Some Aspects of Graft Polymerization of Vinyl Monomers onto Cellulose by Use of Tetravalent Cerium. VI

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Synopsis

The state of cellulose as defined by its crystallinity, grinding, and average degree of polymerization (D.P.) highly influences the grafting yield. Grinding of cellulose with a Wiley mill results in decreased grafting, while grinding with a ball mill or treatment with ethylenediamine, both of which lead to decrystallization of cellulose, nearly inhibits the grafting reaction from taking place. On the other hand, decreased D.P. leads to increased grafting yield. The governing factor being attributed to the specific surface of the cellulose. Increased specific surface, as decreased D.P., brings about an increase in the active sites formed on the cellulose and hence an increase in the grafting yield. However, this occurs up to a limit beyond which further increase in the specific surface, respectively, the formed active sites, as grinding with a Wiley mill and decrystallization, brings about termination reactions through disproportionation and coupling of the exceedingly increased free radicals, and hence grafting is decreased or nearly inhibited. Drying of cellulose at 105°C resulted in decreased grafting yield. This was attributed to condensation of the cellulose structure. It has been also found that the grafting yield is influenced by the type and origin of cellulose whose reactivities differ for different monomers.

INTRODUCTION

In parts I through III of this series,[1-3] it was shown that the factors influencing the graft polymerization of vinyl monomers onto cellulose by use of tetravalent cerium are similar to those affecting free-radical vinyl homopolymerization reactions. The order of addition of reactants had an effect on polymerization, better reaction being achieved when initiator was added before monomer. In parts IV and V,[4,5] the influence of agitation as well as the influence of occluded oxygen and of the different solvents on the grafting reaction were studied.

In the present work, the influence of the state of cellulose on graft polymerization is studied as regards mechanical grinding, average degree of polymerization (D.P.), and crystallinity. The influence of drying as well as the type and origin of the cellulose are also investigated.

Ogiwara and Kubotu[6] showed that the percentage of graft and number of grafted chains decreased with an increase in the degree of beating. Josef[7] found that increase in the specific surface of bleached sulfite straw pulp from 26.9×10^3 to 102.4×10^3 cm^2/g, corresponding to a Schopper–Riegler freeness of 10 to 67°, increased the grafting rates of acrylonitrile. Dilli, Ernst, and Garnett[8] stated that mechanical grinding effectively reduces radical concentration.

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EXPERIMENTAL

Graft polymerization was carried out under purified nitrogen in a well-stop-pered glass bottle of 50-ml capacity where 0.5 g purified cellulose (oven dry) was placed together with ceric ammonium sulfate (CAS), 0.08 g/100 ml 1% sulfuric acid, at a 30:1 liquor-to-cellulose ratio.   Monomer was added in a ratio of 3 ml to 1 g cellulose.   The monomers used were acrylonitrile and ethyl acrylate.   Light agitation was then applied to the bottles to keep the monomer and the other constituents suitably dispersed during the reaction period, which ranged from $\frac{1}{4}$ to 4 hr at a reaction temperature of 30°C.   At the end of the reaction period, the samples were washed thoroughly by extraction with several portions of water, dried, and then weighed.   The crude grafting yield C was calculated as follows:

$$C = B - Z/Z \%$$

where Z is the weight of cellulose (in g) and B is the weight of the grafted product before extraction.

The crude grafted celluloses were extracted for a period of 72 hr with a suitable solvent for the removal of the homopolymer—dimethylformamide (DMF) for polyacrylonitrile (PAN) and tetrahydrofuran (THF) for poly(ethyl acrylate)
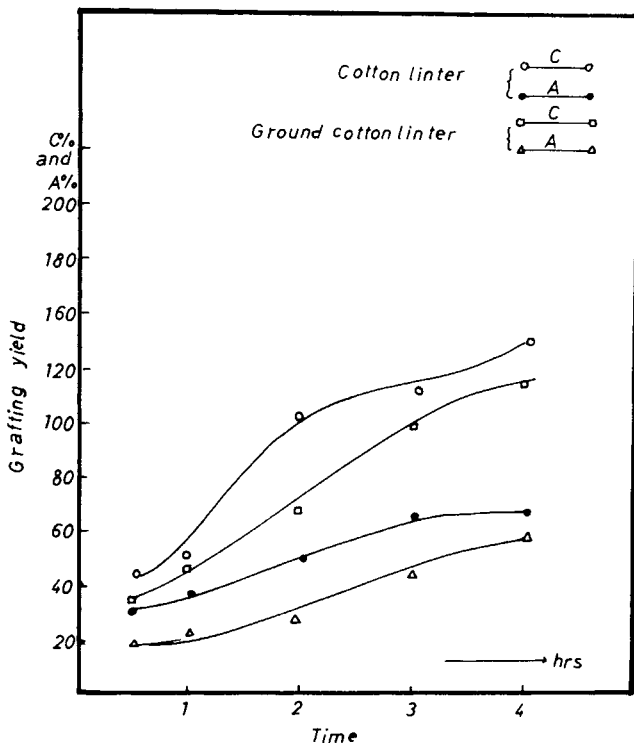

Fig. 1. Influence of state of cellulose "grinding."   Monomer = acrylonitrile: C, grude grafting yield %; A, true grafting yield %.
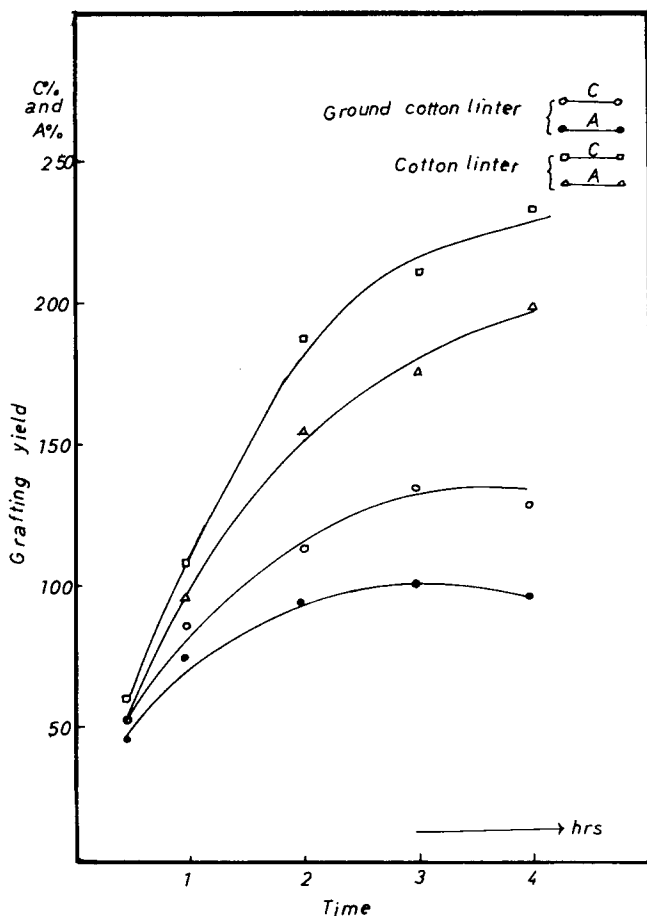
Fig. 2. Influence of state of cellulose "grinding." Monomer = ethyl acrylate: C, crude grafting yield %; A, true grafting yield %.

(PEA). Thorough washing with distilled water followed. Finally, the samples were dried and weighed. The true grafting yield A was calculated as follows:

$$A = G - Z/Z \%$$

where G is the weight of grafted product (weight of the grafted cellulose after extraction).

The ceric consumption was determined according to the method of Mino and Kaizerman[9] as nanomole ceric ammonium sulfate (CAS) per 100 g cellulose and is calculated in this work as the percent of ceric consumed to the ceric added, as follows:

$$\text{percent ceric consumed} = \frac{\text{nanomole CAS consumed}}{\text{nanomole CAS added}} \times 100$$
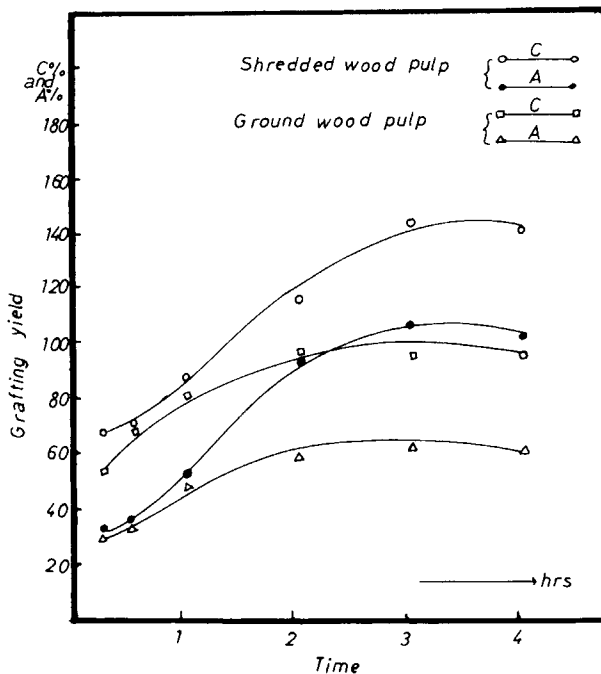
Fig. 3. Influence of state of cellulose "grinding." Monomer = acrylonitrile: C, crude grafting yield %; A, true grafting yield %.

RESULTS AND DISCUSSION

Influence of State of Cellulose

Mechanical Grinding

Cotton linter as well as beech sulfite wood pulp are mechanically ground using a Wiley mill so as to pass through mesh of Din 50. These are to be compared with unground cotton linter and shredded beech sulfite wood pulp, respectively. Shredding was carried out using a Werner–Pfleider shredder.

Figures 1, 2, and 3 show that both crude and true grafting yields decrease on grinding. This may be attributed to the fact that the specific surface of the cellulose increased enough as a result of grinding so that exceedingly more hydroxyl groups became available leading to the formation of exceedingly active sites, namely, free radicals, on the cellulose. Radical-destroying reactions thus take place through coupling and disproportionation between the highly formed free radicals,[10] giving rise to a decrease in grafting yield. This is consistent with the ceric ion consumption (Fig. 4), where due to the exceedingly exposed hydroxyl groups through increasing the specific surface by grinding, a higher ceric ion consumption was observed as compared with the unground cotton linter. Also, for the same reason, ground cotton linter showed a progressive increase in the ceric ion consumption with reaction time, while it leveled off after 2 hr for unground cotton linter.
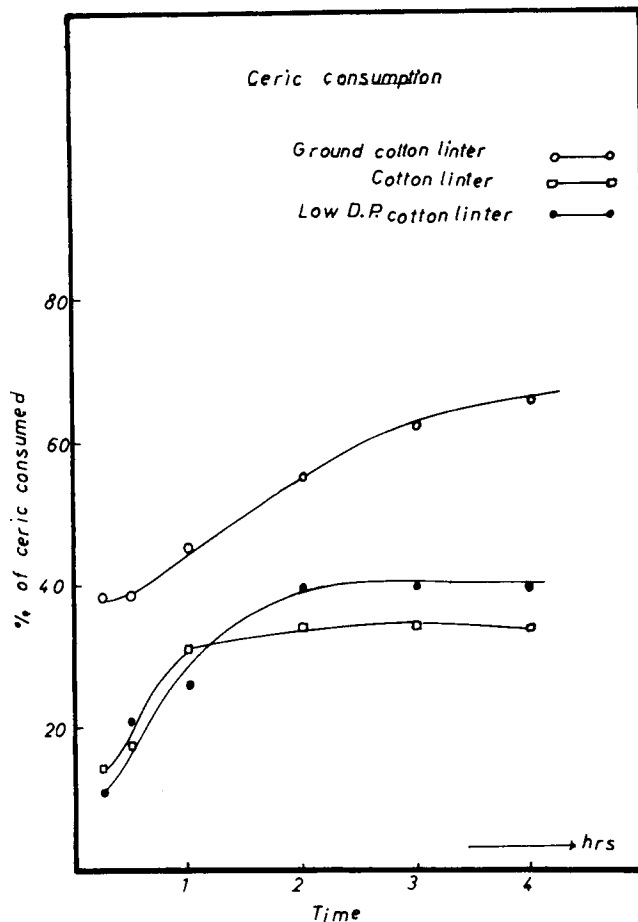
Fig. 4. Ceric consumption. Concentration of ceric ammonium sulfate (CAS) 0.08 g/100 ml 1% H_2SO_4, liquor-to-cellulose ratio 30:1, at 30°C.

Again, considering Figures 1, 2, and 3, it is evident that the reactivity of the monomer and the type of cellulose have an influence on the rate of decrease in graft polymerization due to grinding. Thus, with the more reactive ethyl acrylate,[2] the rate of decrease of both the crude and true grafting yields due to grinding is much more than with acrylonitrile (Figs. 1 and 2). This may again relate to the production of exceedingly more free radicals with the more reactive ethyl acrylate and hence a higher rate of termination reactions.

The same result is achieved by considering the influence of the type of cellulose on the rate of decrease in grafting due to grinding where the decrease was greater with beech sulfite wood pulp (Fig. 3) than with cotton linter (Fig. 1), probably due to the higher reactivity of the former.

Average Degree of Polymerization

The average degree of polymerization (D.P.) was measured according to the method of Brown,[11] making use of the relationships between intrinsic viscosity and molecular weight and D.P.
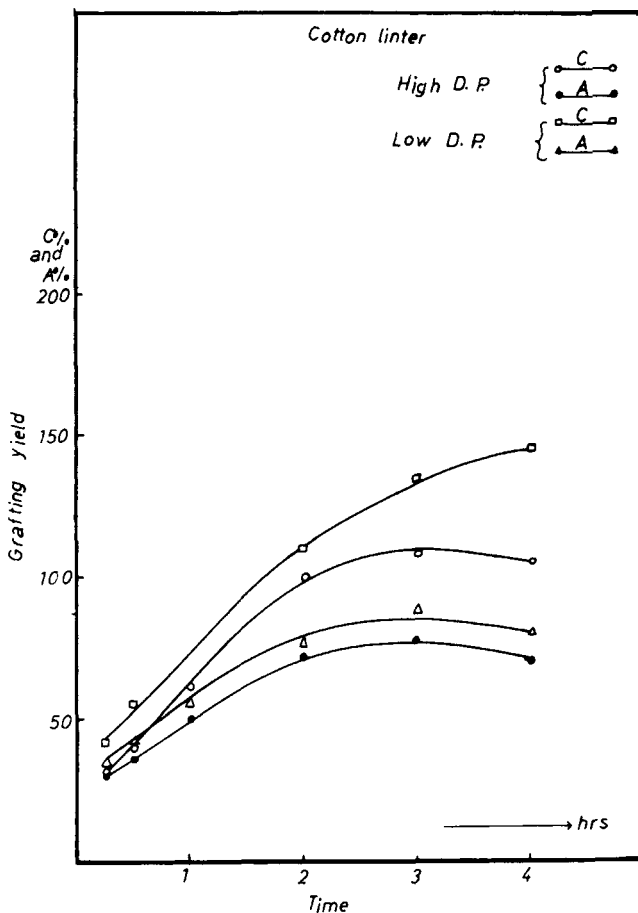
Fig. 5. Influence of D.P. Monomer = acrylonitrile: C, crude grafting yield %; A, true grafting yield %.

Hydrolysis of cotton linter with 1.5% sulfuric acid at 100°C for 1 hr leads to a distinct decrease of the D.P., as the intrinsic viscosity $[\eta]$ dropped from 7.5 to 1.5. Such decrease in D.P. was accompained by an increase in graft polymerization. Figures 5 and 6 show that both the crude and true grafting of acrylonitrile and ethyl acrylate onto cellulose increased with decreased D.P. Such increase is attributed to the formation of new hydroxyl groups which takes place as a result of hydrolysis with sulfuric acid. This is consistent with the ceric ion consumption (Fig. 4), which was higher for cotton linter of low D.P. Therefore, one may say that the specific surface, namely, the active sites formed onto cellulose, increased with decreasing D.P., however to an extent which is still below the limit that allows termination reactions through disproportionation or coupling to take place and hence increased grafting yield.

Crystallinity

Cotton linter was decrystallized according to the method of Klinkova,[12] in which anhydrous ethylenediamine was used at 0°C for $\frac{1}{2}$ hr. The treated cellulose was then washed with chloroform in order to remove the ethylenediamine
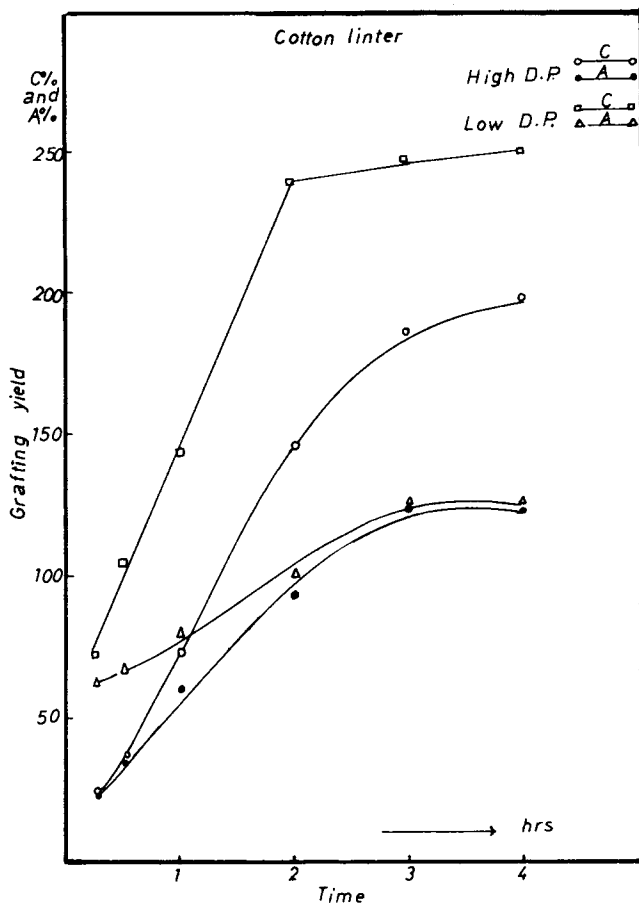
Fig. 6. Influence of D.P. Monomer = ethyl acrylate: C, crude grafting yield %; A, true grafting yield %.

and to decompose the complex compound formed between the latter and the hydroxyl groups of cellulose.   The last traces of cloroform were completely removed by means of a high vacuum.

The results of Table I show that decrystallizing of cellulose with ethylenediamine resulted in true grafting yields of 6.08% and 7.59% when grafting with acrylonitrile and ethyl acrylate, respectively, as compared with 65.50% and 151.78% for the corresponding untreated samples.   A blank experiment was also

TABLE I
Effect of Decrystallization and Drying on True Grafting Yield[a]

Monomer	True grafting yield, %			
	Untreated cellulose	Treatment with ethylenediamine	Grinding with ball mill	Drying
Acrylonitrile	65.50	6.08	2.80	52.0
Ethyl acrylate	151.78	7.59	4.60	65.83

[a] Ceric ammonium sulfate concentration 0.08 g/100 ml 1% H_2SO_4; liquor-to-cellulose ratio 30:1; monomer-to-cellulose ratio 3:1; temperature 30°C; time of reaction 3 hr.

carried out using ethyl acrylate, but in the absence of ethylenediamine, and it gave a true grafting yield of 135.0%.

Decrystallization was also affected by grinding with a ball mill to mesh 60. Results of Table I again show that due to such grinding, the true grafting yield decreased to 2.80% and 4.60% on grafting with acrylonitrile and ethyl acrylate, respectively, as compared with 65.50% and 151.78% for the corresponding untreated cellulose.

From the above results, it is evident that grafting is nearly inhibited by decrystallization of cellulose. This indicates that grafting does not take place on the amorphous regions of cellulose and that grafting occurs only on the crystalline regions. This may be attributed to the fact that in the amorphous regions all the hydroxyl groups become available and hence the active sites, that is, the free radicals formed, are at a maximum, thus leading to maximum disproportionation or coupling reactions with which no grafting occurs.
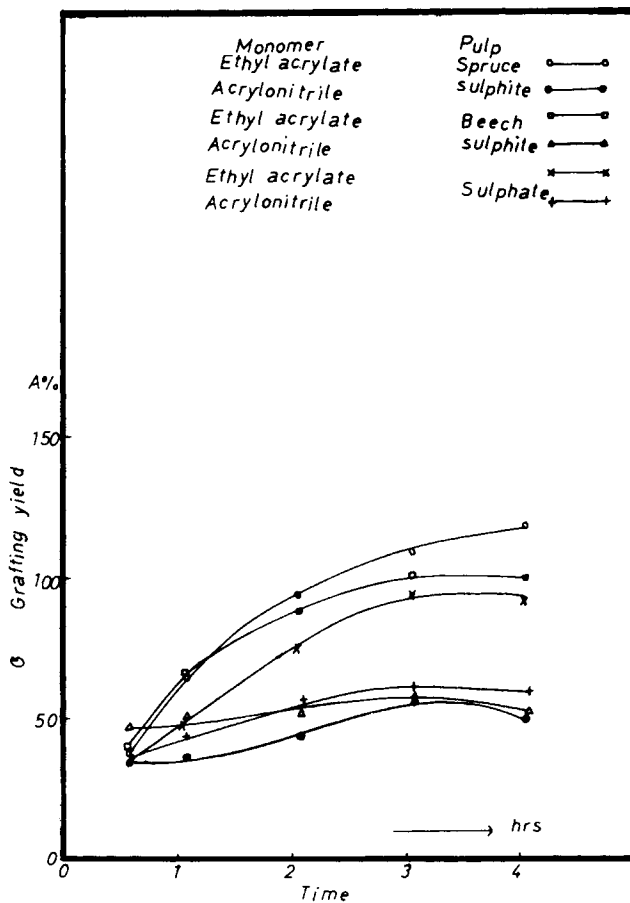

Fig. 7. True grafting yield (A) of different ground wood pulps (Et = ethyl acrylate, Ac = acrylonitrile).
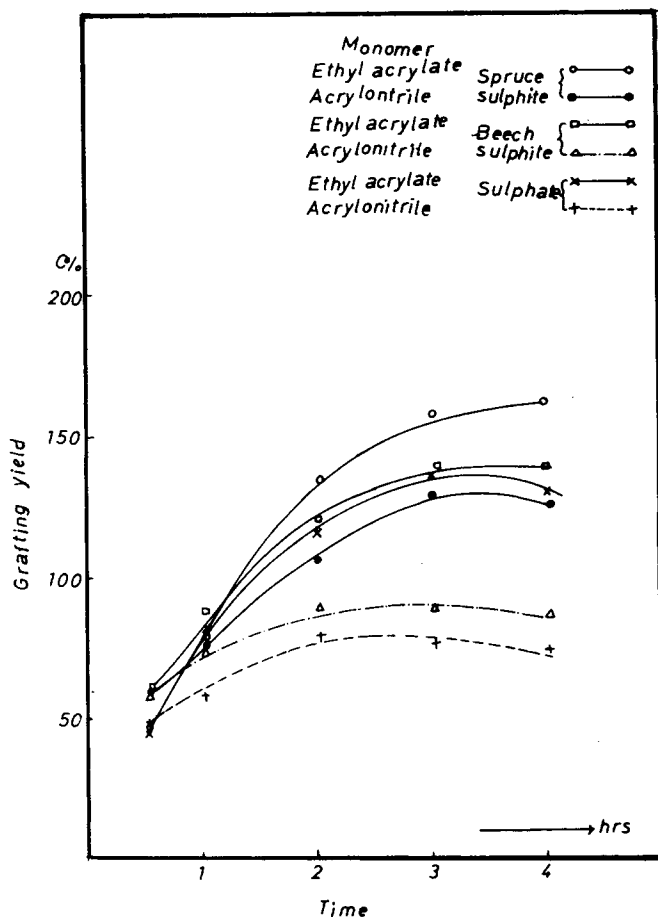
Fig. 8. Crude grafting yield (C) of different ground wood pulps (Et = ethyl acrylate; Ac = acrylonitrile).

Conclusions

Grafting yield may be increased by increasing the active sites formed on the cellulose. This may be achieved through increasing the cellulose specific surface. However, this occurs up to a limit beyond which further increase of the specific surface, that is, the formed active sites, brings about termination reactions through disproportionation and coupling of the exceedingly increased number of free radicals formed and hence decreased grafting yield.

Influence of Drying

Samples of cotton linter were dried at 105°C for 8 hr in a drying oven. Results listed in Table I show that predrying of cellulose leads to decreased grafting yield. This may relate to the condensation of the cellulose structure which then makes the penetration of the reacting chemicals more difficult through the collapsed fiber capillaries and the cellulose hydroxyl less available because of the formation of interfibrillar hydrogen bonds.

Influence of Type and Origin of Cellulose

To elucidate this influence on graft polymerization, ground cotton linter, spruce and beech sulfite pulps, and also sulfate pulp were used for grafting ethyl acrylate and acrylonitrile.

From Figures 2 and 7 the reactivities of the different celluloses at the maximum true grafting yields of poly(ethyl acrylate) were in the order spruce sulfite > beech sulfite = cotton linter > sulfate, while from Figures 2 and 8 the order of reactivity at the maximum crude grafting yield was spruce sulfite > beech sulfite > sulfate ≃ cotton linter.

For grafted polyacrylonitrile cellulose, the reactivities at the maximum true grafting yields, as shown from Figure 1 and 7, are in the order sulfate ≃ cotton linter ≃ beech sulfite = spruce sulfite, while from Figures 1 and 8 the order of reactivities at the maximum crude grafting yield is spruce sulfite > cotton linter > beech sulfite > sulfate.

From the above it is clear that the order of reactivities of celluloses of different types, namely, cotton linter, sulfate, and sulfite pulps, and of different origins, namely, spruce and beech, differs for the different monomers. Also, each of the true and crude grafting yields is independently influenced by the type and origin of the cellulose. This may relate to the Trommsdorff effect,[13] contributed to the presence of noncellulosic incrustants which differ in the different celluloses and hence variably influence both crude and true grafting. In this connection, Dilli et al.[14] showed that additives such as aromatic and nonaromatic compounds and free-radical scavengers in the radiation-induced copolymerization of monomers to cellulose caused the peak of the Trommsdorff effect to increase or decrease.

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