CHAPTER I

GRAFT COPOLYMERIZATION ONTO JUTE AND FLAX FIBERS

" A SHORT REVIEW "

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INTRODUCTION :

The shortage of oil and natural gas has been reflected in shortages and spiraling prices for polymers based on petrochemical resources. Providentially, such polymers may be in part replaced by lignocellulosic materials that are the most abundant and most economical organic renewable resources available. In their natural state as wood and plant fibers and as the principal constituent used in the manufacture of paper, textile fibers and many other industrial products, lignocellulosic materials will continue to be fundamental to human welfare. Lignocellulosic materials are eternally renewable raw materials that can be used in their polymeric form without degradation. However, their properties and performance must be improved before they can compete with petrochemically derived synthetic polymers. Many new techniques for improving the competitive position of lignocellulosic materials are available. The grafting of vinyl monomers onto lignocellulosic fibers is one of these techniques [ 1 ]. Grafting reactions provide a versatile route for significantly altering the physical, mechanical, chemical and biochemical properties of substrate
polymers. Grafting possesses great potential for tailoring material properties to specific end uses. The improvement in properties that has been achieved by natural and synthetic polymers and fibers through graft copolymerization include; improved tensile strength, rot-resistance, dyeuptake ability, abrasion resistance, thermal stability, electrical conductance, adhesion to a variety of substances, improved wash and wear rating, wrinkle recovery angle, bacteriocidal and fungicidal properties, settability, wettability, biocompatibility, etc. [1 - 3].

Lignocellulotic fibers like jute and flax are the most abundant renewable, agricultural raw materials that are easily transformed into multifarious products affecting every phase of our daily life due to their wide applications as clothing, housing and industrial products [ 4,5 ]. Although jute fibers possess high dimensional stability certain unfavourable textile properties like high stiffness, very low elasticity, susceptibility towards sunlight and
certain chemical reagents etc. have tremendously limited its use [6]. Similarly even though flax fibers have long since been used for manufacture of certain cloths and ropes but these materials do not have significant durability. Further flax fibers have low elasticity, poor dyeuptake ability and are susceptibility towards common chemical reagents such as mineral acids and alkalis [4,5] which have somewhat limited their uses in the textile field. With a view to minimizing such undesirable properties of both the fibers and simultaneously to improve their effectiveness for intensified textile uses graft copolymerization onto these fibers are now been tried. The present author has also paid much interest in upgrading the textile properties of these two natural lignocellulosic fibers and in this thesis includes the results of her studies on graft copolymerization of vinyl monomers onto jute and flax fibers using chemical method of initiation, involving non-metal and metal ion initiators like Potassium Peroxydisulphate \((K_2S_2O_8)\), Potassium monopersulphate \((KHSO_5)\), and Ceric ion Ce (IV) and the changes in textile properties
imparted by the grafted fibers. In this connection she feels it essential to outline a comprehensive up to date review on chemical methods of initiation of graft copolymerization of vinyl monomers onto the aforesaid fibers and the changes in textile properties of the grafts reported by various workers.

**REVIEW ON JUTE FIBERS**

Recently Mohanty [7] has reviewed various methods of grafting of vinyl monomers onto jute fibers. The various methods of grafting reported by him are radiation initiation, photochemical initiation and chemical methods of initiation involving metal and non-metal ion oxidisers. However, the author feels that such review is not up to date so far as the chemical methods of initiation is concerned. Irrespective of the number of methods available for affecting graft copolymerization of vinyl monomers onto jute fibers the chemical method of initiation has attracted the attention of the researchers in recent years because of the selectivity of the systems in affecting graft
copolymerization, and exclusion of concurrent formation of homopolymers in most of the systems.

**CERIC ION SYSTEM:**

Ceric ion initiation of graft copolymerization onto preformed polymers is the most promising and practical method. It was first proposed by Mino and Kaizerman in 1958. These authors found out that certain ceric salts such as nitrate and sulphate form very effective redox systems when coupled to organic reducing agents such as alcohols. The oxidation and reduction produces cerousion and transient organic free radical species capable of initiating vinyl polymerization [8]. The mechanistic path leading to the formation of transient free-radicals was proposed by Duke and co-workers [9,10], who suggested intermediate complex formation between the organic substrates and the ceric ion. The complex subsequently disproportionates in an unimolecular fashion to free radical species. In the case of alcohols the reaction can be written as;
Ce(IV) + R - CH₂ - OH → [Ceric alcohol complex] → Ce(III) + H⁺ + R - CH - OH OR (R - CH₂ - O)

If a polymeric reducing agent is employed, such as cellulose and the oxidation with ceric ion is conducted in the presence of vinyl monomers, graft copolymer formation will occur. This method of grafting of vinyl monomers onto cellulosic substrates were extended by Stanette and co-worker [11]. By using this technique in both aqueous and emulsion system, Mino & co-workers were also able to graft acrylonitrile, acrylamide and methyl acrylate onto cellulose [12]. Ceric ion initiated graft copolymerization of vinyl monomers onto cellulose, cellulose derivatives and lignocellulose has recently been reviewed by Samal and co-workers [13]. The authors have elaborately discussed the conditions leading to maximum graft yield, the mechanism of graft initiation and termination and the improved properties of the grafts for many individual systems. Mehta and co-workers [14] have reported ceric ion initiated graft copolymerization of Acrylonitrile (AN) onto defatted and bleached jute fibers.
The effect of initiator concentration, temperature, lignin content, monomer concentration, and reaction time on the extent of grafting has been studied. The author could notice that the extent of lignin content in jute fibers was responsible for affecting grafting of acrylonitrile onto it. For instance, with a lowering of lignin content from 14 to 1.8% grafting increases to a maximum of 45%. However, a further decrease in lignin content did not increase percentage of grafting. The graft yield also increases with the increase of other reaction parameters. Haque and co-workers [15] have reported the graft copolymerization of methyl methacrylate onto both defatted and bleached jute fibers using ceric ammonium sulfate as the initiator. In order to obtain the optimum conditions for grafting, the effect of initiator concentration, temperature, time of reaction, lignin content of jute and monomer concentration was studied. Under optimum reaction condition, the maximum percent grafting and grafting efficiency were found to be 13.2% and 0.71 respectively. Kinetic study showed that at 0.03 M of ceric ammonium sulfate the reaction appeared to
be second order process. The activation energies were 7.74 and 5.12 K cal/mole, for defatted (lignin content 15.7%) and chlorite bleached (lignin content 10%) jute respectively. The activation energies in the graft copolymerization of methyl methacrylate onto jute fibers were compared with the energies of activation in graft copolymerization of acrylonitrile onto the same fibers. Haque and Habibuddowla [16] have studied the tenacity of methyl methacrylate grafted jute fibers prepared by ceric ion initiation method. The tensile strength of methyl methacrylate grafted jute fibers were determined and compared with those of the ungrafted fibers. For chlorite bleached jute with lignin content of 4.6% and graft yield of 6%, the tenacity decreased by $\s\ \text{G}_{0.3} \text{g/denier}$ whereas for chlorite bleached jute with lignin content of 10.85% and graft yield 38.5%, the tenacity increased by $\s\ \text{G}_{0.40} \text{g/denier}$. When the lignin content gradually decreased from 15% to 11% there was a sharp fall in tenacity from 2.5 g/denier to 0.46 g/denier. However, decreasing the lignin content from 11% to 5% did not considerably decrease the tenacity with the final tenacity
being 0.39 g/denier. Dutta and co-worker [17] have studied the tensile properties of Jute-g-poly (acrylonitrile) graft copolymer prepared by using ceric ammonium sulfate as the initiator. Habibuddowla [18] has studied the grafting of methyl methacrylate onto both bleached and defatted jute fibers using ceric ammonium sulfate as the initiator under variable reaction conditions and has determined the tensile modulus at-break of the grafts. It has been observed that so far as the tensile modulus at-break (stiffness) is concerned the bleached jute fibers showed decreased in stiffness. In case of defatted jute fibers increasing of grafting temperature from 30th 50°C reduces tensile modulus at-break (stiffness). With bleached jute fibers irregularities of tensile modulus (stiffness) was observed when grafting was carried out from 30th 50°C. The overall results showed that the effect of grafting of methyl methacrylate on the tensile properties of the jute fibers was rather obscure to propose any definite mechanism. Singh et. al. [19] have reported ceric ion/hippuric acid redox initiated graft copolymerization of acrylonitrile
onto jute fibers. The effect of time, temperature, concentration of monomer, metal ion (Ce⁴⁺), hippuric acid, sulphuric acid and amount of jute fibers on graft yield were studied. IR spectra of chemically modified bleached jute and grafted jute was taken and their characteristics bands were identified. More than 90% graft yield was achieved in the present system. Varma and Murali [20] have reported the ceric ion initiated graft copolymerization of methyl methacrylate onto jute fibers at variable reaction conditions with a view to impart significant hydrophobicity to the fibers. The grafted fibers were used for the fabrication of hybrid composites with glass fibers and unsaturated polyster resins and the properties of composites were evaluated and compared. Grafted jute fibers based composites had better tensile, flexural and interlaminar shear strength than those composites fabricated using unreacted jute fibers. Das, Nayak, Das, Mishra and Singh [21] have reported the influence of Dimethyl sulfoxide on the ceric ion initiated graft copolymerization of acrylonitrile onto jute fibers. The effect of concentration
of monomer, Ce(IV), DMSO, HNO\textsubscript{3} and reaction time and temperature on the grafting reaction was studied. The optimum condition leading to high graft yield was established. The grafting mechanism has also been suggested.

**Mechanism:**

In a system containing jute fibers, ceric ion and monomer, the following reaction mechanism has been proposed by most of the authors.

1. **Complex formation:**

   \[ \text{J - H} + \text{Ce(IV)} \stackrel{k}{\rightleftharpoons} \text{J - H} \rightarrow \text{Ce(IV) complex} \]

   (where \( \text{J - H} = \text{Jute} \) and \( \text{J - h} \rightarrow \text{Ce(IV)} = \text{Ceric Jute complex.} \))

2. **Jute Radical Generation:**

   \[ \text{J - H} \rightarrow \text{Ce(IV)} \xrightarrow{k_r} \text{J} + \text{Ce(III)} + \text{H}^+ \]
3. Initiation :

   a) \[ J + M \xrightarrow{k_i} J - M \] (Initiation of grafting)

   Where, \( M \) = Vinyl monomer.

   b) \[ \text{Ce(IV)} + M \xrightarrow{k_i} \text{M} + \text{Ce(III)} + \text{H}^+ \]

   (Initiation of homopolymerization)

4. Propagation :

   a) \[ J - M + nM \xrightarrow{k_p} J - M_{n+1} \] (Propagation of grafting)

   b) \[ \text{M} + m\text{M} \xrightarrow{k_p} \text{M}_{m+1} \] (Propagation of homopolymerization)

5. Termination :

   a) \[ J - M_{n+1} + \text{Ce(IV)} \xrightarrow{k_{t1}} \text{Graft-copolymer} + \text{Ce(III)} + \text{H}^+ \]

   b) \[ \text{M}_{m+1} + \text{Ce(IV)} \xrightarrow{k_{t2}} \text{Homopolymer} + \text{Ce(III)} + \text{H}^+ \]

   c) \[ J - M_{n+1} + J - M_{m+1} \xrightarrow{k_{t3}} J - M_{(n+m+2)} - J \]
6. Oxidation:

\[ \text{J} + \text{Ce(IV)} \underset{k_0}{\overset{\text{Oxidized product} + \text{Ce(III)} + \text{H}^+}{\longrightarrow}} \]

**QUINQUEVALENT VANADIUM (V\textsuperscript{+5}) SYSTEM**

In a quantitative survey, Waters and Littler [22] reported the oxidation of a multitude of organic substrates (alcohols, acids, aldehydes, ketones, amines etc.) by Quinquevalent vanadium V (v) in aqueous sulfuric acid. Most such oxidation were found to proceed through a free radical path that effectively initiates vinyl polymerization [23 - 27]. Further quinquevalent vanadium has a similar affinity towards polymeric substrates containing characteristic pendant groups (-OH, -CHO, -CONH\textsubscript{2}, -NH\textsubscript{2}, -SH, -COOH etc.) on their backbone. Interaction of V(V) with such groups forms free-radical sites on the polymer backbone. These macroradicals attack vinyl monomers at the immediate vicinity, resulting in the formation of graft copolymers without simultaneous formation of homopolymers as has been
reported by Rogovin and co-worker [28] in the synthesis of dialdehyde cellulose - g - poly (acrylonitrile), polyacrylamide - g - poly (2 - methyl - 5 vinyl pyridine). Polymethacrolein - g - poly (acrylonitrile) a cellulose derivative containing aromatic amine-g-poly (acrylonitrile) etc. Quinquevalent Vanadium (V$^{+5}$) initiated graft copolymerization of vinyl monomers onto cellulose, cellulose derivative and lignocellulose have recently been reviewed by Samal et. al. [13]. Initiation of graft copolymerization of vinyl monomers onto lignocellulosics substrates like jute involving quinquevalent vandium (V$^{+5}$) as initiator has been reviewed by Mohanty [7]. The present review includes the work cited by Mohanty and in addition it also includes the recent reports on (V$^{+5}$) ion initiated graft copolymerization of vinyl monomers onto jute fibers. Singh and co-workers [29 – 30] have reported graft copolymerization of methyl methacrylate and acrylonitrile onto jute and chemically modified jute fibers, initiated by quinquevalent vanadium (V$^{+5}$) / organic substrate redox systems. In their studies on (V$^{+5}$) / Cyclohexanone system initiated graft copolymerization of methyl methacrylate onto jute fibers [29] the authors have reported the effect of concentration of monomer, acid, (V$^{+5}$), reaction time and
temperature on graft yield. The effect of some organic solvents and inorganic salts on the graft yield were also investigated. The optimum condition leading to high percent grafting were also determined by the authors. A suitable reaction mechanism was put forth by the authors and various kinetic rate expressions has also been derived. More than 100% grafting could be achieved by this system. Secondly in their studies on $V^{+5}$ / cyclohexanol redox system initiated graft copolymerization of methyl methacrylate onto jute fibers [30] the authors have investigated the effect of reaction time, concentration of $V^{+5}$, MMA, cyclohexanol, sulfuric acid, amount of jute fibers and reaction temperature on graft yield. The effects of some organic solvents and inorganic salts on the graft yield were also studied. A grafting mechanism was proposed and kinetic rate expressions were derived. Grafting improved the thermal stability and light fastness of jute fibers dyed with basic dyes. More than 170% graft yield could be achieved with the present system. In another report of $V^{+5}$ / cyclohexanol redox initiated graft copolymerization methyl methacrylate onto modified jute fibers [31], the authors have given a
comparative account of grafting onto various jute substrates. They observed that the high lignin content of natural jute was responsible for low grafting yield. The softening of jute fibers however after removal of certain impurities and lignin enhanced grafting considerably. In their recent report [32] of V$^{+5}$ / cyclohexanone redox initiated graft copolymerization of acrylonitrile onto acetylate jute, the authors have studied the effect of reaction time, temperature, concentration of V$^{+5}$, monomer, cyclohexanone, on the percent grafting. The effect of organic solvents and inorganic salts on percentage of grafting were also studied. The IR spectra of acetylated and grafted jute was taken and their characteristic bands were indentified. Grafting improved the thermal stability and also the light fastness rating of jute fibers dyed with basic dyes.

MECHANISM :

In a system containing V$^{+5}$, monomer, organic substrate and jute fibers; V$^{+5}$ may interact with the organic substrate (R) to form a complex that dissociates in a unimolecular
fashion giving rise to primary free radicals. These radicals along with \( V^{+5} \), abstracts hydrogen from the jute to yield free radical sites on its fiber backbone to which monomer addition takes place resulting in graft initiation. The termination of the growing grafted chains may be due to interaction with \( V(v) \) primary radical (\( R' \)) and through mutual combination of growing grafted chains on neighbouring matrix in jute.

**PRIMARY RADICAL FORMATION:**

1. \[ V^{+5} + R \xrightarrow{k} \text{complex} \xrightarrow{k_d} R' + V^{+4} + H^+ \]
   
   (\( R = \text{Organic substrate} \))

2. Jute radical formation:
   
   a) \( JH + R' \xrightarrow{k_f} J' + RH \)
   
   Where \( JH = \text{Jute molecule} \)

   b) \( J - H + V(v) \xrightarrow{k_i} \text{complex} \xrightarrow{k_d} J' + V(IV) + H^+ \)

3. Initiation:
   
   \( J' + M \xrightarrow{k_i} JM' \)
4. Propagation:

\[ J M^* + M \xrightarrow{k_p} J M_n' \]

\[ J M_{n-1}^* + M \xrightarrow{k_p} J M_n \]

5. Termination:

a) \[ J M_n^* + V^{5+} \xrightarrow{k_{t1}} \text{Graft copolymer} + V(IV) + H^+ \]

b) \[ J - M_n^* + R^* \xrightarrow{k_{t2}} \text{Graft copolymer} \]

c) \[ J - M_n^* + J - M_m \xrightarrow{k_{t3}} J - M_{n+m} - J \]

6. Oxidation:

\[ J^* + V^{5+} \xrightarrow{k_0} \text{Oxidation product} + V(IV) + H^+ \]

Permanganate System:

Permanganate ion is one of the most versatile oxidising agents and the oxidation of a multitude of inorganic and organic substrates involving this ion has been reviewed.
by Stewart [33]. Permanganate ion when coupled to suitable organic substrates forms effective redox systems which smoothyl initiate vinyl polymerization [34 - 54]. However, scanty reports on the use of this ion as the initiator of graft copolymerization are available. The use of permanganate ion for graft copolymerization has been reported by Toyo Rayon Co. [55]. Tiechmann and co-workers have reported permanganate ion initiated graft copolymerization acrylonitile [56,57], ethylacrylate [58] and acrylamide [57,59] onto viscose and cotton fibers. Graft copolymerization of vinyl monomers onto modified cotton using permanganate ion as initiator have also been reported [60].

Even though the above few reports on permanganate ion initiated graft copolymerization of vinyl monomers onto some cellulosic fibers are available but the review of the literature reveals that only two reports are available on the use of this ion as the initiator for graft copolymerization of vinyl monomers onto jute fibers. Singh and co-workers [61] have reported the kinetics of graft
copolymerization of methyl methacrylate onto jute fibers using KMnO₄ / Malonic acid redox system as the initiator. The authors have studied the effect of the concentration of malonic acid, monomer, KMnO₄, reaction temperature and time on the graft yield. The effect of some organic solvents and inorganic salts on graft yield have also been investigated. The mechanism of graft copolymerization have been proposed and various kinetic rate expressions have been derived. The graft copolymers have been characterized by thermal analysis.

Tripathy and co-workers [62] have reported grafting of methyl methacrylate onto jute fibers initiated by KMnO₄. The effect of concentration of KMnO₄, MMA, Mineral acid, reaction time and temperature on the percent grafting was studied. The reaction follows a second order kinetics. The activation energy for the system was found to be 4.434 Kcal/mole. The grafted fibers were characterized by TG, and DT analysis. The grafting however did not improve the mechanical properties of jute fibers.
PERSULPHATE ($S_{2}O_{8}^{2-}$) SYSTEM:

The persulphate ion is known to act as a strong oxidising agent in aqueous solution. Persulphate, either alone or with activators has been extensively used as an initiator of vinyl polymerization [63 - 70]. However, the use of persulphate ion redox system for initiation of graft copolymerization of vinyl monomers onto lignocellulosic substrate was recognised in 1963. Persulphate ion initiated graft copolymerization of vinyl monomers onto cellulose, cellulose derivatives and lignocellulosic substrates has been reviewed by Samal et al [13]. Only a few reports reviewed by Mohanty [7] are available on the use of persulphate ion as the initiator of graft copolymerization of vinyl monomers onto jute fiber. Singh and co-workers [71] have reported the graft copolymerization of methyl methacrylate onto jute fibers initiated by $S_{2}O_{8}^{2-}$/ thiourea redox system. The authors have studied the effect of concentration of monomer, $S_{2}O_{8}^{2-}$, thiourea, reaction time and
temperature on graft yield. The effects of some organic solvents and inorganic salts on graft yield were also investigated. The mechanism of graft copolymerization has been suggested. The graft copolymers were characterized by IR and thermogravimetric analysis. Grafting improved the light fastness on jute fibers dyed with basic dydes. More than 200% of graft yield could be achieved with the present initiating system.

Ghosh and co-workers [72] have studied the improvement in rot-resistance and dyeability of methyl methacrylate grafted raw, dewaxed and phenol formaldehyde treated simple and oxidised jute fibers. The grafting was initiated by photochemical method involving $K_2S_2O_8$ as the radical generating species and maleic anhydride or methacrylic acid as co-monomers. The grafting reaction was studied under varying concentration of monomer, initiator, reaction time. Nature of the chemically modified fiber on the extent of grafting was also investigated. The grafted samples exhibited 80-90% of rot resistance and nearly 80% dye fixation. The
authors also tested the washing fastness and light fastness properties of dyed fibers. All these properties for various samples of jute fibers were examined and results have been compared.

**FENTON'S REAGENTS \([\text{H}_2\text{O}_2/\text{Fe(II)}]\) SYSTEM:**

Evans and his school \([64,73]\) observed the potentiality of Fenton's reagent \([\text{FeSO}_4 / \text{H}_2\text{O}_2]\) as an effective redox initiator for vinyl polymerization where \(\text{OH}\) radical is known to be a chain initiating species. The mechanism of this redox reaction is primarily due to Haber and Weiss \([74,75]\). Various aspects of Fenton's reagents initiated vinyl polymerization has been reviewed by Mishra \([76]\). The use of Fenton's reagent \("\text{H}_2\text{O}_2 / \text{Fe(II)}"\) as an effective pair for grafting of vinyl onto preformed macromolecules was reported for the first time by Rogovin and co-workers \([77 - 81]\). Those authors \([81]\) and Ogiwara et. al. \([82]\) suggested that the decomposition of hydrogen peroxide by Ferrous ion \((\text{Fe}^{+2})\) is a typical redox reaction for producing...
OH radical that initiated grafting.

\[
\text{HO - OH + Fe(II) } \rightarrow \text{Fe(III) + OH + OH}
\]

The OH radical so formed may abstract hydrogen atom from the cellulosic substrates and creates grafting sites, to which monomer addition takes place. Fenton's reagent \([H_2O_2/Fe(II)]\) initiated graft copolymerization of vinyl monomers onto cellulose, cellulose derivatives and lignocellulosic substrates has been reviewed by Samal and co-workers [13]. However, the above review seems not to include Fenton's reagent [Fe(ii)/H\(_2\)O\(_2\)] initiated graft copolymerization of vinyl monomers onto jute fibers.

Hebeish and co-workers [83] have studied the effect of various jute components like water soluble materials, waxes, peptins, lignin, hemi-cellulose and \(\alpha\)-cellulose on graft copolymerization of methyl methacrylate, styrene and acrylonitrile onto this fiber initiated by Fenton's reagent \([H_2O_2/Fe^{+2}]\) at 80°C. It was observed that water soluble materials, pectins, and lignin accelerated graft
copolymeryization of these monomers during the initial stage. Grafting decreased the tensile strength and imparted rot proofing properties to the substrates. Singh and co-workers [84] have reported graft copolymerization of acrylonitrile onto chemically modified jute fibers initiated by Fent ions's reagent. The authors have studied the effect of reaction time, temperature, concentration of $\text{H}_2\text{O}_2$, $\text{Fe}^{+2}$, Acrylonitrile (AN), amount of jute fibers and acid on percentage of grafting. The effect of some organic solvents and inorganic salts on the grafting reaction has also been investigated. Singh, Mohanty and Das have also reported the grafting of methyl methacrylate [85] and Acrylonitrile [86] onto jute and chemically modified jute fibers initiated by Fenton's reagent $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$. Defatted, delignified, ethylene diamine treated and zinc chloride treated jute fibers were subjected to grafting at varying concentration of the monomers initiator and catalysts. The graft yield increased with increase in methyl methacrylate concentration from 0.094 M to 0.47 M and then decreased. Increase of $\text{H}_2\text{O}_2$ concentration beyond 0.088 M resulted in decrease
in graft yield. The graft yield increases on increasing the Fe(II) concentration from 0.0025 to 0.075 M and then decreased. The maximum graft yield was obtained at 40°C for reaction, time 2 hours. The role of solvent on the grafting reaction has been reported. In acrylonitrile grafting [86] the authors have studied the grafting reaction at varying concentration of H₂O₂, Fe(II), AN, at a number of temperatures for various time intervals. The graft yield increases for reaction time upto 4 hours at 40°C for H₂O₂ = 0.132 M, Fe(II) = 0.025 M and at fixed monomer concentration. However, the graft yield under the above condition increases with increase in monomer concentration.

The mechanism of graft copolymerization has been proposed. The chemically modified jute fibers and graft copolymers have been characterized by IR spectra.

POTASSIUM MONOPERSULPHATE (KHSO₅) SYSTEM:

Although the existance of Peroxygen acid of sulphur and
their salts was recognised since nearly a century ago but the use of such compounds like ammonium persulphate, $(NH_4)_2S_2O_8$ as the initiator of vinyl polymerization was recognised in 1946 by Bocon [63]. Evans [64] and Morgen [65]. However, no report was available on the use of potassium monopersulphate (KHSO$_5$) either as an oxidising agent and/or the initiator of vinyl polymerization. Kennedy and co-workers [87] for the first time reported the versatile oxidising action of potassium monopersulphate in the oxidation of a multitude of organic substrates for preparative purpose. Samal and co-workers have pioneered in evaluating the detailed chemistry of potassium monopersulphates especially as regards to its mode of decomposition in solution either alone or under the catalytic action of salts, complexing agents, salts / complexing agents couples and the effectiveness of the systems in causing high rate of initiation in vinyl polymerization [88 - 99] and graft copolymerization of vinyl monomers onto cotton cellulose [100 - 102], jute [103 - 106], Dextran [107] and wool fibers [108 - 110]. In their
studies on decomposition and vinyl polymerization involving KHSO₅, the authors have extensively studied the effect of various reaction components such as the concentration of salts, complexing agents, KHSO₅, minerals acids, monomers, reaction time, temperature and organic solvents of varying composition on the course of decomposition of KHSO₅, and on the rate of vinyl polymerization. In their grafting studies involving KHSO₅, the authors have studied the effect of concentration of monomer, acid, metal salts, complexing agents, reaction time, temperature on graft percentage and the grafting efficiency. The effect of various organic solvents on the extent of percent grafting and grafting efficiency have also been studied. The change in textile properties of the grafted fibers in connection with their tensile strength, rot-resistance, extent of absorption of water and water vapours; dye-uptake ability, thermal stability, behaviour towards the action of mineral acids and alkali etc. have been reported.
REVIEW ON FLAX FIBERS

As has been cited earlier in this chapter, even though flax fibers have wide applications as clothing, housing and industrial products but these materials do not have significant durability and as such the parent fibers have low elasticity, poor dye-uptake ability and susceptibility towards the common chemical reagents such as mineral acids and alkalis [4,5] which have somewhat limited their uses in the textile field. With a view to minimizing such undesirability of flax fibers and simultaneously improve their textile properties they are presently been modified through vinyl grafting. However, the review of the literature reveals that the reports on modification of flax fibers through vinyl grafting is scanty. Gongsheng and co-workers [111 - 112] have reported the grafting of vinyl monomers onto flax fibers using ceric ion as initiator. One of the reports [111] includes their studies on the kinetics of graft copolymerization of methyl methacrylate and ethyl acrylate onto flax fibers with ceric ammonium nitrate in
nitric acid as initiator in heterogeneous system. The percent grafting was dependent on the concentration of ceric ion, monomers, $H^+$ and temperature. The grafting reaction was studied at ceric ion concentration between $4.5 - 6.5 \times 10^{-3}$ mol/l, monomer concentration $6 - 9 \times 10^{-1}$ mol/l, $H^+$ concentration $5 - 8 \times 10^{-2}$ mol/l at 30-40°C within 2-3 hours. An overall rate equation of graft copolymerization was derived. The other report [112] includes their studies on the breaking strength and Young's modulus of ethylacrylate grafted flax fibers prepared by ceric ion method. The maximum grafting level was obtained at ceric ion concentration of 0.006 M, ethylacrylate concentration between 0.4 - 0.9 M, $H^+$ concentration of 0.06 M at reaction temperature of 30-40°C for 3 hours. The authors observed that ethylacrylate grafted flax fibers have higher breaking strength and lower Young's modulus than those of the pristine fibers. Yuje and co-workers [113] have reported the grafting of ethyl acrylate onto flax fibers using $K_2S_2O_8$/thiourea as the redox initiating system. The grafting rate was high at $K_2S_2O_8 = 0.015$ M, $Tu = 0.002$ M, $EA = 0.216$ M, $[H^+] = 0.01$ M for
reaction time of 2 hours at 60°C. The grafted fibers were
found to have increased elongation at break and flexibility,
while the Young's modulus of the grafted fibers decreased in
comparison to the virgin fibers.

Hebeish and co-worker [114] have reported the grafting of Acrylamide onto flax - polyester blend fabrics through thiocarbonation followed by \( K_2S_2O_8 \) catalysis. The graft yield increased with increase in temp. \( \leq 70^\circ C \) and increasing \( K_2S_2O_8 \) concentration \( \leq 40 \) moles/litre, but dropped sharply at higher concentration of \( K_2S_2O_8 \). The graft yield also showed maximum as a function of pH (\( \leq 6 \)) and Fe(II) conc. = 1M. The authors have established that the grafting exclusively takes place on the flax component of the blend.
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