

CHAPTER I

INTRODUCTION



1.1 Cellulose

Cellulose, the most abundant renewable agricultural raw material, is transformed into various products affecting every phase of our daily life due to their wide applications as clothing, housing, absorbent product and other industrial products. At the present time the demand of using water absorbent product is increasing. Cellulose fibre is the natural polymer which is preferable used in commercial for production of water absorbent product. It is used as fluid absorbant in different products, for examples, disposable diaper, absorptive pads and incontinent underpads etc. In addition, it can be used in agriculture application and so on.

Cellulose fibre, itself, can absorb water about 7-8 times by weight. Improvement in absorbency of cellulose fibre can be achieved by modification of its chemical structure (1), for examples;

1. Introduction of new group followed by crosslinking.
2. Substitution with new chemical group at original hydroxyl group of cellulose fibre.
3. Crosslinking the cellulose chain to form network structure.
4. Grafting polymer side chain onto cellulose backbone.

Among these four methods, the most popular method that gives the high absorbency is the graft copolymerization. It can be carried out easily and does not greatly change properties of the cellulose. Cellulose used in graft copolymerization can be prepared from various natural materials such as cotton, bagasse, wood pulp, hemp, rayon, ethers or esters of cellulose, etc.

1.2 Background of Grafting on Cellulose

Graft copolymerization of vinyl monomer onto cellulose, cellulose derivatives and lignocellulosic fibre has been the subject of extensive studies since 1950. Many hundreds of papers and patents have been published.

In 1961 Ide et al.(2) studied the grafting of vinyl acetate, methyl methacrylate, methyl acrylate, acrylonitrile and styrene onto cellulose. They showed that the factors which effect on graft copolymerization were temperature, type of initiator, concentration of monomer and amount of nitric acid.

In 1962 Daniel and Moore (3) studied the effect on the physical properties of paper grafted with acrylonitrile using ceric ion. The grafted paper showed improved resistance to acids, improved wet and dry strength properties, dimensional stability together with increased stiffness and resistance to abrasion.

Recently, attempts have been made to use ceric ion as an initiator for grafting vinyl monomers onto lignocellulosic fibres.

Lin et al.(4) reported ceric ion initiation of graft copolymerization of methyl methacrylate and acrylonitrile onto bamboo. The grafting reaction was found to depend strongly on ceric ion concentration, and maximum grafting occurred in a range around 0.15 mol/L at 40°C. In addition, the effect of lignin contained in bamboo on the graft copolymerization reaction was also examined.

Mansour et al.(5) reported graft copolymerization of ethyl acrylate and acrylonitrile onto lignocellulosic fibres with the use of ceric ammonium sulfate in 1% H₂SO₄. They observed that the graft percentage of ethyl acrylate decreased from 240 to less than 10 with an increase in lignin percentage from 0 to 1.33. Furthermore, with acrylonitrile the graft yield decreased from 175 % to 10 % with an increase in the percentage of lignin from 0.0 to 0.27.

In 1982, Fanta and co-workers (6) reported graft copolymerization of acrylonitrile and methyl acrylate onto hemicellulose and purified (low lignin) wheat straw hemicellulose using Ce⁴⁺ as initiator. The result indicated that ceric ion was suitable for grafting onto low lignin hemicellulose, but it was inert with crude wheat straw hemicellulose containing 11% lignin.

Morin et al.(7) reported graft copolymerization of cellulose xanthate with vinyl monomers, initiated by metal ions. With a number of metal ions as initiators [V⁵⁺, Cr⁶⁺, Fe³⁺], it was observed that V⁵⁺ was the most efficient one with a high rate of grafting and no homopolymer formation.

Nayak et al. (8) studied various kinetic aspects in the V^{5+} initiated graft copolymerization of methyl methacrylate onto cellulose. They observed that an increase of V^{5+} concentration increased graft yield, beyond the concentration of 0.0025 M, however, the graft yield decreased. The increases of monomer concentration and reaction temperature also increased the graft yield but an increase of acid concentration had an adverse effect on the grafting reaction.

Klenin et al. (9) reported the kinetics of graft copolymerization of vinyl monomers onto cellulose with Co^{3+} -salt as initiator. The result indicated that monomers like acrylamide and 2-methyl-5-vinyl pyridine had been successfully grafted.

Samal et al. (10) recently reported that hexavalent chromium, Cr^{6+} , initiated graft copolymerization of methyl methacrylate onto cotton cellulose in aqueous perchloric acid. The grafting reaction was studied at varying concentration of monomer, initiator, $HClO_4$ and temperature. It was found that the graft percent increased with increasing concentration of monomer upto 0.657 M and then decreased. High percent graft was obtained at $[Cr^{3+}] = 6.66 \times 10^{-3}$ M at $50^\circ C$. The order of graft percent with various acids had been found to be $HClO_4 > HNO_3 > H_2SO_4$. In addition, they had also investigated the effects of radical inhibitors on the graft reactions which were retarded or inhibited by the addition of $FeCl_3$, $CuSO_4$ solution, and hydroquinone.

Mishra et al. (11) reported graft copolymerization of methyl methacrylate onto cellulose using Fe^{3+} -acetylacetonate, Al^{3+} -acetyla-



cetonate, and Zn^{2+} -acetylacetonate complexes as initiators. The highest extent of grafting (21.96 %) was obtained with Fe^{3+} -acetylacetonate, whereas grafting with Al^{3+} -acetylacetonate and Zn^{2+} -acetylacetonate gave the yields up to 14.08 and 10.32 %, respectively.

Bardhan, Mukhopadhyay, and Chatterjee (12) studied the kinetics of graft copolymerization of acrylamide onto methylcellulose using persulfate ion as initiator. The highest efficiency of grafting was obtained at an initiator concentration of 3.1×10^{-4} M.

Kislenko and co-workers (13) reported graft copolymerization of methyl acrylate onto methylcellulose using persulfate ion as initiator. The investigations indicated that the atmospheric oxygen had little influence on the rate of graft copolymerization after the initiation period.

Hirose and Hatakeyama (14) used peracetic acid coupled with Fe^{2+} and Fe^{3+} salts as initiators for grafting methyl methacrylate, acrylamide, and acrylic acid onto cellulosic substrates. They found that the optimum concentration of initiator for a high conversion of monomer to polymer and a high yield of graft copolymer were at the temperature higher than $60^{\circ}C$ (up to $75^{\circ}C$). They also suggested that the addition of a complexing agent like ethylene diamine tetracetate to the ferrous ions made it possible to operate the grafting process at high pH.

1.3 The Objectives of This Research

- 1.3.1 Synthesizing polymer material with high absorbency from cellulose.
- 1.3.2 Studying the various properties of water - retaining material obtained.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

1.4 Scope of Work

