persulphate ($K_2S_2O_8$, M.W. 270.31) were purchased from Central Drug House (P) LTD. N,N'-Methylene Bisacrylamide 3x cryst ($C_7H_{10}N_2O_2$, M. W. 154.17), Sodium Hydroxide (NaOH, M.W. 40) were purchased from Sisco Research laboratories Pvt. Ltd. Silver Nitrate ($AgNO_3$, M.W. 169.87) was procured from Merck Specialities Pvt. Ltd. All the experiments are carried out in distilled water.

3.2. Methods

3.2.1. Grafting of bamboo fabric with acrylic acid

Initially the bamboo rayon fabric was washed with non-ionic detergent to remove the finishing agent applied to the fabric. Aqueous solution of potassium persulphate (KPS, initiator (w/v)) was prepared; the fabric of known weight was immersed onto it and heated to a temperature of 90° C for 15 minutes to dissociate the initiator. The sample was thoroughly washed with distilled water several times and squeezed between two filter papers to remove excess solution. In a typical reaction, the above KPS treated fabric was placed on a round bottom flask containing acrylic acid (w/v). The flask containing KPS treated fabric was heated with a water bath arrangement, to a temperature of 60° C. After 30 minutes, required amount of N, N'-Methylene Bisacrylamide (crosslinking agent, w/v) was added and the reaction was continued for another 30 minutes. After completion of reaction, the grafted fabric was then washed with hot water several times, to remove the homopolymer and dried.

The grafting (%) was calculated using the formula;

Grafting (%) = $\frac{W_2 - W_1}{W_1} \times 100$

Where w_1 and w_2 are the weight of ungrafted and grafted fabric respectively.

Further the bamboo grafted with acrylic acid was immersed in aqueous solution of NaOH (0.1N) for 24 hours. The –COOH group present in the grafted fabric converted to –COONa. The AA grafted bamboo rayon converted to NaAA grafted bamboo rayon fabric.

3.2.2. Preparation of antimicrobial absorbent layer

The above NaAA grafted bamboo rayon fabric was placed in $AgNO_3$ (0.1N) solution. The possible ion exchange reaction takes place between ions Na^+ present in the grafted bamboo fabric and Ag^+ ions present in the solution. After 24 hours the sample was collected and dried.

3.2.3. Determination of mass swelling (S_m, %)

The swelling behavior of grafted bamboo fabric was studied in water and synthetic urine. The composition of synthetic urine was Urea-9.3 gpl, Chloride-1.87 gpl, Sodium 1.17 gpl, Potassium 0.75 gpl, Creatine 0.67 gpl. Dried samples were weighed and immersed in the distilled water/synthetic urine to swell. The samples were taken out of the water/synthetic urine, the liquid was precisely removed from their surfaces and the samples were weighed at different time. The swelling ratio was calculated using the following equation:

$$SR = \frac{W_t - W_0}{W_0} \times 100$$

Where, SR, W_t and W_0 are the swelling ratio, weight of swelling grafted bamboo fabric at time t and dried grafted bamboo fabric. When there is no change in weight of the grafted bamboo rayon fabric, it is in chemical equilibrium with its surrounding solution. The Equilibrium Swelling Ratio (ESR) was calculated using following equation:

$$ESR = \frac{W_{max} - W_0}{W_0} \times 100$$

Where W_{max} is the maximum AA grafted bamboo rayon weight that occurs at equilibrium state.

3.2.4. Measurement of hydrophilic group

To measure the amount of hydrophilic group (–COOH groups), the optimised AA grafted bamboo rayon fabric was immersed in an excess of NaOH solution (0.1N) for 24 hours.The bamboo grafted fabric swell in the NaOH solution and –COOH groups converted to –COONa groups completely.

$$R—COOH + NaOH = R—COONa + H_2O$$

The residual NaOH was titrated by using HCl(0.05N) solution. The amount of —COOH in the sample was calculated according to the following equation:

$$—COOH\ (mol\ \%) = (C_{NaOH} \times V_{NaOH} - C_{HCl} \times V_{HCl}) \times 71 / W_{sample} \times 100\ \%$$

3.3.5. Characterization of NaAA grafted bamboo rayon fabric

3.3.5.1. Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. Parent bamboo fabric and acrylic acid grafted bamboo fabric were analysed by FTIR using Transmittance Mode on Thermo Scientific Nicolet 380 Spectrophotometer (Nicolet) USA. FTIR spectra were obtained in the range of wave number from 1800 to 650 cm^{-1}.

3.3.5.2. Energy dispersive X-ray spectroscopy (EDXS)

The elemental composition of sodium hydroxide treated bamboo grafted fabric and silver modified fabric was analyzed with Energy dispersive X-ray analyzer attached with scanning electron microscope (S-3700N) at a voltage of 20kv.

3.3.5.3. Scanning electron microscopy (SEM)

Surface morphology of parent fabric and grafted fabric were observed by a scanning electron microscope (HITACHI, S-3700N SEM, Germany) at a voltage of 20 kV. Surface of specimen was coated with gold before analysis.

3.3.6. Antibacterial testing

The Antibacterial activity of grafted bamboo fabrics was evaluated using disc diffusion method by using Gram positive bacteria *Staphylococcus aureus* (ATCC 19636) and Gram negative bacteria *Escherichia coli (ATCC 43886)* . The bacteria were grown in Luria Agar (Hi media) medium. In this test, 7 mm diameter discs of the parent fabric, grafted fabric and silver modified fabric (sterilized by autoclaving for 30 min at 120^{o}C) were gently pressed on to the surface of the plate and incubated at 37 ° C for 24 hours. The antibacterial activity of films is demonstrated by the diameter of the zone of inhibition in comparison to the parent fabric and calculated using the following equation:

$$W = \frac{T - D}{2}$$

Where W is the width of clear zone of inhibition in mm, T is the width of test specimen and clear zone in mm and D is the width of test specimen in mm.

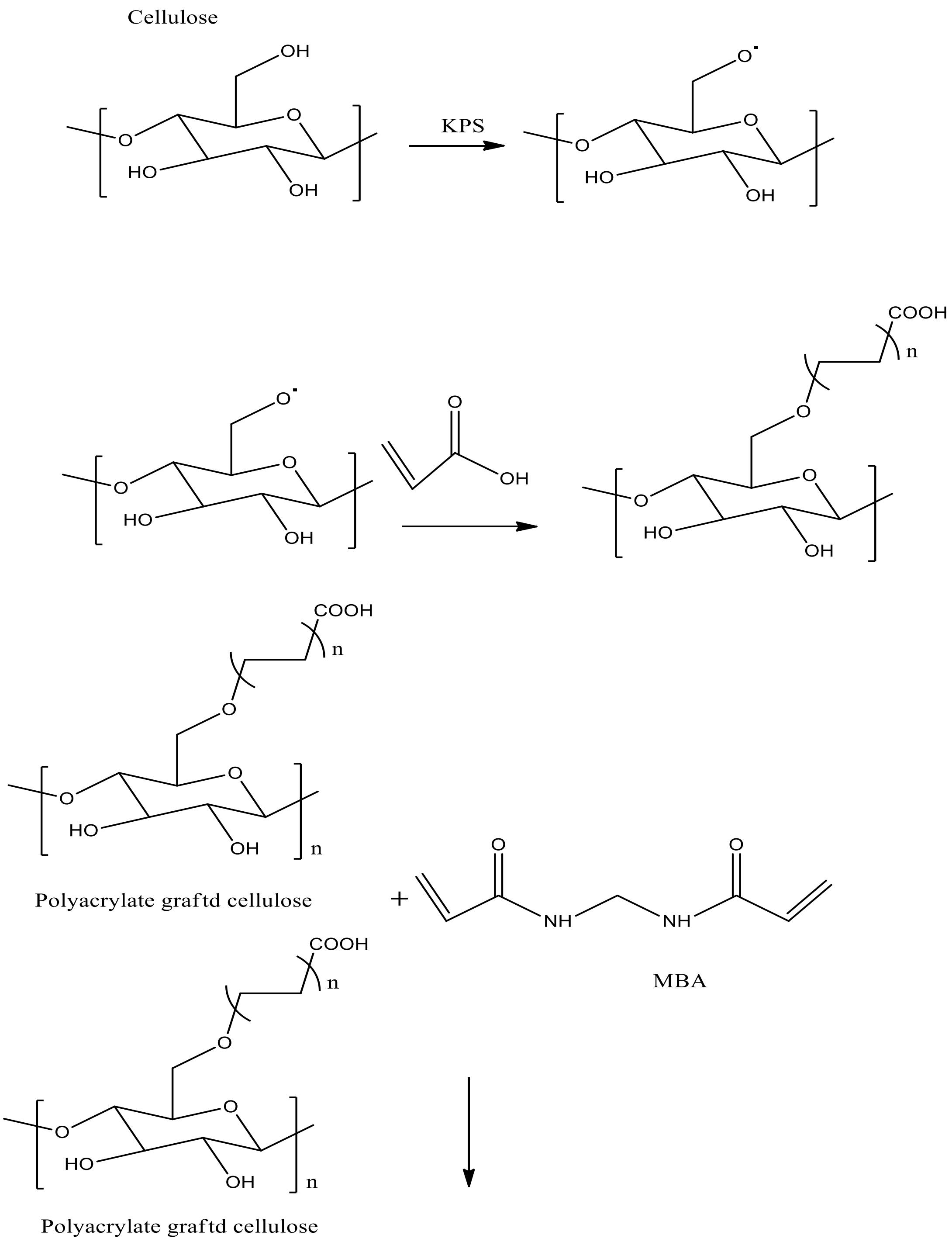
CHAPTER 4

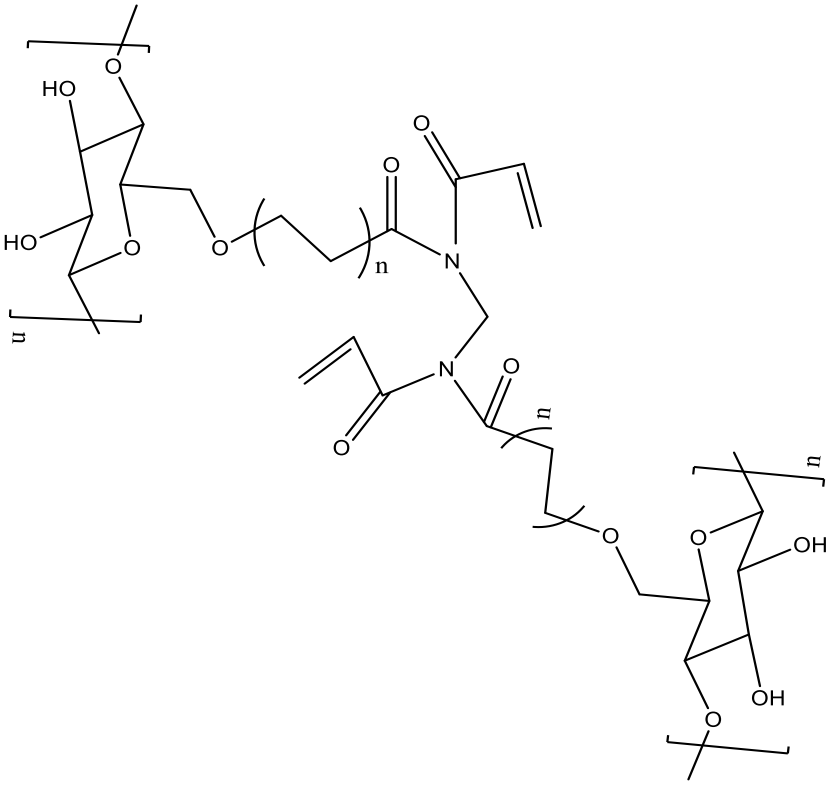
RESULTS AND DISCUSSION

Disposable baby diaper generally used beads or powder of superabsorbent polymer. This superabsorbent polymer (sodium polyacrylate) is either dispersed or blended with fluff cellulose pulp. The polymer may not be uniformly dispersed or blended throughout the cellulosic pulp. Urine and other exudates absorbed into the absorbent article are converted to ammonia by urease produced by skin-flora, i.e., a group of normal microorganisms on the skin. This ammonia, in turn, may cause dermatitis, rash and other forms of skin irritation. Such disease of the skin in infants can be a serious medical matter.

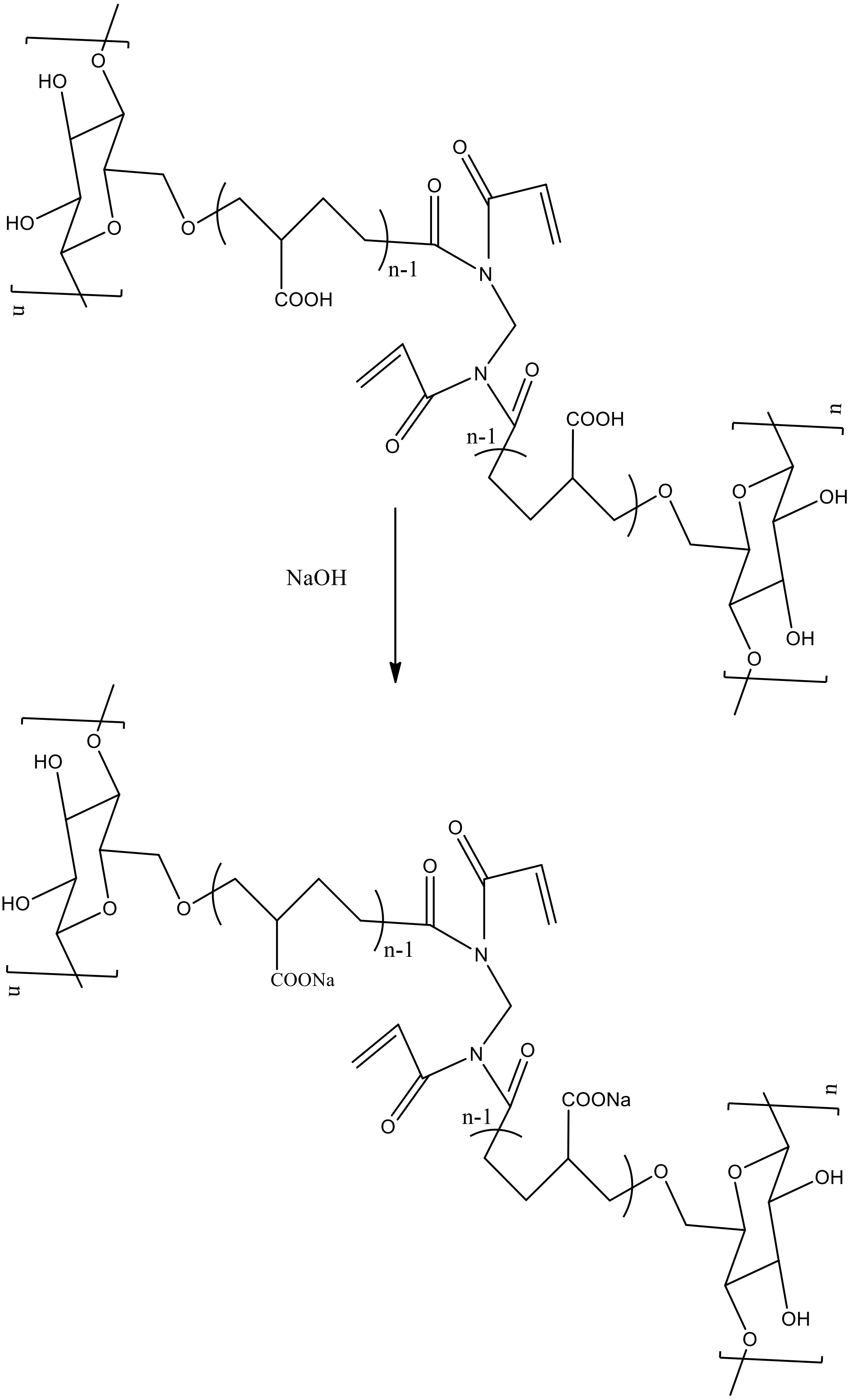
Also the sodium polyacrylate hold more liquid but this create a breeding ground for bacteria causing a bacterial illness called toxic shock syndrome. To overcome these difficulties an attempt has been made to construct antimicrobial absorbent layer for baby diaper. In this research, acrylic acid is grafted onto the bamboo rayon fabric to form a cross-linked hydrogel layer on the surface of fabric with the help of methylenebisacrylamide (MBA) as a crosslinker and potassium persulfate (KPS) as an initiator. Further the absorbent layer is modified by Silver (Ag) to inhibit the growth of bacteria.

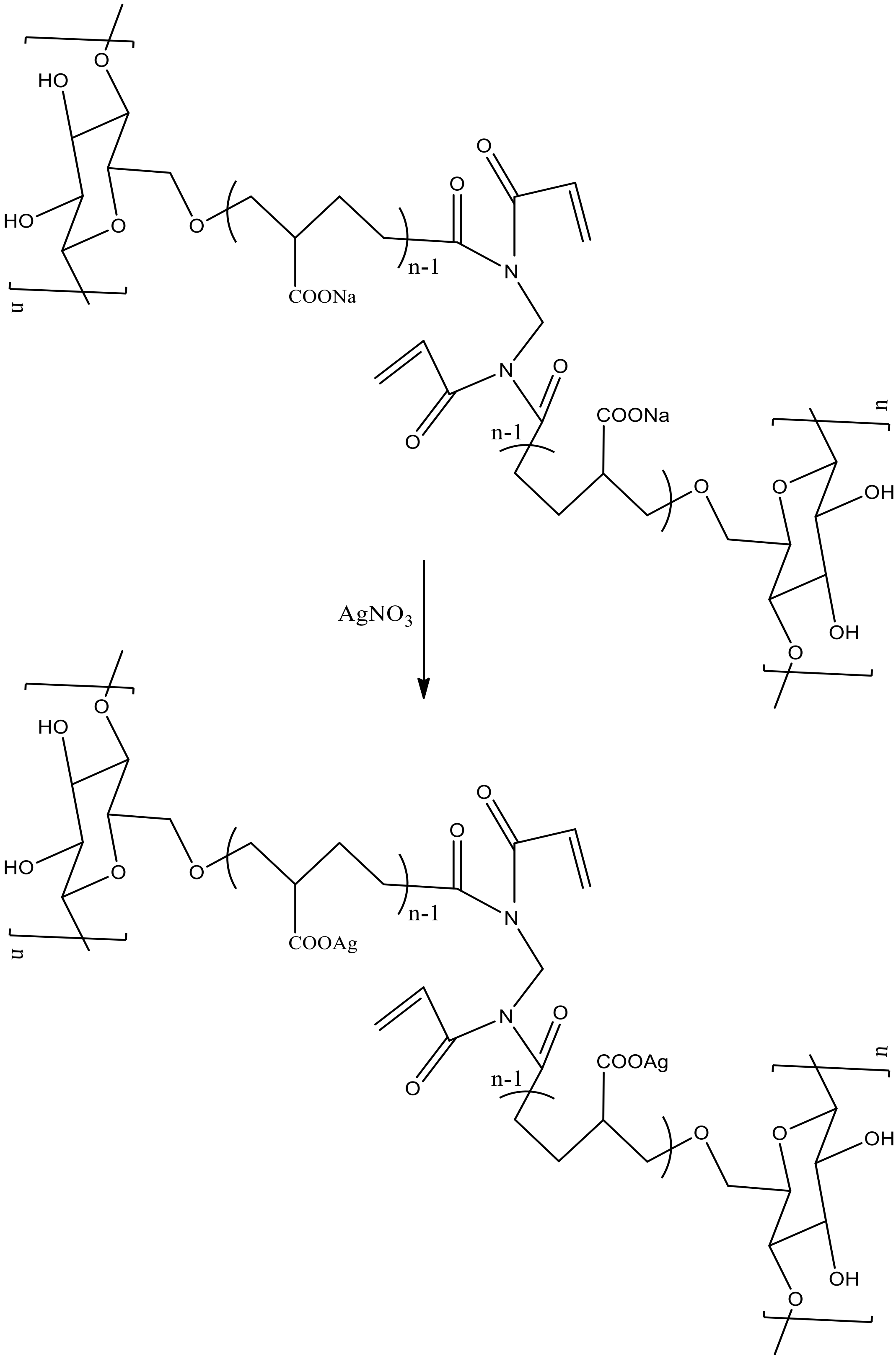
The effects of various parameters on grafting of acrylic acid onto the bamboo rayon fabric backbone are studied. The effects of different concentrations of initiator (0.5%, 1.00%, 2.00% and 3.00% (w/v)) and cross-linker (0.05%, 0.1% and 0.2% (w/v)) on the grafting (%) and swelling (%) are studied. The acrylic acid (AA) concentration and temperature are fixed as 10% (w/v) and 60 °C respectively. The mechanism of grafting of AA onto bamboo rayon fabric in the presence of MBA is shown in the following scheme:



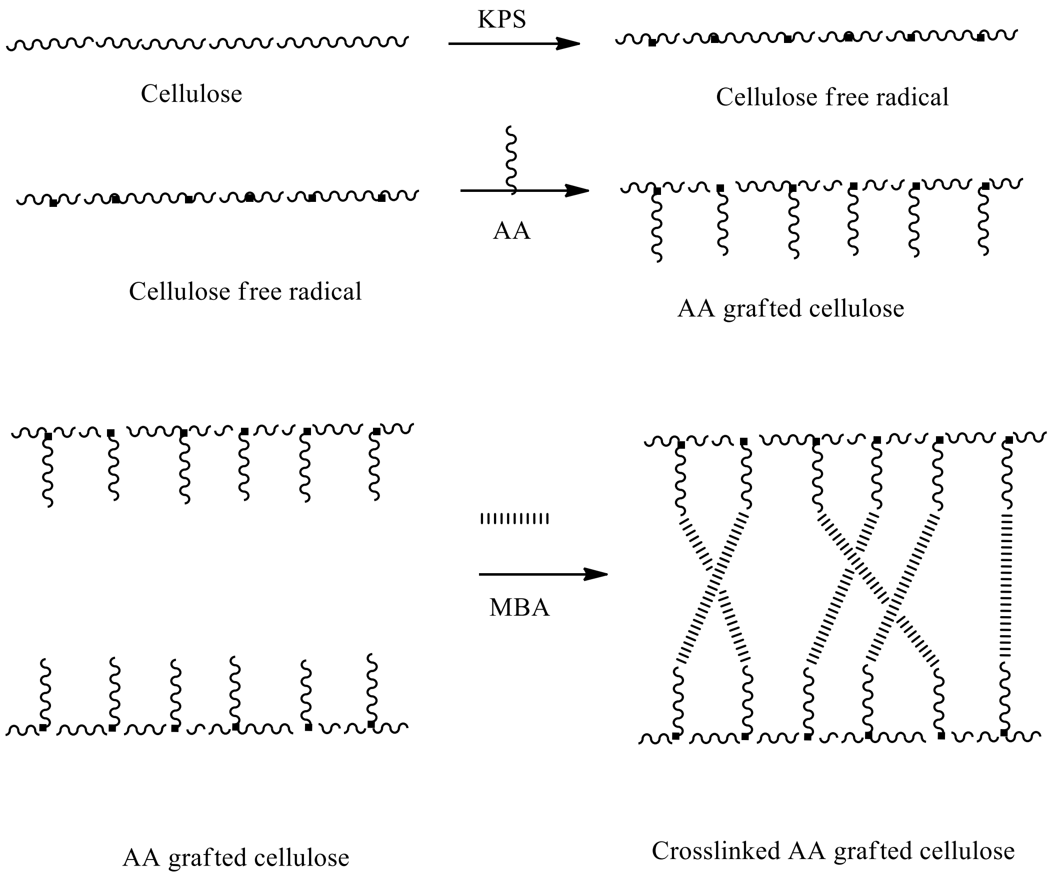


Crosslinked AA grafted bamboo rayon fabric


HO
HO
O
O
O
O
O
COOH
n-1
N
N
n
NaOH
COONa
OH
OH



(Scheme for reaction)



Diagrammatic representation of grafting reaction

The persulfate initiator is decomposed under heating to generate sulfate anion radical. The radical abstracts hydrogen from the hydroxyl group of cellulose (bamboo rayon fabric) substrate to form alkoxy radicals on the substrate. So, this persulfate–cellulose redox system is resulted in active centres on the substrate to radically initiate polymerization of AA led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a cross-linked structure. The AA grafted bamboo rayon fabric layer was further treated with NaOH to make it more absorbent. Further the NaAA grafted layer was modified with silver ion using ion exchange method to give it antibacterial effect. Finally the NaAA grafted bamboo rayon fabric characterized for its swelling (%), structural and antimicrobial analysis.

4.1. Study on grafting percentage

Results in Table 1 and Figure 1 indicate the variation of grafting (%) with respect to different concentration of initiator (KPS) and crosslinker (MBA). In these series of experiment the AA (10%, w/v) and temperature (60°C) remain constant. From the fig it has been observed that, for a particular MBA concentration, the grafting (%) increases with increase in KPS concentration. Which may be due to increase in the number of radicals generated which leads to more active site for the grafting reaction. With increase in KPS concentration from 2% (w/v) to 3% (w/v) for MBA concentration 0.1% (w/v) the grafting (%) slightly increases and for MBA concentration 0.2% (w/v) grafting (%) decreases. This may be due to homopolymer formation simultaneously causing reduction in concentration of available monomer for grafting. It is well known that high initiator concentrations lead to short chain polymers, therefore it can be expected that a higher concentration of KPS might result in decreasing grafting (%).

Table 1: Effect of initiator (KPS) and crosslinker (MBA) concentration on grafting (%)

Sl No.	KPS (%, w/v)	MBA (%, w/v)	Grafting (%)
1	0.5	0.05	54.84
2	0.5	0.1	69.70
3	0.5	0.2	109.37
4	1	0.05	243.75
5	1	0.1	618.18
6	1	0.2	620.00
7	2	0.05	650.00
8	2	0.1	915.38
9	2	0.2	960.71
10	3	0.05	900.00
11	3	0.1	937.50
12	3	0.2	945.45

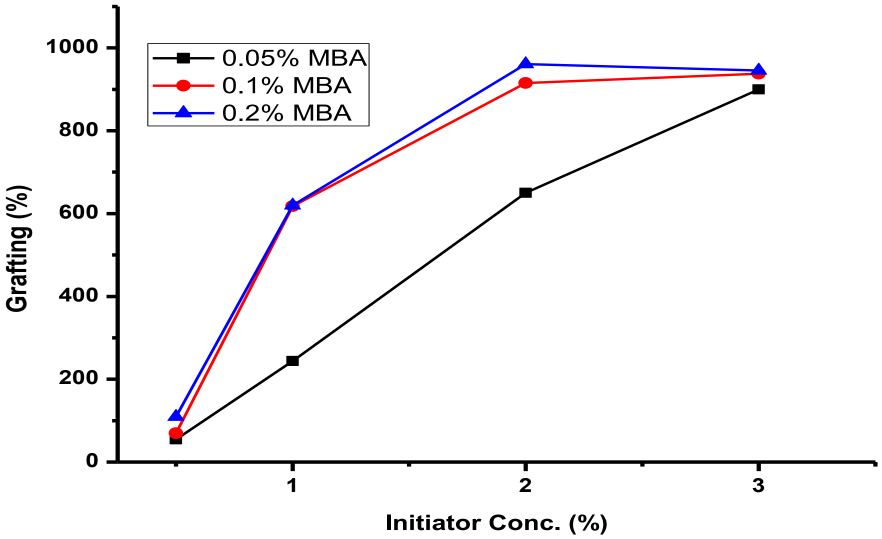


Figure 1: Effect of initiator (KPS) and crosslinker (MBA) concentration on grafting (%)

4.2 Optimisation based on swelling data analysis

The cross-linker concentration is the important variable which affects the swelling capacity of hydrogel. Crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. Efficiency of crosslinker incorporation controls the overall crosslink density in the final hydrogel. The swelling capacity of NaAA grafted bamboo rayon fabric in water and synthetic urine with various concentrations of KPS and MBA are studied.

4.2.1. Mass swelling in water

The mass swelling (S_m) behavior of NaAA grafted Bamboo rayon fabric in water is shown in the Table 2. The Figure 2, 3, 4 and 5 shows the swelling (%) in water for KPS concentration 0.5%, 1%, 2% and 3% (w/v) respectively for three different MBA concentrations 0.05%, 0.1% and 0.2% (w/v).

From the Table 2 it has observed that, the mass swelling (S_m, %) increases with respect to time with increase in KPS concentration. This may be due to the number of primary free radicals increases and the polymeric chains with relatively higher molecular weight are produced. With increase in MBA concentration, (w/v) for different KPS concentration (0.5% and 1% w/v) the mass swelling (%) increases (Figure 2 and 3). The possible reason for increasing the mass swelling (S_m, %) by increasing the crosslinker concentration is related to crosslink density. If the polymer network acts only as a barrier against diffusing water, less water molecules will diffuse to the highly crosslinked network. Thus, decreasing crosslink density should increase rate of water uptake. But a superabsorbent hydrogel is a strongly hydrophilic polymer, which attracts water molecules instead of repelling them. Higher crosslink density may cause stronger thermodynamic force that makes water to diffuse faster. As a result, it may be expected that a denser network offer a higher rate of water absorption.

But in case of 2% and 3% (w/v) KPS concentration (Figure 4 and 5), with increase in MBA concentration upto 0.1% (w/v) the mass swelling (S_m, %) increases after that decreases. Higher crosslinker concentration produce more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling when it is brought into contact with the solvent. Similar observations have been reported in the literature.

Table 2: Swelling (%) of NaAA grafted bamboo rayon fabric in water

Sl no.	**KPS (%)**	**MBA (%)**	**Time (minute)** **5**	**10**	**20**	**45**	**60**	**120**	**180**	**240**	**360**
1	0.5	0.05	4.34	8.70	8.70	17.39	17.39	21.74	21.74	21.74	21.74
2	0.5	0.1	5.55	11.11	13.89	16.67	19.44	22.22	22.22	25.00	25.00
3	0.5	0.2	8.00	12.00	16.00	24.00	28.00	28.00	32.00	36.00	36.00
4	1	0.05	7.41	14.81	22.22	25.93	33.33	40.74	55.56	66.67	70.37
5	1	0.1	12.07	18.97	20.69	25.86	29.31	34.48	53.45	68.97	77.59
6	1	0.2	11.76	17.65	23.53	29.41	32.35	41.18	64.71	67.65	76.47
7	2	0.05	13.11	18.03	22.95	31.15	40.98	57.38	63.93	68.85	73.77
8	2	0.1	19.09	23.64	29.09	35.45	41.82	48.18	68.18	72.73	82.73
9	2	0.2	13.00	19.00	26.00	29.00	32.00	34.00	45.00	59.00	63.00
10	3	0.05	13.95	23.26	34.88	39.53	41.86	52.33	62.79	69.77	75.58
11	3	0.1	16.28	36.05	43.02	48.84	52.33	60.47	69.77	75.58	89.53
12	3	0.2	16.36	20.91	25.45	29.09	35.45	44.55	53.64	59.09	66.36

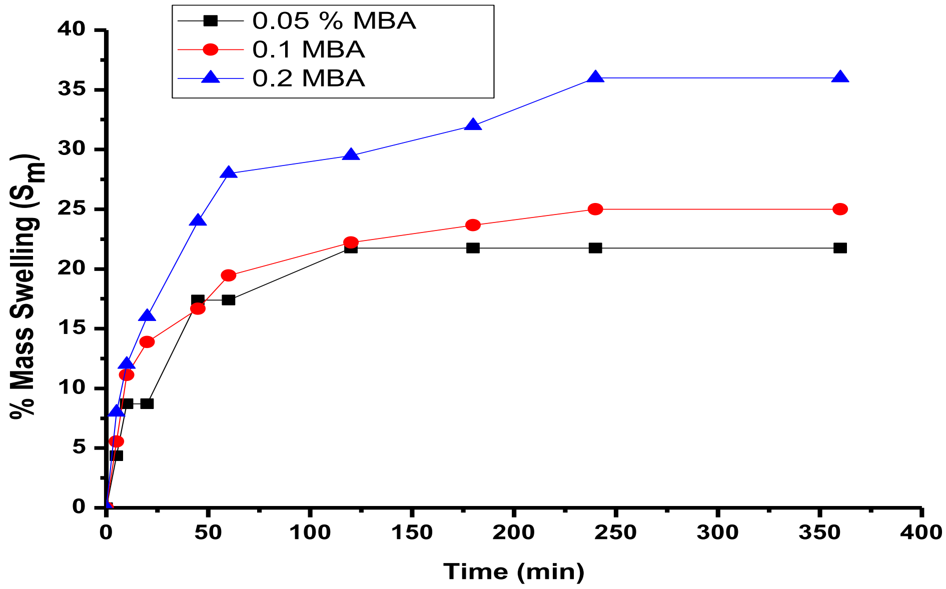


Figure 2: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 0.5% KPS and three different concentration of MBA.

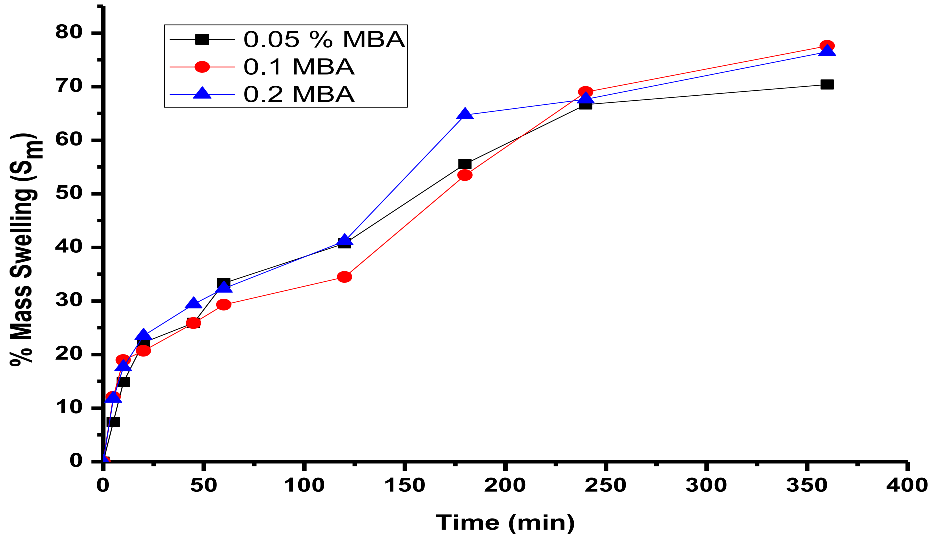


Figure 3: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 1.00% KPS and three different concentration of MBA.

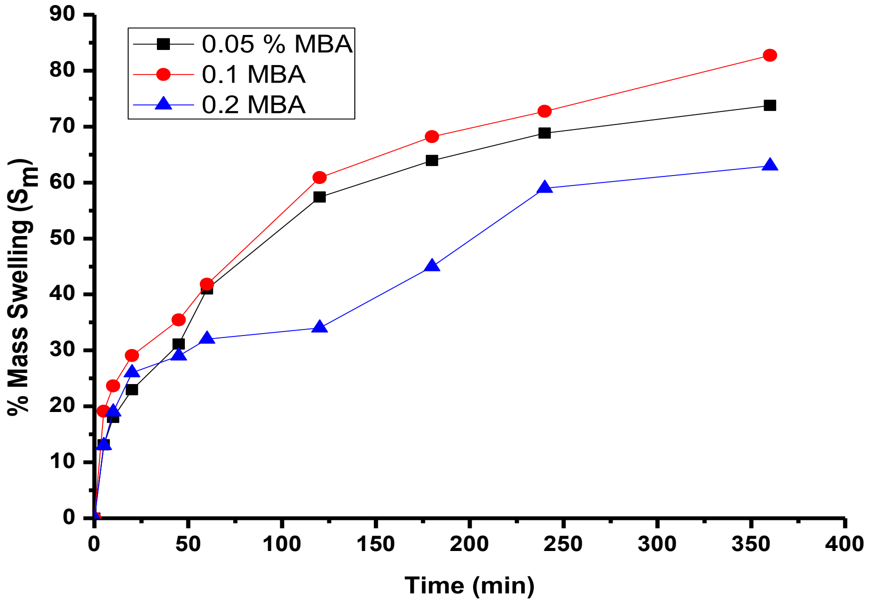


Figure 4: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 2.00% KPS and three different concentration of MBA.

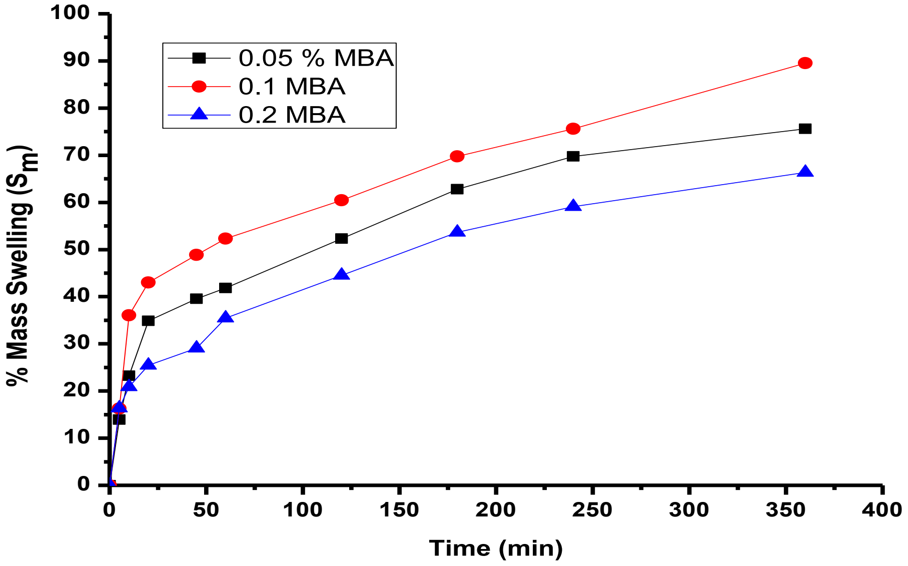


Figure 5: Mass of water absorbed by NaAA grafted bamboo rayon fabric as a function of time for 3.00% KPS and three different concentration of MBA.

4.2.2. Mass swelling in synthetic urine

The mass swelling (S_m, %) behavior of NaAA grafted Bamboo rayon fabric in synthetic urine is shown in the Table 3. The Figure 6, 7, 8 and 9 shows S_m in synthetic urine for KPS concentration 0.5%, 1%, 2% and 3% (w/v) respectively for three different MBA concentrations 0.05%, 0.1% and 0.2% (w/v). The major constituent of urine is urea and it also contains potassium, sodium, chloride and traces of creatine. Due to presence of amine group and potassium and sodium ion, the AA grafted bamboo rayon fabric absorbed more urine than distilled water.

Initially (Table 3, Figure 6), when the concentration of initiator is 0.5% (w/v) for three different concentration of MBA (0.05%, 0.1%, 0.2% (w/v)), the minimum mass swelling (S_m, %) of AA grafted bamboo rayon fabric may be due to the fact that the network does not form efficiently with a small number of free radicals. However, with the increase in KPS content, the number of primary free radicals increases and the polymeric chains with relatively higher molecular weight are produced. However, when the KPS concentration is increased beyond 2% (w/v), S_m again begins to decrease. This may be attributed to the fact that the concentration of free radicals becomes so high that the growing macromolecular chains are terminated at a faster rate. This results in the formation of low molecular weight grafted polymeric segments within the fabric network. So the resulting NaAA grafted bamboo rayon fabric demonstrates a decrease in the synthetic urine uptake.

For the initiator concentration 1%, 2% and 3% (w/v), with increase in MBA concentration upto 0.1% (w/v) the S_m increases after that decreases. Higher crosslinker concentration produce more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling when it is brought into contact with the synthetic urine.

Table 3: Swelling (%) of NaAA grafted bamboo rayon fabric in synthetic urine

			Time (minute)								
Sl no.	**KPS (%)**	**MBA (%)**	**5**	**10**	**20**	**45**	**60**	**120**	**180**	**240**	**360**
1	0.5	0.05	9.09	18.18	27.27	40.91	40.91	40.91	40.91	40.91	40.91
2	0.5	0.1	9.37	18.75	28.13	34.38	40.63	46.88	46.88	46.88	46.88
3	0.5	0.2	16.00	28.00	40.00	56.00	68.00	80.00	84.00	84.00	84.00
4	1	0.05	50.00	60.00	70.00	100.00	120.00	130.00	140.00	140.00	140.00
5	1	0.1	40.91	86.36	109.09	168.18	186.36	209.09	222.73	231.82	236.36
6	1	0.2	35.71	78.57	114.29	157.14	178.57	192.86	207.14	214.29	214.29
7	2	0.05	38.46	61.54	76.92	115.38	126.92	146.15	165.38	169.23	176.92
8	2	0.1	137.50	162.50	187.50	225.00	254.17	295.83	329.17	333.33	341.67
9	2	0.2	42.86	85.71	121.43	157.14	185.71	214.29	242.86	257.14	278.57
10	3	0.05	39.02	58.54	73.17	107.32	124.39	141.46	148.78	151.22	151.22
11	3	0.1	97.30	140.54	159.46	197.30	213.51	227.03	240.54	248.65	256.76
12	3	0.2	47.37	89.47	123.68	157.89	171.05	205.26	213.16	218.42	223.68

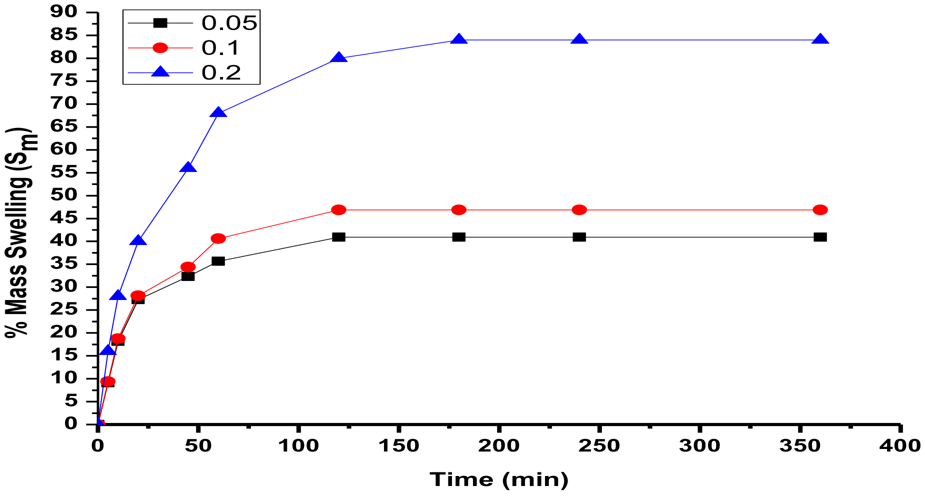


Figure 6: Mass of synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 0.05% KPS and three different concentration of MBA.

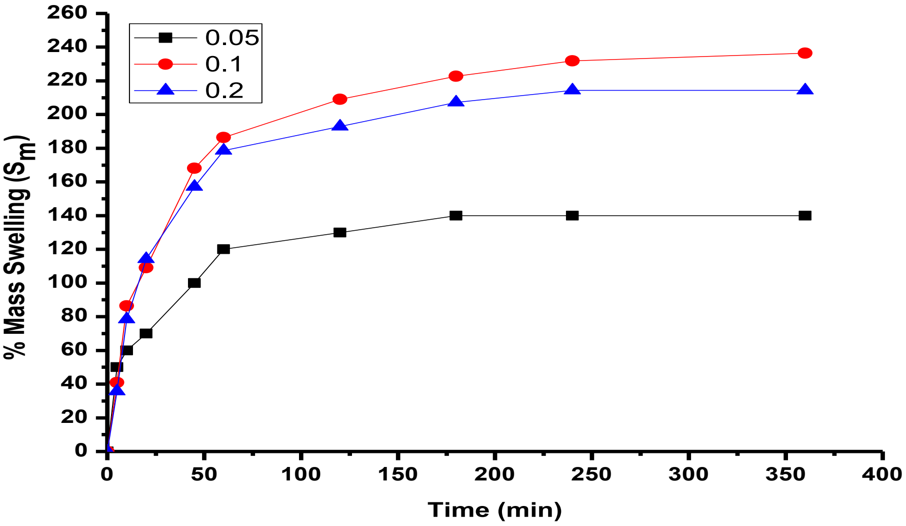


Figure 7: Mass of synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 1.00% KPS and three different concentration of MBA.

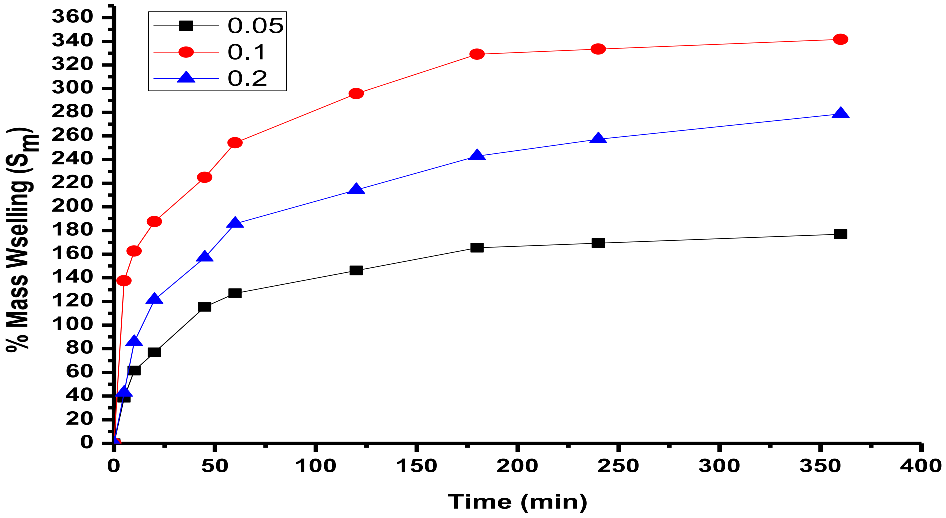


Figure 8: Mass of synthetic urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 2.00% KPS and three different concentration of MBA.

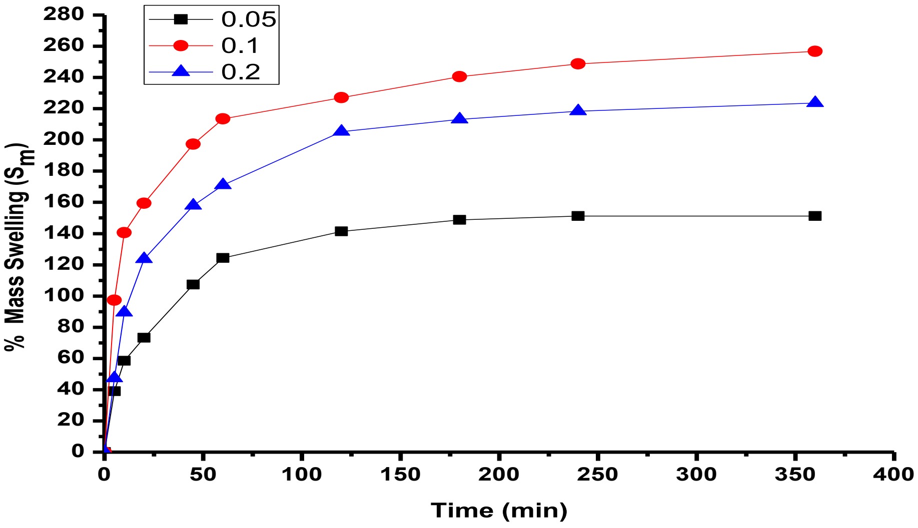


Figure 9: Mass of Synthetic Urine absorbed by NaAA grafted bamboo rayon fabric as a function of time for 3.00% KPS and three different concentration of MBA.

From the above swelling data analysis, it has been observed that for 2% (w/v) KPS and 0.1% (w/v) concentration the resulted NaAA grafted bamboo rayon fabric gives better mass swelling (S_m, %) in water and synthetic urine i.e. 94.55% and 341.67% respectively.

4.3. Study on swelling kinetics

The swelling kinetics of NaAA grafted bamboo rayon fabric in water and synthetic urine were studied. The power law equation is commonly used to determine the mechanism of diffusion in polymeric networks [43]:

$$\frac{M_t}{M_\infty} = kt^n$$

Where M_t (Swelling Ratio, SR) is the mass of water absorbed at time t, M_∞ (Equilibrium Swelling Ratio, ESR) is the water uptake at equilibrium, k and n are the kinetic/swelling constant, characteristic of polymer network and the diffusional exponent characterizing the mechanism of diffusion of the solvent into the network. The constant n and k is calculated from the slopes and intercepts of the plots of log (SR/ESR) versus log t (time) from the experimental data.

Peppas *et al.* were the first to give an introduction to the above equations [49]. For hydrogel, n= 0.45 indicates Fickian diffusion, $0.5 < n < 0.89$ indicates anomalous transport (non Fickian) and $n \geq 0.89$ implies CASE II (relaxation-controlled) transport. When the water penetration rate is below the polymer chain relaxation rate, it is possible to record the n values below 0.5. This situation is called Less Fickian behaviour.

The plots of log log (SR/ESR) versus log t for different samples in both water and synthetic urine are shown in the Figure 10 to 17. The Swelling constant (K) and diffusion exponent (n) value for the above mentioned samples are shown in the Table 4 to 11. For all the cases the diffusion co-efficient value ranges 0.21 to 0.49, which indicates the less Fickian behavior of the NaAA grafted bamboo rayon fabric.

Deviations from the fixed boundary Fickian behavior are usually attributed to some of the following phenomena: (i) variable surface concentration, (ii) a history dependent diffusion coefficient, (iii) stresses between parts of the gel swollen to different extents and (iv) polymer relaxation.

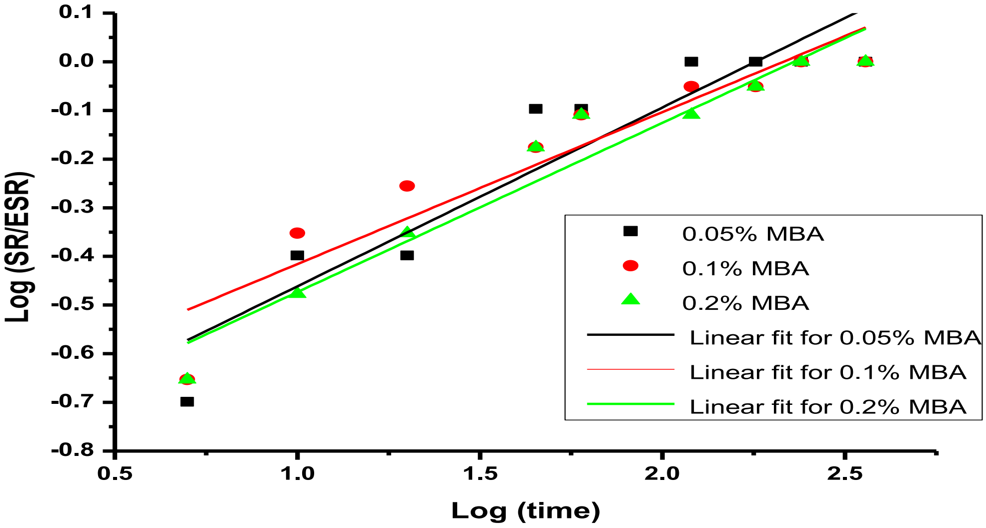


Figure 10: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 0.5% KPS and three different concentration of MBA.

Table 4: Swelling constant (K) and diffusion exponent (n) for sample of 0.5% KPS and three different concentration of MBA in water

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.82	-0.73	-0.82
Diffusional exponent (n)	0.37	0.31	0.35

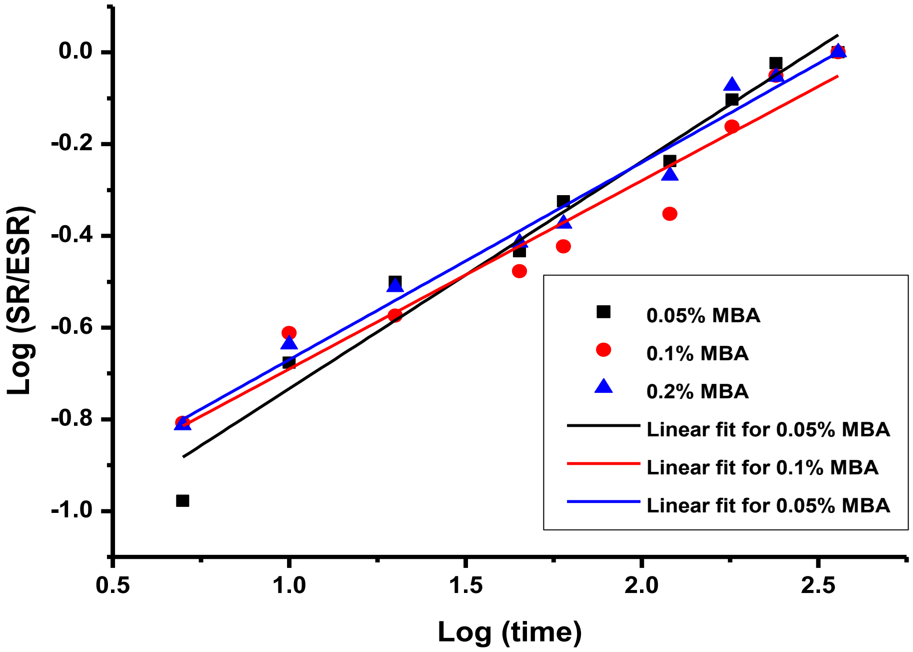


Figure 11: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 1.0% KPS and three different concentration of MBA.

Table 5: Swelling constant (K) and diffusion exponent (n) for sample of 1.0% KPS and three different concentration of MBA in water

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-1.23	-1.01	-1.10
Diffusional exponent (n)	0.49	0.41	0.43

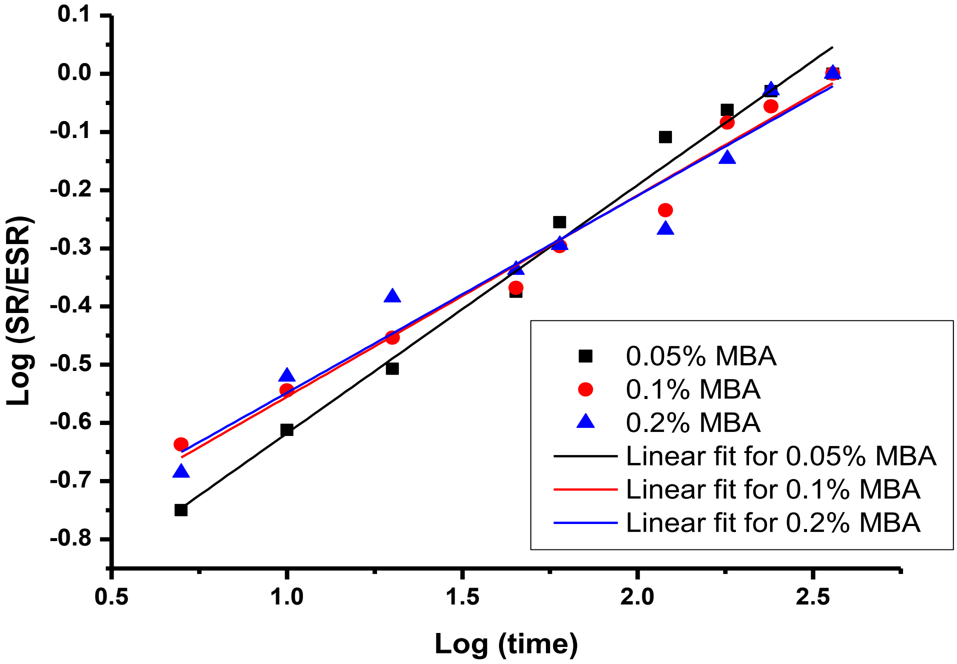


Figure 12: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 2.0% KPS and three different concentration of MBA.

Table 6: Swelling constant (K) and diffusion exponent (n) for sample of 2.0% KPS and three different concentration of MBA in water

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-1.04	-0.90	-0.89
Diffusional exponent (n)	0.43	0.35	0.34

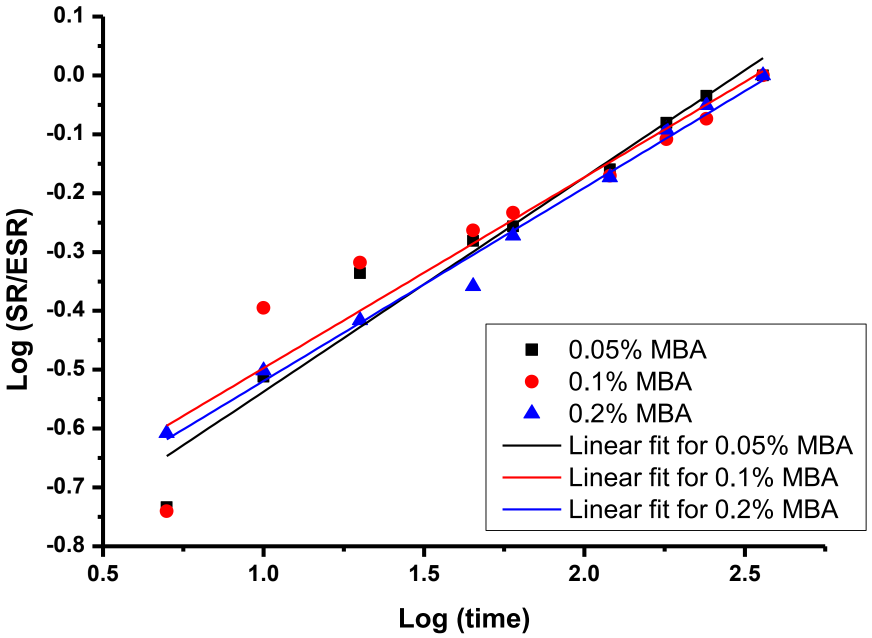


Figure 13: Swelling mechanism analysis of NaAA grafted bamboo rayon in water for 3.0% KPS and three different concentration of MBA.

Table 7: Swelling constant (K) and diffusion exponent (n) for sample of 3.0% KPS and three different concentration of MBA in water

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.90	-0.82	-0.85
Diffusional exponent (n)	0.36	0.32	0.33

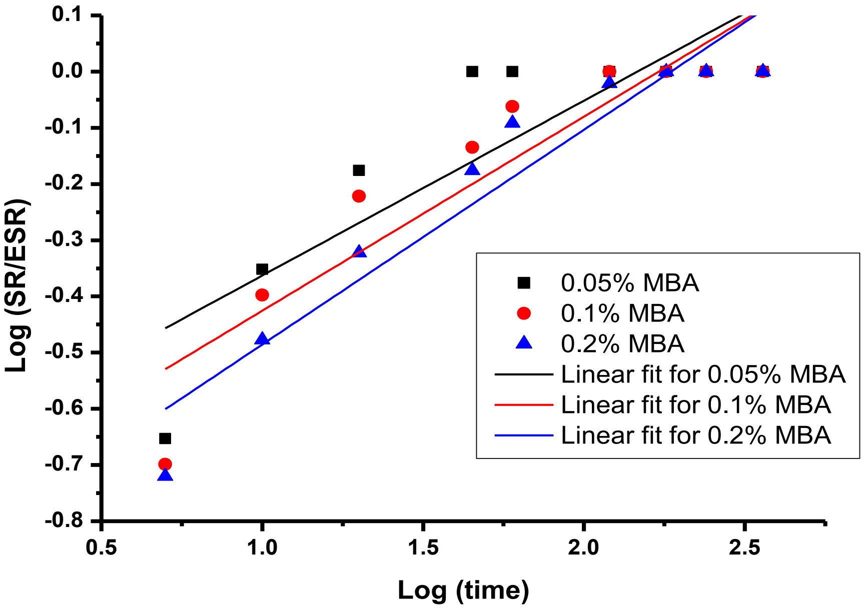


Figure 14: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 0.5% KPS and three different concentration of MBA.

Table 8: Swelling constant (K) and diffusion exponent (n) for sample of 0.5% KPS and three different concentration of MBA in synthetic urine

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.67	-0.77	-0.87
Diffusional exponent (n)	0.31	0.34	0.38

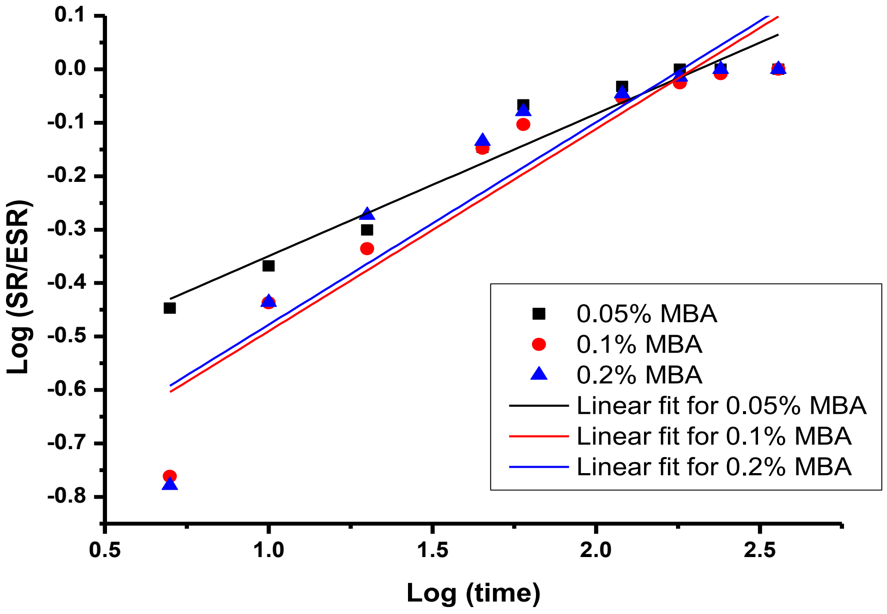


Figure 15: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 1.0% KPS and three different concentration of MBA.

Table 9: Swelling constant (K) and diffusion exponent (n) for sample of 1.0% KPS and three different concentration of MBA in synthetic urine

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.62	-0.87	-0.86
Diffusional exponent (n)	0.27	0.38	0.38

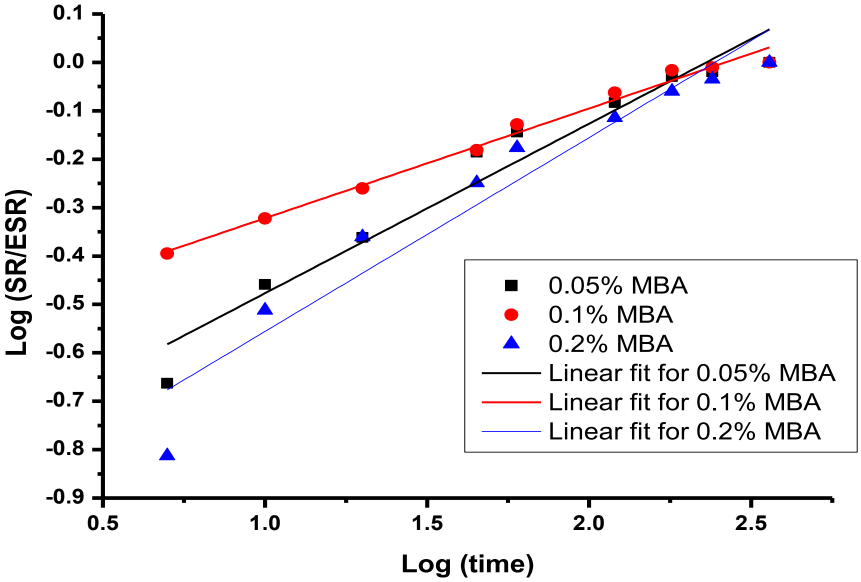


Figure 16: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 2.0% KPS and three different concentration of MBA.

Table 10: Swelling constant (K) and diffusion exponent (n) for sample of 2.0% KPS and three different concentration of MBA in synthetic urine

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.83	-0.55	-0.96
Diffusional exponent (n)	0.35	0.27	0.40

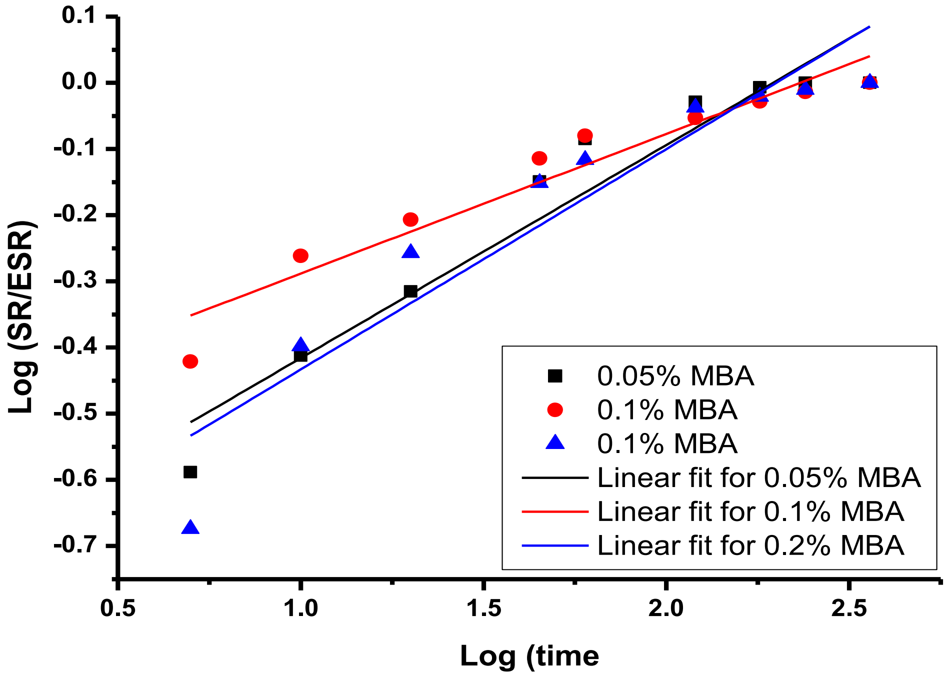


Figure 17: Swelling mechanism analysis of NaAA grafted bamboo rayon in synthetic urine for 3.0% KPS and three different concentration of MBA.

Table 11: Swelling constant (K) and diffusion exponent (n) for sample of 3.0% KPS and three different concentration of MBA in synthetic urine

Sample	0.05% MBA	0.1% MBA	0.2% MBA
Kinetic /swelling constant (k)	-0.74	-0.50	-0.76
Diffusional exponent (n)	0.32	0.21	0.33

The swelling kinetics of optimised NaAA grafted bamboo rayon fabric sample is shown in the figure 18. For both the cases i.e. for swelling of NaAA grafted bamboo rayon fabric in water and synthetic urine the diffusional exponent (n) was found to be 0.23 and 0.34 (Table 12) respectively, which shows the Less Fickian diffusion.

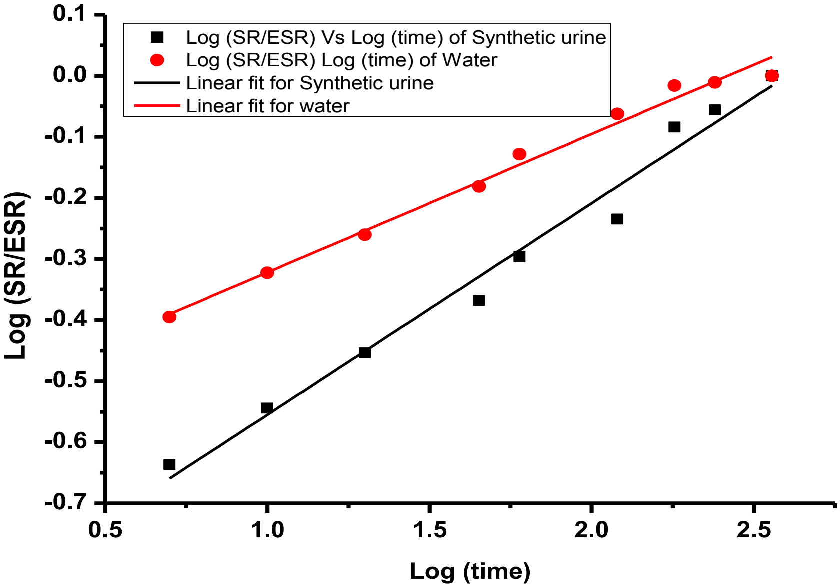


Figure 18: Swelling mechanism analysis of optimized NaAA grafted bamboo rayon

Table 12: Swelling constant (K) and diffusion exponent (n) for optimized AA grafted bamboo rayon

Sample	Kinetic /swelling constant (k)	Diffusional exponent (n)
Swelling in Water	- 0.55	0.23
Swelling in Synthetic urine	- 0.90	0.34

4.4. Analysis of –COOH group in the optimized sample

The optimized NaAA grafted sample (0.1% MBA and 2% KPS) was analysed for –COOH group determination. From the titration it was found that amount of free –COOH groups in the AA grafted bamboo fabric was 65 mol %. So, it is clear that rest of the mol (%) of the –COOH group have crosslinked with MBA.

4.5. Determination of silver ion on hydrogel

Elemental chemical analysis by EDXS was carried out for both the samples i.e. NaOH treated grafted bamboo fabric and Silver modified grafted bamboo fabric. The weight percentages obtained through EDXS analysis of different elements are shown in the Table 13. The NaOH treated grafted layer contains Na^+ (88.46 %) and K^+ (11.54 %) in its inter layer spaces. The silver modified grafted bamboo fabric layer shows the presence of Na^+ (1.32 %), K^+ (2.17 %). After ionic exchange, the total silver content was 96.51 % for the Silver modified sample. It has been reported that Na^+ is preferentially exchangeable by Ag^+; therefore, the decrease in sodium content can be associated with the incorporation of Ag^+ ions in the samples by cation exchange.

Table 13: Elemental analysis (wt. %) of parent and silver treated sample

Element	Parent	Silver treated sample
C	0.00	0.00
N	0.00	0.00
O	0.00	0.00
Na	88.46	1.32
K	11.54	2.17
Ca	0.00	0.00
Ag	0.00	96.51
Total	100.00	100.00

4.6. Structural analysis through FTIR

The FTIR spectrum of plain bamboo rayon fabric and NaAA grafted bamboo fabric is shown in the Figure 19. The FTIR spectrum of NaAA grafted fabric when compared with that of the ungrafted fabric clearly indicated the peak for –COOH group at 1723 cm^{-1} that is due to introduction of polyacrylic acid graft on to bamboo rayon backbone.

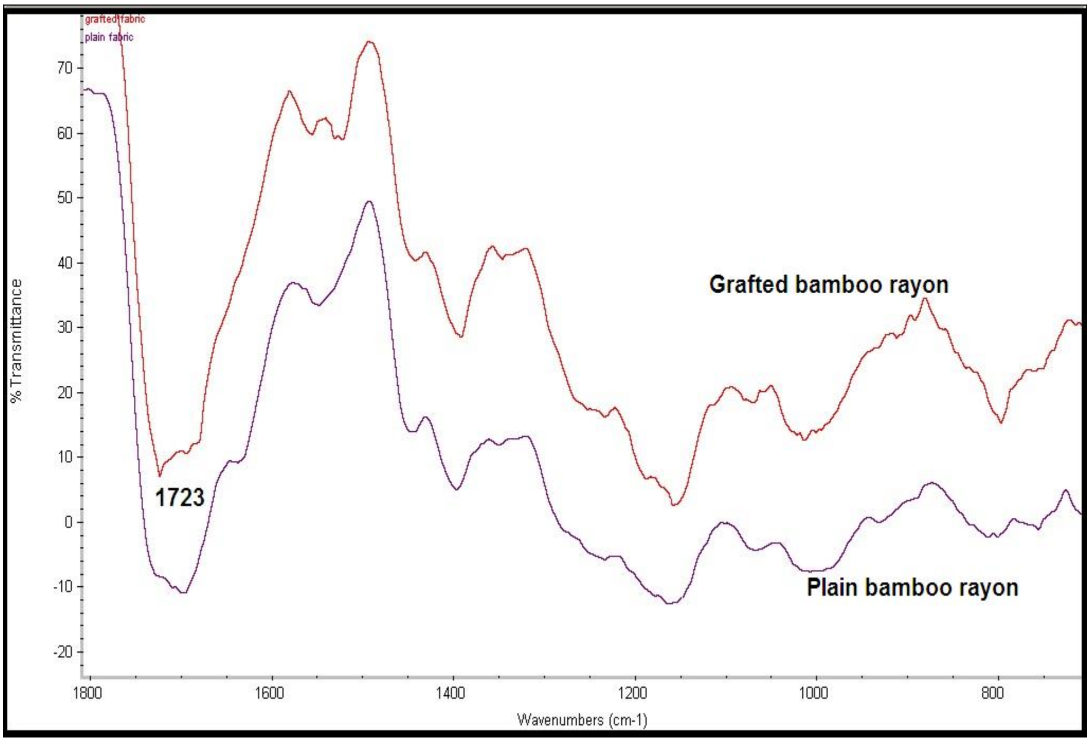


Figure 19: FTIR spectra of plain bamboo rayon fabric and NaAA grafted bamboo rayon fabric

4.7. Morphological analysis

The surface morphology of parent bamboo fabric and NaAA grafted bamboo fabric are analysed by scanning electron microscopy. The SEM micrographs are shown in Figure 20. The SEM images of grafted bamboo fabric shows hydrogel layer on the surface of the bamboo fibres, which is absent in the parent bamboo fabric. This further supports the presence of grafted acrylic acid on the cellulosic backbone of bamboo fabric.

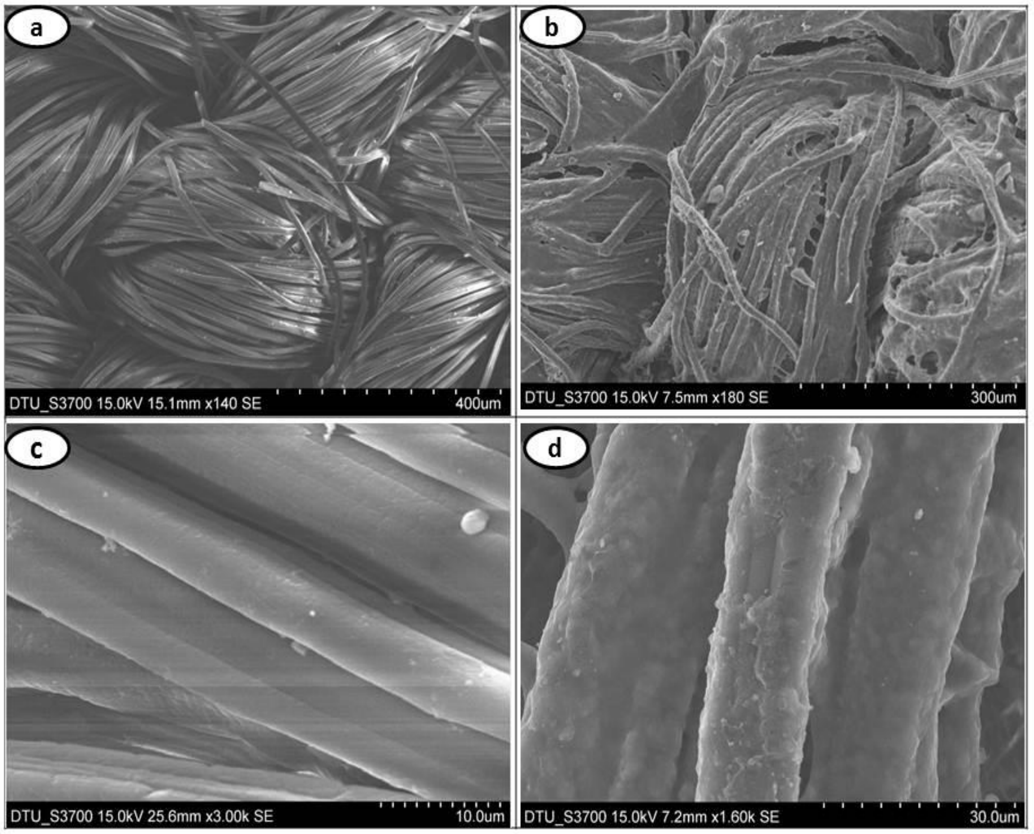


Figure 20: SEM micrographs for (a) & (c) parent bamboo rayon fabric and (c) & (d) NaAA grafted bamboo rayon fabric

4.8. Antibacterial testing

The disc susceptibility tests are shown in Figure 21, and the results are given in Table 14 and 15. The clear zone of inhibition is given in mm. The parent bamboo rayon fabric and acrylic acid grafted bamboo rayon fabric show no zone of inhibition for both the strain E. coli and S. aureus. But the silver modified grafted bamboo fabric shows clear zone of inhibition 6.5 mm and 8 mm for the strain E. coli and S. aureus respectively. The presence of Silver increased the antibacterial activities of the grafted fabric. The antibacterial properties of silver modified grafted fabric layer has been attributed to the attraction, by electrostatic forces, of the negatively charged membrane of the bacteria to the surface of the clay, where the positive charged silver ions kills the bacteria or renders them unable to replicate.

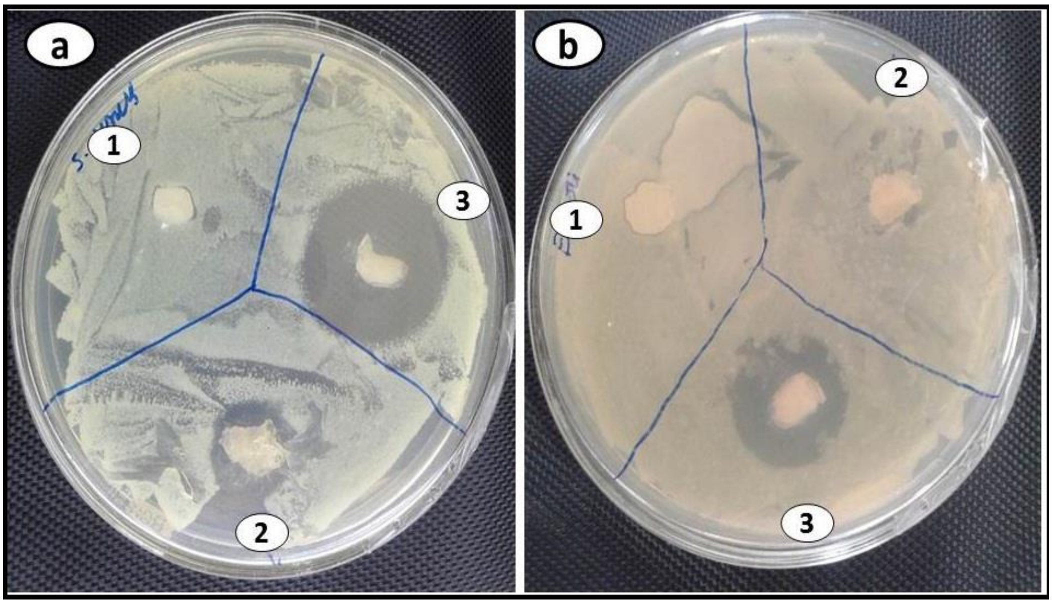


Figure 21: Zone of inhibition (a) S. aureus treated (b) E. coli treated (1) plain bamboo rayon fabric (2) NaAA grafted bamboo rayon fabric (3) silver modified NaAA grafted bamboo rayon fabric.

Table 14: Zone of inhibition for sample treated with E. coli

Sl no.	sample	Width of Specimen (D, mm)	Width of specimen and clear zone (T, mm)	Clear Zone of Inhibition (W, mm)
1	Parent bamboo fabric	7	7	No growth
2	Grafted bamboo fabric	7	7	No growth
3	Silver modified grafted bamboo fabric	7	20	6.5

Table 15: Zone of inhibition for sample treated with S. aureus

Sl no.	sample	Width of Specimen (D, mm)	Width of specimen and clear zone (T, mm)	Clear Zone of Inhibition (W, mm)
1	Parent bamboo fabric	7	7	No growth
2	Grafted bamboo fabric	7	7	No growth
3	Silver modified grafted bamboo fabric	7	23	8

Chapter 5

Conclusions and future scope

5.1. Conclusions

Bamboo rayon fabric was successfully grafted with acrylic acid hydrogel using KPS as initiator and MBA as crosslinking agent. In the grafting reaction the 10 % (w/v) acrylic acid is taken and temperature is maintained at 60 °C. Different concentration of MBA and KPS were studied and optimized according to swelling (%) analysis. The grafted layers were further treated with NaOH to make it superabsorbent. The optimized NaAA grafted bamboo rayon (2% KPS and 0.1% MBA) shows mass swelling (S_m, %) 94.55% and 341.67% in water and synthetic urine respectively. From the titration it was found that amount of free –COOH groups in the AA grafted bamboo fabric was 65 mol %. From the swelling kinetics study, the grafted layer shows less Fickian behavior, which means the water penetration rate is below the polymer chain relaxation rate. The peak at 1723 cm^{-1} for –COOH group on FTIR Spectra confirms the NaAA grafted onto the bamboo rayon fabric. The SEM micrographs shows bumpy layer structure on bamboo rayon fabric, which further confirms the NaAA hydrogel grafted onto the bamboo rayon fabric. The optimized sample was loaded with silver ion to make it antimicrobial resistance. The EDXS result shows the silver ion (96.51%) is present on the surface of hydrogel layer. From the disc diffusion test, the absorbent layer shows excellent antibacterial activity against Gram positive (*S. aureus*) and Gram negative (*E. coli*) bacteria.

5.2. Future scope

The grafted layer can be made using other different types of vinyl monomers like acrylamide, methacrylic acid, methacrylamide and combination of one or more monomers. Also one may use different types of crosslinking agent to stabilize the hydrogel structure. Other different types of antimicrobial agent like Zn or Cu can be used. The AA grafted bamboo rayon can be used in the area of biomedical for wound dressing, scaffold.

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