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CHEMICAL MODIFICATION OF CELLULOSE

BY

VINYL MONOMERS (ACRYLONITRILE)

A Thesis Submitted to
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By

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A C K N O W L E D G E M E N T

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C O N T E N T S

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SUMMARY

Grafting of acrylonitrile onto cellulose was studied in detail, using ceric sulphate as the initiator. The reaction was studied in aqueous (nitric) acid medium using cotton hanks. The influence, on the extent of grafting, of all the variables like reaction time, temperature and concentrations of ceric sulphate, nitric acid and acrylonitrile were studied in detail. The tensile strength of the grafted products were compared and their resistance to microbial attack evaluated.

The extent of grafting increased proportionately with time upto a period of 4 hours above which the increase was marginal. The percentage grafting was found proportional to the square of the monomer concentration. There was increase in grafting with increase in acid concentration upto 0.6 N, beyond which there was once again gradual decrease. The effect of ceric sulphate concentration was studied in the range of 0.0078 - 0.0312 M. It was noticed that an increase in its concentration upto 0.025 M increases the percentage grafting to a marked extent, above which the increase in grafting is comparatively less. Temperature has no marked influence on the reaction.

There is an increase in tensile strength to the extent of

about 20% in the grafted fibre. However, at high acid concentrations or when the fibre comes into contact with acid for a longer period of time, there is a decrease in tensile strength indicating degradation of the cellulose backbone. Similarly, the product is markedly resistant to microorganisms, excepting when there is degradation in the cellulose backbone.

Optimum conditions for the grafting reaction were established when a product grafted with acrylonitrile to the extent of about 70% can be obtained without any degradation in the cellulose backbone. Convincing evidence has been adduced to show that the product is a graft polymer and not a mere mechanical mixture.

Special applications have been suggested especially in view of its resistance to microorganisms. Further modifications of the grafted fibre have also been shown to be feasible which widens the scope of this product. A few envisaged modifications and their applications have been indicated.

The reaction is very smooth and facile and easy to carry out even when scaled up, without requiring any costly equipment. Hence it has got potentials to be taken up by the textile industry.

CHAPTER - I

I N T R O D U C T I O N

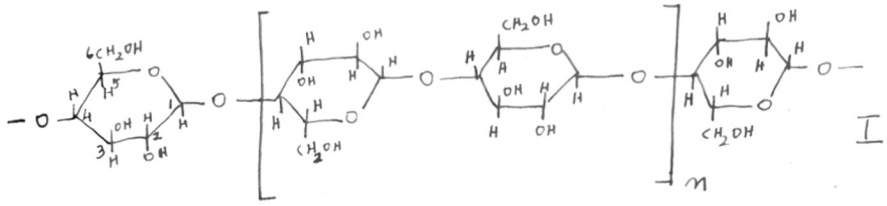
Cellulose is the only material in a wide range of extensively used polymers whose resources, far from diminishing, are each year renewed in practically unlimited amounts. Cellulose makes up about a third of all vegetable matter. Fibres are obtained from vegetable sources (cotton, flax, jute etc.) and cellulose is the main constituent of all of them; but it never occurs in pure form. Cotton seed hairs are the richest source containing about 90% cellulose by weight.

The use of cotton as the prime textile material is by no means entirely due to its cheapness and abundance, but rather to the fact that it provides material whose laundering properties are excellent. Other contributory factors to the popularity of cotton are its strength, durability, feel to hand, and its breathing and moisture uptake that make it ideal for wear in hot and humid climate.

1.1 STRUCTURAL FEATURES OF CELLULOSE

Cotton mainly contains alpha-cellulose, and beta-and gamma-cellulose only to a very limited extent and in general the term cellulose refers to alpha-cellulose only. Alpha-cellulose refers to cellulose which is insoluble in 18% sodium hydroxide solution at 20°C. Beta-cellulose (presumably degraded α-cellulose of low degree of polymerization[1]), is soluble in 18% sodium hydroxide solution at 20°C but is precipitated on slight acidification, while gamma-cellulose remains in solution even on acidification. Beta- and gamma-celluloses are not necessarily true celluloses in the sense that they contain only polymers of anhydroglucose units. Gamma-cellulose represents the major portion of the poly-saccharides known as 'hemi-celluloses', such as xylan, mannan, araban, galactan, uronic acids and other plant gums.

Cellulose is an unbranched linear polymer, formed by the condensation of β-glucose molecules linked together through 1 and 4 positions. Each glucose unit in cellulose has one primary and two secondary hydroxyl groups. The number of glucose residues or anhydroglucose units usually runs into several thousands in cellulose. The cellulose chain molecule has the structure (I). On the basis of conformational analysis the chair structure (II) can be a better representation.



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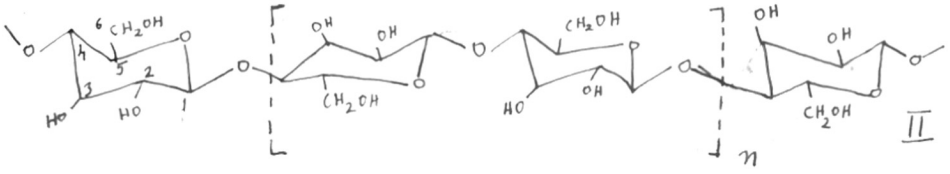


II

1.1.1 Hydrogen bonding

Whenever the distance between the various oxygen and hydrogen atoms in the cellulose molecule reaches 3 Å or less they interact with each other to form intra-molecular and inter-molecular hydrogen bonds[2]. With its three hydroxyl groups per anhydroglucose unit and the chair configuration of the glucose rings, cellulose has the capability of forming many hydrogen bonds along the length of the polymer chain. These bonds, combined with other secondary valence forces (principally the vander Waals attraction) bind together, portions of the molecular chains into various degrees of lateral order, ranging from perfect geometrical packing of the crystalline lattice to random conditions.

1.1.2 Crystallinity

The amount of crystallinity as measured from the intensities of x-ray powder diagrams[3,4] was found to be about 70%

for natural cellulose, about 50% for mercerised cellulose and about 40% for regenerated cellulose. Even at the same crystallinity level, however, the structure and the physical and chemical properties of cellulose will be dependent upon the size-distribution of the crystallites.

The non-crystalline areas give a diffuse background blackening in x-ray studies and therefore lack distinct orientation. In the crystalline regions, the chains are parallel or nearly so and in the amorphous areas, the chain molecules may deviate from each other or may cross each other; they might have a different length in the amorphous regions and some of them might be twisted around the main valence bonds. Infrared analysis has pointed out that almost all the hydroxyl groups in the amorphous areas take part in hydrogen bonding as well, presumably with the restriction that their bonding partners will show no periodicity as in the crystalline regions. Probably a transitional region of intermediate order will exist between the crystalline and amorphous regions, and the same molecular chains will sometimes run through from one region to another. Alteration of the size, type and proportion of the crystalline regions has a marked effect on both the physical properties and the reactivity of cellulose. The increase in crystallinity leads to the increase of tensile strength, Young's modulus, dimensional stability and density and the decrease of elongation, moisture sorption, swelling, dye sorption, chemical reactivity and flexibility. The hydroxyl groups located in the amorphous regions react readily in all chemical reactions,

being in a highly accessible environment. In the crystalline regions, where there is a close packing and strong interchain bonding, these groups are not readily accessible to reactant molecules. When water molecules enter the amorphous region, the individual cellulose molecules are pushed farther apart from each other, and thus the fibre swells. If the swelling is considerable, some of the crystalline regions in the proximity of the amorphous regions may also be opened up - thus permitting water or other reactants into those regions which were previously inaccessible. The outstanding feature of materials rich in hydroxyl groups is their solubility in water. Cellulose fibres are, however, insoluble in water due to very high degree of polymerization and mutual attraction between the hydroxyl groups of adjacent chains. These forces confer stability on the structure and make it difficult for water molecules to find their way into it.

1.1.3 Reactivity of hydroxyl groups in cellulose

The involvement of the hydroxyl groups in hydrogen bonding as well as general dispersion forces determined by the proximity of neighbouring atoms, impart a different reactivity to the three hydroxyl groups available for chemical reactions. It is to be anticipated that the primary hydroxyl groups will exhibit a greater degree of reactivity than the secondary. In sugars, however, it has been found that of the available hydroxyl groups, the primary on carbon atom 6 and the secondary on carbon 2 are more readily esterified, and the differences in reactivity between these two are not as

great as with simple alcohols. Esterification and etherification studies have shown that the C-6-OH group is esterified ten times as fast as the other -OH groups. On the other hand the C-2-OH group is etherified twice as fast as the C-6-OH groups and the C-6-OH group twice as fast as the C-3-OH group. The primary alcoholic group at C-6 is distinguished from the other two secondary alcoholic groups in that it has an axis of free rotation around the C-5 to C-6 bond, which is however, somewhat restricted by the hydrogen bonds[5]. In esterification, tosyl chloride reacts with the primary group[6] whereas benzoyl chloride gives the 2 and 6-derivatives of D-glucose[7]. In etherification, trityl chloride prefers the primary groups and reaction with methyl iodide or dimethyl sulphate yields derivatives substituted in the 2- and 6- positions[8]. The hydroxyl group on position 3 turns out to be the least reactive. To make a general statement as to the different reactivities of the groups in cellulose is difficult. Although it seems that the primary group has a somewhat higher reactivity, some conditions favour conversion of secondary groups probably at the C-2 rather than the C-3 position[9].

1.2 CELLULOSE DERIVATIVES

Synthesis of new derivatives of cellulose and application of new methods of treatment help to produce cellulose materials with such combinations of technically valuable properties, which we do not find in natural and regenerated cellulose

fibres. Cellulose derivatives originated mainly from the fact that they enabled short fibres of cotton and of wood pulp to be converted into filaments, films, coatings and moulded products. Thus, before fully synthetic polymers were developed for the same purpose, these derivatives started a major industry based on a virtually unlimited source of raw material.

1.2.1 Cellulose esters and ethers

Cellulose is capable of forming esters and ethers, which differ in their degree of esterification or substitution upto the maximum given by the reaction of the three hydroxyl groups attached to each anhydroglucose unit. Characterisation of an ester or ether requires not only a knowledge of the degree of polymerization (DP) but also a knowledge of the degree of substitution (DS).

(a) Cellulose esters

Cellulose nitrate is the best known ester of cellulose, which is prepared by the nitration of cellulose with mixtures of nitric and sulphuric acids. Cellulose acetate is prepared by acetylation of cellulose with acetic anhydride, glacial acetic acid and sulphuric acid. Cellulose acetate butyrate is prepared by esterification of cellulose by acetic and butyric acids.

Cellulose nitrate is used in the manufacture of celluloid, lacquer, enamel, artificial leather cloth and gun cotton used in explosives which contains more than 12% of nitrogen (DP around 2000 and DS 2.4). Cellulose acetate with DS 2.4 and

DP 350-400 is soluble in acetone and is known as secondary acetate, which is mainly used in the manufacture of acetate rayon. Its moisture content is only 6.5%. The fabrics made from it drape well. It is resistant to cold dilute acids, moths and mildew. It is used for trubenising and insulation. It is also used in the manufacture of plastics. Cellulose acetate-butyrate is non-inflammable, highly flexible and soluble in many cheap solvents. It is also used as cable lacquer. Its water and weather resistance are good and many mouldings are made from it.

(b) Cellulose ethers

These are prepared by the action of the etherifying agent on cellulose which has been treated with a swelling and solvating agent like sodium hydroxide.

Methyl cellulose is used as a protective colloid, dispersing agent in emulsions and textile finishing and printing. Ethyl cellulose with DS (2.2 - 2.5) is used in varnishes, adhesives, cable lacquers, plastics etc. Carboxy methyl cellulose is used as a thickener and a protective colloid.

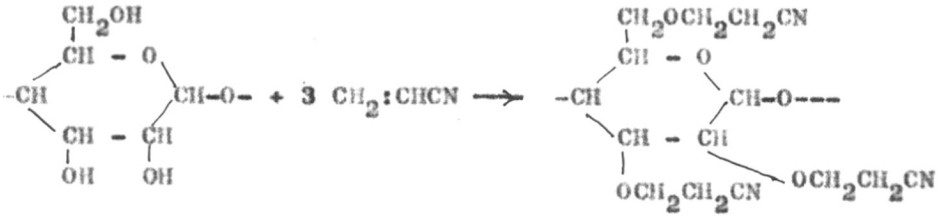
i) Cyanoethyl ether of cellulose

Cellulose pre-treated with alkali reacts fairly easily with acrylonitrile[10,11,12].

$$\text{Cell-OH} + CH_2{:}CHCN \longrightarrow \text{Cell-O}CH_2CH_2CN$$

When cellulose reacts with acrylonitrile, there is an increase in weight. The reaction can go to completion (as

shown in the equation below):



with a resultant gain in weight by 98% and a nitrogen content of 13%. However, in practice, the cyanoethylation of cellulose is usually restricted so that the product has a nitrogen content of only 3%. The improvement of properties that cellulose has gained from cyanoethylation are:

(i) a considerable increase in resistance to mildew, bacteria and heat; and

(ii) about 40% increase in resistance to abrasion.

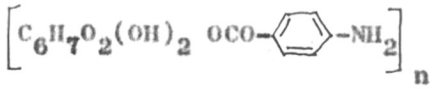
1.3 MODERN TRENDS IN THE DERIVATIVES OF CELLULOSE

During recent years, the number of synthesized cellulose ethers and esters is continuously increasing[13].

Phenyl ethers of cellulose were synthesized by the reaction of sodium phenolate with a solution of tosyl ether of cellulose in phenol at 110-120°C. The nitration of cellulose phenyl ether leads to the formation of nitrate and nitro groups in cellulose

$$\left\{ C_6H_7O_2(OH)_{0.45}(ONO_2)_{1.8}\left[OC_6H_3(NO_2)_2\right]_{0.75} \right\}_n$$

molecule, which is of fundamental interest.



... (A)

The reaction of cellulose with p-nitrobenzoyl chloride, followed by the subsequent reduction of the nitro group to amino group makes it possible to dye the cellulose with acidic dyes, leading to structure (A).

The synthesis of cellulose esters with acids containing phosphorous is carried out by reacting cellulose with chloromethyl phosphonic acid. Cellulose esters containing about 1.5% phosphorous exhibit non-flammable properties.

1.3.1 Introduction of new functional groups into the cellulose macromolecule

The classical modification of the structure and properties of cellulose by forming derivatives is limited to the transformation of only the hydroxyl group of the cellulose molecule as it is a monofunctional compound. However, the number of cellulose derivatives can be increased by first converting the hydroxyl group into a variety of functional groups such as aldehyde, carboxyl, amino, amide and nitrile groups which in turn undergo further reactions[13]. Such modified cellulose include deoxy cellulose[14,15], amino deoxy cellulose[16], chloro deoxy cellulose[17,18] and iodo deoxy cellulose[19].

1.4 MODIFICATION OF CELLULOSE

There is a vast development in the production of various synthetic fibres during the last 15 years. The synthetic polymers have better properties over the natural polymers in several aspects. The main advantages of cellulose fibres are high hygroscopicity, higher thermal stability and good mechanical properties. The main short-comings of cellulose fibres as compared to synthetic fibres can be briefly formulated as follows:

(a) low resistance to chemicals,

(b) low resistance to micro-organisms and moulds,

(c) flammability,

(d) poor elasticity and hence, lower resistance to distortion and creasing, and

(e) low resistance to abrasion.

Attention has been paid to the way in which the above-mentioned short-comings of cellulose can be eliminated to a considerable extent by either physical or chemical modification of cellulose. The crystal structure of cellulose can be changed by treating native cellulose to render it soluble and then regenerating it from solution. The regenerated cellulose (rayon and cellophane) has modified physical properties, but the improvement of properties of cellulose brought by the change in its physical structure is very limited.

The chemical structure of cellulose can be changed by preparing:

(a) a derivative of cellulose,

(b) a crosslinked cellulose[20-23] i.e. a net structure, and

(c) a branched cellulose, i.e. a graft polymer of cellulose.

Of these three ways of modifying the chemical structure of cellulose, the preparation of a cellulose derivatives is, of course, the oldest and most widely used, which is already described in the previous pages. However, in the preparation of a cellulose derivative, such as cellulose ester or ether with a high degree of substitution, certain desirable properties of cellulose are lost. This occurs because these treatments affect the structure of each individual anhydroglucose unit in the cellulose molecule, thereby reducing the ability of the chains to crystallize, or preventing the formation of hydrogen bonds with a resulting loss of solvent and heat resistance.

The crosslinking of cellulose is also a well known and established technique for the treatment of cellulose to impart crease resistance, shrink resistance, and a number of other properties but owing to the fact that the cellulose chains become part of a three-dimensional net work, the material becomes harder and more rigid, thus resulting in the loss of some desirable textile properties.

The grafting approach, on the other hand, presents a means of modifying the cellulose molecule through the creation of branches which impart to the cellulose certain desirable properties without destroying the useful properties of cellulose. This accounts for the great interest in cellulose graft polymers and it is described in detail, in the forthcoming pages.

1.5 GRAFTING ON CELLULOSE

It was observed that properties of cellulose such as resistance to mildew, heat etc. could be improved by cyanoethylation (refer page 8). Attempts were made to obtain similar improvements of properties by the incorporation of polyacrylonitrile inside the cellulose fibre[24-26]. The two methods adopted for this purpose are:

(i) polymerization of acrylonitrile vapour, in the individual cellulose fibre; and

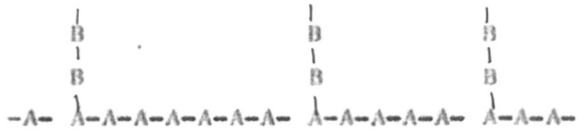
(ii) by swelling the cellulose fibre with water in the presence of ferrous ion, drying and then treating with acrylonitrile and hydrogen peroxide.

The properties were found to be materially improved in breaking strength, resistance to rot, acid, abrasion resistance and high frictional characteristics between adjacent yarns.

A further improvement in this direction is made by graft polymerization of acrylonitrile onto cellulose fibre. This results in chemical bonding of polyacrylonitrile side chains to the cellulosic chains through chemical bonding. The chemical bonding leads to greater uniformity and improved stability, thus combining the properties of both polyacrylonitrile and cellulose. A number of methods have been successfully developed to prepare graft polymers of cellulose and its derivatives which are reviewed in the literature[27-31].

The technique of graft polymerization permits tailor-making of the polymer structure, with widely different

combinations of backbone and side chains. The typical graft polymer is represented as:



where the macromolecule consists of a backbone or trunk of poly-A with branches of poly-B. It is actually a segmented polymer containing sequences of repeating units of various length.

Since graft polymerization involves the polymerization of monomers onto a polymer backbone, the various methods of accomplishing polymerization reactions can be utilised for the synthesis of graft polymers. Thus, addition polymerization reaction of vinyl monomers initiated by free radical or ionic means and condensation or ring opening polymerization reactions of compounds containing reactive functional groups are suitable tools and they are described below.

1.5.1 Methods based on chain transfer reaction

Growing polymer radicals are capable of abstracting hydrogen or other labile atoms like halogen, sulphur etc., from the backbone polymer resulting in the creation of free radical centres on the latter. Graft polymerization is initiated by these free radical centres on the backbone:

$$AX + R^{\bullet} \longrightarrow A^{\bullet} + RX$$

$$A^{\bullet} + nB \longrightarrow AB_{n-1} - B^{\bullet} \xrightarrow{\text{termination}} A\text{-}B_n$$

where AX is the backbone polymer with X as the labile atom,

B is the monomer molecule (to be grafted), R$^{\cdot}$ is the polymeric free radical, A$^{\cdot}$ is the backbone radical, AB_{n-1} —— B$^{\cdot}$ is the graft polymer radical, and AB_n is the graft polymer. In addition to graft polymer, the reaction product contains unreacted backbone as well as free (unbound) side chain polymer.

Grafting on cellulose by chain transfer process has been studied in some detail[31]. The yields were low but appreciable grafting was observed[32] by introducing -SH groups into the cellulose before grafting. Chaudhuri and Herman[33] incorporated mercapto groups onto cellulose backbone by the reaction of cellulose with ethylene sulphide.

$$\text{Cell} - OH + \underset{\diagdown\,S\,\diagup}{CH_2\text{-}CH_2} \longrightarrow \text{Cell} - OCH_2SH$$

The mercapto groups have high chain transfer activity resulting in increase in the degree of grafting when vinyl monomers are polymerized. Both the air dry strength and wet strength of regenerated cellulose grafted by styrene are about 10% higher when compared to the ungrafted fibre. The modulus of elasticity is increased by 100%.

1.5.2 Graft polymerization by mechano-chemical methods

Polymers in visco-elastic state when subjected to mechanical stresses, such as mastication, extrusion, milling etc. undergo main-chain scission to form polymeric free radicals:

$$P\text{-}P \longrightarrow P^{\cdot} + P^{\cdot}$$

In presence of oxygen, peroxide formation also takes place.

$$P^{\cdot} + O_2 \longrightarrow POO^{\cdot} \longrightarrow POOH$$

Block polymerization is initiated by these polymeric radicals or peroxides[34,35]. The polymeric free radicals thus, formed are also capable of abstracting hydrogen or other labile atoms from the backbone of the polymer molecule[36,37], thus creating grafting sites. The mastication data for cellulose and its derivatives (methyl, ethyl, benzoyl cellulose, cellulose acetate, starch etc.) in the presence of vinyl monomers like acrylonitrile, styrene, vinyl acetate and methyl methacrylate, has been summarized by Ceresa[38] et al[39]. This process leads to the formation of mixture of block and graft polymers.

1.5.3 Grafting on modified cellulose, containing aromatic amino groups

Sodium salt of carboxy methyl cellulose or soda cellulose[40] is reacted with a halogenated amine.

$$Cell - ONa + ClCH_2COC_6H_4NH_2 \longrightarrow Cell\text{-}OCH_2COC_6H_4NH_2$$

$$Cell - OCH_2COONa + Cl\ CH_2COC_6H_4NH_2 \longrightarrow Cell\text{-}OCH_2COOCH_2COC_6H_4NH_2$$

The product is diazotized and heated. The following reaction is believed to take place:

$$Cell -- C_6H_4N_2^{+}\ Cl^{-} \longrightarrow Cell -- C_6H_4^{\cdot} + Cl^{\cdot} + N_2$$

The free radical sites formed on the backbone as a result of the decomposition of the diazonium salt initiate polymerization of vinyl monomers. Considerable homopolymerization also occurs by initiation by Cl. This may be suppressed by

addition of ferrous ions as follows:

$$\text{Cell}\text{--}C_6H_4N_2^+Cl^- + Fe^{2+} \longrightarrow \text{Cell}\text{--}C_6H_4^{\cdot} + Fe^{3+} + Cl^- + N_2$$

This method has advantage in that the grafted chains can be removed by hydrolysis of ester linkages so that the molecular weight of the grafted side chains etc. may be evaluated.

1.5.4 Grafting on modified cellulose containing peroxy groups

Peroxide and hydroperoxides of cellulose esters may be decomposed yielding free radical sites for grafting[41]. When the o-chlorobenzoyl ester of cellulose is allowed to stand in air, peroxide groups are introduced into the polymeric molecule. These peroxide groups are the reactive sites for the initiation of polymerization of styrene to yield graft polymers.

Ozonization is a more effective technique for producing active sites on a polymeric backbone than air oxidation and has been applied to a series of backbone-monomer systems. The polymer may be in the form of a fibre or film to give surface grafting or may be ozonized in solution. Cellulose and starch[42,43] treated in this manner are modified by graft polymerization.

1.5.5 Radiation methods

(a) Low energy radiation

Polymers containing appropriate labile groups may be irradiated directly to produce grafting sites. Irradiation

of a polymer-monomer mixture in the presence of a photo-sensitizer yields graft polymer, as a result of the activation (creation of free radicals) of backbone by the photo-sensitizer. Photosensitizing action has been found in well known radical producing catalysts such as 2-2′-azo-bis-isobutyronitrile[44] and in dyes like eosin and safranine. For instance, anthraquinone dyes have been employed as photosensitizers in the grafting of various monomers, including acrylonitrile, methyl methacrylate and vinyl acetate, onto cellophane[45-47]. The grafting is particularly effective with polymers containing methylol groups. The dye molecule is photo-excited and abstracts a hydrogen atom from the cellulose to yield a free radical grafting site. By the incorporation of various dyes into polymer molecules, photosensitized graft polymerization can be carried out. The dye creates the grafting sites on cellulose when exposed to light in the presence of a reducing agent-oxygen system.

$$P \longrightarrow P^*$$

$$\text{Cell} - \text{CHOH} + P^* \longrightarrow \text{Cell} - \text{C}^{\cdot}\text{OH}$$

$$\text{Cell} - \text{C}^{\cdot}\text{OH} \xrightarrow{\text{Acrylonitrile}} \text{Cell} - \underset{\displaystyle \underset{\displaystyle AN}{|}}{\overset{\displaystyle \overset{\displaystyle AN}{|}}{\text{C}^{\cdot}\text{OH}}}$$

where P is a photo-sensitizer, P* is an excited photo-sensitized molecule.

(b) <u>High energy irradiation</u>

γ-radiation from a Co^{60} source, high energy electrons

from linear accelerator and high energy x-rays have been used to create active sites on polymers for graft polymerization.

Free radical centres on a polymer may be created by irradiation of the latter with γ-rays from Co^{60} at dose rates $1\text{-}100 \times 10^4$ r/hr. This method has been widely employed for grafting on cotton fibres, regenerated cellulose as well as synthetic fibres like terylene. Two main techniques are employed for grafting by γ-rays[48-50] viz. (i) simultaneous grafting or mutual grafting, and (ii) post-irradiation or pre-irradiation grafting (involving either air pre-irradiation method or vacuum pre-irradiation method).

Grafting by the irradiation of polymers has been one of the most successful of all grafting methods and has been applied to many polymer-monomer systems[51]. Until recently, it was considered impossible to graft more than a few percent to cellulose using radiation without degradation of cellulose. However, considerable grafting could be carried out if the cellulose was rendered accessible to the monomer by swelling techniques. The cellulose was pre-swollen[52] or even solvent exchanged[53] before irradiation in the presence of a suitable monomer such as styrene. Large amounts of acrylonitrile were grafted onto cotton by irradiation in a solution of acrylonitrile in 80% zinc chloride solution, which is an effective swelling agent. Such grafted cellulose was found to have increased elongation and softness[54]. It was considered that the grafted products consist of considerable amounts of block polymers in addition to graft polymers

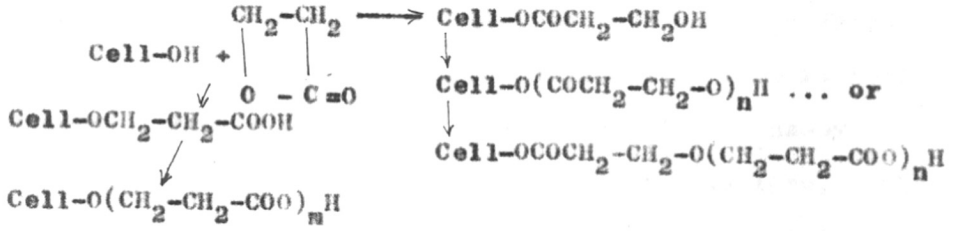
since cellulose undergoes chain scission. In radiation grafting, generally the presence of non-solvents like methanol or water (for the grafts) increases the rate of grafting[55,56]. Usmanov and coworkers[57] irradiated mixtures of cellulose and acrylonitrile solution in various solvents over a wide range of radiation doses and monomer concentrations. For cellulose substrate, a minimum of 10^5 rad of irradiation was required. Grafting occurred only when cellulose fibres absorbed the monomer-solvent mixture. The monomers used were styrene, methyl methacrylate, 2-methyl 5-vinyl pyridine and vinyl acetate. Cellulose when grafted by γ-rays with methyl methacrylate, methyl acrylate, methacrylic amide, acrylonitrile and styrene, gets considerably modified. Grafting of cellulose increases its thermostability, resistance to micro-organisms, its dyeability and adhesion capacity. The thermostability and resistance to micro-organisms of cellulose grafted with methacrylic amide and acrylonitrile increase with the degree of grafting.

1.5.6 Ionic initiation

The reaction of cellulosic hydroxyl groups with an aluminium alkyl forms an alkyl aluminium alkoxide group attached to cellulose: cell - $OAlR_2$. On addition of a transition metal compound, ethylene, propylene and styrene are polymerized onto the cellulosic fibres[58]. The fibres are encapsulated by the vinyl polymer, and no actual chemical bond may be formed between the cellulose and the vinyl polymer.

1.5.7 Cyclic monomers

The reaction of cotton with β-propiolactone yields graft polymers as a result of etherification and polyesterification[59]. The polymers are mixed ethers and ethers of cellulose.



The ether linkages are stable to saponification, while the ester linkages are broken. Therefore, saponification removes all but the carboxyethyl groups attached directly to the cellulose molecule. Dehydration of the β-propiolactone treated cotton results in the production of unsaturated groups in the hydracrylic acid ester groups attached to the cellulose molecule.

$$\text{Cell-OCOCH}_2\text{CH}_2\text{OH} \longrightarrow \text{Cell-OCOCH=CH}_2 + \text{H}_2\text{O}$$

These are sites for polymerization of vinyl monomers.

1.5.8 Chemical activation

The free radical sites for graft polymerization can be induced by a variety of redox systems, such as those described below:

Hydrogen peroxide reacts with cellulose containing absorbed ferrous ions to yield free radical sites:[60]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$$

$$Cell\text{-}CHOH + {}^{\cdot}OH \longrightarrow Cell\text{-}{}^{\cdot}COH + H_2O$$

Graft polymerization is initiated at these reaction centres in presence of vinyl monomers.

It was observed by Duke[61] that glycols can be oxidized by Mn^{3+} by electron transfer process involving free radical mechanism. This principle is employed by Singh, Thampy and Chippalkatti[62] to obtain graft polymers, of cellulose, carboxy methyl cellulose, starch etc. using methyl methacrylate, acrylonitrile, methyl acrylate, styrene and vinyl acetate. Manganic sulfate in the presence of excess of sulphuric acid has been employed and the initiation was believed to be:

$$Mn^{3+} + RCH_2OH \longrightarrow Mn^{2+} + H^+ + R\dot{C}HOH \text{ or } RCH_2O^{\cdot}$$

The free radical produced, initiated graft polymerization in the case of carboxy methyl cellulose, the reduction in the available hydroxyl groups reducing the extent of grafting. Grafting was not achieved in the case of styrene and vinyl acetate presumably because of their insolubility in water. The graft polymers after isolation from homopolymers by solvent extraction were characterised by I.R.spectra.

The same authors obtained graft polymers of cellulose with methyl methacrylate using pentavalent vanadium as initiator[63]. Vanadium pentanitrate was employed and grafting occurred at room temperature. The I.R.spectra of grafted cellulose showed the presence of $-COOCH_3$ frequency at 1720 cm^{-1}.

It was believed that grafting occurred by redox process but mechanism was not discussed.

The system sodium thiosulphate/potassium persulphate was found to be an initiator for polymerization of acrylonitrile in presence of cellulose[64]. Traces of copper were found to accelerate the rate of polymerization. The substrates used were secondary cellulose acetate, mercerised cotton and cellophane. The fabrics were resistant to micro-organisms.

The system ceric^{4+} -reducing agent (polymeric substrate)-monomer was extensively studied by a number of workers and a detailed discussion of various grafting studies involving Ce^{4+} is described in the following section.

1.6 GRAFT POLYMERIZATION INITIATED BY CERIC IONS

1.6.1 Oxidation by cerium(IV)

Ceric ion in acid medium is a very good oxidising agent and extensive studies of oxidation of various organic substrates have been carried out by many workers. Oxidation studies of alcohols by ceric ions indicate that the oxidation proceeds through the disproportionation of a co-ordination complex[61-65,66] between alcohol and ceric ion. Studies on absorption spectra and kinetics of oxidation indicate complex formation. Ardon[67], for example, described the oxidation of ethanol in aqueous solution of ceric perchlorate by the reaction:

$$Ce^{4+} + EtOH \underset{}{\overset{K}{\rightleftharpoons}} \text{complex}$$

$$\text{complex} \xrightarrow{k} Ce^{3+} + H^{+} + \text{oxidation products.}$$

The concentration c of the complex was given by:

$$C = (1+KA)^{-1} KA [Ce]$$

where A represents the alcohol concentration, and [Ce] the total ceric content. The rate at which ceric is reduced was given by $K' [Ce]$ where $K' = k\,KA(1+KA)^{-1}$. The equilibrium constant K of the complex was obtained from a plot of $\frac{1}{K'}$ vs $\frac{1}{A}$. The complex formation was also verified independently by spectrophotometric studies.

1.6.2 State of ceric in aqueous solutions

In aqueous solutions of ceric sulphate the following species have been postulated[68-70], $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ and the stability constants of these complexes were evaluated. Ce^{4+} shows less complex formation in nitric acid medium and complex formation is still less in perchloric acid medium. However, according to Hardwick and Robertson[68] and Sherrill[71], ceric ions in perchloric acid medium even at low pH are complexed with hydroxyl ions giving rise to $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$. Furthermore, dimers and polynuclear complexes of ceric ion also exist depending on pH and other factors.

The stability constant of the ceric-ethanol complex depends on pH. This dependance was explained by Ardon[67] on the basis of the equilibrium:

$$Ce^{4+} + H_2O \rightleftharpoons CeOH^{3+} + H^+$$

Addition of neutral sulphate to ceric sulphate solutions,

however reduces the rate of oxidation. On the other hand, addition of sulphuric acid ~~to ceric~~ to ceric sulphate may lead to increased oxidation rates. Hargreaves et al[72] explained this by postulating a special complexing scheme involving both sulphate ions and hydrogen ions. It will be clear from these data that the quantitative results in one series of experiments may depend very much on the concentration of the various species present.

1.6.3 Mechanism of initiation by Ce^{4+} ions

Mino, Kaizerman and Rasmussen[73] studied in detail, the oxidation of pinacol by ceric sulphate. The concentration of ceric sulphate was varied from 0.03 - 0.16 M. The rate of oxidation was proportional to $[Ce][\text{pinacol}]$. Two moles of acetone were produced for every two moles of Ce^{4+} reduced. The rate determining step was:

$$Ce^{4+} + (CH_3)_2\overset{OH}{\underset{|}{C}}-\overset{OH}{\underset{|}{C}}-(CH_3)_2 \longrightarrow (CH_3)_2CO + (CH_3)_2\dot{C}OH + H^+ + Ce^{3+}$$

followed by:

$$Ce^{4+} + (CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CO + H^+ + Ce^{3+}$$

In the presence of excess acrylamide, only one mole of acetone was produced which was explained by the fact that the free radical species first formed by ceric oxidation participates in the initiation of polymerization of acrylamide.

1.6.4 Oxidation of cellulose by Ce^{4+} and graft polymerization

Mino and Kaizerman[74] pointed out that certain ceric salts such as the nitrate and sulphate form very effective redox

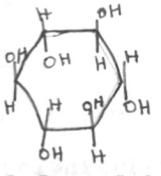
systems in the presence of organic reducing agents, such as alcohols and glycols:

$$Ce^{4+} + RCH_2OH \rightleftharpoons B \xrightarrow{K_d} Ce^{3+} + H^+ + R\dot{C}HOH \text{ (or } RCH_2O^\bullet)$$

where Ce^{4+} represents the ceric complexes as they exist in aqueous solution, B the ceric alcohol complex and $R\dot{C}HOH$ a free radical. If a vinyl monomer is present, the free radical initiates polymerization.

If a polymeric substrate such as cellulose, polyvinyl alcohol etc. is used as a reducing agent, the free radical centre formed on polymeric substrate (backbone) initiates graft polymerization.

In order to get an insight into the mechanism of initiation of grafting, a series of polymerization studies of acrylamide were carried out using the aqueous redox systems of ceric nitrate and various model compounds[75]. Of the model compounds studied, it was found that glucose-ceric salt and trans-1,2-cyclohexanediol-ceric salt redox systems were very effective.



trans-1,2-cyclohexanediol.

The trans-1,2-cyclohexanediol is very similar to 1,2-glycol unit of cellulose molecule. Glucose which has a hemiacetal unit was the most effective reducing agent among the model compounds chosen. This fact proves the observation that

grafting occurs most easily at a hemiacetal unit in the end of the cellulose molecule. The conclusion was that the grafting occurred both at hemiacetal and 1,2-glycol units.

Mino and Kaizerman carried out extensive studies of grafting of vinyl monomers onto cellulose and other substrates containing -OH groups employing Ce^{4+} as an oxidising agent. In all cases ceric ion and substrate (containing -OH groups) formed a redox system. The substrate was oxidised by Ce^{4+} in acid medium giving rise to free radical centres on the polymeric backbone. These free radical centres initiate vinyl polymerization so that a chemical bonding is established between the polymeric backbone and the new vinyl polymer. Homopolymerization also invariably occurred to a minor extent.

Mino, Kaizerman and Meinhold[76] employed two main techniques for grafting vinyl monomers onto cellulose in the presence of Ce^{4+} salts. The cellulose was oxidised by Ce^{4+} and the free radical centres formed on cellulose initiated graft polymerization. In solution technique the cotton fabric was immersed in monomer solution containing Ce^{4+} and acid in nitrogen atmosphere. In vapour saturation technique, acidified solution of Ce^{4+} was applied to the fabric by padding and the fabric was suspended in the vapour of the monomer for 5 minutes at the boiling point. Acrylonitrile, methyl and ethyl acrylate, methyl methacrylate etc. were grafted in this way. Good rot and mildew resistance were obtained without sacrificing any mechanical properties.

Mino, Kaizerman et al[77] also employed cellulose in the form of cotton fibres or paper treated with 0.01 M ceric-

ammonium sulphate solution in 0.1 M sulphuric acid. The material was exposed to vapours of boiling acrylonitrile-water azeotrope. After removal of acrylonitrile and ceric salts, it was found that 21.7% of polyacrylonitrile was deposited on the fibre. The grafted fabric showed outstanding resistance to degradation by micro-organisms and no loss of strength after six weeks burial in soil whereas untreated fabric degraded completely in less than two weeks.

The grafting of acrylonitrile and methyl, ethyl and butyl acrylates in two types of celluloses, one rich and the other poor in hemicellulose content, was studied by the procedure of Mino and Kaizerman employing Ce^{4+} in nitric acid medium. It was found that the grafting was more rapid ~~than~~ in the case of hemicellulose rich sample[78].

It was observed that ultrasonic waves of 420 KC and 2000 W accelerated the graft polymerization of vinyl monomers such as methyl methacrylate onto viscose sponge in the presence of ceric ammonium nitrate and salts of metals of group VIII[79].

Acrylamide was grafted onto cotton linters, bleached sulphite and sulphate pulp in the presence of Ce^{4+} at 0.02% and pH 2.4. Grafting increased with increase of time and [acrylamide]. When the degree of polymerization of grafted polyacrylamide side chain is > 3000 that of ungrafted (free) polyacrylamide was significantly higher indicating block polymer formation[80].

The graft polymer of cellulose-acrylonitrile prepared using ceric ammonium nitrate as initiator was isolated by removing free polyacrylonitrile by treatment with 55% zinc chloride and 5% ammonium chloride solution at 70°C and free cellulose by extracting with hexa sodium ferric tartarate[81].

Acrylonitrile was grafted onto cellulose using Ce^{4+} ions in aqueous medium[82]. To avoid homopolymer formation, the cellulose was first treated with aqueous solution containing Ce^{4+}. Then it was treated with acrylonitrile vapour in nitrogen atmosphere.

Recent studies of graft polymerization kinetics employing Ce^{4+} for grafting of acrylonitrile and acrylamide onto granular wheat starch[83] indicated that homopolymerization increased with increase in [monomer] and grafting decreased with increase in $[Ce^{4+}]$. The grafting efficiency was 87% for acrylonitrile and 43.8% for acrylamide.

Acrylamide was grafted onto dextran[84] by ceric nitrate in aqueous medium at 25°C. It was observed that ceric ion and dextran formed a complex with equilibrium constant $K = 3.0 \pm 1.6$ l/mole and the specific rate of dissociation of the complex $K_d = 3.0 \pm 1.2 \times 10^{-4}$ sec.$^{-1}$. The number-average degree of polymerization was directly proportional to the ratio [Monomer] / $[Ce^{4+}]$ and found to increase exponentially with increase in degree of conversion. The initial fast reaction was accounted for by the high reactivity of ceric ion with cis-glycol groups on ends of dextran chains.

1.7 SCOPE OF THE PRESENT WORK.

The problem of modifying the characteristics of natural fibres such as cellulose, wood etc. has attracted increasing attention in recent years. The properties like crease recovery, wrinkle resistance, resistance to microorganisms, etc. were considerably improved by incorporation of polymers like polyacrylonitrile into fibre. This was achieved by graft polymerization of vinyl monomer onto the fibre wherein a chemical bond is established between the fibre and the vinyl polymer.

It is well known that reducing agents like glycols etc. are oxidised by ceric ions when free radicals are formed onto the reducing agents. This was extended to the case where the reducing agent was cellulose. The free radicals formed on cellulose molecule by oxidation by Ce^{4+}, initiate graft polymerization of vinyl monomers like acrylonitrile, and a chemical bonding is established between the backbone and side chains.

In this present work, polymerization of acrylonitrile onto cellulose fibre using Ce^{4+} in nitric acid medium has been carried out, since the system Ce^{4+} - nitric acid has a fairly high redox potential (1.61). Acrylonitrile was selected as the monomer because of its water solubility, and the excellent fibre characteristics of its polymer (resistance to chemicals, microorganisms etc.). Optimum reaction conditions to obtain maximum degree of grafting without destroying the desirable properties of cellulose are established. The effect of reaction conditions on the properties of cellulose(tensile strength, resistance to microorganisms) are studied.

CHAPTER-II

EXPERIMENTAL AND RESULTS

2.1 MATERIALS

Cellulose

Scoured and bleached cotton hanks of 28s count supplied by Rajabahadur Motilal Poona Mills Ltd., Poona, each weighing about 1.8 gms. were used in the grafting experiments.

Acrylonitrile

B.D.H. reagent grade acrylonitrile was purified by successive washings with 5% dilute sulphuric acid, 1% dilute sodium carbonate solution and distilled water. After drying thoroughly with anhydrous calcium chloride, it was distilled at atmospheric pressure and stored over calcium chloride, so as to remove the monomer absorbed water. Immediately before use, the monomer was filtered and distilled.

Dimethyl formamide

Dimethyl formamide (commercial grade) was kept over phosphoric oxide at room temperature for several hours, then decanted and distilled. It was used as a solvent for the extraction of homopolymer (polyacrylonitrile) formed during the grafting experiments.

Ceric sulphate

Analar grade ceric sulphate was used as initiator in the grafting experiments which was supplied by Bhabha Atomic Research Centre, Trombay, Bombay. 0.1 M ceric sulphate solution was prepared by dissolving about 33.3 gms.

of it in one litre of 1.0 N nitric acid solution. Ceric sulphate solution was standardised by titrating it against 0.1 N ferrous sulphate solution using $\mathcal{O}$-phenanthrolene as an internal indicator.

2.2 APPARATUS AND POLYMERIZATION PROCEDURE

2.2.1 Constant temperature bath

A water thermostat was set up with a heating arrangement upto 50°C and with a cooling arrangement upto 10°C. The temperature of the bath was maintained constant with an accuracy of $\pm$ 0.1°C.

2.2.2 Nitrogen supply

Nitrogen gas, regulated from a cylinder, was freed from oxygen by passing through Fieser's solution containing a 3:4 mixture of sodium hydrosulphite and sodium hydroxide with a small quantity of sodium anthraquinone- β-sulphonate in water. The gas was then passed through a trap containing lead acetate solution to remove any sulphurous impurities, then through concentrated sulphuric acid to free it from moisture.

2.2.3 Polymerization procedure

Scoured and bleached cotton hanks were washed with methanol and acetone and dried in a vacuum oven at 40°C and 20 mm. pressure for 6 hours. Then maintaining the same pressure, they were brought to the room temperature.

Then they were quickly transferred to a dessicator containing phosphoric oxide and weighed. Cotton hanks approximately about 1.8 grams in weight were taken in dried and well-stoppered 250 ml. pyrex conical flasks.

Just before starting the experiments, oxygen-free nitrogen gas was bubbled through nitric acid and ceric sulphate solutions and distilled water to remove any oxygen present in the solutions.

Total volume of the aqueous solution in the reaction mixture was kept at 128 ml. in all the experiments, i.e. material: liquor ratio of about 1:70 was maintained. Calculated quantities of distilled water, 1.0 N nitric acid solution and acrylonitrile were added successively from different microburettes to the reaction flask containing weighed cotton hank. The flask was shaken by a microid flask shaker for 5 minutes and then the calculated quantity of the initiator (0.1 M ceric sulphate solution) was added quickly from microburette. The flask was immediately stoppered and shaken for the required time at 30°C.

For the study of the effect of temperature on the grafting reaction, two-necked 250 ml. round bottomed pyrex flask was used as the reaction vessel. The flask was dipped upto its neck in the water thermostat. Throughout the reaction the thermostat was maintained at the desired temperature with an accuracy of $\pm$ 0.1°C. The grafting reaction was carried out as usual but the contents in the flask were gently stirred throughout the reaction time with

a glass stirrer fitted with a mercury seal, which was rotated by a motor.

2.3. WASHING OF THE SAMPLE AFTER GRAFTING REACTION

After carrying out the reaction for the required time, the stirring was stopped. The solution in the reaction flask was found to be clear and no precipitated homopolymer (polyacrylonitrile) was observed. The cotton hank was removed quickly from the reaction flask and it was observed that a little quantity of homopolymer was adhering to its surface. Immediately it was washed thoroughly with distilled water to remove loosely held homopolymer. Then the cotton hank was shaken in 250 ml. conical flask for 5 minutes with 100 ml. of 1.0 N nitric acid solution at room temperature. Similarly, it was shaken for another 5 minutes with a fresh quantity of acid. Nitric acid treatment was given to the cotton hank in order to remove any ceric sulphate precipitated as ceric hydroxide during the grafting reaction and held inside the cellulosic material. The sample was made acid-free by repeated washings with distilled water. Then it was washed with methanol and then with acetone and then air-dried.

2.4 REMOVAL OF HOMOPOLYMER (POLYACRYLONITRILE) FROM GRAFTED SAMPLE

Dimethyl formamide was used as a solvent for the removal of homopolymer formed inside the cotton hank during

the grafting reaction. The grafted sample was shaken with 100 ml. of pure dimethyl formamide in a 250 ml. well-stoppered conical flask for about 24 hours at room temperature. The flask was shaken by a microid flask shaker. The shaking of the sample with fresh quantities of solvent was continued until the solvent was free of any homopolymer. Presence of even a small quantity of homopolymer in the solvent can be detected by adding excess methanol to a small portion of solvent, in which case the homopolymer precipitates. Usually it takes 8-10 days with several fresh charges of dimethyl formamide for the complete removal of the homopolymer.

Alternatively, the homopolymer can also be extracted with dimethyl formamide in a soxhlet apparatus in vacuum (98°C/45mm.) under anhydrous conditions until the extract is free of solute. To avoid any yellowing of the sample, it was always desirable to avoid high temperatures and hence extraction at room temperature was preferred, even though it was time consuming.

2.5 ESTIMATION OF PERCENTAGE GRAFTING

There are three reliable methods to estimate the percentage grafting. They are (i) gravimetric, (ii) volumetric, and (iii) chemical analysis (nitrogen content determination by Kjeldahl's method).

In the present work, gravimetric method was adopted but to confirm the correctness of the results so obtained, estimation for a few samples was also carried out by the

other two methods. The results obtained by all the three methods were found to be in good agreement.

2.5.1 Gravimetric method

The untreated sample was dried at 40°C and 20 mm. pressure in a vacuum oven and weighed accurately, as mentioned earlier. The final weight of the sample after grafting reaction was computed after the complete removal of the adhering homopolymer by extracting with dimethyl formamide at room temperature until the washings no longer gave any turbidity when poured into excess of methanol. Before taking the final weight, the sample was dried thoroughly at 40°C and 20 mm. pressure in vacuum, as usual. The drying, cooling and weighing of the sample was repeated until a constant weight was obtained. The degree of grafting was calculated, as follows:

Weight of the untreated sample = w_1 gms.

Weight of the sample after grafting and removal of homopolymer = w_2 gms.

Increase in weight (due to grafting) = $(w_2 - w_1)$ gms

% increase in weight i.e. % grafting .. = $\frac{w_2 - w_1}{w_1} \times 100$

As the cotton absorbs moisture very quickly, the weight of the sample before and after the grafting reaction should be taken under identical conditions.

2.5.2 **Volumetric method**

About 0.5 gm. of the grafted cellulose and 20 ml. of 10% sodium hydroxide solution were placed together in a 100 ml. conical flask. A few pieces of unglazed porcelain were added, a reflux water condenser was fitted and the contents were boiled gently for about 20 minutes. The flask was cooled and the sample was washed with 10% sodium hydroxide solution, distilled water, sulphuric acid solution (1%) and finally with distilled water before drying thoroughly.

$$\text{Cell --CN} + \text{NaOH} + H_2O \longrightarrow \text{Cell -- COONa} + NH_3$$

$$\text{Cell --COONa} \xrightarrow{\text{sulphuric acid}} \text{Cell -- COOH}$$

The nitrogen content of this grafted and saponified sample was estimated by Kjeldahl's method to check whether all the -CN groups were converted into -COOH groups or not. No nitrogen was found in the saponified sample and hence it was assumed that under the above mentioned reaction conditions, all the -CN groups were converted into -COOH groups.

To the grafted and saponified sample, 50 ml. of $\frac{N}{10}$ sodium hydroxide solution was added and stirred well for 10 minutes. Then 10 ml. of solution was taken from the above mixture and titrated against $\frac{N}{10}$ sulphuric acid using phenol-phthalien as an indicator. The carboxyl content of the saponified sample was estimated and from the carboxyl content, the percentage grafting was

calculated as follows:

Weight of the grafted sample = w gms.

10 ml. of the alkali solution = v ml. of $\frac{N}{10}$ acid

Carboxyl content of the grafted and saponified sample = (50-5v) ml. $\frac{N}{10}$ acid

$= \frac{10-v}{2000}$ equivalents

(Correction is to be made in the volume of v for the carboxyl content of the grafted sample without saponification by carrying out a blank experiment)

w gms. of the grafted cellulose contains $\frac{10-v}{2000}$ equivalents of -(COOH) groups after hydrolysis.

Since each unit of acrylonitrile in the grafted chain, produces one equivalent of -(COOH), w gms. of the grafted product contains $\frac{10-v}{2000}$ units of acrylonitrile, i.e. w gms. of the grafted product contains $\frac{10-v}{2000}$ x 53 gms. of polyacrylonitrile where 53 is the molecular weight of acrylonitrile.

Weight of the cellulose before grafting = $w - \frac{53(10-v)}{2000}$ gms.

$w - \frac{53(10-v)}{2000}$ gms. of cellulose is grafted with $\frac{(10-v)}{2000}$ x 53 gms. of polyacrylonitrile.

$\therefore$ Percentage grafting $= \frac{5300\ (10-v)}{2000\ w-53(10-v)}$

For every sample, three readings were taken each time taking about 0.5 gm. of the sample. The average of the three readings was taken and the percentage grafting was calculated.

2.5.3 Chemical analysis (Kjeldahl's method)

The nitrogen content of the grafted sample was estimated by Kjeldahl's method. About 50 mg. of the sample was digested with 5 ml. of concentrated sulphuric acid (A.R.grade) in presence of 1 gm. catalyst mixture (1 gm. of selenium, 1 gm. cupric sulphate pentahydrate, 20 gms. of potassium sulphate finely powdered and mixed). The mixture was heated over a micro burner, boiled gently for 5 minutes and vigorously for 45 minutes. The liquid was cooled and diluted with 10 ml. of distilled water. 20 ml. of 40% sodium hydroxide was carefully added and the Kjeldahl's flask was quickly connected to the distillation apparatus. A 100 ml. conical flask containing 25 ml. of 0.04 N HCl was used as a receiver of the distillation apparatus. The contents of the Kjeldahl's flask were distilled with steam for 45 minutes. The distilled ammonia was absorbed in excess acid. The excess acid was titrated with 0.04 N sodium hydroxide. A blank was also carried out.

v_1 = Vol. of 0.04 N HCl consumed in determination

v_2 = Vol. of 0.04 N HCl consumed in blank experiment

w = Weight in mg. of the sample taken

$$\% \text{ nitrogen} = \frac{100(v_1 - v_2) \times 0.5603}{w}$$

$$\% \text{ of acrylonitrile in the grafted sample} = \% \text{ of nitrogen} \times \frac{53}{14}$$

(where 53 is the molecular weight of acrylonitrile)

$$\therefore \text{ Weight of cellulose} = 100 - \% \text{ of nitrogen} \times \frac{53}{14}$$

i.e. $(100 - \%\text{ of nitrogen} \times \frac{53}{14})$ of cellulose contains $(\%\text{ of nitrogen} \times \frac{53}{14})$ of acrylonitrile.

100 gms. of cellulose contains.... $\frac{100 \times \%\text{ of nitrogen} \times \frac{53}{14}}{(100 - \%\text{ of nitrogen} \times \frac{53}{14})}$ of acrylonitrile

$$\therefore \%\text{ grafting} = \frac{5300 \times \%\text{ of nitrogen}}{1400 - 53 \times \%\text{ of nitrogen}}$$

2.6 VARIATION OF DIFFERENT PARAMETERS OF GRAFTING REACTION

In order to obtain a maximum degree of grafting on cellulose without damaging the textile properties of the original cellulosic material, the determination of optimum conditions of the grafting reaction is essential.

2.6.1 Acid concentration

The influence of nitric acid concentration on degree of grafting was studied by varying the overall acid concentration in the reaction mixture mainly from 0.4 - 1.0 N. The reaction was carried out at 30°C for 4 hours under the following conditions.

	Acid concentration (N)	Initiator concentration (M)	Monomer concentration (M)
(1)	0.4 - 1.0	0.0250	0.9500
(2)	0.4 - 1.0	0.0250	0.7110
(3)	0.28- 1.0	0.0195	0.5925

The desired final acid concentration was obtained by adding a calculated quantity of 2.0 N nitric acid stock solution. Below 0.4 N acid concentration of the reaction mixture, excessive precipitation of ceric sulphate as ceric hydroxide was noticed and hence the low acid concentrations were mainly avoided. Higher acid concentrations in the reaction mixture above 1.0 N for a considerable period of time may effect the tensile strength of cellulose and hence the maximum acid concentration selected was 1.0 N.

2.6.2 Monomer concentration

The monomer concentration was varied between 0.1185 - 0.950 M. The reaction was carried out at 30°C under the following conditions.

	Monomer concentration (M)	Initiator concentration (M)	Acid concentration (N)	Time (hrs.)
(1)	0.5925 - 0.950	0.0262	0.50	6.0
(2)	0.5925 - 0.950	0.0262	0.50	3.5
(3)	0.1185 - 0.950	0.0195	0.60	4.0

Further increase of monomer concentration is not feasible in view of its limited solubility in water.

2.6.3 Initiator (ceric sulphate) concentration

The initiator concentration was varied between 0.0078-0.0312 M. The reaction was studied at 30°C for 4 hours

at an acid concentration of 0.6 N and at two different monomer concentrations i.e. 0.95 M and 0.711 M. Further increase in the concentration of the initiator did not have much effect on the degree of grafting.

2.6.4 Time

The reaction time was varied from 1-6 hours. The reaction was studied at 30°C, 0.025 M initiator concentration, 0.950 M monomer concentration and at two acid concentrations (0.6 N and 0.4 N). Longer times were considered to be not necessary and keeping the cellulose in acid for longer periods is not desirable.

2.6.5 Temperature

The reaction temperature was varied from 15-40°C. The reaction was studied for 4 hours at 0.025 M initiator concentration, 0.6 N acid concentration and at two monomer concentrations in 0.950 M and 0.711 M.

2.7 CUPRAMMONIUM SOLUBILITY OF GRAFTED SAMPLES

The solubility behaviour of the grafted samples along with the untreated sample in cuprammonium hydroxide solution was tested. The cuprammonium hydroxide solution was prepared by bubbling air over small pieces of metallic copper covered with aqueous ammonia solution. Cuprammonium solution containing 15 gms. of copper and 240 gms. of ammonia per litre was used.

It was noticed that the untreated sample was completely soluble whereas the samples above 15% grafting were insoluble in cuprammonium hydroxide solution under the above mentioned conditions. However, when the percentage grafting is in between 8-10, about 10% solubility was observed.

2.8 PROPERTIES OF GRAFTED SAMPLES

The tensile strength and the resistance to micro-organisms of the samples grafted under various conditions were measured and compared with untreated samples.

2.8.1 Measurement of tensile strength

The grafted and untreated cotton hanks were conditioned at 70°F and 65% R.H. for three days before testing. The breaking strength of the samples was measured on Zweigle machine, Strength Tester No.39, kept in a chamber at 70°F and 65% R.H. 50 cms. length of each sample was tested for 20 seconds under the above conditions and the tensile strength (in gms.) was directly read out on 0-500 gms. scale. The tensile strength of the fibre after grafting with acrylo-nitrile under varied conditions of the experiment - acid, monomer, initiator concentrations and time and temperature was determined and compared with the untreated sample (Tables XV-XIX).

2.8.2 Resistance to microorganisms

The grafted and untreated samples were kindly tested by Defence Research & Development Organisation, Defence Research Laboratory (Materials), Kanpur-4, for the resistance

to microbiological attack. We are very much thankful to them for their assistance.

The grafted samples along with the untreated sample were subjected to tests according to specification No.IND/TC/0279. The following test organisms were used:

i) Pencillium Sp
ii) Aspergillus fumigatus
iii) Aspergillus niger
iv) Chaetomium globosum
v) Memnoniella echinata, and
vi) Rhizopus Sp

Of the above test organisms used, Chaetomium globosum, Aspergillus fumigatus, Memnoniella echinata and Pencillium Sp are cellulolytic fungi, their cellulolytic activity decreasing in that order, the activity of the first organism being very strong. The most widely used organisms for testing in the laboratory are: Chaetomium globosum and Memnoniella echinata.

The microbial resistance of the fibre after grafting with acrylonitrile under different conditions of acid and monomer and time, was studied (Tables XX-XXII).

2.9 RESULTS

The experimental results pertaining to the effect of reaction conditions on degree of grafting, estimation of percentage grafting, influence of grafting reaction on tensile strength of cellulose and resistance of grafted cellulose samples to microorganisms, are included in the following Tables I-XXII. (Fig.1-5).

Table I

Effect of acid concentration on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.950 M
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Nitric acid concentration(N)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.40	1.804	2.712	0.908	50.34
0.50	1.810	2.990	1.180	65.19
0.60	1.813	3.083	1.270	70.04
0.65	1.802	2.974	1.172	65.04
0.70	1.805	2.890	1.085	60.12
0.80	1.833	2.786	0.953	51.99
0.90	1.821	2.725	0.904	49.65
1.00	1.816	2.717	0.901	49.62

Table II

Effect of acid concentration on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.711 M
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Nitric acid concentration (N)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.40	1.806	2.319	0.513	28.41
0.50	1.804	2.467	0.663	36.76
0.60	1.812	2.534	0.722	39.84
0.65	1.808	2.471	0.663	36.67
0.70	1.804	2.416	0.612	33.93
0.80	1.810	2.342	0.532	29.39
0.90	1.815	2.324	0.509	28.04
1.00	1.818	2.327	0.509	28.00

Table III

Effect of acid concentration on degree of grafting

Initiator concentration = 0.0195 M
Monomer concentration = 0.5925 M
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Nitric acid concentration (N)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.28	1.803	2.002	0.199	11.04
0.36	1.806	2.097	0.291	16.12
0.44	1.810	2.182	0.372	20.55
0.52	1.804	2.241	0.437	24.23
0.60	1.812	2.277	0.465	25.66
0.68	1.816	2.217	0.401	22.08
0.76	1.808	2.173	0.365	20.18
0.84	1.805	2.140	0.335	18.56
0.92	1.810	2.137	0.327	18.06
1.00	1.810	2.136	0.326	18.01

Table IV

Effect of monomer concentration on degree of grafting

Initiator concentration = 0.0262 M
Acid concentration = 0.50 N
Total volume = 128 ml
Temperature = 30°C
Time = 6.0 hours

Monomer concentration (mole/litre)	Square of monomer concentration (mole/litre)^2	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.5925	0.351	1.812	2.324	0.512	28.26
0.6517	0.425	1.808	2.425	0.617	34.13
0.7110	0.506	1.816	2.544	0.728	40.09
0.7702	0.593	1.804	2.655	0.851	47.18
0.8295	0.688	1.807	2.794	0.987	54.63
0.8897	0.791	1.812	2.957	1.145	63.19
0.9500	0.902	1.802	3.091	1.289	71.53

Table V

Effect of monomer concentration on degree of grafting

Initiator concentration = 0.0262 M
Acid concentration = 0.50 N
Total volume = 128 ml
Temperature = 30°C
Time = 3.5 hours

Monomer concentration (mole/litre)	Square of monomer concentration $(\text{mole/litre})^2$	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.5925	0.351	1.805	2.103	0.298	16.51
0.6517	0.425	1.803	2.191	0.388	21.52
0.7110	0.506	1.800	2.288	0.488	27.11
0.7702	0.593	1.810	2.418	0.608	33.59
0.8295	0.688	1.813	2.541	0.728	40.15
0.8897	0.791	1.821	2.685	0.864	47.44
0.9500	0.902	1.807	2.803	0.996	55.13

Table VI

Effect of monomer concentration on degree of grafting

Initiator concentration = 0.0195 M
Acid concentration = 0.60 N
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Monomer concentration (mole/litre)	Square of monomer concentration $(\text{mole/litre})^2$	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.1185	0.014	1.814	1.833	0.019	1.047
0.2370	0.056	1.809	1.882	0.073	4.035
0.3555	0.126	1.806	1.971	0.165	9.137
0.4740	0.225	1.812	2.106	0.294	16.220
0.5925	0.351	1.830	2.293	0.463	25.300
0.7110	0.505	1.825	2.490	0.665	36.430
0.8295	0.688	1.803	2.696	0.893	49.530
0.9500	0.902	1.810	2.979	1.169	64.600

Table VII

Effect of initiator concentration on degree of grafting

Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Initiator concentration (mole/litre)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.0078	1.812	2.501	0.689	38.02
0.0102	1.816	2.634	0.818	45.05
0.0126	1.803	2.728	0.925	51.30
0.0156	1.808	2.863	1.055	58.35
0.0195	1.816	2.987	1.171	64.49
0.0216	1.807	2.996	1.189	65.83
0.0234	1.821	3.070	1.249	68.58
0.0250	1.818	3.092	1.274	70.08
0.0273	1.806	3.085	1.279	70.82
0.0312	1.809	3.120	1.311	72.47

Table VIII

Effect of initiator concentration on degree of grafting

Monomer concentration = 0.711 M
Acid concentration = 0.60 N
Total volume = 128 ml
Temperature = 30°C
Time = 4.0 hours

Initiator concentration (mole/litre)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
0.0078	1.802	2.187	0.385	21.36
0.0102	1.810	2.268	0.458	25.30
0.0126	1.808	2.330	0.522	28.87
0.0156	1.805	2.398	0.593	32.86
0.0195	1.823	2.485	0.662	36.34
0.0216	1.817	2.490	0.673	37.04
0.0234	1.809	2.507	0.698	38.59
0.0250	1.822	2.542	0.720	39.51
0.0273	1.811	2.533	0.722	39.87
0.0312	1.813	2.552	0.739	40.76

Table IX

Effect of reaction time on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml
Temperature = 30°C

Time (hrs.)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
1.0	1.802	2.524	0.722	40.05
1.5	1.819	2.682	0.863	47.44
2.0	1.808	2.786	0.978	54.09
2.5	1.806	2.891	1.085	60.09
3.0	1.809	2.966	1.157	63.96
3.5	1.811	3.036	1.225	67.64
4.0	1.807	3.073	1.266	70.08
4.5	1.805	3.097	1.292	71.58
5.0	1.814	3.131	1.317	72.61
6.0	1.820	3.146	1.326	72.85

Table X

Effect of reaction time on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.950 M
Acid concentration = 0.40 N
Total volume = 128 ml
Temperature = 30°C

Time (hrs.)	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
1.0	1.807	2.135	0.328	18.16
1.5	1.803	2.254	0.451	25.01
2.0	1.812	2.402	0.590	32.56
2.5	1.809	2.488	0.679	37.54
3.0	1.815	2.567	0.752	41.43
3.5	1.801	2.642	0.841	46.70
4.0	1.800	2.706	0.906	50.32
4.5	1.817	2.760	0.943	51.90
5.0	1.802	2.760	0.958	53.16
6.0	1.806	2.786	0.980	54.26

Table XI

Effect of temperature on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml
Time = 4.0 hours

Temperature °C	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
15	1.808	3.007	1.199	63.33
20	1.812	3.036	1.224	67.54
25	1.806	3.047	1.241	68.71
30	1.813	3.083	1.270	70.04
35	1.810	3.102	1.292	71.39
40	1.815	3.144	1.329	73.21

Table XII

Effect of temperature on degree of grafting

Initiator concentration = 0.025 M
Monomer concentration = 0.711 M
Acid concentration = 0.60 N
Total volume = 128 ml
Time = 4.0 hours

Temperature °C	Initial weight of cotton hank (gms)	Final weight of cotton hank (gms)	Increase in weight (gms)	% increase in weight (% grafting)
15	1.803	2.452	0.649	35.99
20	1.810	2.505	0.695	38.40
25	1.806	2.512	0.706	39.09
30	1.812	2.534	0.722	39.84
35	1.807	2.541	0.734	40.62
40	1.809	2.562	0.753	41.63

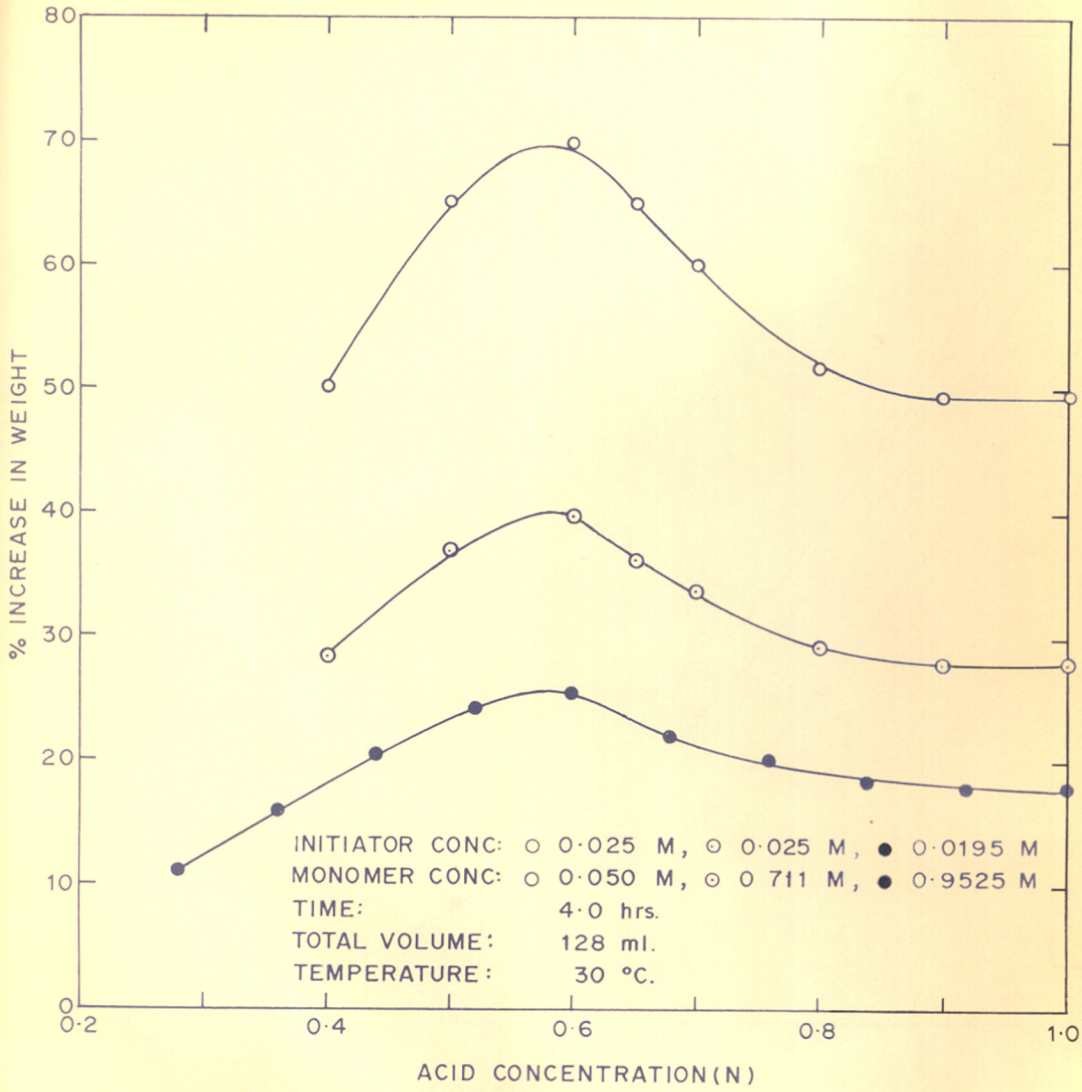

80
70
60
50
40
30
20
10
0
% INCREASE IN WEIGHT
0·2
0·4
0·6
0·8
1·0
ACID CONCENTRATION (N)
INITIATOR CONC: ○ 0·025 M, ⊙ 0·025 M, ● 0·0195 M
MONOMER CONC: ○ 0·050 M, ⊙ 0 711 M, ● 0·9525 M
TIME: 4·0 hrs.
TOTAL VOLUME: 128 ml.
TEMPERATURE: 30 °C.

FIG. 1.

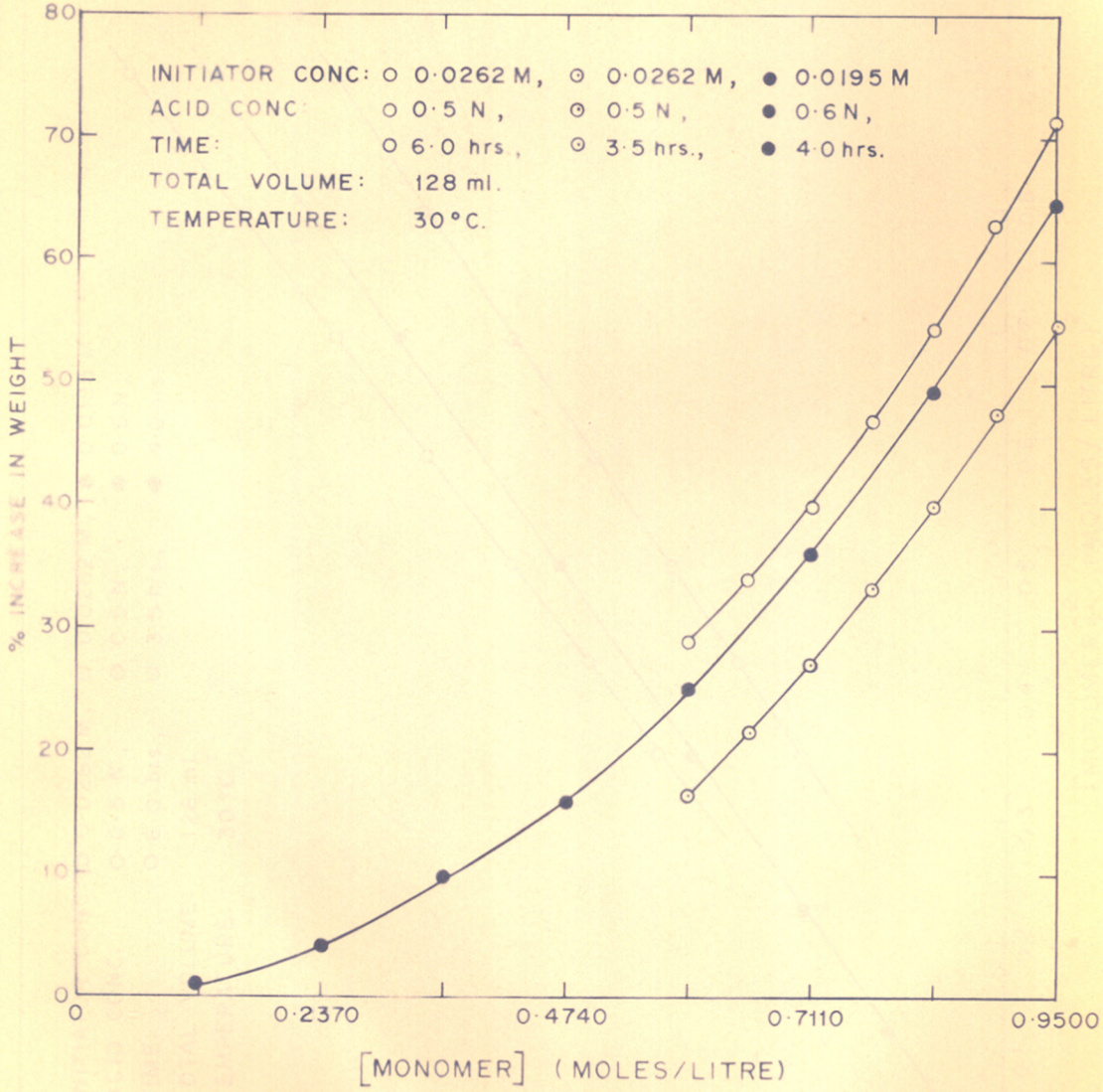

INITIATOR CONC: ○ 0·0262 M, ⊙ 0·0262 M, ● 0·0195 M
ACID CONC: ○ 0·5 N, ⊙ 0·5 N, ● 0·6 N,
TIME: ○ 6·0 hrs., ⊙ 3·5 hrs., ● 4·0 hrs.
TOTAL VOLUME: 128 ml.
TEMPERATURE: 30°C.
% INCREASE IN WEIGHT
80
70
60
50
40
30
20
10
0
0
0·2370
0·4740
0·7110
0·9500
[MONOMER] (MOLES/LITRE)

FIG. 2

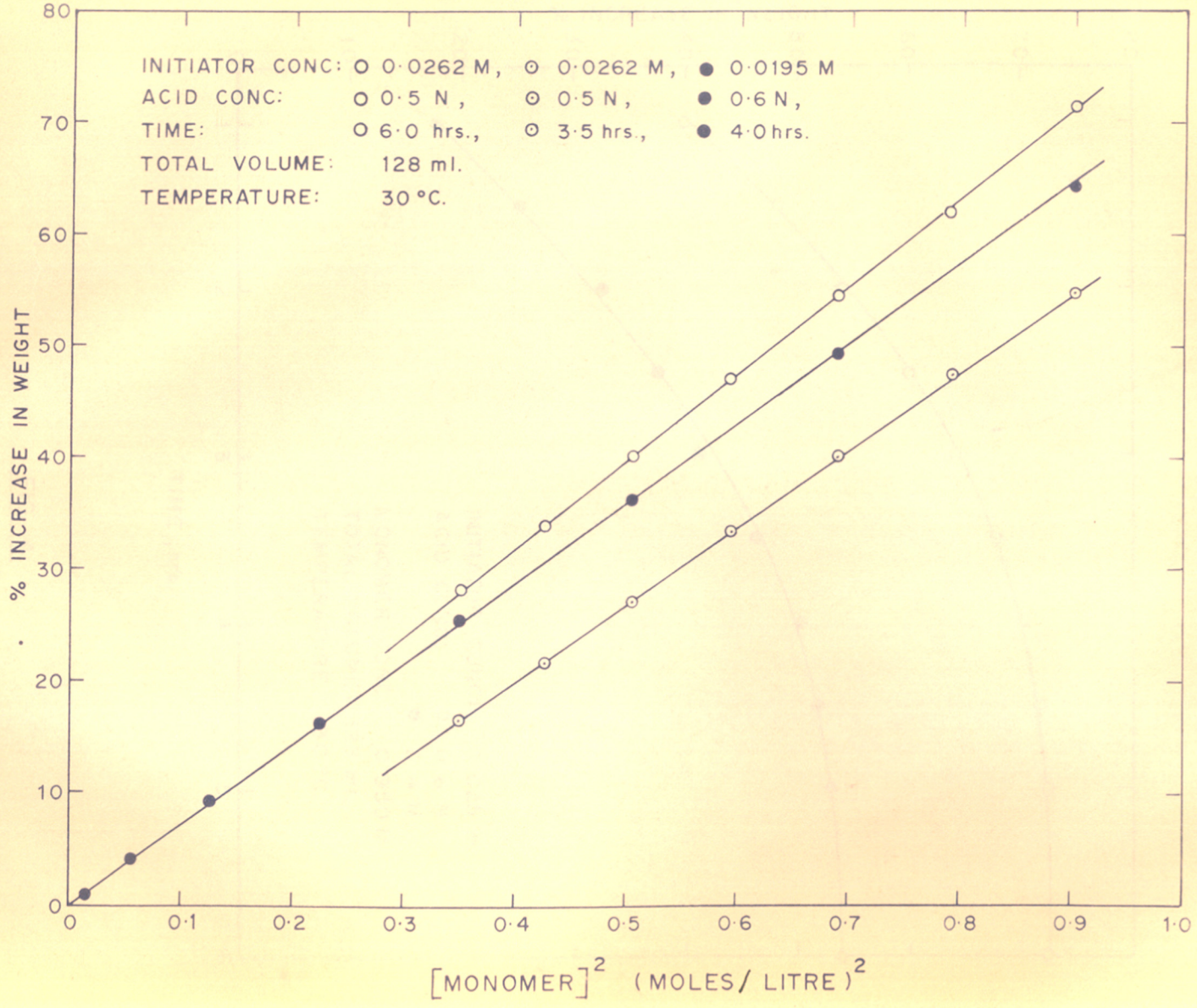

INITIATOR CONC: ○ 0·0262 M, ⊙ 0·0262 M, ● 0·0195 M
ACID CONC: ○ 0·5 N, ⊙ 0·5 N, ● 0·6 N,
TIME: ○ 6·0 hrs., ⊙ 3·5 hrs., ● 4·0 hrs.
TOTAL VOLUME: 128 ml.
TEMPERATURE: 30 °C.
% INCREASE IN WEIGHT
0
10
20
30
40
50
60
70
80
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
[MONOMER]² (MOLES/ LITRE)²

FIG. 3

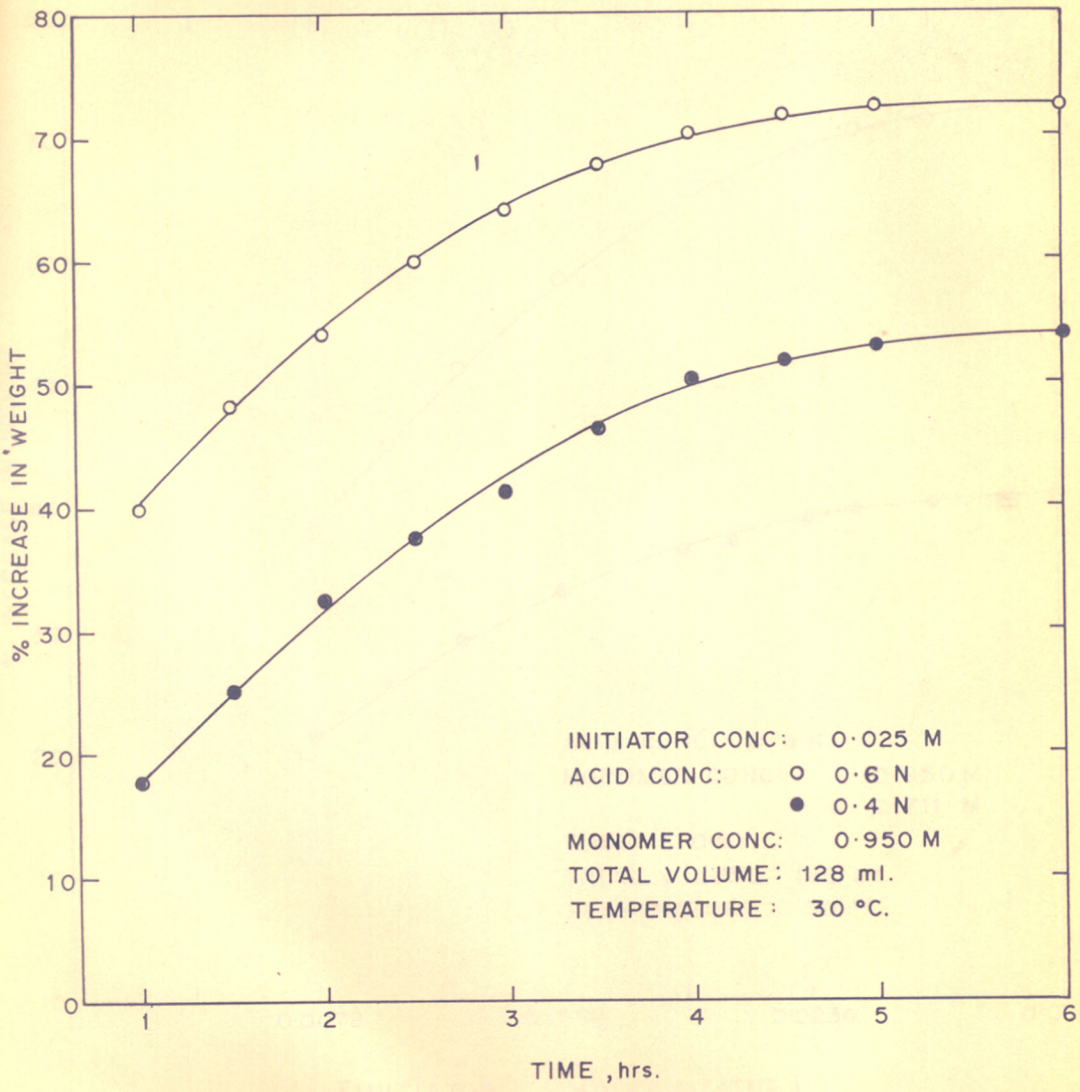

80
70
60
50
40
30
20
10
0
% INCREASE IN WEIGHT
1
INITIATOR CONC: 0·025 M
ACID CONC: ○ 0·6 N
● 0·4 N
MONOMER CONC: 0·950 M
TOTAL VOLUME: 128 ml.
TEMPERATURE: 30 °C.
1
2
3
4
5
6
TIME , hrs.

FIG. 4

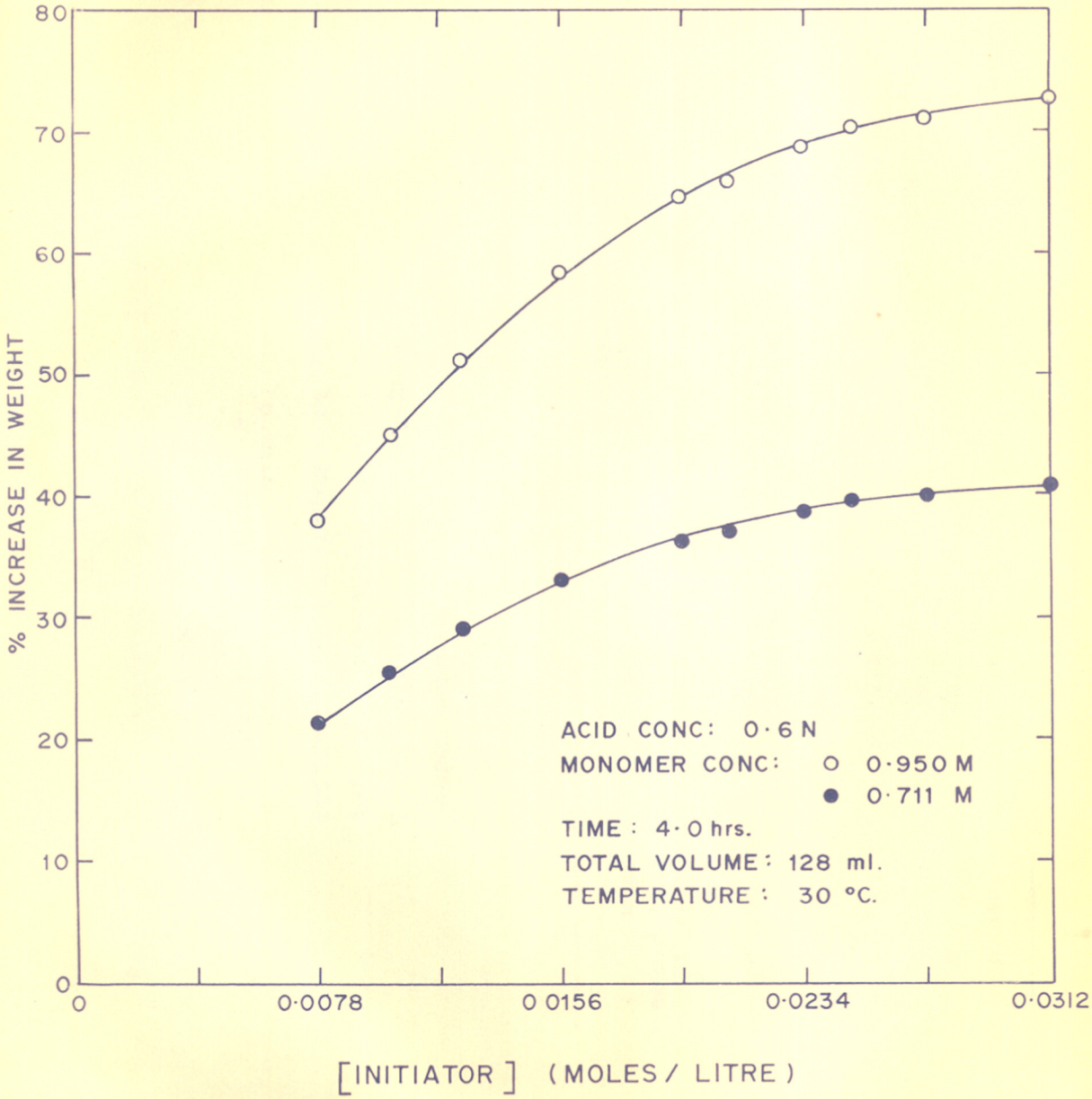

80
70
60
50
40
30
20
10
0
% INCREASE IN WEIGHT
0
0·0078
0 0156
0·0234
0·0312
[INITIATOR] (MOLES / LITRE)
ACID CONC: 0·6 N
MONOMER CONC: ○ 0·950 M
● 0·711 M
TIME : 4·0 hrs.
TOTAL VOLUME : 128 ml.
TEMPERATURE : 30 °C.

FIG. 5.

Table XIII

Comparison of the degree of grafting as estimated by:

i) Gravimetric method
ii) Volumetric method
iii) Nitrogen analysis
(Kjeldahl's method)

Initiator concentration = 0.0195 M
Acid concentration = 0.60 N
Total volume = 128 ml.
Temperature = 30°C
Time = 4.0 hours
Weight of the cotton hank = 1.817 ± 0.017 gms.

Monomer concentration (mole/litre)	% grafting as estimated by		
	Gravimetric method	Volumetric method	Nitrogen analysis
0.2370	4.035	4.008	3.892
0.3555	9.137	9.103	8.987
0.4740	16.220	16.010	15.860
0.5925	25.300	25.060	24.830
0.7110	36.430	36.070	35.860
0.8295	49.530	49.120	49.010
0.9500	64.600	64.210	64.030

Table XIV

Comparison of the degree of grafting as estimated by:

i) Gravimetric method
ii) Volumetric method
iii) Nitrogen analysis (Kjeldahl's method)

Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml.
Temperature = 30°C
Time = 4.0 hours
Weight of cotton hank = 1.817 ± 0.017 gms.

Initiator concentration (mole/litre)	% grafting estimated by		
	Gravimetric method	Volumetric method	Nitrogen analysis
0.0156	58.35	58.04	57.85
0.0195	64.49	64.21	64.02
0.0216	65.83	65.49	65.08
0.0234	68.58	68.13	67.76
0.0250	70.08	69.63	69.21
0.0273	70.82	70.36	69.85
0.0312	72.47	71.92	71.31

Table XV

Effect of acid concentration on tensile strength

Initiator concentration = 0.025 M

Monomer concentration = 0.950 M

Total volume = 128 ml.

Temperature = 30°C

Time = 4.0 hours

Weight of the cotton hank = 1.817 ± 0.017 gms.

Tensile strength of hank= 320 gms.
(count 28s)

Nitric acid concentration (N)	% grafting	Tensile strength in (gms)	% increase or decrease in tensile strength
0.40	50.34	390	(+) 21.88
0.50	65.19	386	(+) 20.63
0.60	70.04	380	(+) 18.75
0.65	65.04	365	(+) 14.06
0.70	60.12	334	(+) 4.37
0.80	51.99	282	(-) 11.88
0.90	49.65	236	(-) 26.25
1.00	49.62	180	(-) 43.75

Table XVI

Effect of monomer concentration on tensile strength

Initiator concentration = 0.0262 M
Acid concentration = 0.50 N
Total volume = 128 ml.
Temperature = 30°C
Time = 3.5 hours
Weight of the cotton hank = 1.817 ± 0.017 gms
Tensile strength of hank (count 28s) = 320 gms.

Monomer concentration (mole/litre)	% grafting	Tensile strength (gms)	% increase or decrease in tensile strength
0.5925	16.51	340	(+) 6.25
0.6517	21.52	348	(+) 8.75
0.7110	27.11	355	(+) 10.94
0.7702	33.59	363	(+) 13.44
0.8295	40.15	370	(+) 15.63
0.8897	47.44	376	(+) 17.50
0.9500	55.13	382	(+) 19.37

Table XVII

Effect of initiator concentration on tensile strength

Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml.
Temperature = 30°C
Time = 4.0 hours
Weight of the cotton hank = 1.817 ± 0.017 gms.
Tensile strength of hank (count 28s) = 320 gms.

Initiator concentration (mole/litre)	% grafting	Tensile strength (gms)	% increase or decrease in tensile strength
0.0126	51.30	370	(+) 15.63
0.0156	58.35	372	(+) 16.25
0.0195	64.49	375	(+) 17.19
0.0216	65.83	376	(+) 17.50
0.0234	68.58	378	(+) 18.12
0.0250	70.08	380	(+) 18.75
0.0273	70.82	372	(+) 16.25
0.0312	72.47	361	(+) 12.81

Table XVIII

Effect of time on tensile strength

Initiator concentration = 0.025 M

Monomer concentration = 0.950 M

Acid concentration = 0.60 N

Total volume = 128 ml.

Temperature = 30°C

Weight of the cotton hank = 1.817 ± 0.017 gms

Tensile strength of hank (count 28s) = 320 gms.

Time (hrs.)	% grafting	Tensile strength (gms)	% increase or decrease in tensile strength
1.0	40.05	392	(+) 22.50
2.0	54.09	390	(+) 21.88
3.0	63.96	386	(+) 20.63
4.0	70.08	380	(+) 18.75
5.0	72.61	304	(-) 5.00
6.00	72.65	195	(-) 39.06

Table XIX

Effect of temperature on tensile strength

Initiator concentration = 0.025 M
Monomer concentration = 0.950 M
Acid concentration = 0.60 N
Total volume = 128 ml.
Time = 4.0 hours
Weight of the cotton hank = 1.817 ± 0.017 gms.
Tensile strength of the hank (count 28s) = 320 gms.

Temperature °C	% grafting	Tensile strength in (gms)	% increase or decrease in tensile strength
15	63.33	396	(+) 23.75
20	67.54	392	(+) 22.50
25	68.71	387	(+) 20.94
30	70.04	380	(+) 18.75
35	71.39	369	(+) 15.31
40	73.21	350	(+) 9.37

Table XX

Effect of acid concentration on resistance of the grafted sample to microorganisms

Initiator concentration	= 0.025 M
Monomer concentration	= 0.950 M
Total volume	= 128 ml.
Temperature	= 30°C.
Time	= 4.0 hours
Weight of the cotton hank	= 1.817 ± 0.017 gms.

Acid concentration (N)	% grafting	Resistance to microorganisms	% increase or decrease in tensile strength
Untreated sample:		Profuse fungal growth	
0.70	60.12	Show slight fungal growth	(+) 4.37
0.80	51.99	Show slight fungal growth	(-) 11.88
0.90	49.65	Show slight fungal growth	(-) 26.25
1.00	49.62	Show moderate fungal growth	(-) 43.75

Table XXI

Effect of time on resistance of the grafted sample to microorganisms

Initiator concentration	= 0.025 M
Monomer concentration	= 0.950 M
Acid concentration	= 0.60 N
Total volume	= 128 ml.
Temperature	= 30°C
Weight of the cotton hank	= 1.817 ± 0.017 gms.

Time (hrs.)	% grafting	Resistance to microorganisms.	% increase or decrease in tensile strength
4.0	70.08	Do not show any fungal growth	(+) 18.75
5.0	72.61	Show slight fungal growth	(-) 5.00
6.0	72.65	Show moderate fungal growth	(-) 39.06
6.0*	71.53	Show moderate fungal growth	(-) 36.02

* Acid concentration = 0.50 N
Monomer concentration = 0.0262 M

Table XXII

Effect of monomer concentration on resistance of the grafted sample to microorganisms

Initiator concentration	= 0.0195 M
Acid concentration	= 0.60 N
Total volume	= 128 ml.
Temperature	= 30°C
Time	= 4.0 hours
Weight of the cotton hank	= 1.817 ± 0.017 gms.

Monomer concentration (mole/litre)	% grafting	Resistance to microorganisms.	% increase or decrease in tensile strength
0.1185	1.047	Show slight fungal growth	-
0.2370	4.035	Show very slight fungal growth	(+) 2.50
0.3555	9.137	Show very slight fungal growth	(+) 5.31
0.5925	25.300	Do not show fungal growth	(+) 9.69

CHAPTER-III.

D I S C U S S I O N

3.0 The main object of the present work is to investigate the optimum conditions to get maximum percentage grafting without affecting the textile properties of cellulose. All possible parameters such as acid, monomer and initiator concentrations and time and temperature, have been varied and the results are presented in Tables I-XII and in Figures 1-5. From these results, it is evident that the percentage grafting is dependent on all the variable parameters. But the influence of acid and monomer CONCENTRATIONS on the reaction is remarkable and affects the percentage grafting to a great extent. The effect of the parameters on the reaction is discussed in detail.

3.1. EFFECT OF REACTION CONDITIONS ON DEGREE OF GRAFTING

3.1.1 Effect of acid

The effect of acid concentration was studied by keeping the reaction time for four hours at 0.025 M initiator concentration and 0.95 M monomer concentration (Table I). The acid concentration was varied from 0.4 N - 1.0 N. The percentage grafting increases with an increase in acid concentration upto 0.6 N and with further increase in acid concentration, the percentage grafting decreases. From 0.6 - 0.8 N acid concentration, a decrease of percentage grafting (70.04 - 49.62) is noticeable above which it has not much effect on the reaction. In another set of experiments (Table II),

the same effect was observed by varying the monomer concentration from 0.95 M - 0.711 M and keeping the other ~~variable~~ factors constant.

In another set of experiments (Table III) the effect of acid concentration on the reaction was studied from 0.28 N - 1.0 N. The reaction was carried out for four hours which was the same for the above two sets of experiments, but the initiator and monomer were kept at lower concentrations and the results in grafting were similar to the previous experiments.

In all the experiments, the maximum percentage grafting was obtained at 0.6 N acid concentration (Fig.1). The low acid concentration (about 0.3 N) is not preferable because of the hydrolysis of ceric ions. At higher acid concentrations the tensile strength of the cellulose decreases (Table XV) and hence it is not preferable to keep acid concentrations above 0.6 N.

The system ceric-nitric acid has a redox potential of 1.61 compared to that of ceric-sulphuric acid system (1.44). Hence grafting was carried out in nitric acid medium.

It is generally known that the ceric ion forms various species with anions depending upon acid concentration. The species present at 0.6 N nitric acid concentration might be favouring the complex formation with cellulose which further initiates the graft polymerization. Richards et al[85] also studied the effect of acid concentration on degree of grafting of acrylonitrile onto paper using ceric ammonium

nitrate as initiator. They observed maximum percentage of grafting at 0.25 N sulphuric acid.

3.1.2 Effect of monomer

The effect of monomer concentration on the grafting reaction was studied varying its concentration from 0.1185 - 0.95 M at acid concentrations of 0.5 and 0.6 N, which was found to be the most suitable range. In one set of experiments, the reaction was carried out for six hours keeping the initiator and acid concentrations at 0.0262 M and 0.5 N respectively (Table IV, Fig.2). In these experiments, it was observed that the percentage grafting was proportional to the monomer concentration. The same effect was noticed even when the reaction was conducted only for 3½ hours (Table V). In another set of experiments, the reaction was carried out for 4 hours at the initiator and acid concentrations of 0.0195 M and 0.6 N respectively (Table VI), for which the effect was found to be similar. Because of the solubility limitations of the monomer in water (7.35% at 20°C) its maximum concentration employed was 0.95 M. In all the experiments, an interesting phenomenon is observed that the percentage grafting is directly proportional to the square of the monomer concentration (Fig.3).

3.1.3 Effect of initiator

The effect of initiator concentration on the grafting reaction was studied varying its concentration from

0.0078 - 0.0312 M. In one set of experiments, the reaction was carried out for 4 hours, keeping the monomer and acid concentrations at 0.95 M and 0.6 N respectively (Table VII). In these experiments, it was noticed that an increase in initiator concentration upto 0.025 M increases the percentage of grafting to a marked extent, above which the percentage increase of grafting is comparatively less. The same effect was noticed even when the reaction was conducted at 0.711 M monomer concentration (Table VIII).

It is generally believed that the termination of free radicals during oxidation of cellulose and of growing polymer chains during grafting, occurs through conversion of Ce^{4+} ions to Ce^{3+} ions. Hence it is expected that the ceric ions not only initiate but also terminate the graft polymerization and homopolymerization of acrylonitrile. High ceric ion concentration may increase the percentage grafting but at the same time it may favour the formation of more homopolymer.

Katai et al[88] have derived a relationship for the rate of polymerization in an ethylene glycol-acrylonitrile-ceric ion system, according to which the rate of polymerization is inversely related to the ceric ion concentration. They have also indicated the possibility of using this system as typical of what may be used if it is desired to graft a water insoluble polymer onto cellulose. Although the initial rate of polymerization may be higher at low ceric ion concentration, the subsequent rate may slow down due to

exhaustion of ceric ions in the reaction bath. Hence avoiding of very high and very low ceric ion concentrations is preferred and optimum concentration is 0.025 M.

3.1.4 Effect of time

The effect of time on the grafting reaction was studied varying its period from 1 to 6 hours. In one set of experiments, the reaction was carried out keeping the initiator, monomer and acid concentrations at 0.025 M, 0.95 M and 0.6 N respectively (Table IX). In these experiments, it was found that the percentage grafting was progressively increasing with time. When the reaction time was increased from 1-4 hours, the percentage grafting increased from 40.05 to 70.08. But when the reaction time was further increased to 6 hours, the percentage grafting was only 72.85. Hence it is clear from these experiments that the increase of reaction time beyond 4 hours increases the percentage grafting to a negligible extent. The same effect was noticed even when the reaction was carried out at 0.4 N acid concentration (Table X). As the reaction proceeds, conversion of monomer takes place, thereby decreasing its concentration in the reaction bath. As the percentage grafting is directly proportional to the square of the monomer concentration, further increase in reaction time decreases the rate of graft polymerization.

The samples are found to have an increase in tensile strength when grafted for 4 hours at 0.6 N acid concentration.

If the reaction was carried out for more than 4 hours, a loss in tensile strength was observed (Table XVIII). The decrease in tensile strength may be attributed to prolonged contact of cellulose with nitric acid. Hence a reaction time of 4 hours is preferred.

3.1.5 Effect of temperature

The grafting reaction was carried out by varying the temperature from 15-40°C. In one set of experiments, the reaction was carried out for 4 hours at various temperatures, keeping the initiator, monomer and acid concentrations at 0.025 M, 0.950 M and 0.6 N respectively (Table XI). The percentage grafting was found to increase very slightly with increase of temperature. The same effect was noticed even when the reaction was carried out at 0.711 M monomer concentration (Table XII). When the grafting reaction was carried out at higher temperatures, the strength of the cellulose was found to decrease (Table XIX).

As the influence of monomer concentration on the degree of grafting is greater than that of ceric ion concentration, it is desirable to ~~start~~ conduct the reaction at high monomer concentration. Due to the limited solubility of the monomer in water, its maximum concentration was kept at 0.95 M and in all the experiments, a material to liquor ratio of about 1:70 was maintained; total volume being 128 ml.

Conclusion

In the light of the above observations, in regard to the effect of different parameters on the degree of grafting, it may be concluded that about 70% grafting can be attained by maintaining the following reaction conditions:

Initiator concentration	= 0.025 M
Monomer concentration	= 0.950 M
Acid concentration	= 0.60N
Time	= 4.0 hours
Total volume	= 128 ml.
Temperature	= 30°C.

3.2 ESTIMATION OF PERCENTAGE GRAFTING

The percentage increase in weight of samples was taken as percentage grafting. It is believed that the increase in weight was due to grafting only and not due to homopolymer of acrylonitrile. The accuracy of this method was checked by estimating the percentage grafting for a few samples by volumetric analysis and nitrogen estimation (Kjeldahl's method) and the results were found to be in good agreement (Tables XIII and XIV).

3.3 PROOF OF GRAFTING

A number of methods are available for establishing whether a given polymeric material is a graft polymer or a mechanical mixture of the two homopolymers, even though most of them are not completely satisfactory. The exact

method to be employed for a particular system will, however depend on the characteristics of the constituent polymers.

In general, the product obtained by the grafting reaction will be made up of a mixture of the unreacted backbone polymer, the graft polymer and the pure homopolymer of the monomer used for grafting. The first method involves in employing suitable solvent-nonsolvent mixture for fractional precipitation, or selective extraction if the backbone and side chain polymers have widely different solubility characteristics. The graft polymer, thus, isolated can be characterised by comparison of its properties either with the ungrafted backbone, pure side chain polymer or a mechanical mixture of the latter two.

Secondly, if the graft polymer thus isolated can be brought into solution in a suitable solvent system, a measure of its average molecular weight by osmometry or light scattering will conclusively prove that grafting has taken place, if its molecular weight is much higher than that of the backbone.

If in a graft polymer, the grafted side-chains are linked to the backbone by easily hydrolysable groups like ester, amide etc. it becomes possible to indirectly prove the grafting by a comparison of the properties of the grafted sample before and after the breaking up of the link. Especially the solubility characteristics of the latter, which is only a mechanical mixture of the two polymeric parts, will be quite different from that of the graft polymer.

Unfortunately, for the present system of cellulose grafted with polyacrylonitrile, none of the above methods is applicable. For, the cellulose backbone is a highly insoluble material requiring inorganic complexing agents like cuprammonium hydroxide for dissolving it. Polyacrylonitrile is also a difficultly soluble material, being insoluble in any of the common solvents and soluble to a certain extent only in dimethyl formamide or dimethyl sulfoxide. Consequently, their graft polymer is a completely insoluble substance.

It is quite difficult to completely extract out the homopolymer of acrylonitrile from the grafted cotton hanks even with dimethyl formamide, since the homopolymer may be present (deposited) inside the fibres. Hence, it is impossible to conclude prima facie that repeated extraction with dimethyl formamide alone will completely remove the homopolymer of acrylonitrile. Similarly, solubility characteristics in cuprammonium hydroxide solution are also inconclusive. For example, cellulose with an increase in weight of 15% or more due to grafting, is found insoluble in this system; but this can as well be due to the entanglement of the polyacrylonitrile chains with the cellulose fibres as due to chemical grafting. At lower polyacrylonitrile content, lesser entanglement and hence easier extraction with dimethyl formamide can be expected. A product of this type containing about 10% of polyacrylonitrile, is found to be partially soluble in cuprammonium hydroxide. Perhaps, this is due to the presence of some unreacted cellulose in

the product, which has gone into solution, together with the graft polymer of very low polyacrylonitrile content.

A reliable method, as described below, has been established for proving that grafting has taken place and also for its quantitative determination.

The grafted product, after thorough extraction with dimethyl formamide, is saponified by treatment with 10% sodium hydroxide solution (see p.37 for the procedure). Thus, all the nitrile groups present in the polyacrylonitrile side chain, as well as in the residual homopolymer of acrylonitrile is converted to the -COONa groups. The resultant product is a mixture of cellulose grafted with polyacrylic acid together with pure polyacrylic acid, both in their sodium salt form. Since the polyacrylic acid is readily soluble in alkali, its complete dissolution in the sodium hydroxide solution can be expected, especially since the cellulose fibres are fully swollen in the alkali, facilitating diffusion of the occluded homopolymer to the solvent phase. The pure grafted products can hence be isolated by filtration and washing with 10% alkali solution, water, 1% sulphuric acid solution and finally with distilled water. The estimation of its -COOH content by the volumetric titration method conclusively proves that about 99% of the acrylonitrile present is chemically grafted, the rest (about 1%) perhaps being the residual homopolymer (Tables XIII and XIV).

3.4 THE MECHANISM OF GRAFTING REACTION

The mechanism of oxidation by ceric ion was studied extensively by many workers. Mino and Kaizerman[68] pointed out that oxidation of alcohols by Ce^{4+} in acid medium proceeds by intermediate complex formation between Ce^{4+} and alcohol, which decomposes, giving Ce^{3+} and alcohol with a free radical:

$$Ce^{4+} + RCH_2OH \rightleftharpoons (Ce\ RCH_2OH)$$

Complex

$$\xrightarrow{K_d} Ce^{3+} + H^+ + RCH_2O^{\cdot}\ (R\dot{C}HOH)$$

The rate determining step is the dissociation of the ceric-alcohol complex[61,71,72]. The free-radical in the alcohol molecule initiates vinyl polymerization. If a polymeric substrate such as cellulose, polyvinyl alcohol etc. is used as a reducing agent, the free-radical created on the polymeric backbone initiates graft polymerization of a vinyl monomer.

Study of model compounds analogous to cellulose structure[69] e.g. trans-1,2-cyclohexanediol (containing 1,2 glycol units) and glucose (containing hemiacetal unit) indicated that oxidation of Ce^{4+} occurred most rapidly when glucose was a reducing agent. Since cellulose molecule contains hemiacetal unit at the ends, it was observed that oxidation by Ce^{4+} occurred easily at the ends of the cellulose molecule, at the site of hemiacetal units in

addition to oxidation at 1,2 glycol units.

Wallace and Young[84] recently carried out a detailed kinetic study of grafting of acrylamide initiated by ceric nitrate-dextran polymeric redox systems. The sustrate dextran closely resembles cellulose in structure and like cellulose, it is composed of glucoside units. The following mechanism was given:

$$Ce(X)_6 + R \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \text{Complex} \xrightarrow{K_d}$$

$$R^{\cdot} + Ce(X)_4 + 2X + H^+$$

where X is either OH^- or NO_3^- ions or water molecules. R represents the substrate (dextran), and $R^{\cdot}$ the polymeric free radical formed. The polymeric free radical formed initiates graft polymerization.

$$R^{\cdot} + M \xrightarrow{K_i} RM^{\cdot}$$

$$R\,Mn^{\cdot} + M \xrightarrow{K_p} R\,Mn_{+1}\,I^{\cdot}$$

Termination of the growing graft polymer occurs by ceric ions:

$$Ce\,(X)_6 + R\,Mn^{\cdot} \xrightarrow{K_t} \underset{\text{(dead)}}{\text{Graft polymer}} + Ce(X)_4 + 2X + H^+$$

The equilibrium constant K_{eq} for the complex formation between ceric ion and dextran was 3.0 ± 1.6 l/mole and the decomposition rate constant of the complex:

$$K_d = 3.0 \pm 1.2 \times 10^{-4} \text{ sec}^{-1}.$$

From the kinetic scheme, the K_p/K_t ratio for the grafting reaction was evaluated and found to be equal to 0.44 ± 0.15.

The foregoing discussion based on the kinetic studies of graft polymerization of vinyl monomers onto polymeric substrates like glucose, dextran etc. initiated by Ce^{4+} ions in acid medium leads to the conclusion that a similar mechanism is operating in the system cellulose-acrylonitrile-Ce^{4+} in the present study. In all probability the following mechanism may be presumed to be operating.

$$Ce(X)_6 + \text{Cellulose} \underset{}{\overset{K}{\rightleftharpoons}} \text{Ceric-cellulose complex}$$

$$\downarrow K_d$$

$$\text{Cell-}CH_2O^{\cdot} \text{ (or Cell-}\dot{C}HOH) + Ce(X)_4 + 2X + H^+$$

$$\text{Cell-}CH_2O^{\cdot} + M \xrightarrow{K_i} \text{Cell-}CH_2O - M^{\cdot}$$

$$\downarrow K_p \; M$$

$$\text{Cell} - CH_2O-(M)-M^{\cdot}$$

$$\downarrow K_p \; M$$

$$\text{Cell-}CH_2O-(M)_{n-1} - M^{\cdot}$$

$$\downarrow K_t \; Ce(X)_6$$

$$\text{Cell-}CH_2O-M_n + Ce(X)_4 + 2X + H^+$$

where X is either OH^- or NO_3^- or water,

K, the equilibrium constant for complex formation between cellulose and ceric ions,

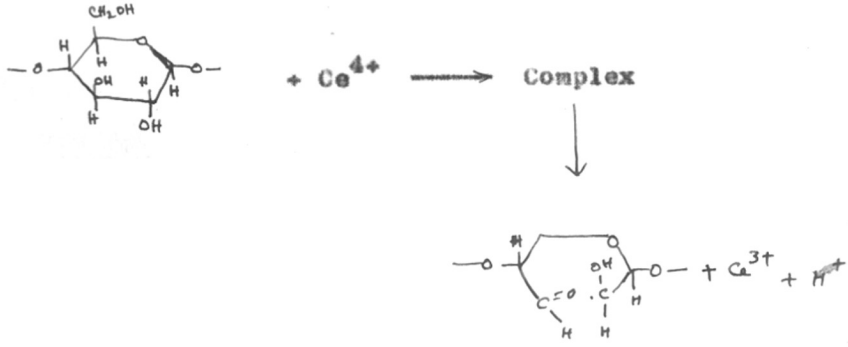
K_d, the dissociation constant of the above complex,

K_i, K_p and K_t the rate constants for the initiation, propagation and termination of the grafting reaction respectively,

M, acrylonitrile molecule.

Apart from the extent of grafting, the concentration of the initiator (ceric ion) will also influence the number and length of the polyacrylonitrile side chains. It is obvious that higher concentrations of the initiator will lead to greater number of grafting sites at the cellulose backbone and the build up of shorter chains since the ceric ion participates in the termination reaction as well. At lower ceric ion concentrations, we can expect less number of grafted chains of greater length.

The location of the site of grafting on the cellulose backbone is also of interest. There are at least two views on this issue. Terasaki et al[86] are of the opinion that the most reactive region in cellulose is the C_1-O- linkage in the end unit of the chain which is initially oxidised. Rogovin et al[87], however conclude that the reaction proceeds as follows, at the body of the chain also and not necessarily at the ends alone.



It is however known that the hydroxyl groups present in the amorphous regions of cellulose are more susceptible to grafting. Hence the extent of grafting depends on the degree of crystallinity which in turn depends on the nature of cellulose used. Further, grafting of vinyl monomers onto cellulose can be achieved without degradation of cellulose, and therefore this method is superior to the grafting method by radiation.

3.5 THE INFLUENCE OF GRAFTING REACTION ON TENSILE STRENGTH OF CELLULOSE

The tensile strength of the grafted cotton hanks and a standard hank (untreated cotton hank) was measured under the same conditions. The results were tabulated in Tables XV to XIX. On the whole, in most of the samples, an increase in the tensile strength of about 18-20% was noticed. But some reaction conditions of grafting affected the strength of the fibre and sometimes instead of an increase in strength, a drastic decrease in tensile strength was noticed.

Of all the reaction conditions of grafting, the acid concentration and reaction time influence the strength of cellulose to a marked extent. For instance, an increase in acid concentration upto 0.6 N even though increases percentage grafting, reduces the percentage increase in tensile strength. Further increase in acid concentration (i.e. above 0.7 N) results only in loss of tensile strength (refer Table XV).

The increase in reaction time upto 4 hours, resulted in the increase of degree of grafting, decreasing the percentage increase in tensile strength. When the reaction time was 5 hours or more, loss in tensile strength was noticed (Table No.XVIII). This behaviour may be attributed to the prolonged contact of the sample with acid.

An increase in reaction temperature increases the degree of grafting to a minor extent, but reduces the percentage increase in tensile strength. This may be due

to the increase in the reactivity of acid with cellulose (Table No.XIX).

An increase in the initiator concentration (ceric sulphate) upto 0.025 M increases both degree of grafting and tensile strength. Further increase in ceric sulphate concentration results in, only a slight increase of degree of grafting and considerable reduction in increase of tensile strength (Table No.XVII). It is desirable to maintain a low ceric ion concentration during grafting reaction keeping in view that ceric salts are very powerful oxidising agents.

The increase of monomer concentration results in an increase in the degree of grafting and tensile strength (Table No.XVI). The increase in tensile strength is attributed to the increase in degree of grafting because monomer as such has no effect on the strength of cellulose.

Hence it can be concluded that the tensile strength of the grafted cellulose is not only dependent on the degree of grafting but also on the reaction conditions under which the degree of grafting is obtained. Higher acid and initiator concentrations, longer reaction times and higher temperatures should be avoided in order to have a definite improvement in tensile strength.

3.6 RESISTANCE OF THE GRAFTED CELLULOSE SAMPLES TO MICROORGANISMS

The resistance of the grafted cotton hanks along with the untreated cotton hanks to different microorganisms

(page 44) was tested and the results are presented in Tables XX-XXII. The untreated cotton hanks when subjected to the attack of test organisms, showed profuse fungal growth, whereas to a similar attack, some of the grafted hanks showed very good resistance. In general, the resistance of the grafted hanks to microorganisms is dependent both on the degree of grafting and the reaction conditions. Another observation was that when there was a decrease in tensile strength, the resistance of the grafted hanks to the microorganisms was limited.

As the acid concentration increases above 0.7 N in the grafting reaction, there is a loss in tensile strength and not much resistance to microorganisms was observed.

It seems the degree of grafting is not the only criterian for the microbial resistance. Though the degree of grafting increases with increase of time, there is a considerable decrease in tensile strength and microbial resistance (Table XXI). Even with a low degree of grafting, (about 10%) good resistance to microorganisms can be obtained (Table XXII).

From the above observations, it can be concluded that high degree of grafting is not essential to make cellulose resistant to microbial attack. In fact about 25% grafting is sufficient to make cellulose completely resistant to microbial attack, provided high acid concentrations (above 0.6 N) and longer periods of reaction (above 4 hours) are avoided.

3.7 CONCLUSION

By the detailed study of cellulose-acrylonitrile-ceric ion system, it has been possible to establish a convenient method for modifying cellulose by grafting with polyacrylonitrile. The standardised conditions are:

Ceric sulphate concentration	0.025 M
Acrylonitrile concentration	0.950 M
Nitric acid concentration	0.60N
Time	4.0 hours
Temperature	30°C
Weight of cotton hank: total volume	1:70

Under these conditions, a product containing $\sim$70% of polyacrylonitrile grafted to the cellulose is obtained having no deleterious effect on the fibre structure. Its tensile strength is enhanced by about 20% and there is remarkable resistance to microorganisms unlike pure cotton.

The experimental technique is very simple and scaling up of the process does not present much difficulties. No costly equipment is required, the reaction being carried out at room temperature in a closed vessel under nitrogen, with gentle shaking. The direct utility of the product in the field of textiles remains to be worked out keeping in view the improvement in the tensile strength and the resistance to rot. The latter property suggests that the product is especially suitable for high altitude military tents etc. where the resistance to soil and humid climate is essential.

However, a few other applications can also be envisaged by suitable modifications of the product or by modifying the grafting process itself. As already shown, grafted product can be completely saponified with alkali and the resulting polyacrylic acid side chains incorporate certain ion exchange properties to the fibre, which behaves as a weakly acidic ion exchanger. Hence, there is a potential for employing fabrics made out of this as filter cloth for fruit juice refining where the cloth will act as deioniser as well.

The nitrile groups in the polyacrylonitrile side chains can also be partially hydrolysed under controlled conditions to amide-($-CONH_2$) groups. On partial conversion of the nitrile groups to amides and reaction with formaldehyde the product will contain both the amide groups condensed with formaldehyde to give crease recovery and the nitrile groups to give resistance to microbial attack. The same product can also be prepared by using a mixture of acrylamide and acrylonitrile monomers for the grafting reaction.

It may also be added that fairly high solubility of acrylonitrile in water (7.35% at 20°C and 7.9% at 40°) enables the grafting reaction to be conducted in aqueous medium. The properties of the reinforced cellulose fibre may also be studied using other water soluble monomers like acrylamide, vinyl pyridine etc.

It is needless to say that a more uniform blending of the properties of both the constituents may be achieved

by graft polymerization than by mechanical blending of the two fibres. For example, cellulose fibre, when grafted with polyacrylonitrile, gets reinforced, the properties of polyacrylonitrile fibre such as greater dimensional stability, press retention, wrinkle recovery, soft feel, pleasing texture, resistance to heat, moisture and micro-organisms etc. being incorporated into cellulose. The properties of the reinforced cellulose depend on the degree of grafting as well as on the length and number of grafts and other factors.

CHAPTER-IV

R E F E R E N C E S

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