

# Graft Polymerization of Some Vinyl Monomers onto Alkali-Treated Cellulose

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## SYNOPSIS

Treatment of cellulose by different concentrations of alkali, namely, 5–30% NaOH, changed its fine structure and transferred cellulose I into cellulose II. The decreased crystallinity due to alkali treatment and the transformation of cellulose I into cellulose II lowered the reactivity of cellulose toward the grafting polymerization reactions. Compactness of the structure as a result of the treatment of cellulose with 5% sodium hydroxide concentration decreased the rate of the grafting reaction and the grafting yield. On the other hand, such treatment of cellulose with different concentrations of alkali increased the rate of ceric consumption, i.e., increased the rate of oxidation of cellulose. Thus, the termination reaction of the grafting polymerization process may occur as a result of such oxidation and because of the increase of the active sites onto cellulose, leading to a decrease of the grafting yields and rate of grafting polymerization reaction by using the free-radical grafting process. The use of the ionic-xanthate method of grafting polyvinyl- and polyallyl-on alkali-treated cellulose shows an increase of grafting efficiency and grafting yields. Maximum grafting efficiency and yields were achieved when cellulose was treated with sodium hydroxide concentration below 15%, and maximum crystallinity indices were obtained. Using 15–25% sodium hydroxide lowered the indices of crystallinity, and lower grafting yields and grafting efficiency were achieved. Thus, transformation of cellulose I into cellulose II decreased the reactivity of these treated celluloses toward graft polymerization reactions by the use of the ionic-xanthate method. In our opinion, termination reactions may also occur and affect the results.

## INTRODUCTION

Mansour et al.<sup>1</sup> studied the effect of the state of cellulose defined by its crystallinity, grinding, and average degree of polymerization (D.P.) on the grafting yield. Decrystallization of cellulose nearly inhibits the grafting reaction. On the other hand, decreased D.P. leads to increased grafting yields, the governing factor being attributed to the specific numbers, 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 a further increase in the specific number, respectively, the formed active sites on grinding and decrystallization, brings about termi-

nation reactions through disproportionation and coupling of the exceedingly increased free radicals, and, hence, grafting is nearly inhibited. Compactness of the structure contributing to the drying of cellulose at 105°C resulted in decreased grafting yield.

Hori et al.<sup>2</sup> studied the effect of cellulose fine structure on its reactivity to graft copolymerization in the acrylamide–ceric system. They found that grafting yield decreased as the crystallinity and the ratio of diffraction intensities for the crystal planes (101), (002), and (101) increased. Results indicated that graft copolymerization forms mainly in the amorphous region and in the space between micelles oriented perpendicular to (101) plane.

Beating of dissolving pulp (96.1%  $\alpha$ -cellulose) in a PFI mill produced certain microstructural changes, increased the amorphous region, and decreased the D.P. It also increased the ceric ion reactivity of the cellulose and affected the percentage of grafting and

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the number of grafted chains per cellulose molecule; the initial grafting increases with a rapid initial rate and that of beaten celluloses reached a constant value earlier than did unbeaten pulp. Beating reduced the percentage of grafting and the number of grafted chain in the final copolymerization stage, despite the increase in ceric ion affinity. It is thought that beating resulted in a high consumption of cellulose radicals by ceric ion without initiating grafting and an early decrease in the concentrations of monomer and ceric ions without being used effectively for grafting.<sup>3</sup>

Gaylord and Anand<sup>4</sup> considered that the cellulose : monomer interaction in the grafting process depends on the crystallinity of cellulose and that the complexes are essentially aligned on the surface of the cellulose matrix and the propagating chains terminate in the more accessible amorphous areas.

In this work, the state of cellulose changed due to alkali treatment of cellulose with different sodium hydroxide concentrations was considered in regard to the graft polymerization reactions using different initiating systems, namely, ceric ions and sodium bisulfite–china clay for the free-radical method. The ionic-xanthate method was also used for studying the influence of the state of cellulose on the course of the reaction.

## EXPERIMENTAL

### Preparation of the Samples

Alkali treatment of cotton linter was carried out using 5, 10, 15, 20, 25, and 30% sodium hydroxide (wt/vol), at liquor ratio of 1 : 20° and temperature of 25°C for 1 h. The alkali-treated cellulose was washed with distilled water until free from alkali, then treated with 10% acetic acid for 10 min, washed again with distilled water until neutral, and then left to dry at room temperature. The dried samples were subjected to graft polymerization by the two methods described below.

### Free-Radical Polymerization

The polymerization reaction was carried out by using the monomers acrylonitrile, ethyl acrylate, and methyl methacrylate in the presence of ceric–ammonium sulfate (CAS) of 0.08% concentration in 1% sulfuric acid. The reaction was carried out at 30, 40, and 60°C. Graft reaction of methyl methacrylate was also carried out at 40°C, using sodium bisulfite–china clay system as initiator. The free radical methods of grafting were carried out according to

the processes mentioned by Mansour et al.,<sup>5,6</sup> and the ceric consumption was calculated in the presence and absence of grafting as follows<sup>7</sup>:

$$\begin{aligned} \text{Ceric consumed (\%)} \\ = \frac{\text{nmol CAS consumed}}{\text{nmol CAS added}} \times 100 \end{aligned}$$

### Ionic-Xanthate Method of Grafting

The graft polymerization was carried out by a two-stage method: The first stage was the formation of cellulose xanthate and the second was the polymerization stage.

**Formation of Cellulose Xanthate.** Cellulose xanthate was formed from the reaction between cotton linter with purified carbon disulfide and sodium hydroxide (17.5 wt %/vol), in the ratio of 1 : 3 : 6, respectively. This stage of reaction was carried out at 30°C for 1 h, with light hand-shaking every  $\frac{1}{4}$  h applied.

**Polymerization Stage.** The produced cellulose xanthate from the first stage was polymerized with different types of vinyl and allyl monomers in the ratio of 1 : 3 (cellulose : monomer). The polymerization reaction was carried out also at 30°C for 2 h, using a dilute HCl as a precipitating agent for the produced grafted cellulose. The precipitated grafted cellulose was filtered and washed with distilled water until neutralization through a sintered glass crucible ( $G_3$ ), then dried at 60°C for 24 h under vacuum.

True grafting yield and grafting efficiency were determined by extracting the homopolymer for a period of 48 h, using a Soxhlet apparatus with a suitable solvent according to the following table:

Monomer	Solvent of Extraction
Methyl methacrylate	Acetone
Methyl acrylate	Dimethyl sulfoxide
Ethyl acrylate	Tetrahydrofuran
Allyl alcohol	Distilled water
Allyl chloride	Dimethyl sulfoxide
Acrylonitrile	Dimethylformamide

The grafting parameters in both methods were calculated according to the following equations:

$$\text{Crude grafting yield (\%)} = \frac{(C - B)}{(B)} \times 100$$

$$\text{True grafting yield (\%)} = \frac{(A - B)}{(B)} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{(A - B)}{(C - B)} \times 100$$

where  $A$  is the weight of product after copolymerization and extraction in grams,  $B$  is the weight of dry cotton also in grams, and  $C$  is the weight of product after copolymerization.

### Chemical and Physical Analysis of the Treated Samples

Analyses of the alkali-treated celluloses were carried out according to standard methods regarding  $\alpha$ -cellulose, water retention value, solubility in 8% sodium hydroxide, ash content, and D.P.

Crystallinity indices (Cr.I.) and crystallinity ratio (Cr.R.) were calculated from the X-ray analysis according to the following equations<sup>8</sup>:

$$\text{Cr.I.} = \frac{(H - h)}{(H)} \times 100; \quad \text{Cr.R.} = 1 - \frac{(h)}{(H - h)}$$

where ( $h$ ) is the height of the minimum between 18 and 19° for cellulose I; for cellulose II, ( $h$ ) is the height of the minimum between 13 and 15°; for cellulose I,  $H$  is the height of the maximum between 22° and 23°, but for cellulose II, it is the height of the maximum between 19 and 20°.

### X-Ray Generator

The X-ray generator used in our work was a Hilger and Watts Y90 X-ray generator with a Philips 1KW sealed tube having a copper anode and beryllium windows. The tube had four shuttered windows, and the diffractometer system was positioned on one of them. The generator was operated at 38 KV and mA. The characteristic wavelength is  $\text{CuK}\alpha$  ( $\lambda = 0.154$  nm), which separated from the other wavelengths such as the  $\text{CuK}\beta$  doublet ( $\lambda = 0.139$  nm) with white radiation by passing the incident beam through a thin nickel filter fitted over a slit collimator.

## RESULTS AND DISCUSSION

### Influence of the Alkali Treatment of Cellulose on the Free Radical Graft Polymerization

Grafting reactions were carried out using the monomers ethyl acrylate, acrylonitrile, and methyl meth-

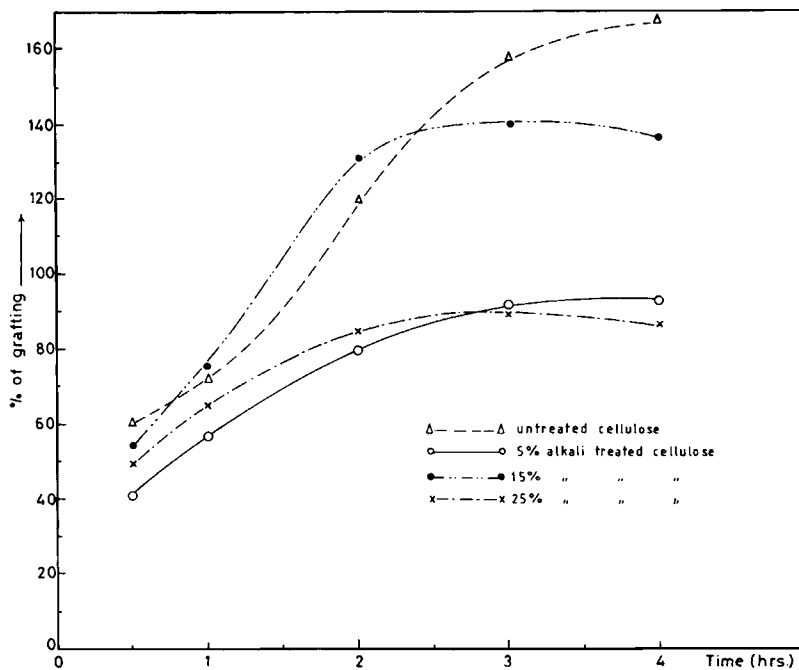
acrylate in the presence of ceric ammonium sulfate as initiator and the native and alkali-treated cotton linters as substrates. The temperatures used were 30, 40, and 60°C to trace the influence of the change of the structure of cellulose as a result of the alkali treatment on the graft yields and the rate of grafting. The results are illustrated on Figures 1–9. Ceric consumptions due to the oxidation of these alkali-treated celluloses at 30 and 60°C were plotted against time in Figure 10.

Figures 1 and 2 show that the rate of grafting of ethyl acrylate as well as the graft yields onto the alkali-treated cotton linters with 5, 15, and 25% sodium hydroxide concentrations were lower than those of the native cotton linter. The grafting temperatures used for these reactions were 30 and 40°C. From Figures 1 and 2, it can be seen that the treatment of cotton linter with 15% sodium hydroxide concentration was more reactive than was other the treated cotton linter toward graft polymerization.

Using the temperature of 60°C for the grafting reaction, which has been found to be the ceiling temperature of the grafting system of ethyl acrylate-cotton linter-ceric ammonium sulfate,<sup>3</sup> we show in Figure 3 that the 15% alkali-treated cellulose is still the most reactive substrate toward graft polymerization using the aforementioned system compared with the other treated celluloses. Also, the graft yield and the rate of grafting of the untreated cellulose (native) showed more reactivity toward grafting than did the treated ones. The other treatments of celluloses using 20, 25, and 30% sodium hydroxide concentrations, i.e., the alkaline concentrations that transfer cellulose I into cellulose II, showed a nearly similar effect on the reactivity of such treated celluloses on the rate of grafting reactions, which were, however, still lower than those of the native cellulose and the cellulose treated with 15% sodium hydroxide concentration. In conclusion, cellulose II showed little passivation toward graft polymerization by the free-radical method.

The chemical analysis of these alkali-treated celluloses, namely,  $\alpha$ -cellulose, solubility in 8% sodium hydroxide, and ash content, showed no relation between the different cellulose contents and the results of the graft yields and the rate of grafting (see Table I). No relation was found between the physical analyses, such as of the water retention value (W.R.V.) and average degree of polymerization (D.P.), of the alkali-treated celluloses (Table I) and the rate of grafting and the graft yield results.

On using acrylonitrile as the monomer to be grafted onto alkali-treated celluloses with 5, 15, 20, and 25% sodium hydroxide concentrations at 30, 40,

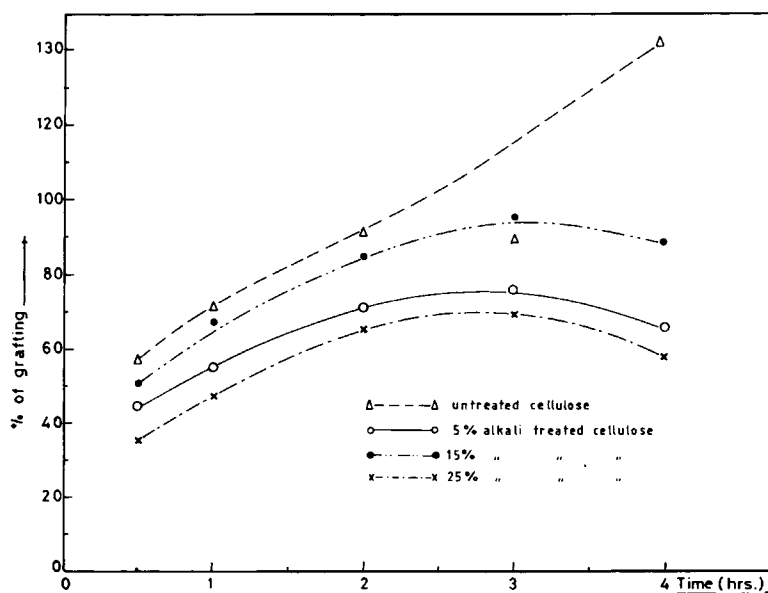


**Figure 1** Graft polymerization of ethyl acrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 30°C.

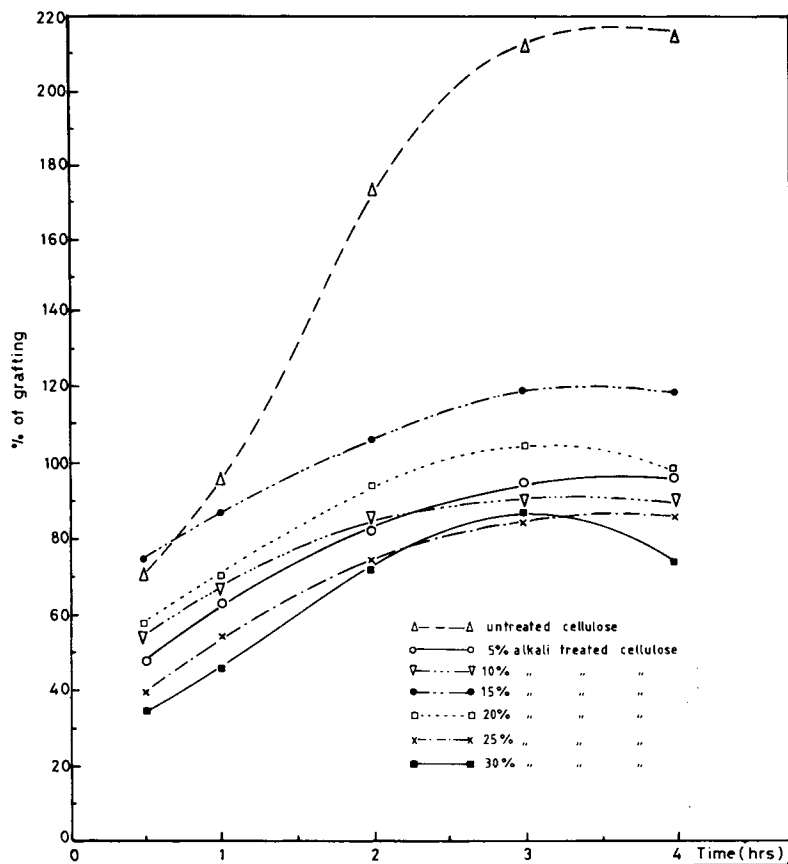
and 60°C, the results in Figures 4-6 showed that the graft yield and rate of grafting of the alkali-treated cotton linters are lower than those of the native cellulose. Even at the ceiling temperature, namely, 30°C,<sup>5</sup> the 15% alkali-treated celluloses still showed higher reactivity toward grafting than did

those treated with other sodium hydroxide concentrations.

With methyl methacrylate used for graft polymerization onto alkali-treated cotton linters with 5, 15, and 25% sodium hydroxide concentrations using ceric ammonium sulphate as initiator and at 30°C,



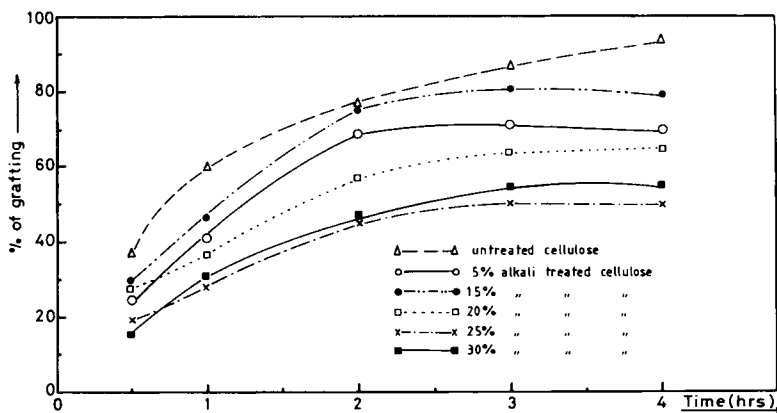
**Figure 2** Graft polymerization of ethyl acrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 40°C.



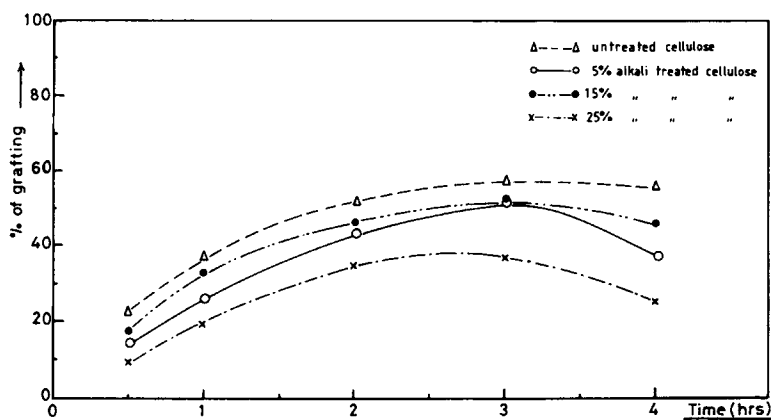
**Figure 3** Graft polymerization of ethyl acrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 60°C.

the rate of grafting and the grafting yields showed a reverse order of reactivity (Fig. 7). The alkali treatment in this case activates the celluloses toward graft polymerization, and the 25% alkali-treated cellulose is more reactive than are the 15% alkali-

treated ones, followed by those treated with 5%; the other treated celluloses and the untreated one are the least reactive. The same order of reactivity was achieved on carrying out the graft polymerization reaction using the same system of initiator and the



**Figure 4** Graft polymerization of acrylonitrile onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 30°C.

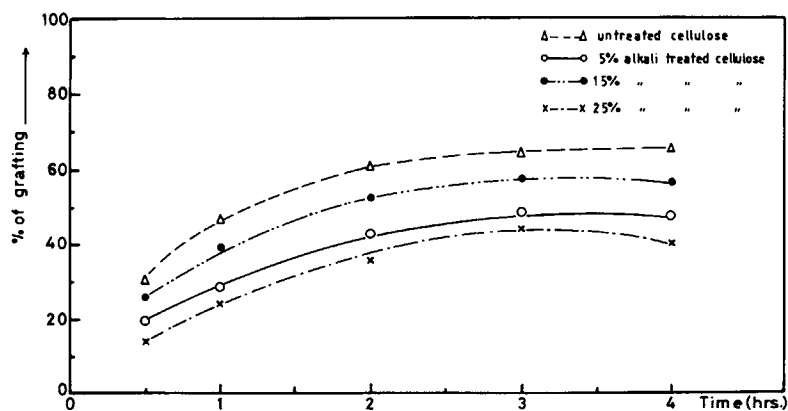


**Figure 5** Graft polymerization of acrylonitrile onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 40°C.

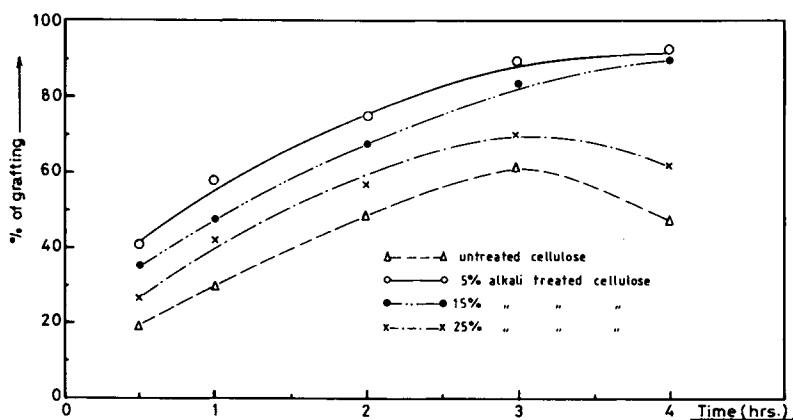
same monomer on the different alkali-treated celluloses at 40 and 60°C (Figs. 8 and 9, respectively). It is noteworthy that ceric ammonium sulfate has been proved to be an unsuitable initiator for graft polymerizing methyl methacrylate.<sup>6</sup> The suitable initiator for grafting such monomer onto cellulose is the sodium bisulfite-soda lime glass,<sup>6</sup> and it is possible to use china clay instead of soda lime glass.<sup>9</sup> Therefore, grafting reactions were carried out on the alkali-treated cotton linters using the initiator system sodium bisulfite-china clay at 30, 40, and 60°C (Figs. 11-13, respectively). The order of the reactivity of these treated celluloses toward graft polymerization using this system are parallel to the order of reactivity achieved before for both ethylacrylate and acrylonitrile monomers in the presence of ceric ammonium sulfate as initiator.

In regard to the ceric consumed by these alkali-treated celluloses at 30, 40, and 60°C, it can be seen in Figure 10 that the rate of the ceric consumption

after 3 h decreased in the following order: 25% alkali-treated cellulose at 60°C; that treated at 30°C; then 15% alkali-treated cellulose at 30°C; cellulose treated with 5% sodium hydroxide concentration at 60°C; then that treated one at 30°C. The least amount of ceric was consumed by the native cellulose carried out at both 30 and 60°C. However, at the initial stage of the ceric oxidation, the rate of the ceric consumption by different celluloses decreased in the following order: 5% alkali-treated cellulose at 60°C; that treated at 30°C; then untreated cellulose at 60°C. The rate of the ceric consumption by the 25% alkali-treated cellulose at 30°C and at 60°C is the same, whereas the rate of consumption by the untreated cellulose at 30°C is less and that of the other treated and untreated celluloses, both at 30 and 60°C is the least (Fig. 10). However, the rate of the ceric consumption cannot be taken as an indicator of the change of the rate of the reactivity of celluloses toward the graft polymerization reaction,



**Figure 6** Graft polymerization of acrylonitrile onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 60°C.

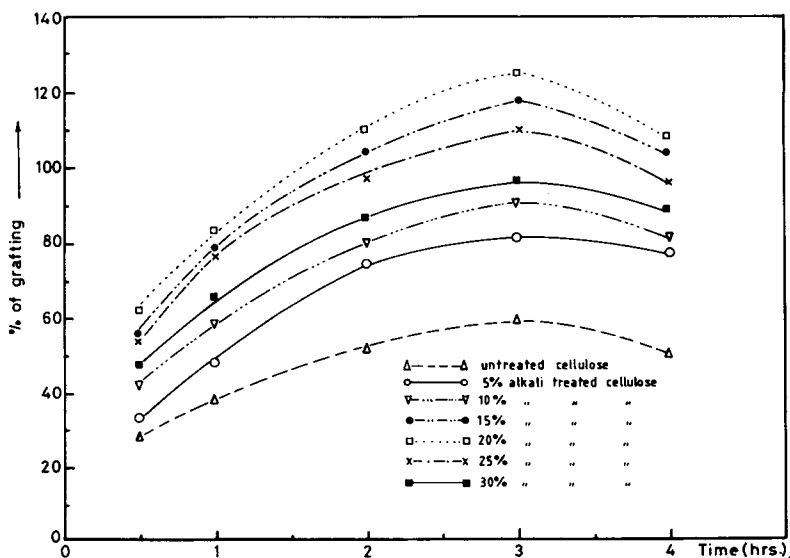


**Figure 7** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 30°C.

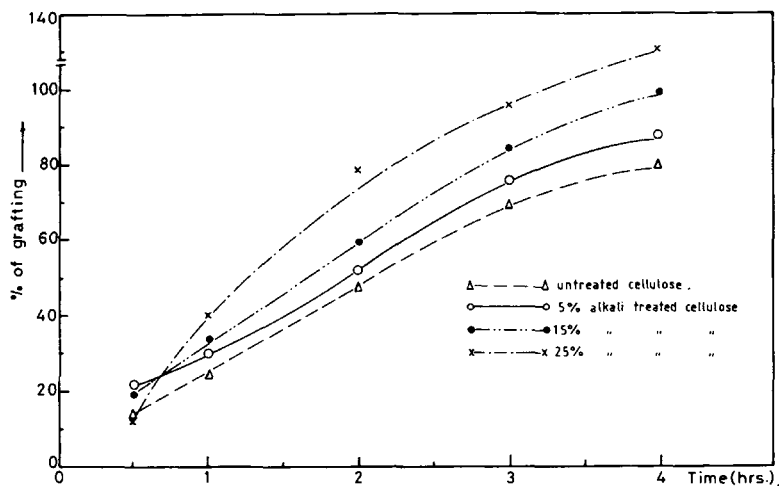
although it is shown that the lowest rate of ceric consumption was achieved for the untreated celluloses showing the highest rate of grafting reaction and graft yields. Thus, it can be concluded that alkali treatment of celluloses, namely, cotton linter, increased the rate of the reactivity of these treated celluloses toward consuming ceric ions; consequently, either a ceric-oxidation reaction or the formation of more active sites that may lead to graft polymerization, or both reactions, may have occurred. In both cases, the rate of grafting and the graft yields may be decreased because the oxidation of celluloses with ceric ion is not suitable for the grafting reaction; also, the formation of more active sites may lead to the termination reactions by both

coupling and disproportionation reactions. Additionally, Hori et al.<sup>2</sup> stated that the graft copolymerization forms mainly in the amorphous regions.

Investigation of the different celluloses, treated and untreated, was carried out using an X-ray diffractometer to trace the influence of the alkali treatment on the degree of crystallinity (Figs. 14 and 15) and, consequently, to understand the effect of this variable on the reactivity of cellulose toward the graft polymerization reaction. The results shown in Figure 15 indicate that the crystallinity indices increased for the 5% alkali-treated cellulose until maximum and then decreased until minimum for the treatment of cellulose with sodium hydroxide solution until 20% alkali concentration. When using



**Figure 8** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 40°C.

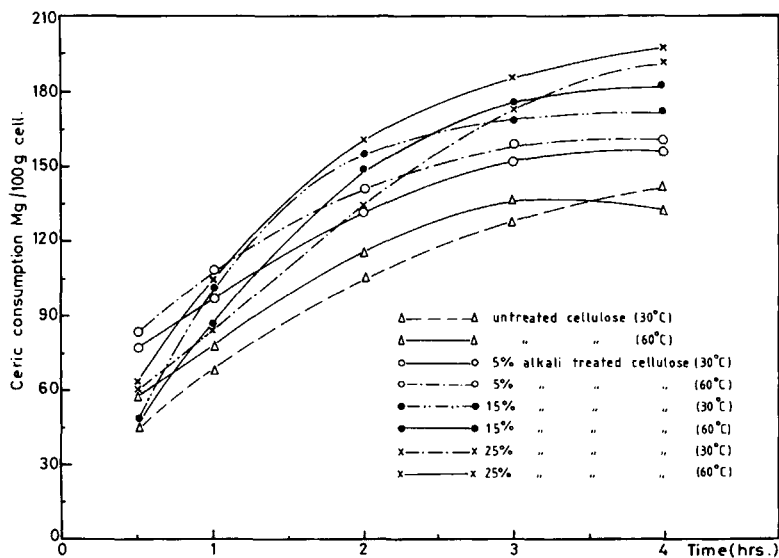


**Figure 9** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of ceric ammonium sulphate as initiator at 60°C.

a sodium hydroxide concentration of 25% and 30% for treating celluloses, increases in the crystallinity indices were achieved until maximum again, but they were still lower than the degree of crystallinity of the native cellulose. On the other hand, the crystallinity ratio clearly decreased for the alkali-treated celluloses and, hence, the amorphous regions increased. The increase in the degree of crystallinity for the 5% alkali-treated cellulose (Fig. 14, chart 2) may be due to the compactness of the fibers, namely, condensation of the structure of cellulose, as has been stated by Mansour et al.<sup>10</sup> Such condensation of the structure affects the affinity of the cellulose

to adsorb the reagent, and, hence, a decrease in the rate of graft polymerization and the graft yields was achieved. The X-ray charts (Figs. 4-7) show that the use of a sodium hydroxide concentration above 15% for the treatment of cellulose transferred cellulose I into cellulose II, which is defined by the presence in it of forked bands in the range 19-22 $\theta$ . Hence, transformation of cellulose I into cellulose II takes place when sodium hydroxide concentrations range between 15 and 30%.

On the other hand, the decrease of the degree of crystallinity achieved as a result of the alkali treatment and, consequently, the increase of the amor-



**Figure 10** Ceric consumption. Concentration of ceric ammonium sulphate (CAS) 0.08 g/100 ml 1% H<sub>2</sub>SO<sub>4</sub>, liquor to cellulose ratio 30 : 1.



**Table I** Chemical and Physical Analyses of the Untreated and Alkali-Treated Cotton Linters

Alkali Concentration (%)	Wt Loss (%)	Ash (%)	W.R.V. (%)	Solubility (%) in 8% NaOH	$\alpha$ -Cellulose (%)	$\overline{D.P_w}$
Untreated	6.4	0.66	18.19	0.25	99.33	731.00
5	9.5	0.38	34.08	2.16	96.90	688.95
10	3.4	0.13	13.13	2.66	95.30	677.05
15	9.3	0.20	15.25	5.62	93.67	659.29
20	3.2	0.10	30.69	4.73	94.40	641.64
25	2.1	0.46	39.50	3.09	97.46	600.92
30	2.7	0.49	33.46	4.00	95.22	538.26

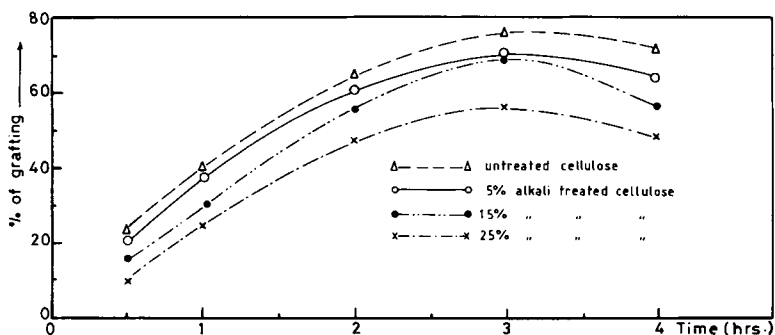
phous regions may be responsible for the decrease of the rate of grafting reaction and the graft yields. The increase in the amorphous regions means an increase in the number of the active sites that may undergo a termination reaction through disproportionation and coupling reactions.

Summing up, it can be said that using alkali-treated celluloses as a substrate for the free-radical graft polymerization of some vinyl monomers using a suitable initiating system, such as the sodium bisulfite-china clay system for the monomer used for the grafting reaction, leads to a decrease in the graft yields and the rate of grafting as compared to that of native cellulose. Using an unsuitable initiating system, such as ceric ions, for initiating the grafting of methyl methacrylate onto treated and untreated cotton linters leads to a greater increase in the rate of grafting and graft yields of the treated cotton linters than of the untreated ones. In other words, alkali treatment of cotton linters increased their reactivities toward grafting in this case. However, alkali treatment activates celluloses toward ceric consumption, which may have caused the decrease in reactivities of these treated celluloses toward grafting as the termination reaction increased because of the grafting reactions. The increased ter-

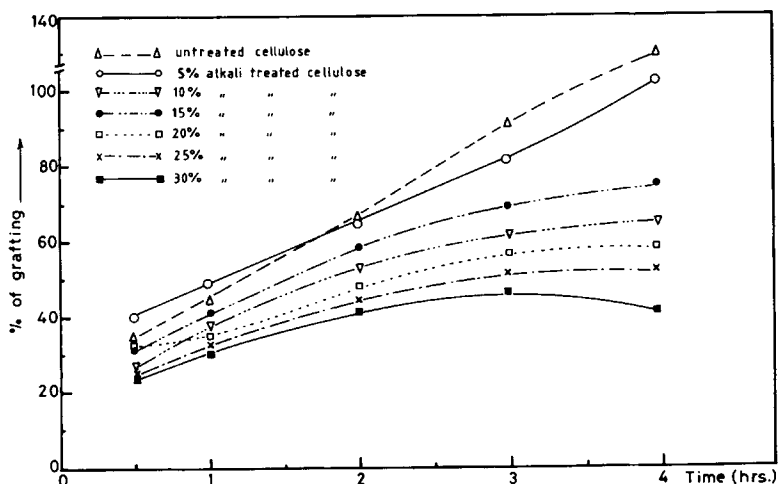
mination reactions may have occurred due to the formation of more active sites that undergo disproportionation and coupling reactions. Thus, the decreased crystallinity index, i.e., the increased amorphous regions indicated by X-ray analysis, leads to a decrease both in the rate and grafting yields. Also, the decreased rate of grafting and graft yields due to alkali treatment of celluloses may, in turn, be due to that the increased specific surface of these treated celluloses contributed to the swelling occurring in the presence of sodium hydroxide and the deswelling as a result of the washing of celluloses with distilled water. The increase of the specific surface as well as the decrease of the average degree of polymerization (D.P.) (Table I) increased the rate of termination reactions by disproportionation and coupling reactions and, hence, led to an overall decrease of the rate of graft polymerization reaction and grafting yields.

#### Influence of the Alkali Treatment of Cellulose on the Ionic-Xanthate Method of Grafting

Graft polymerization of some vinyl and allyl monomers onto cellulose, using the ionic-xanthate method



**Figure 11** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of sodium bisulfite-china clay as initiator at 30°C.



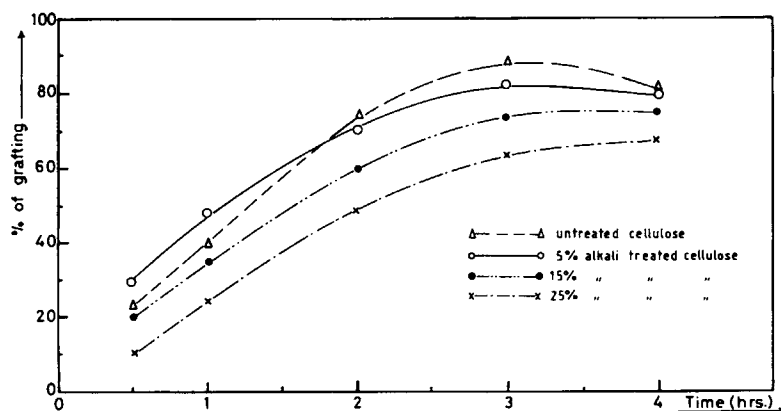
**Figure 12** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of sodium bisulfite-china clay as initiator at 40°C.

of grafting, depends mainly on the formation of cellulose xanthate in the presence of sodium hydroxide.

The ionic-xanthate method of grafting was used to graft polymerize acrylonitrile, ethyl acrylate, methyl methacrylate, methyl acrylate, allyl alcohol, and allyl chloride monomers onto native and alkali-treated celluloses. The results obtained, i.e., the graft yields after 2 h of grafting reactions, are plotted against the concentration of sodium hydroxide used for the alkali treatment of cotton linters (Fig. 16A and B). In this method of grafting, the extent and the rate of graft polymerization depends more or less on the concentration of sodium hydroxide used for the formation of the xanthate groups,<sup>11</sup> and, hence, the swelling of the substrates that contributed to the formation of amorphous regions plays a role. Thus, the results in Figure 16(A and B) showed

that the graft yields achieved for the alkali-treated cotton linters are higher than those for the native cotton linters for all the monomers under investigation. However, sodium hydroxide concentrations used for the alkali treatment and corresponding to the concentration leading to maximum swelling lay in the range 15–25% NaOH.<sup>12</sup> The graft yields for the treated celluloses with these concentrations showed values more decreased than for those treated with sodium hydroxide concentrations lower than 15%. It can be concluded that the transformation of cellulose I into cellulose II leads to some passivation toward the ionic-xanthate method of grafting as in the case of free-radical grafting method.

The grafting efficiencies were calculated for the grafting reactions using the ionic-xanthate method and also for all monomers and substrates under in-



**Figure 13** Graft polymerization of methyl methacrylate onto alkali-treated cellulose in presence of sodium bisulfite-china clay as initiator at 60°C.

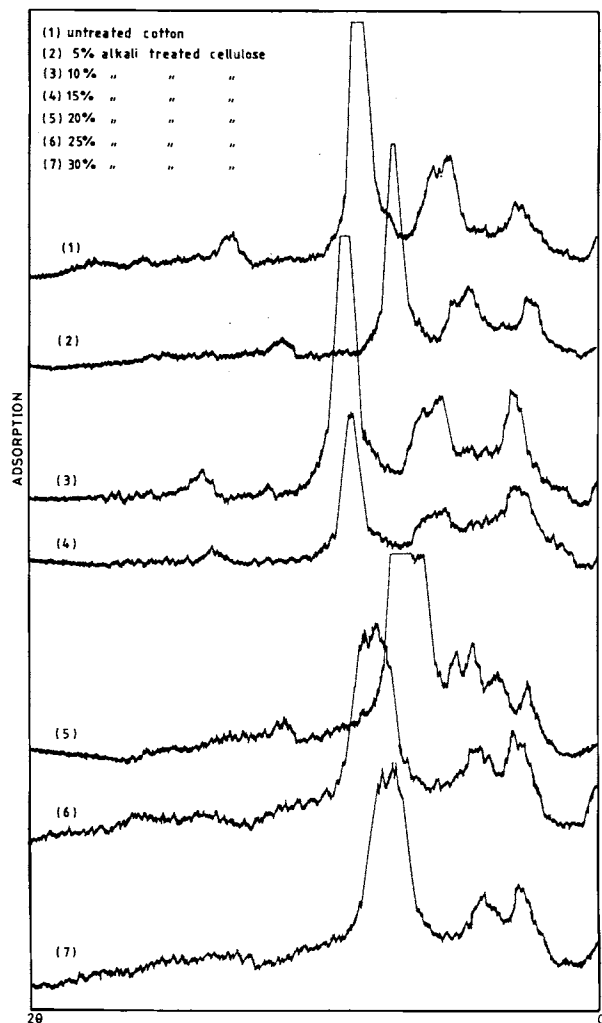


Figure 14 X-Ray analysis of untreated and alkali-treated cotton linters.

vestigation, and the results are shown in Table II. From this table it is clear that the grafting efficiencies of the graft polymerization reactions using alkali-treated celluloses with sodium hydroxide concentrations lower than 15% showed higher values than did those treated with higher concentrations.

Hence, the lowest graft yields of the alkali-treated cotton linters lie in the range of the alkali treatment corresponding to the lowest degree of crystallinity and the transformation of cellulose I into cellulose II, namely 15–25% (Fig. 15 and charts 4–7 in Fig. 14). Thus, the increased amorphous regions and the formation of cellulose II decreased the grafting efficiency and the graft yields. Accordingly, the increased specific surface as a result of the increased amorphous celluloses decreased the reactivity toward grafting reactions using the ionic-xanthate

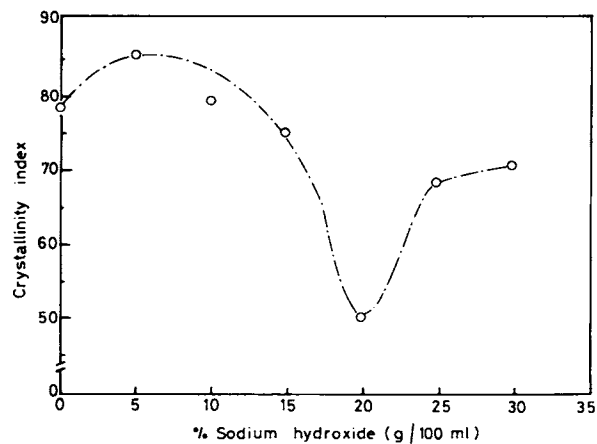


Figure 15 Crystallinity indices of different alkali-treated celluloses.

method. Such a result may contribute to the termination reactions that occurred as a result of the increased specific surface.

On the other hand, the increase of the graft yields achieved for the alkali-treated celluloses with sodium

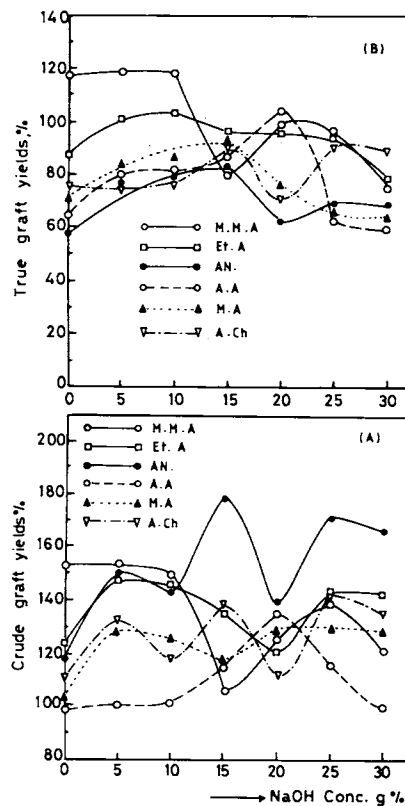


Figure 16 Graft polymerization of the alkali-treated celluloses using the Xanthate-Method of Grafting. *N.B.* Crude graft yields, % = True graft yields, % + extracted homopolymer, %.

**Table II Grafting Efficiency of Graft Polymerization Reaction of the Alkali-Treated Celluloses Using the Ionic-Xanthate Method**

NaOH Used for Treatment (%)	Monomer Used					
	Methyl Methacrylate ( $\pm 0.8$ )	Ethyl Acrylate ( $\pm 1.0$ )	Allyl Alcohol ( $\pm 1.2$ )	Acrylonitrile ( $\pm 1.5$ )	Methyl Acrylate ( $\pm 1.0$ )	Allyl Chloride ( $\pm 1.3$ )
Untreated	76.0	71.9	65.8	49.0	68.3	69.2
5	75.7	69.8	77.5	47.8	65.1	57.1
10	79.1	71.5	79.4	60.6	64.4	64.4
15	76.3	70.6	72.4	49.3	66.0	66.2
20	79.0	62.3	76.5	46.9	70.1	63.9
25	69.3	67.8	72.0	40.2	42.4	66.9
30	60.8	57.3	58.3	40.5	49.5	64.3

Xanthation of the substrate was carried out at 30°C; concentration of NaOH was 17.5%; CS<sub>2</sub>:cellulose = 3:1, for 2 h; monomer:cellulose = 3:1; grafting temp = 30°C.

hydroxide concentrations below 15%, i.e., when cellulose was treated with 5% NaOH, may be due to the increased crystallinity indices as shown in Figure 15. Such results may emphasize the consideration of Gaylord and Anand<sup>4</sup> that cellulose–monomer interactions in the grafting process depend on the crystallinity of cellulose and that the complexes are essentially aligned on the surface of the cellulose matrix and the propagating chains terminate in the more accessible amorphous areas.

## CONCLUSIONS

- Free-radical polymerization reactions are greatly influenced by the alkali-treating of cellulose; the decrease in crystallinity that accompanied the alkali treatment with 5–15% sodium hydroxide leads to a decrease in graft yields and rate of grafting compared with untreated cotton linter. However, opposite results were obtained on using the ionic-xanthate method of grafting.
- Transformation of cellulose I into cellulose II, by treating with 20–25% NaOH, leads to some passivation toward both the free-radical and ionic-xanthate method of grafting.

## REFERENCES

- O. Y. Mansour et al., *J. Appl. Polym. Sci.*, **VI**, **23**, 2425–2434 (1979).
- Y. Hori, T. Takahashi, M. Nagata, and T. Sats, *J. Soc. Fiber Sci. Technol. Jpn. Sen Gakkaishi*, **22**(10), 443 (1966).
- H. Kurosu and K. Horiike, *J. Jpn. Wood Res. Soc.*, **22**(2), 92 (1976).
- N. G. Gaylord and L. C. Anand, *J. Polym. Sci. Polym. Lett. Ed.*, **10** (1972).
- O. Y. Mansour and J. Schurz, *Svensk Papperstidning*, **76**, 258 (1973).
- O. Y. Mansour and A. Nagaty, *J. Polym. Sci.*, **13**, 2785–2793 (1975).
- M. Rebek and J. Schurz, *Osterreich Chem. Kerzeitung*, **68**, 376 (1967).
- J. Segal, J. J. Geely, and C. M. Connad, *Textile Res. J.*, **29**, 786–793 (1959).
- O. Y. Mansour and A. B. Moustafa, *J. Polym. Sci.*, **13**, 2795–2805 (1975).
- O. Y. Mansour, M. El Saayd, and A. Mottaleb, *Indian Pulp Paper*, **26**, 89 (1972).
- A. H. Basta, M.Sc. Thesis, Cairo University, 1983.
- O. Y. Mansour, *Indian Pulp Paper*, **26**(10), 124–128 (1972).

Received September 20, 1990

Accepted January 4, 1991