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### Cellulose Graft Copolymers

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## Cellulose Graft Copolymers

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### SUMMARY

Graft copolymerization reactions of fibrous cellulose with vinyl monomers were initiated at free radical sites formed on the cellulose molecule by interaction with high-energy radiation, by reaction with  $Ce^{4+}$  ions in acidic solution, or by H abstraction by  $\cdot OH$  radicals formed by reaction of  $Fe^{2+}$  ions with  $H_2O_2$  in aqueous solution. The effects of experimental conditions on the nature, half-lives, location of these free radical sites on the cellulose molecule, and on the copolymerization reactions were studied by the use of electron spin resonance spectroscopy. The molecular weights of the grafted polymers varied over a range from about  $3 \times 10^4$  to  $1 \times 10^6$ . The distributions of the grafted polymers within the fibrous cellulosic structure were determined. Some of the changes in physical properties of the cellulose graft copolymers, as compared with cellulose, were decreased permanent set, development of thermoplasticity, decreased stiffness, increased rot resistance, and increased abrasion resistance.

### INTRODUCTION

Cellulose is one of the world's most widely used and important polymers. Fibrous cellulose, including both natural and regenerated cellulosic fibers,

comprise the major fraction of the world's textile fibers [1]. The modification of the textile properties of cellulosic fibers to add new properties, while retaining the desirable natural properties, has been of great interest in recent years [2, 3]. It is not possible to modify the chemical structure and physical properties of cellulosic fibers in a manner similar to that followed for man-made chemical polymers prior to or during their formation.

In recent years, particularly since 1960, the preparation of graft copolymers of cellulose has been actively investigated. The grafted polymer usually has a high molecular weight which may be comparable to that of cellulose. The cellulose graft copolymer retains some of the natural properties of cellulose and also has some of the properties of the grafted polymer [4, 5].

The graft copolymerization reactions of monomers or preformed polymers with cellulose may be initiated by free radical, ionic, or condensation mechanisms [4, 5]. This discussion is concerned with free radical mechanisms in which free radical sites, as detected by electron spin resonance spectroscopy, were formed on the cellulose molecule by dehydrogenation reactions initiated by high energy radiation, by complexing cellulose with ceric ion, or by hydrogen abstraction from cellulose by hydroxyl radicals formed by reaction of ferrous ion with hydrogen peroxide, as reported by our laboratory. Some of the properties of the cellulose graft copolymers are discussed.

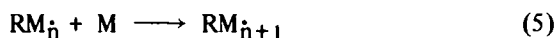
### FREE RADICAL REACTION MECHANISMS

Formation of free radical sites on cellulose can be initiated by dehydrogenation, depolymerization, or oxidation. Commonly used methods include high energy radiation, ultraviolet irradiation, oxidation-reduction systems, decomposition of peroxy compounds, and chemical modification. The use of corona or arc discharge, electrochemical, mechanical, and thermal methods to initiate the formation of free radical sites on cellulose has also been reported [5]. When the activated cellulose is immersed in vapors or solutions of vinyl monomers, chain copolymerization reactions are initiated. Elementary steps for free radical initiated copolymerization reactions of cellulose (R) and vinyl monomer (M) may be written as shown in Eqs. (1) to (9):

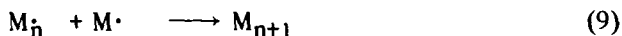
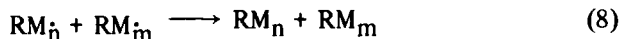
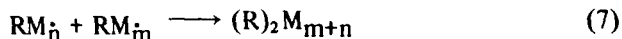
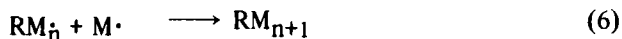
## Initiation



## Propagation



## Termination



Where  $R^*$  = activated cellulose,  $M^*$  = activated monomer,  $R\cdot$  = cellulose radical, and  $M\cdot$  = monomer radical.

## High Energy Radiation

The interaction of high energy radiation with cellulose initiates dehydrogenation and depolymerization reactions of the cellulose molecule. After four or five cleavages per cellulose molecule, the depolymerization reactions lead to significant losses in the breaking strength of cellulosic fibers [6]. Consequently, radiation dosages used for initiation of copolymerization reactions must be held to a minimum. For example, when cobalt-60 gamma-radiation is used, dosages of 1 megarad or less, where chain cleavages per molecule are about four to five, are indicated. Due to the presence of a high degree of order or crystalline regions within the cellulosic structure, long-lived or trapped free radical sites are formed in these regions. The localization of energy on the anhydroglucose ring of the cellulose molecule probably leads to dehydrogenation at carbon  $C_5$ , as indicated by the triplet electron spin resonance spectrum recorded for irradiated cellulose which has lattice type I and contains regain moisture [7, 8].

When vinyl monomer is in contact with cellulose during irradiation [9-12], copolymerization reactions could be propagated as shown in Eqs. (3), (4), and (5). Homopolymer could be formed as shown in Eq. (9). The presence of trapped radicals in the irradiated cellulose makes possible the formation of activated cellulose as shown in Eq. (1) and then the initiation of the copolymerization reaction as shown in Eq. (3). If this two-step reaction is used, homopolymer formation is minimized. However, dependent on the solvent used for the monomer, chain transfer from the activated cellulose to the monomer and then homopolymerization of the monomer can occur.

When the two-step reaction is used, solvents for the monomer can be selected which interact with the cellulosic structure to cause dimensional changes [13-15]. The location of the grafted polymer within the macrostructure of cellulosic fiber can be determined. In the two-step reaction, the free radical concentration in the irradiated cellulose decreases during the copolymerization reaction; however, the shape of the electron spin resonance spectrum does not change [8]. Based on determination of the molecular relationships between grafted polymer and cellulose and on changes in free radical concentration during the copolymerization reaction [16, 17], about 30% of the free radicals are inaccessible to solutions of monomer. Of the remaining 70% of the free radical sites, graft copolymerization reactions are initiated at only 1 to 3% of the sites. The remainder of the free radicals, which are accessible, are likely scavenged by the solvent for the monomer.

### Ceric Ion

Ceric ions in acidic solution form chelates with cellulose which initiate an oxidative degradation of the cellulose molecule and the formation of short-lived free radical sites, probably on carbon  $C_2$  and/or carbon  $C_3$ . A fairly narrow, symmetrical, singlet-type electron spin resonance spectrum is generated when cellulose reacts with ceric ion. If vinyl monomer is present in the solution which contains ceric ion, graft copolymerization reactions with cellulose can be initiated. During the copolymerization reaction, the electron spin resonance spectrum rapidly changed from a singlet-type spectrum to a spectrum for that of the free radical expected on the end of the grafted polymer chain. In the case of reactions initiated by high energy radiation, about one free radical site on the grafted polymer chain was present for about thirty trapped radicals which were not terminated during the reaction, so that this change was not detected [8]. The free radicals formed by ceric ion reaction with cellulose were all accessible to solutions

of monomer, and either initiated copolymerization reactions or were terminated during the reaction [18].

The decay of the free radicals, as well as their formation, on cellulose was also dependent on the concentration of ceric ion. That is, ceric ion reacts with cellulose to form an activated complex  $R^*$ , and after transfer of one electron from the cellulose molecule to ceric ion, a short-lived free radical site  $R\cdot$ , probably on carbon  $C_2$  or  $C_3$ , is formed on cellulose. Then ceric ion can react with the free radical and is reduced to cerous ion. Cellulose is oxidized with anhydroglucose ring cleavage between carbon  $C_2$  and  $C_3$  and with the formation of carbonyl groups at these carbons [18].

### Oxidation-Reduction Systems

Oxidation-reduction systems, in which reactive radicals, such as  $\cdot OH$  and  $HO_2\cdot$ , are formed, are used to initiate graft copolymerization reactions with cellulose. The reactive radicals interact with the cellulose molecule to abstract hydrogen atoms and to form free radical sites on the cellulose  $R\cdot$ . Then graft copolymerization reactions of monomers with cellulose at the free radical sites on cellulose can be initiated. For example, cellulose is immersed in a solution of ferrous sulfate and dried in a nitrogen atmosphere; then a solution of hydrogen peroxide is drawn on the dried cellulose. If this sample is immediately frozen in liquid nitrogen, an electron spin resonance spectrum for the sample can be recorded which has three intense lines with a ratio of intensities of about 1:2:1. If the temperature of the sample is increased, the electron spin resonance spectrum becomes very weak and undefined within a few seconds. The lifetime of the free radical sites is very short. However, if monomers are present in either of the solutions, graft copolymerization reactions are initiated. The electron spin resonance spectrum of the grafted cellulosic product is characteristic of that expected for a free radical site on the end of the growing graft polymer chain [19].

### COPOLYMERIZATION REACTION METHODS

Methods for free radical initiated graft copolymerization of monomers with cellulose are generally limited to bringing the monomer (in either vapor phase or in solution) into contact with cellulose in the solid phase (either before, during, or after activation of free radical sites on the cellulose molecule). In grafting onto fibrous cellulose, crystalline structure

and morphology, as they affect the rate of diffusion of monomer and/or solvent to the free radical sites, are important factors in determining the extent of grafting and the localization of the grafted polymer within the fibrous structure [5].

Cellulose is generally immersed in solutions of monomers for graft copolymerization reactions. Solvents, which also interact with the cellulosic fibers to cause desired dimensional changes in the fibers, are selected for the monomers. The experimental conditions have to be such that the vinyl monomer can compete with the solvent for the free radical sites. For example, when high energy radiation is used to initiate the reactions, the scavenging of the radicals by the solvent in less ordered celluloses is greater than in more ordered celluloses. Usually, at a given radiation dosage, a lower amount of polymer is grafted onto less ordered cellulose than onto more ordered cellulose [5].

### MOLECULAR RELATIONSHIPS

The molecular relationships between cellulose and grafted copolymer are dependent on the method of initiation of the free radical sites on the cellulose molecule and the composition of the solution of monomer, particularly as this affects the propagation and termination reactions. The degree of grafting can be as much as 1 or 2 polymer grafts per cellulose molecule when ceric ion and aqueous systems or high energy radiation combined with grafting from organic solvents is used; molecular weights of the grafted polymer range from 84,000 to 33,000, respectively. When high energy radiation is combined with grafting from aqueous salt solutions, which cause large dimensional changes in the cellulosic fibers, the degree of grafting can be as low as 1 polymer graft per 100 cellulose molecules, with molecular weights of the grafted polymer ranging to as high as 1,000,000 [17].

### PROPERTIES

The use of fibrous cellulose graft copolymers as textiles depends on the advantages which they may offer over just physical blending of other fibers with cotton or regenerated cellulosic fibers. There is no clear relationship between the carbon on the anhydroglucose unit of the cellulose molecule at which the graft copolymerization reaction was initiated, the molecular

weight of the grafted polymer, and the degree of grafting and the properties of the fibrous cellulose graft copolymers [20]. Probably the most significant advance is that in the case of cotton cellulose the morphology of and the distribution of grafted polymer in the macrostructure of the fiber can be experimentally determined [21, 22].

Variations in the shape of the cross section of cotton fibers from collapsed to rounded can be obtained by selection of solvents for the monomers which also have a swelling effect on the macrostructure of the fibers. Also, the method of initiating the graft copolymerization reaction, type of monomer used, and chemical modification of cellulose prior to grafting are factors in determining the morphology of the product. For example, the effects of grafting of acrylonitrile on fibrous cotton can be selectively varied by choice of experimental conditions. When a one-step radiation process with 75% aqueous zinc chloride solution as the solvent for acrylonitrile was used, the fibrous cross section was rounded, and the poly(acrylonitrile) was concentrated about midway between the lumen and outer layers of the fiber. When cyanoethylated cotton was graft copolymerized with acrylonitrile by the same process, the fibrous cross section was rounded, and the grafted poly(acrylonitrile) was uniformly distributed. When either ceric ion or oxidation-reduction systems was used, the fibrous cross section was collapsed and the poly(acrylonitrile) was uniformly distributed [22].

When a two-step radiation process with saturated aqueous zinc chloride solution as the solvent for the monomer was used, the fibrous cross section retained its natural shape, and the poly(acrylonitrile) was distributed from the outer layers of the fiber toward the lumen of the fiber. If aqueous zinc chloride solution was used which caused the fiber to swell, the cross-section of the fiber was rounded, and the poly(acrylonitrile) was more concentrated in the outer layers of the fiber. When an organic solvent, such as N,N-dimethyl formamide, was used in this process, the fibrous cross section of the product resembled that of the natural fiber, and the poly(acrylonitrile) was uniformly distributed [22].

Opening and layering effects on the fibrous cross section were obtained when styrene or methacrylates were dissolved in organic solvents and grafting was initiated by radiation [21, 22].

Other important changes in physical properties of cotton cellulose graft copolymers as compared with cotton were increased elastic recovery, thermoplasticity, increased abrasion resistance, increased wrinkly recovery, increased soil release through changes in surface properties, and increased rot resistance [4, 5, 15, 20, 23-25].



## REFERENCES

- [1] J. C. Arthur, Jr., in *Encyclopedia of Polymer Science and Technology*, Vol. 4 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Wiley (Interscience), New York, 1966, p. 244.
- [2] J. C. Arthur, Jr., and F. A. Blouin, *Amer. Dyestuff Repr.*, **51**, 1024 (1962).
- [3] J. C. Arthur, Jr., and F. A. Blouin, *U. S. At. Energy Comm. Doc. TID-7643*, 319 (1962).
- [4] J. C. Arthur, Jr., in *Polymerization and Polycondensation Processes*, (Advances in Chemistry Series, No. 91) (N. Platzer, ed.), American Chemical Society, Washington, 1969, p. 574.
- [5] J. C. Arthur, Jr., in *Advances in Macromolecular Chemistry*, Vol. 2 (W. Pasika, ed.), Academic, London, 1970, p. 1.
- [6] J. C. Arthur, Jr., in *Energetics and Mechanisms in Radiation Biology* (G. O. Phillips, ed.), Academic, London, 1968, p. 153.
- [7] J. C. Arthur, Jr., T. Mares, and O. Hinojosa, *Textile Res. J.*, **36**(7), 630 (1966).
- [8] P. J. Baugh, O. Hinojosa, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **11**(7), 1139 (1967).
- [9] J. C. Arthur, Jr., and F. A. Blouin, *J. Appl. Polym. Sci.*, **8**(6), 2813 (1964).
- [10] J. C. Arthur, Jr., and R. J. Demint, U. S. Patent 3,109,798 (Nov. 5, 1963).
- [11] J. C. Arthur, Jr., and R. J. Demint, U. S. Patent 3,157,460 (Nov. 17, 1964).
- [12] J. C. Arthur, Jr., J. A. Harris, and T. Mares, *Textile Ind.*, **132**(9), 77 (1968).
- [13] F. A. Blouin and J. C. Arthur, Jr., *Polym. Preprints*, **6**(1), 359 (1965).
- [14] F. A. Blouin and J. C. Arthur, Jr., *Textile Res. J.*, **33**(9), 727 (1963).
- [15] F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., *Textile Res. J.*, **36**(4), 309 (1966).
- [16] J. C. Arthur, Jr., and D. J. Daigle, *Textile Res. J.*, **34**(7), 653 (1964).
- [17] N. J. Morris, F. A. Blouin, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **12**(2), 373 (1968).
- [18] J. C. Arthur, Jr., P. J. Baugh, and O. Hinojosa, *J. Appl. Polym. Sci.*, **10**(10), 1591 (1966).
- [19] J. C. Arthur, Jr., O. Hinojosa, and M. S. Bains, *J. Appl. Polym. Sci.*, **12**(6), 1411 (1968).
- [20] F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., *Textile Res. J.*, **38**(7), 710 (1967).

- [21] F. A. Blouin, A. M. Cannizzaro, J. C. Arthur, Jr., and M. L. Rollins, *Textile Res. J.*, **38**(8), 811 (1968).
- [22] M. L. Rollins, A. M. Cannizzaro, F. A. Blouin, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **12**(1), 71 (1968).
- [23] J. C. Arthur, Jr., and J. N. Grant, *Textile Res. J.*, **36**(10), 934 (1966).
- [24] J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, *Textile Res. J.*, **33**(11), 896 (1963).
- [25] R. J. Demint, J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, *Textile Res. J.*, **32**(11), 918 (1962).