Graft Copolymerization of Acrylonitrile onto Bagasse and Wood Pulps

SALWA O. HEIKAL and SAMIRA F. EL-KALYOUBI, *National Research Centre, Cellulose and Paper Laboratory, Dokki, Cairo, Egypt*

Synopsis

Graft copolymerization of acrylonitrile onto bagasse and wood pulps has been studied using ceric ammonium nitrate as initiator. The effect of order of reactants addition on grafting was examined: three methods were studied. Addition of the pulp to a mixture of initiator and monomer (method A) resulted in more efficient grafting than the other two methods. The reaction produced more grafting at 50°C than at 30°C or at 40°C. The results showed that the monomer and initiator concentrations are the major factors influencing the grafting rate of acrylonitrile. Increasing the acrylonitrile or initiator concentration was accompanied by a substantial increase in graft yields. Increasing the initiator concentration is more effective on polymerization rate than the increase in monomer concentration. The extent of grafting of this monomer can best be controlled by reaction time. Water swelling of pulps significantly affected the grafting rate of acrylonitrile as well as the ceric consumption during grafting. The reactivity of bagasse pulp towards grafting of acrylonitrile is higher than that of wood pulp due to a more open structure of cellulose in bagasse pulp as well as the presence of some lignin which accelerates grafting. Ceric consumption during grafting depends on the nature of the pulp as well as the monomer and initiator concentrations, time, temperature, and the method of grafting. More Ce(IV) is consumed during grafting than during oxidation of the pulps under identical reaction conditions, due to homopolymer formation which accompanied grafting. The ceric consumption by bagasse during grafting or oxidation is somewhat greater than that consumed by wood pulp under similar reaction conditions.

INTRODUCTION

The use of ceric ions to initiate graft copolymerization of vinyl monomers on various cellulosic materials (wood pulp, cotton, rayon, and paper) has gained considerable importance. Since the ceric ion is a powerful oxidizing agent, it therefore has high efficiency on both grafting and oxidation of cellulose.[1-5] Kaizerman et al.[2] have reported that ceric ammonium nitrate is more efficient for graft polymerization than the corresponding sulfate. It has been postulated that the initiation of free radicals on the cellulose molecule occurs through a single-electron transfer according to a mechanism proposed by Mino and Kaizerman.[5] This mechanism favors grafting much more than homopolymer formation. Cleavage of the C_2—C_3 glycol bond occurs during this system of grafting initiation.

This paper reports the results of a study designed to show the influence of water swelling of cellulose fibers as well as the order of reactants addition on grafting. Another object of this work was to study the parameters which affect the grafting reaction of acrylonitrile onto bagasse pulp as compared with wood pulp.

CCC 0021-8995/82/083027-15$02.50

HEIKAL AND EL-KALYOUBI

EXPERIMENTAL

Materials

Pulp Preparation

Unbleached commercial bagasse pulp provided by Edfo Mill, Egypt, was used in this study. The pulp was bleached by applying the conventional three-stage process. The bleached pulp has the following analysis: 73.71% α-cellulose, 22.74% pentosan, 1.50% lignin, 0.38% ash, and 909 D.P. Also commercial bleached birch sulfate pulp of 85% α-cellulose, D.P.; SCAN C_{15}, 1045 was used as a reference.

Ceric ammonium nitrate (CAN), BDH reagent grade, aqueous solution containing concentrated nitric acid (1%) was used after standardization with ferrous sulfate.[6] Freshly distilled acrylonitrile (AN) was used.

Methods

Graft copolymerization of AN onto pulps was carried out according to different methods.[7-12] The procedures were carried out as follows.

(Method A)[7]

Polymerization was carried out by adding monomer to 30 mL CAN then 1 g water-swollen pulp, based on dry weight, was immediately introduced into the reaction flask.

Conventional Ceric Ion Method[8-11] *(Method B)*

Polymerization was initiated by the addition of 30 mL ceric salt aqueous solution of known concentration to a system containing 1 g swollen pulp (based on dry weight), water, and monomer.

Adsorbed Ceric Ion Method[11,12] *(Method C)*

One gram of swollen pulp sample (based on dry weight) was immersed, after adjusting the liquor ratio, in 30 mL ceric salt aqueous solution of known concentration and then the polymerization was carried out by adding monomer to the reaction flask.

After the required reaction time, the polymer samples were washed well by extraction with several portions of distilled water, with a little soap to remove the loosely adhering polymer, washed, and dried. In order to calculate the graft yield, some of the polymer samples were Soxhlet extracted with dimethyl formamide for 36 h to remove the homopolymer.

Polymer loading (%) (percent weight increases due to polymerization) is determined from the values of the nitrogen content of the treated samples. The nitrogen content is determined by a standard Kjeldahl procedure.[13] The percent conversion to homopolymer is calculated as follows:

$$\% \text{ homopolymer} = \frac{\text{weight of homopolymer}}{\text{weight of monomer}} \times 100$$

The polymerization conditions are summarized in Table I.

Oxidation of pulps with CAN was carried out under conditions identical with those for grafting, except that the monomer was omitted.

Ceric consumption during grafting and oxidation was determined according to a method reported by Mino et al.[6]

RESULTS AND DISCUSSION

Order of Reactants Addition

In order to investigate the most suitable method for grafting AN onto bagasse and wood pulps for producing maximum grafting, polymerization was performed by using three different methods (A, B, or C) described in the experiment, which differed mainly in the order of reactants addition. The polymerization reaction has been studied with respect to polymer loading and ceric [Ce(IV)] consumption during grafting with CAN as initiator. The results are shown in Figures 1 and 2.

Polymer Loading

Because ceric salts can initiate the polymerization of certain vinyl monomers, such as AN, and can form complexes with both cellulose and the monomer, the effect of mode of addition of the initiator was investigated. The reactions were carried out with identical concentrations of CAN and AN and under identical conditions of temperature, liquor ratio, and time intervals.

Figure 1 shows the rate of grafting of AN onto bagasse and wood pulps using the different grafting methods studied. The percent of polymer loading increases with increasing reaction time, since time enhances swelling of the fibers and diffusion of both monomer and initiator inside them. This is true for all the methods studied. However, the polymer loads obtained differ considerably according to the method used. The polymer loads of bagasse pulp obtained by using method A are significantly higher than those obtained with method C, at the same reaction time.

TABLE I
Polymerization Conditions[a]

Initiation	Initiator concentration (mol/L)	Liquor ratio	Monomer concentration (% based on pulp weight)	Reaction temp. (°C)
Method A	0.02	50:1	100	50
	0.01	50:1	$\left\{\begin{array}{l}100\\200\\300\end{array}\right.$	$\left\{\begin{array}{l}30, 40, 50\\50\\50\end{array}\right.$
	0.002	50:1	100	50
Method B	0.01	50:1	100	50
Method C	0.01	50:1	100	50

[a] The pulp samples (based on dry weight) were initially swelled in water for 24 h, then disintegrated and filtered from water. The CAN aqueous solutiion was initially thermostated for 15 min (after adjusting the liquor ratio) at a specific temperature.
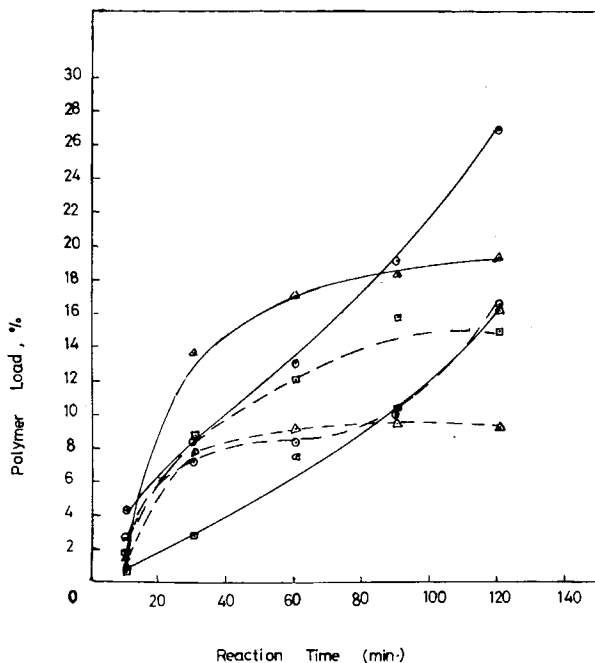
Fig. 1. Effect of grafting method on the rate of polymerization. (⊙) Method A; (△) method B; (▫) method C; temperature = 50°C; liquor ratio = 50:1; AN = 1 g; (——) bagasse pulp; (- - -) wood pulp.

The rate of polymerization of bagasse pulp was considerably lower (Fig. 1), when the initiator was added before the monomer (method C), and there was a significant decrease in the amount of the polymer loads (compared with the other two methods of addition). This is due to a decrease in initiator concentration, method C, since part of it was exhausted in oxidation of pulp before adding the monomer.

In the early stage of reaction, no difference is observed in the polymer loading obtained with methods B or C. However, as the reaction proceeds up to 120 min, method B (in which the monomer was added before initiator) resulted in considerably higher polymer loads than those obtained with method C. This is probably due to the increasing availability of monomer for grafting. Opposite results were obtained in the case of wood pulp. Hence, method C resulted in a considerable increase in polymerization rate as compared with the other two methods. The rate of polymerization using method B leveled off after a certain reaction time and showed a maximum yield. The leveling of the reaction in this case can be attributed to the substantial amount of polymer grafted on the substrate backbone which impedes diffusion of Ce(IV) as well as monomer into cellulosic fibers for further grafting. Whereas the polymerization rate in method A was directly proportional to the reaction time, method A (after a long time) resulted in a greater polymer load than that of method B. This remains true for both bagasse and wood pulps. Moreover, the reactivity of bagasse pulp towards grafting of AN with methods A and B was higher than that of wood pulp. Thus, the highest polymer loads achieved were about 27 and 19% with methods A and B, respectively, for bagasse pulp. In wood pulp a much lower percentage
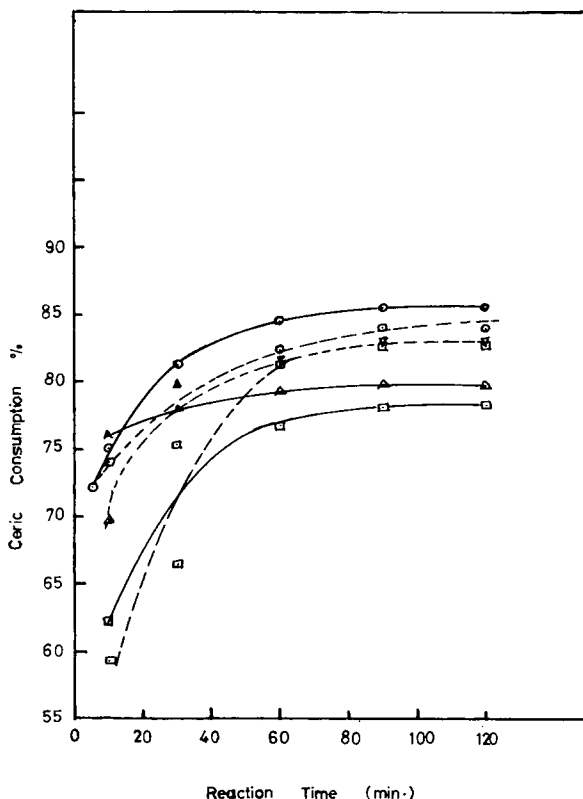
Fig. 2. Ceric consumption during grafting with different methods. (⊙) Method A; (△) method B; (□) method C; temperature = 50°C; liquor ratio = 50:1; AN = 1 g; (——) bagasse pulp; (- - -) wood pulp.

of polymer loads was obtained with the same methods under identical reaction conditions, about 16 and 9% for methods A and B, respectively. This is due to the more open structure of cellulose in bagasse pulp. The maximum polymer loads for both pulps can be achieved by using method A.

Ceric Consumption during Different Grafting Methods

Ceric [Ce(IV)] consumption by bagasse and wood pulps during grafting of AN with methods A, B, and C using CAN as initiator at 50°C are shown in Figure 2. This consumption is expressed as the percent of ceric consumed to ceric added. The consumption increases with increasing reaction time, and is more significant in the initial stages of the reaction than in the latter ones owing to the lowering of ceric concentration as well as shortage of reactive sites on the substrate backbone as the reaction proceeds. This is observed with both pulps and is the same for the three methods studied. Figure 2 shows that the reaction is characterized by an initial fast rate followed by a slower one.

The magnitudes of Ce(IV) consumption during grafting differ considerably depending on the type of the pulp as well as the grafting methods. The Ce(IV) consumption by bagasse pulp during grafting using method A (Fig. 2), was higher than when grafting was carried out by using methods B or C. The same trend

was observed with respect to wood pulp. However, the Ce(IV) consumption by bagasse pulp in the early stages of the reaction was higher than that which occurred in wood pulp. This is in accord with the open structure of cellulose in the case of bagasse pulp as well as the presence of small amounts of lignin which react with the initiator.[14] As the reaction proceeded, the percent of Ce(IV) consumption was higher for wood pulp than for bagasse pulp (except in method A). This is possibly due to the easier swelling of wood pulp (which enhances the diffusion of initiator inside the fibers) than bagasse pulp.

Effect of Different Parameters on the Grafting Reaction

The effect of different variables on the grafting of AN onto bagasse and wood pulps was calculated by using method A, which resulted in the highest polymer loading. The variables studied include concentrations of monomer and ceric salt as well as temperature and reaction time. The grafting process was performed by using Ce(IV) as initiator.

Monomer Concentration

The effect of monomer concentration on the degree of conversion of monomer to polymer as well as the corresponding graft yield and grafting efficiency of bagasse and wood pulps is given in Table II. Increasing the AN concentration increases the rate of polymerization (Figure 3). Consequently, upon increasing the monomer concentration from 100 to 200% (based on dry pulp weight), the grafting yield increased from 6.17 to 28.5% and from 5.69 to 15.30% for bagasse and wood pulps, respectively (Fig. 3). A further increase in AN concentration to 300% (based on dry pulp weight) resulted in a significant additional increase in the grafting yield of bagasse and wood pulps from 28.50 to 70.88% and from 15.30 to 32.76%, respectively. At low AN concentrations (100% based on pulp) bagasse and wood pulp behaved more or less the same since they have nearly the same graft yield (6.17 and 5.69%, respectively). On the other hand, with higher monomer concentration (200 or 300% based on pulp weight) grafting of the monomer onto bagasse pulp proceeds at a rate which is higher than that for wood pulp. Therefore, grafting of AN onto bagasse pulp is considerably faster than

TABLE II
Effect of Monomer Concentration on Grafting of AN onto Bagasse and Wood Pulps[a]

Starting material	AN % based on dry pulp weight	Polymer loading (%)	Degree of conversion (%)	Grafting yield (%)	Grafting efficiency (%)	Homopolymer (%)
Bagasse	100	13.00	13.00	6.17	47.46	2.14
pulp	200	43.22	21.61	28.50	65.94	7.86
	300	95.04	31.68	70.88	74.58	8.05
Wood	100	8.28	8.28	5.69	68.72	1.32
pulp	200	34.85	17.43	15.30	43.90	9.67
	300	85.56	28.52	32.76	38.29	17.60

[a] Reaction temperature = 50°C; 0.01 mol initiator concentration; liquor ratio = 50:1; reaction time = 60 min.
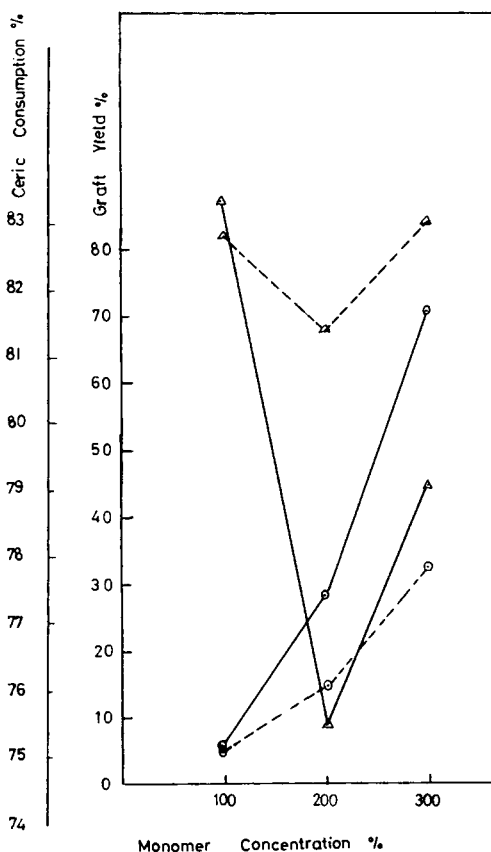
Fig. 3. Effect of AN concentration on grafting rate. (⊙) Graft yield; (△) ceric consumption; temperature = 50°C; liquor ratio = 50:1; time = 60 min; ceric concentration = 0.01 mol; (——) bagasse pulp; (- - -) wood pulp.

onto wood pulp. Thus, at any given concentration, the degree of conversion of monomer to polymer as well as the graft yield of bagasse pulp are higher than that of wood pulp (Table II). The above results can be explained by assuming that the cellulose structure of bagasse pulp is more open than that of wood pulp and hence more diffusion of initiator and monomer occurs. Also, due to the presence of some lignin in bagasse pulp which reacts with ceric ions at a faster rate than cellulose, forming active sites responsible for accelerating the formation of grafts and therefore increasing number of grafts are obtained.[15]

Although the grafting efficiency of wood pulp is higher than that of bagasse pulp with low monomer concentration (see Table II), it is significantly lower with higher monomer concentration. This may be due to the percentage of homopolymer formed. Although the total conversion was low (8–31%) (Table II), the amount of AN converted to homopolymer is always lower than the amount grafted. Consequently the grafting efficiency of bagasse pulp (ratio of graft yield to total amount of monomer converted to polymer) was higher than 50% at all concentrations. Actually, the grafting efficiency increased with AN concentration, and a higher grafting efficiency (74.6%) was obtained at an AN concentration of 300% (based on pulp weight). Whereas, the grafting efficiency of wood pulp increased with the AN concentration and showed a maximum (43.9%) at an AN concentration of 200%.
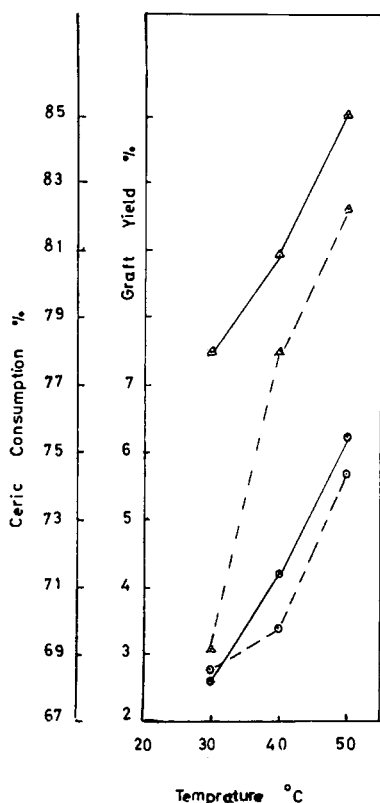
Fig. 4. Influence of temperature on (⊙) graft yield and (△) ceric consumption. (——) Bagasse pulp; (- - -) wood pulp.

Temperature

The effect of temperature on grafting of AN onto bagasse and wood pulps was studied using a low monomer concentration (100% based on pulp weight) at 30, 40, and 50°C. The results are given in Figure 4 and Table III. For both pulps the grafting rate increases with increasing temperature from 30 to 50°C and follows the order 50 > 40 > 30°C. The improvement in graft yields as a result of increasing the reaction temperature is due to the higher rate of dissociation

TABLE III
Effect of Temperature on Grafting of AN onto Bagasse and Wood Pulps[a]

Starting material	Grafting yield (%)			Grafting efficiency (%)			Homopolymer (%)		
Temp. (°C)	30	40	50	30	40	50	30	40	50
Bagasse pulp	2.58	4.17	6.17	99.61	99.68	52.60	—	mdsh	2.14
Wood pulp	2.75	3.35	5.69	63.95	71.58	68.72	—	—	1.32

[a] AN is 100% based on dry pulp weight; liquor ratio = 50:1; reaction time = 60 min; initiator concentration 0.01 mol.

of CAN. This increases the diffusion of monomer from the aqueous phase to the cellulose phase and increase the solubility of monomer. This is found to be in agreement with Hebeish and Mehta.[12] Since increasing the temperature increased the solubility of the monomer, maximum graft yields were obtained for both pulps at 50°C. However, at a given temperature, the grafting yield of bagasse is more than that of wood pulp. This is due to the greater diffusion of the monomer as well as initiator inside the open structure of bagasse pulp fibers and the presence of some lignin. Therefore, increasing the temperature from 30 to 50°C resulted in a 30.13% increase in the graft yield of bagasse pulp over that obtained for wood pulp. On the other hand, the grafting efficiency of both pulps is lower at 50°C than at 40 or at 30°C (Table III). This may be due to homopolymer formation.

Initiator Concentration

Figure 5 shows the effect of CAN concentration on the polymer loading of bagasse and wood pulp using three different concentrations of CAN as initiator (0.002, 0.01, and 0.02 mol). For both pulps, increasing the CAN concentration from 0.002 to 0.01 mol/L has little or no effect on the polymer loads of the pulps
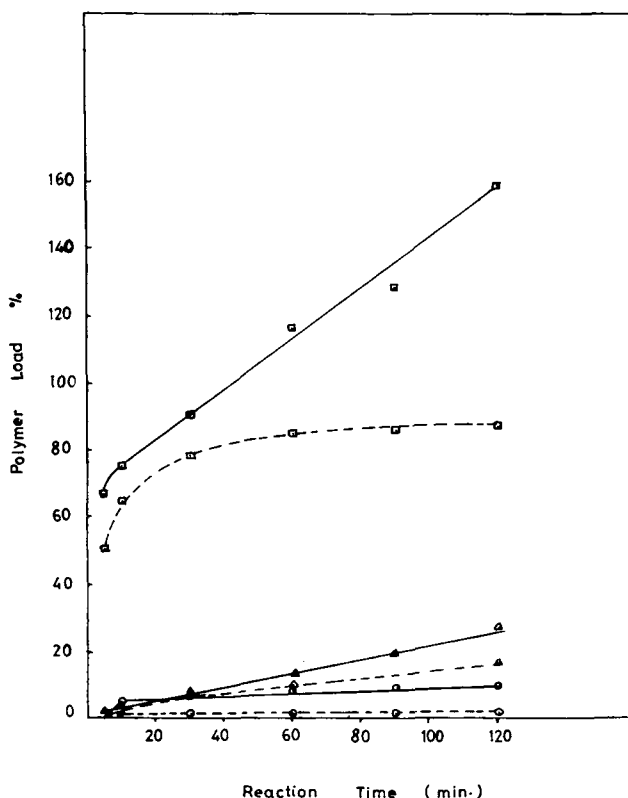

Fig. 5. Effect of ceric concentration on the rate of grafting. Ceric concentration: (⊙) 0.002 mol; (▵) 0.01 mol; (▫) 0.02 mol; temperature = 50°C; liquor ratio = 50:1; AN = 1 g; (——) bagasse pulp; (- - -) wood pulp.

in the early stages of reaction.   As the reaction proceeds, the effect of initiator concentration is more pronounced and the polymer loading of the pulps increases by increasing the CAN concentration up to 0.02 mol.   With both pulps the polymerization reaction is characterized by an initial fast rate followed by a slower one.   This is true for all concentrations used.   However, with high concentrations (0.02 mol CAN), polymerization proceeds at a rate which is higher than those of lower concentrations (0.01 or 0.002M) and hence higher polymer loads.   At low ceric concentration (0.002M), the grafting rate levels off after 60 min and shows a maximum yield.   This may be attributed to the difficult diffusion of Ce(IV) as well as monomer into the fibers for further grafting.   In the case of bagasse pulp increasing the initiator up to 0.02 mol resulted in a greater percent polymer loading than that obtained by increasing the monomer concentration to 300% (Table IV).

The rate of polymerization of bagasse pulp was faster than that for wood pulp with all Ce(IV) concentrations studied.   Therefore, at a given reaction time the polymer loading of bagasse pulp is higher than that obtained for wood pulp under similar reaction conditions.   This observation may also be explained in view of the open structure of cellulose in bagasse pulp.

Swelling of Cellulose Fibers

In order to study the effect of swelling of cellulosic fibers on their graftability, grafting of AN (using procedure A) onto dry and water-swollen bagasse pulp as well as wood pulp has been studied using CAN as initiator.   The results are shown in Figure 6.   The rate of grafting of AN onto the swollen pulps is much higher than that onto the dry pulps.   The lower rate of dissociation of ceric salt through the dry cellulosic fibers would account for this effect, since swelling of cellulosic fibers would be expected to improve their reactivity towards the grafting reaction.[11]   This result agrees in general with the expected behavior of the polymerization reaction.   Consequently, for a given reaction time, the polymer loads obtained with swollen pulps are substantially higher than that with dry pulps.   This is because the diffusion of the monomer as well as the initiator inside the dry fibers would be very difficult.   And as a result, a small amount of graft copolymerization is formed.

The grafting reaction, in dry pulps, slows down and levels off after 60 min, and

TABLE IV
Polymer Loadings at Differing Concentrations of CAN and AN for Bagasse and Wood Pulps[a]

	Starting material	CAN concentration (mol)			AN concentration based on dry pulp (% weight)		
		0.002	0.01	0.02	100	200	300
Polymer loading (%)	Bagasse pulp	8.10	13.37	116.22	13.00	43.22	95.04
	Wood pulp	0.97	9.66	84.74	8.28	34.85	85.56

[a] Reaction temperature = 50°C; liquor ratio = 50:1; reaction time = 60 min.
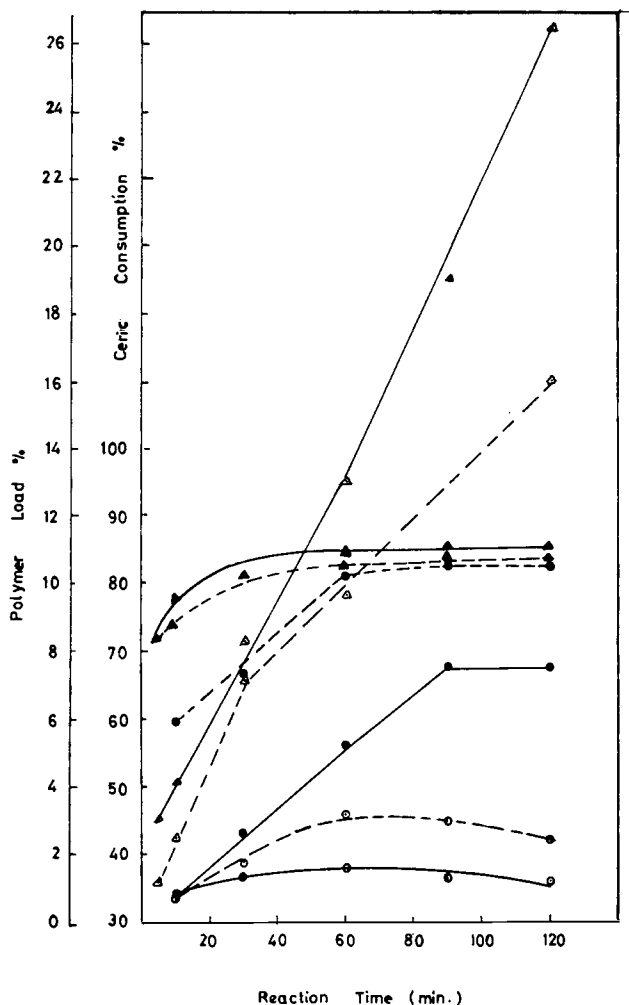
Fig. 6. Effect of swelling of fibers on the rate of grafting and rate of ceric consumption during grafting.   Temperature = 50°C; liquor ratio = 50:1; AN = 1 g; CAN = 0.01 mol.   Polymer loading: (○) dry fiber, (△) swollen fiber.   Ceric consumption: (●) dry fiber, (▲) swollen fiber; (——) bagasse pulp; (- - -) wood pulp.

shows a maximum yield.   The same trend was observed with both pulps.   The maximum yield obtained may be due to the compact structure of the dry pulps (especially bagasse pulp).   Therefore, maximum reaction can be achieved in the outer layer of that structure which is responsible for decreasing the diffusion rate of monomer and initiator to the inner layers.   Opposite results are obtained with respect to swollen pulps, since the percent of polymer loading proportionally increases with the reaction time, without reaching a maximum in the studied range.   Although the rate of polymerization of dry bagasse pulp is lower than that of dry wood pulp (consequently lower polymer loading), that of swollen bagasse pulp is significantly higher than in the case of wood pulp (consequently higher polymer loading).   This occurs because the dry wood pulp is easier to swell in time than bagasse pulp.   Hence, diffusion of the monomer as well as initiator inside the dry bagasse pulp fibers would be very difficult.

Ceric Consumption during Grafting and Oxidation of Bagasse and Wood Pulps

The Ce(IV) consumption depends on the reaction conditions as well as the nature of pulp. The effect of reaction temperature, monomer and initiator concentrations, as well as the water swelling of the pulps, on the Ce(IV) consumption by bagasse and wood pulps during grafting of AN was studied. The results are shown in Figures 3, 4, 6, 7, and 8 and expressed as the percent of CAN consumed per ceric added. Generally, Ce(IV) consumption by bagasse or wood pulps during grafting of AN increases with increasing temperature from 30 to 50°C (Fig. 4). This is due to the greater rate of dissociation of the ceric salt as the temperature increases. However, the consumption is somewhat higher with bagasse pulp than with wood pulp.
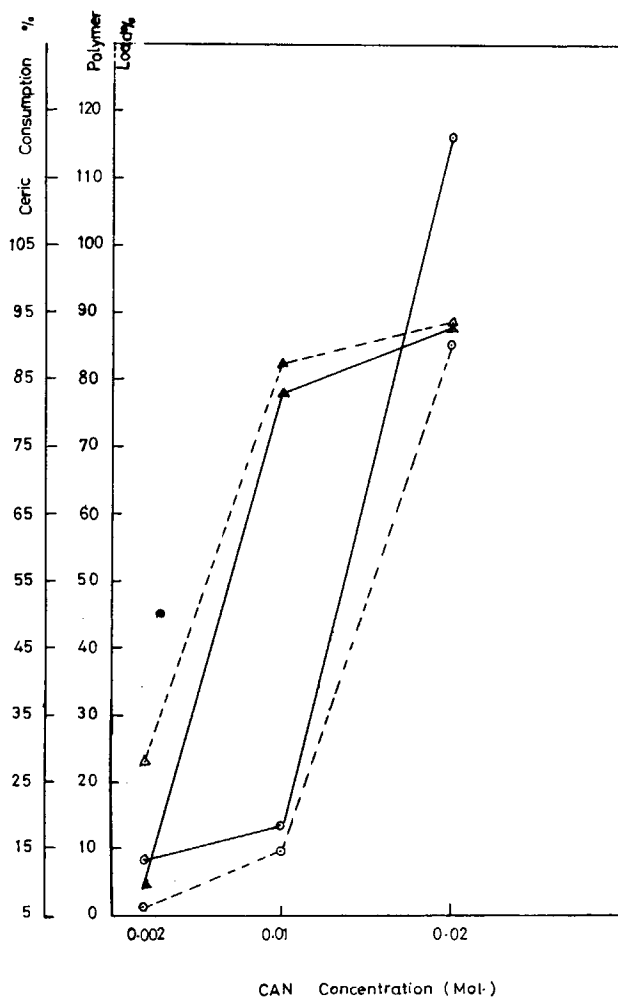

Fig. 7. Effect of CAN concentration on graft yield and ceric consumption during grafting. (⊙) Polymer loading; (▲) ceric consumption; time = 60 min; temperature = 50°C; AN = 1 g; liquor ratio = 50:1; (——) bagasse pulp; (- - -) wood pulp.
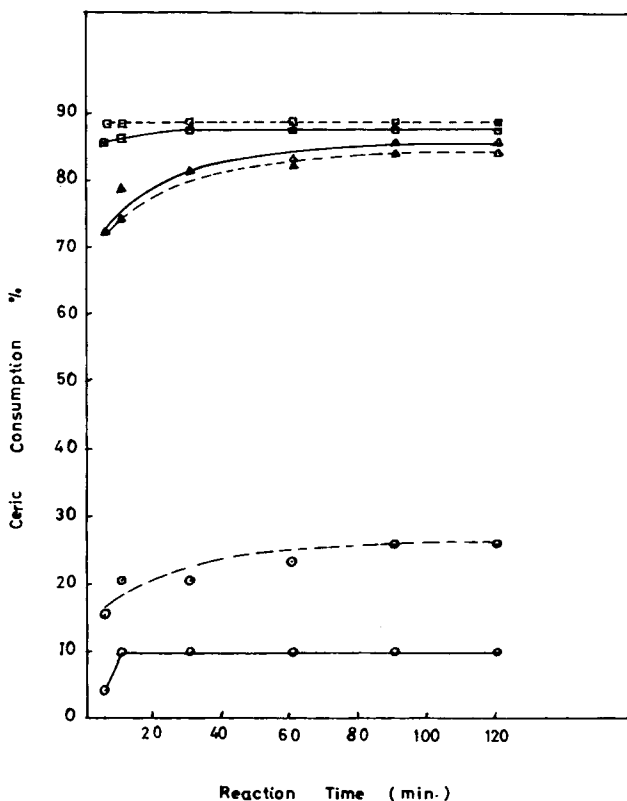
Fig. 8. Effect of CAN concentration on the rate of ceric consumption during grafting. CAN concentration: (⊙) 0.002 mol; (▲) 0.01 mol; (▣) 0.02 mol; temperature = 50°C; liquor ratio = 50:1; AN = 1 g; (——) bagasse pulp; (- - -) wood pulp.

Figure 3 shows that the Ce(IV) consumption is lowered after a certain level of monomer concentration, suggesting that the high Ce(IV) consumption at low monomer concentration, 100% based on pulp weight, is due to a fast termination rate of the growing polymer chain. But at higher concentration, more monomer would be available for grafting as well as for ceric attack. The effect of the latter on the monomer is to bring about a considerable amount of homopolymer formation (Table II). As a result, more Ce(IV) is consumed. The same is true for both pulps. But the ceric consumption by wood pulp is higher than that by bagasse pulp. This is due to an increase in homopolymer formed in the case of wood pulp.

The same trend is observed with respect to the initiator concentration where the consumption increases with increasing initiator concentration (Fig. 7). The polymerization reaction is characterized by an initial fast rate followed by a slower one. The high consumption of Ce(IV) at higher initiator concentrations is due to the fact that Ce(IV) is available in considerable amounts in the reaction medium.

Generally, the results (Fig. 8), show that the ceric consumption during grafting increases with increasing reaction time, and is more significant in the initial stage of the reaction. As the reaction proceeds, the rate of ceric consumption levels off. This may be due to lowering of the ceric concentration in the latter stages
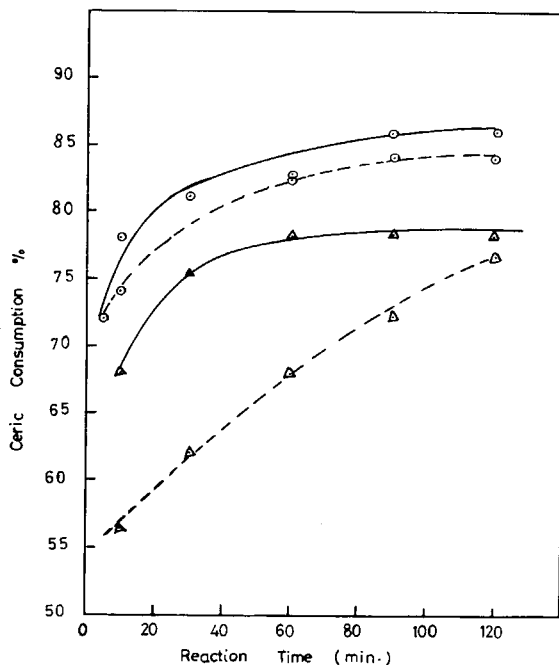
Fig. 9. Ceric consumption during grafting (⊙) of AN and during oxidation (△). Temperature = 50°C; liquor ratio = 50:1; AN = 1 g; CAN = 0.01 mol; (——) bagasse pulp; (- - -) wood pulp.

and to a shortage of reactive sites on the substrate backbone as the reaction proceeds.

Figure 6 shows the rate of ceric consumption by dry and swollen bagasse or wood pulp. The consumption of Ce(IV), by dry or swollen fibers, increases with increasing reaction time. The rate of consumption is characterized by an initial fast rate. The same is true for both dry and swollen fibers. However, the Ce(IV) consumption by dry fibers is much lower than that consumed by the swollen ones because of the difficult diffusion of Ce(IV) inside the dry fibers. The same trend is observed with respect to wood pulp. However, the consumption is much higher with dry wood pulp than with corresponding bagasse pulp.

Furthermore, a comparison was made between the Ce(IV) consumption by bagasse or wood pulp at 50°C in the absence of monomer, i.e., oxidation, and that consumed during grafting of AN onto the above pulps using CAN as initiator. The results are illustrated in Figure 9. The Ce(IV) consumption during grafting increases with increasing reaction time, and is more significant in the initial stages than in the latter stages owing to the lowering of the ceric concentration as the reaction proceeds. The same is observed for the consumption during oxidation. This is true for both bagasse and wood pulps. However, the consumption is somewhat higher with bagasse than with wood pulp. This is possibly explained in terms of lignin content in pulps; lignin in pulp plays an important role in its reactivity towards ceric ions. Because of the higher reactivity of lignin towards ceric ion,[14] an amount of CAN is exhausted in the reaction with lignin. Also the ceric consumption during grafting is greater than that consumed during oxidation, perhaps due to homopolymer formation during grafting.[7]

References

1. F. K. Guthrie, *Tappi*, **46**, 656 (1963).
2. S. Kaizerman, G. Mino, and L. F. Meinhold, *Text. Res. J.*, **32**, 136 (1962).
3. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polym. Sci. A*, **3**, 1185 (1965).
4. R. J. E. Cumberbirch and J. R. Holker, *J. Soc. Dyers Colour.*, **82**, 59 (1966).
5. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **39**, 523 (1959).
6. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
7. A. Hebeish, A. Kuntouch, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **15**, 1921 (1971).
8. L. Neimo and H. Sihtola, *Pap. Puu*, **47**, 369 (1965).
9. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. A-1*, **5**, 2791 (1967).
10. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *Kogyo Kagaku Zasshi*, **70**, 103 (1967).
11. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. A-1*, **6**, 1489 (1968).
12. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1625 (1968).
13. A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961, p. 256.
14. V. Harnof, B. V. Kokta, and J. I. Valade, *J. Appl. Polym. Sci.*, **20**, 1543 (1976).
15. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **13**, 1569 (1969).