A THESIS

ENTITLED

ASPECTS OF THE UTILIZATION OF THE IONIC XANTHATE METHOD OF GRAFTING

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With the name of ALLAH the All-merciful

Nor say of anything "I shall be sure to do so and so tomorrow". * Without adding "If it is Allah's will". And call thy Lord to mind when you forget something and say * "I hope that my Lord will guide me ever closer (even) than this to the right path"

[The Holy Qur'an 18 : 23 - 24]

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AIM OF THE WORK

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SUMMARY

Many unsaturated ketons, esters, nitriles, etc.., undergo addition reactions with active hydrogen containing compounds. Addition of this general type known as Michael reaction, require base catalysts. One of the most powerful catalysts for such reactions is sodium alkoxide. So that sodium cellulosates as well as alkali cellulose, should readily react with certain vinyl compounds. The cyanoethylation of cellulose with acrylonitrile in presence of sodium hydroxide is a type of Micheal addition reaction. The acrylonitrile double bond is activated by the presence of the CN group which withdraws electron and in the case of vinyl monomers, $CH_2 = CHX$, the case of anionic polymerization can be expected to be a function of the electron withdrawing power of X.

In analogy to the anionic polymerization of some vinyl monomers onto alkali-cellulose, the cellulose xanthate in presene of sodium hydroxide was used as an intermediate or substrate for grafting reactions of some vinyl and allyl monomers.

It has been proved that the ionic xanthate method of grafting is capable on undertaking the grafting reactions of several allyl and vinyl monomers onto cotton linters.

The grafting by the xanthate methode either by ionic or free radical processes are based on the introduction of a small number of xanthate groups into the cellulose molecules and then contacting this activated cellulose with polymerizable monomers in presence or absence of peroxide catalysts. This first type of

initiation is based on the grafting by the use of the redox system, between the cellulose xanthate and the peroxide catalyst. The second type of initiation is the ionic grafting reaction which was carried out by the use of cellulose xanthate in absence of any peroxides.

In the first part of this thesis the ionic xanthate method of grafting was used to graft polymerize some vinyl or allyl monomers onto viscose wood or jute pulps as substrates. grafting parameters such as grafting yields and grafting efficiencies increased with the use of suitable preciptating agent such as HCl or HCl in presence of different solvents. High crude grafting yields were obtained on using HCl alone as precipitating agent and acrylonitrile or methyl methacrylate as monomers, while in case of methyl acrylate and allyl alcohol the proper precipitating agent was HCl in presence of acetone. High true grafting yields were obtained on using HCl as precipitating agent for all monomers used and maximum grafting efficiencies were obtained on using HCl, HCl in presence of acetone, HCl and HCl in presence of ethanol when the monomers used were acrylonitrile, methyl methacrylate, methyl acrylate and allyl alcohol. These results represent a true case of using viscose pulp as cellulose substrate. Meanwhile the substrate was jute pulp, high crude grafting yields were obtained on using HCl in presence of isopropanol, HCl in presence of methanol, HCl and HCl in presence of acetone as precipitating agents and the monomers were acrylonitrile, methyl methacrylate, methyl acrylate or allyl alcohol respectively. While high true grafting yields were obtained on using precipitating agents similar to those in case of viscose pulp except in case of methyl methacrylate as monomer, the suitable precipitating agent is HCl in presence of methanol and maximum grafting efficiencies were obtained on using HCl for monomers acrylonitrile, methyl methacrylate and allyl alcohol while HCl in presence of methanol for methyl acrylate. Also, the increase of temperature up to a limit leads to the increase of the grafting parameters. Such increase depends mainly on the ceiling temperature of the monomer used. The ceiling temperature Tc of the polymerization is defined as the temperature at which the rate of addition is equal to the rate of the elimination reaction for a given system. The Tc should be 30°C for the grafting reactions of the monomers acrylonitrile and methyl methacrylate, while it was 40°C and 50°C for monomers allyl alcohol and methyl acrylate respectively.

The increase of sodium hydroxide concentration of the xanthation reaction increased the grafting parameters up to a limit. Such increase in the concentration of sodium hydroxide lead to the increase of the number of xanthate groups which lead to more grafting sities and hence more grafting yield up to a limit which depends on the type of monomers and the cellulose origin.

For the xanthate - ionic method, the monomers reactivity depends on both radical stabilization due to the substituted groups and the strength of the electron affinities of the monomers. The grafting parameters increased with the increase of the monomer concentration till a maximum then decreased. The order of reactivity is as follows : acrylonitrile > methyl methacrylate > methylacrylate > allyl alcohol when the substrate used for grafting is viscose pulp and the use of the proper precipitating agent, while when the substrate was jute pulp the order is as follows : acrylonitrile > methyl acrylate > methyl methacrylate > allyl alcohol.

Generally speaking, viscose pulp give high grafting yields than jute pulp, the difference is attributed to the difference in chemical and physical structure.

Also, the effect of diluent (acetone or dioxane) have been studied in this thesis and has been found that the use of diluent in the ionic - xanthate method of grafting decreased the grafting yields.

In the second part of this thesis, the rheological properties were investigated for the solutions of both cellulose xanthate and cellulose xanthate cografted polymers with different grafting yields dissolved in dilute sodium hydroxide. It has been found that, the origin of cellulose affected greatly on the structure of the solution rather than the grafting yields and also the thixotropic behavior, i.e., the sol-gel transformation depends mostly on the cellulose origin and little on the grafting yields and type of cografted polymers.

In the third part of this thesis, the study is concerned with the manufacturing of the membranes from cellulose xanthate and different cellulose xanthate cografted polymers using different monomers with different grafting yields. The properties of the produced membranes toward that, alkali treatment of the cellulose xanthate ungrafted and cografted with polymers changed the W.R. values. For the ungrafted cellulose xanthate the increase of alkali concentration decreased the W.R.Value approximately similar results were obtained for the grafted cellulose. Also the weight loss decreased with the increase of the alkali concentration.

On treatment of membrane with HCl or H_2SO_4. the weight loss increased till a maximum then decreased. The cografting of cellulose xanthate with polymers decreased the swellability of the membranes but lose some of its weight especially at significantly high grafting yield.

On treatment of membrane with zinc chloride, it has been found that, the low grafting yields lead to membranes of low W.R. values compared with those membranes with high grafting yields. Also the weight loss due to the salt-treatments were low compared with those of high grafting yields. So that on making membranes of cellulose cografted polymers, it is preferable that the samples are of low grafting yields.