Graftability of Beaten Pulps and Acetylated Pulps

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Synopsis

Ce(IV)-induced polymerization of acrylonitrile with acetylated bagasse and wood pulps, having different acetyl contents, has been investigated. The graft yield is dependent on the acetyl content as well as the origin of the pulp. Increasing the acetyl content of pulps caused a significant decrease in the polymer loading. However, the rate of polymerization of acetylated wood pulp is much higher than that of acetylated bagasse pulp. The ceric consumption during grafting decreases as the acetyl content of the pulp increases. The effect of beating of the pulps, to various degrees of freeness, on their reactivity toward grafting process has also been studied. Generally, the state of cellulose, as defined by its degree of beating, and the origin of the pulp strongly influenced the graft yield. Increasing the beating degree of bagasse pulp resulted in a decrease in graft yield, while beating of wood pulp, to a definite degree, inhibits the polymerization reaction. The consumption of Ce(IV) by the beaten pulps during oxidation is somewhat greater than that consumed by the unbeaten pulps, whereas the consumption during grafting of acrylonitrile onto beaten pulps depends on the initial concentration of ceric solution. Also, the effect of grafting of acrylonitrile onto acetylated wood and bagasse pulps on their strength properties as well as the effect of grafting onto beaten pulps on their properties has been investigated. Grafting of acrylonitrile onto acetylated bagasse pulp decreased its strength properties, but improved its beatability comparatively to those of original pulp (0 acetyl content). On the other hand, grafting of acrylonitrile onto acetylated wood pulp resulted in a great improvement in its strength properties compared to those of grafted unacetylated pulp. Grafted unbeaten pulps gave thinner and weaker paper than the original pulp (without grafting). Beating of bagasse pulp before grafting gave pulp which possessed a higher strength properties, at low °SR, than those of pulp beaten after grafting. Raising the °SR by rebeating the pulp after reaction up to the original value had an adverse effect on the strength. Beating of bagasse pulp before grafting did not accelerate the reaction rate, but it saved some power consumption, since the time required for beating of grafted pulp to a given °SR was lower than that of ungrafted pulp.

INTRODUCTION

The extent and the rate of grafting are directly related to the accessibility of substrate under certain conditions. In the previous work[1] it was shown that the order of reactants addition as well as the water swelling of cellulosic fibers had a considerable effect on the rate of polymerization, using tetravalent cerium as initiator, of bagasse and wood pulps. The influence of different variables on their rate of polymerization were also investigated.

Recently, it has been found that substitution of the cellulose hydroxyls of cotton by carboxymethyl[2] or acetyl[3] groups greatly affects the graft yeld. Also, graft yield and the number of grafted chains are greatly affected by the beating degree of pulps.[4]

Graft polymerization of certain monomers, such as acrylamide which produces a hydrophillic polymer, onto pulps increases the dry strength of the paper.[5–7] In contrast, monomers like methyl methacrylate and vinylacetate produce hydrophopic polymer, therefore, have an adverse effect on the strength properties of paper made up of grafted pulps.[6,7]

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The present work has been undertaken to clarify the influence of the change in the physical or chemical structure of cellulose of bagasse and wood pulps brought about when the pulps were either treated mechanically or by introducing a new functional group, such as the acetyl group, into the cellulose molecule on the graftability of the pulp. Studying the effect of grafting of acrylonitrile onto bagasse and wood pulps on their strength properties was another objective of this work.

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% pentosans; 1.5% lignin; 0.38% ash; a degree of polymerization (DP) of 909. Also a commercial bleached birch sulfate pulp of 85% α-cellulose, DP, SCAN C_{15}, 1045 was used as a reference.

In order to study the effect of beating on the rate of grafting of acrylonitrile (AN) onto pulps, the pulp samples were beaten in a Jokro mill to different degrees (30–70°SR).

Acetylated pulps having two different acetyl contents were prepared.[8] The acetyl content, expressed as combined acetic acid %, was determined according to a method described by Genung.[9]

Ceric ammonium nitrate (CAN), BDH reagent grade, was used after standardization with ferrous sulfate.[10]

Freshly distilled acrylonitrile (AN) was used.

Methods

The graft copolymerization of AN was conducted according to a method described in the previous work.[1] In that the polymerization was carried out by adding 1 g monomer to 30 mL ceric ammonium nitrate (CAN) solution of known concentration, containing 1% concentrated nitric acid; then a water-swollen pulp sample was immediately introduced into the reaction flask. The liquor ratio was 50:1 and the reaction temperature was 50°C. Some of the polymer samples were soxhlet-extracted with dimethyl formamide for 36 h to remove the homopolymer.

Oxidation of pulp samples, using CAN, was carried out under conditions identical with those of grafting, except that the monomer was omitted.

Ceric consumption, expressed as percent of ceric consumed/ceric added, during grafting and oxidation was determined according to a method reported by Mino et al.[10]

Polymer loading (%) (percent weight increase due to polymerization) was determined from the value of the nitrogen content of grafted samples. The nitrogen content of treated pulps was determined by standard Kjeldahl procedure.[11]

Papermaking and testing: Grafted bagasse and wood pulps were beaten up to 50°SR using a Jokro mill. In another experimental series grafted reaction was carried out on pulps which were first beaten up to 50°SR. Hand sheets were prepared from the above pulps according to the Swedish Standard Method (SCA). Also hand sheets were prepared from the untreated pulps for comparison. The water retention[12] (WRV) of the sheets was estimated and their strength properties were tested according to the Tappi Standard Method.

RESULTS AND DISCUSSION

The effect of introducing of acetyl groups in cellulose molecule of bagasse and wood pulps on their behavior toward grafting with AN and the properties of grafted pulps has been investigated. The effect of beating degree of pulps on their graftability and on the strength properties of grafted pulps has also been studied. The grafting reaction was studied with respect to the polymer loading or graft yield and ceric consumption.

Influence of Introducing of Acetyl Groups

Graft Yield

Figure 1 shows data for polymer loading obtained with acetylated bagasse and wood pulps, having different percentages of combined acetic acid (8.78%, 18.59% and 10.98%, 19.46% for bagasse and wood pulps, resp.). For comparison, data for polymer loading obtained with unacetylated pulps are also illustrated in the

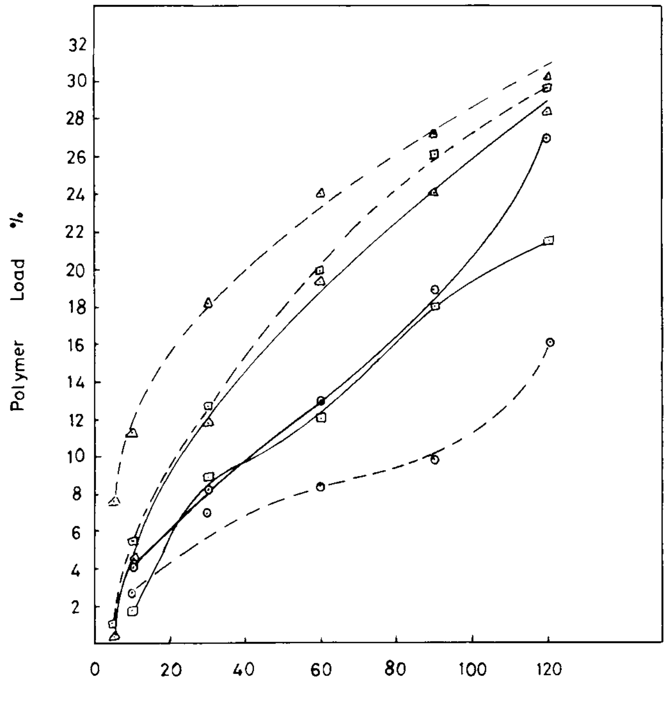

Fig. 1. Effect of introducing acetyl groups on graftability of pulps: (⊙) blank; (△) low acetyl content; (⊡) high acetyl content; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1 g.; (—), bagasse pulp; (---), wood pulp.

figure. It is clear that the polymerization of bagasse pulp proceeds slowly in the early stage of the reaction (within 10 min), and the polymer formation is only considerable at 30 min of reaction. Thereafter, the reaction time causes a significant increment in the polymer loading, within the range studied. This may be due to the introducing of acetyl groups along the cellulosic chain, which reduces the swellability of the pulp. Diffusion and adsorption of the monomer as well as the intiator inside the fiber would consequently be very difficult, especially in the early stage of the reaction. Therefore, a small polymer load is obtained. Sufficient time increased swelling of the fibers, and diffusion of both monomer and initiator resulted in a substantial amount of polymer. A similar trend is observed with respect to acetylated wood pulp having high acetyl content (19.46%). However, with pulp having a low acetyl content (10.98%), the polymerization reaction proceeds very fast.

It is apparent that increasing of acetyl content of the pulps, from 0% to about 11%, for wood pulp, and about to 8.8%, for bagasse pulp, causes an appreciable increment in the rate of polymerization. A further increase in the acetyl content of the pulps to about 19% resulted in a decrease in the obtained polymer loading. This is due to the fact that the presence of the acetyl group, more than a definite limit, in the cellulose resulted in blocking some of the hydroxyl groups along the cellulose chain. This holds true for both pulps. However, the rate of polymerization of acetylated wood pulp is much higher than that of acetylated bagasse pulp. This suggests that the presence of acetyl groups on the cellulose chain of wood pulp offers sites for increased interaction of monomer with the cellulose upon ceric treatment, rather than in case of acetylated bagasse pulp, resulting in more homopolymer formation in the former pulp than in the latter one (Table I).

Ceric Consumption

Ceric consumption during grafting, at 50°C using CAN as initiator, of bagasse and wood pulps before and after acetylation is illustrated in Figure 2. It is apparent that the Ce(IV) consumption is initially very fast, for all pulps (acetylated or not); then it slows down or levels off. This is perhaps due to lowering the ceric concentration as the reaction proceeds. The above observation is true for both bagasse and wood pulps. It is clear that the Ce(IV) consumption during grafting of acetylated bagasse pulp decreases as its acetyl content increases. This may be due to the fact that the susceptability of cellulose to Ce(IV) attack decreases by introducing of acetyl groups into the cellulose molecule which at the same time decreases the number of the cellulose hydroxyles. The ceric consumption, during

TABLE I
Effect of Introducing Acetyl Groups in Cellulose on Its Graft Yield[a]

Sample	Bagasse pulp			Wood pulp		
Acetyl content, %	0	8.78	18.59	0	10.98	19.46
Polymer load, %	13.00	19.27	12.00	8.30	34.80	20.80
Graft yield, %	6.17	18.13	8.17	5.69	21.71	8.02
Homopolymer, %	52.54	5.916	31.917	31.45	37.62	61.44

[a] CAN concentration, 0.01M; AN, 1 g; cellulose, 1 g; liquor ratio, 50:1; temperature, 50°C; time, 60 min.

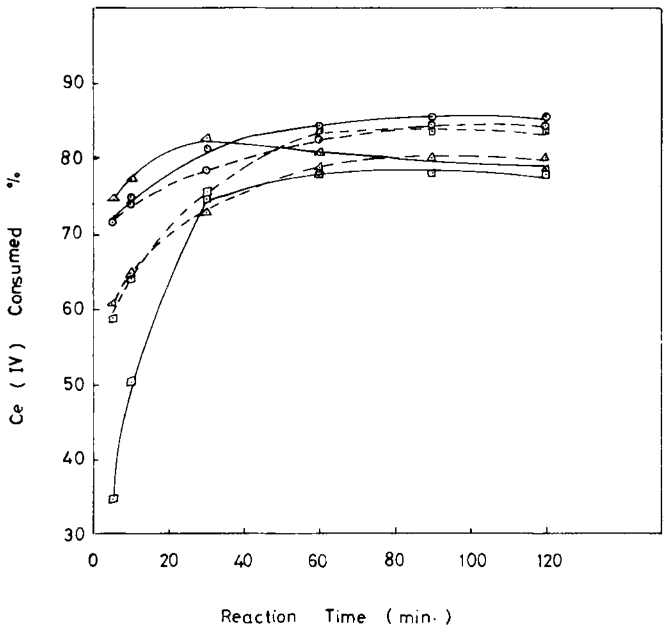

Fig. 2. Effect of introducing acetyl groups in cellulose on ceric consumption during grafting: (⊙) blank; (△) low acetyl content; (⊡) high acetyl content; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1g.; (——). bagasse pulp; (- - -), wood pulp.

the early stages of reaction, by highly acetylated wood pulp is much lower than that observed in case of highly acetylated bagasse pulp. Opposite results are obtained during the latter stages of reaction.

Effect of Beating Degree on Graftability of Pulps

Graft Yield

In order to investigate the influence of beating degree of pulps on their behavior toward grafting, bagasse and wood pulps were beaten to a various degrees (30–70°SR) and then were treated with AN in the presence of ceric ion, Ce(IV), as initiator. The results obtained are compared with those of the unbeaten pulps. Figures 3 and 4 show the rate of grafting of AN onto beaten and unbeaten bagasse and wood pulps. It is obvious that with bagasse pulp, at 30 and 60°SR, the polymer loading obtained increased with increasing reaction time. However, the rate of increasing of the polymer loading of beaten bagasse pulp, at any degree of freeness, is significantly lower than that of the unbeaten pulp. Therefore, the graft yield obtained with unbeaten pulp is higher than that of beaten pulp at any degree, in the range studied, (Table II). This may be attributed to the fact that the specific surface of cellulose increased enough so that exceedingly more acetyl groups became available leading to the formation of exceedingly active sites (free radicals) on the cellulose. Radical-destroying reactions thus take place through coupling and disproportionation between the highly formed free radicals,[13] giving rise to a decrease in grafting yield.

Since the origin of cellulose strongly influenced the rate of polymerization of pulps due to the difference in their reactivity toward grafting, wood pulp

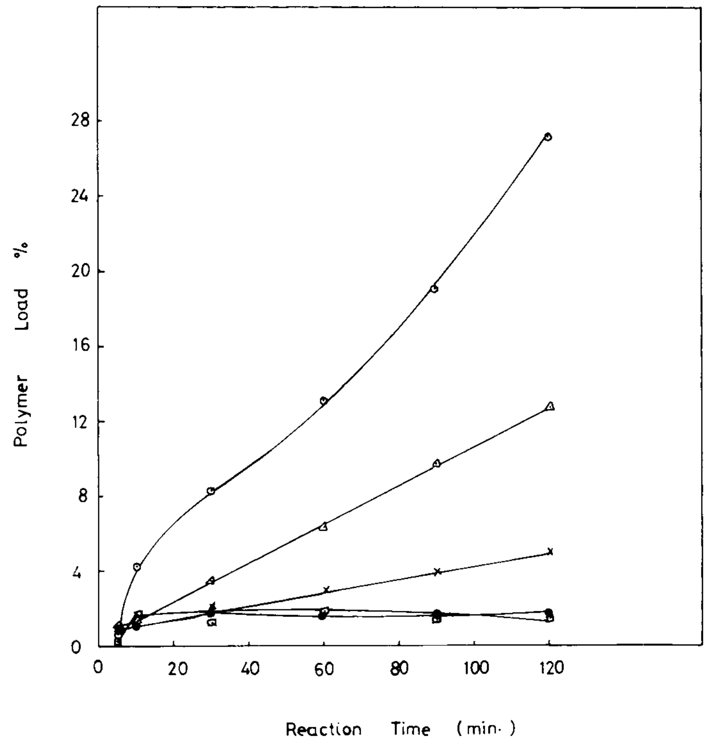

Fig. 3. Effect of beating on graftability of bagasse pulp: (⊙) unbeaten; (△) 30°SR; (⊡) 50°SR; (x) 60°SR; (.) 70°SR; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1 g.

therefore behaved differently (Fig. 4). Thus the rate of increasing of polymer loading of beaten (30–60°SR) wood pulp is significantly higher than that of the unbeaten one. On the other hand, increasing the beating degree up to 70°SR resulted in a lower rate of polymerization than in case of the unbeaten pulp. The maximum polymer load obtained with wood pulp is achieved at 30°SR. Table II shows that increasing the beating degree from 30 to 60°SR resulted in an increase in the graft yield from 2.60% to 7.14%. Although the maximum polymer loading was obtained with beaten pulp at 30°SR, the maximum graft yield was obtained with sample of 60°SR. This is possibly due to the higher homopolymer formation with sample of 30°SR than in case of samples with 60°SR.

The reactivity of pulp fibers toward graft polymerization depends on the character of the fibers and, in particular, on their active surface. It is evident that the rate of polymerization of both bagasse and wood pulps decreased with increasing the beating degree from 30 to 70°SR (Figs. 3 and 4). Since wood pulp is more reactive than bagasse pulp, the rate of decreasing of its polymer load due to increase in the beating degree is much more than with bagasse pulp. This is probably due to the production of exceedingly more free radical with more reactive pulp and hence a higher rate of termination reactions.

Ceric Consumption

Ce(IV) consumption by bagasse and wood pulps, unbeaten and beaten to 50°SR, in the absence of monomer (i.e., oxidation) and the consumption by unbeaten as well as beaten pulps up to 30–70°SR during grafting are given in

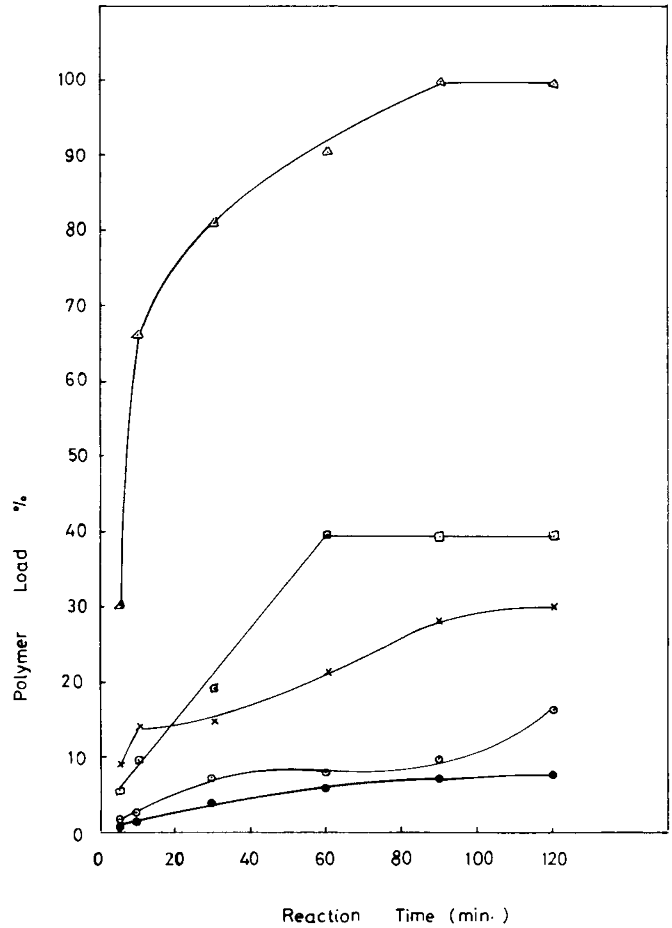

Fig. 4. Effect of beating on graftability of wood pulp: (⊙) unbeaten; (△) 30°SR; (□), 50°SR; (x) 60°SR; (.) 70°SR; temp., 50°C; liquor ratio 50:1; AN, 1 g.; cellulose, 1 g.

Figures 5–7. It is clear from Figure 5 that, with both pulps, the Ce(IV) consumption increases with increasing the reaction time in the initial stages of the reaction then it levels off after certain time. This is due to lowering of the ceric concentration as well as a shortage of reactive sites on the pulp backbone as the reaction proceeds.

The consumption during oxidation of beaten pulps is greater than that of unbeaten ones. This is attributed to the exceedingly exposed hydroxyl groups

TABLE II
Effect of Beating Degree of Pulps on Their Reactivity toward Grafting[a]

Sample	Bagasse pulp				Wood pulp			
Beating degree, °SR	Unbeaten	30	50	60	Unbeaten	30	50	60
Polymer loading, %	13	6.34	1.83	2.90	8.30	90.33	19.06	21.3
Graft yield, %	6.17	2.46	1.90	2.90	5.69	2.60	5.33	7.14
Homopolymer, %	52.54	61.99	—	—	31.45	97.12	72.04	66.5

[a] CAN concentration, 0.01M; AN, 1 g; Cellulose, 1 g; liquor ratio, 50:1; temperature, 50°C; time, 60 min.

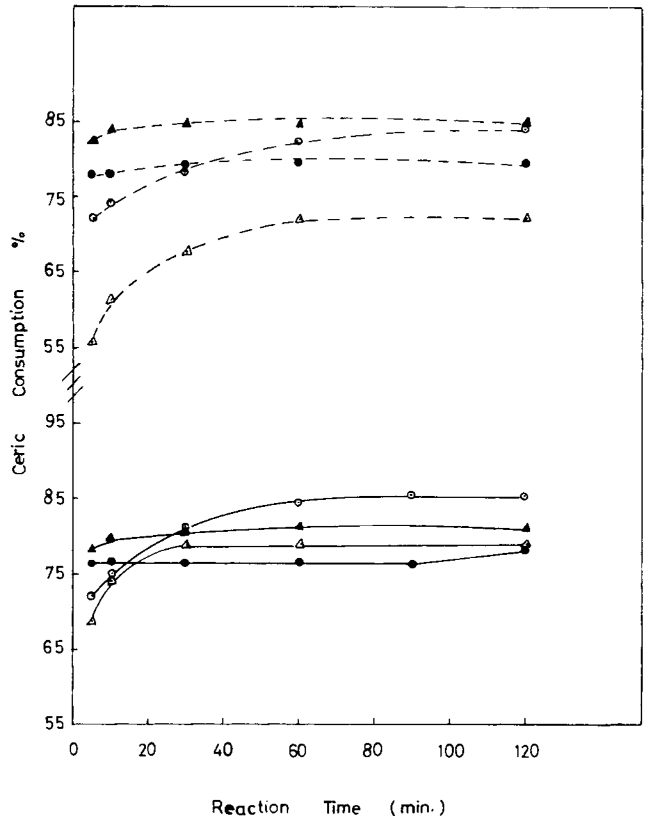

Fig. 5. Effect of beating on ceric consumption during grafting and oxidation of pulps: (○) unbeaten during grafting; (△) unbeaten during oxidation; (●) beaten pulp (50°SR) during grafting; (▲) beaten pulp (50°SR) during oxidation; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1 g.; (——), bagasse pulp; (- - -), wood pulp.

through increasing the specific surface of pulps by beating (Fig. 5), whereas the consumption during grafting of beaten pulps depends on the initial concentration of ceric solution (Figs. 6 and 7). It can be seen from Table III that the reactivity of pulp toward ceric salt is reduced with an increase of the beating degrees. Opposite results are obtained with respect to wood pulp. Although the ceric consumption during oxidation of beaten wood pulp is higher than the corresponding consumption in case of bagasse pulp, the unbeaten pulps behaved oppositely (Fig. 5). Therefore, the magnitude of ceric consumption being dependent on the origin, state of pulp and the rate of intiation and termination of the homopolymer formed in solution.

Paper Properties of Acrylonitrile Grafted Pulps

Effect of Degree of Grafting on The Properties of Pulps

Wood and bagasse pulps were grafted with AN to a different polymer loading using CAN as initiator. Hand sheets were made from the above pulps, and the properties of the produced sheets were studied comparatively to those of sheets prepared from ungrafted pulps. The results are given in Table IV. It can be seen from this table that AN-grafted bagasse pulp gave less denser and weaker

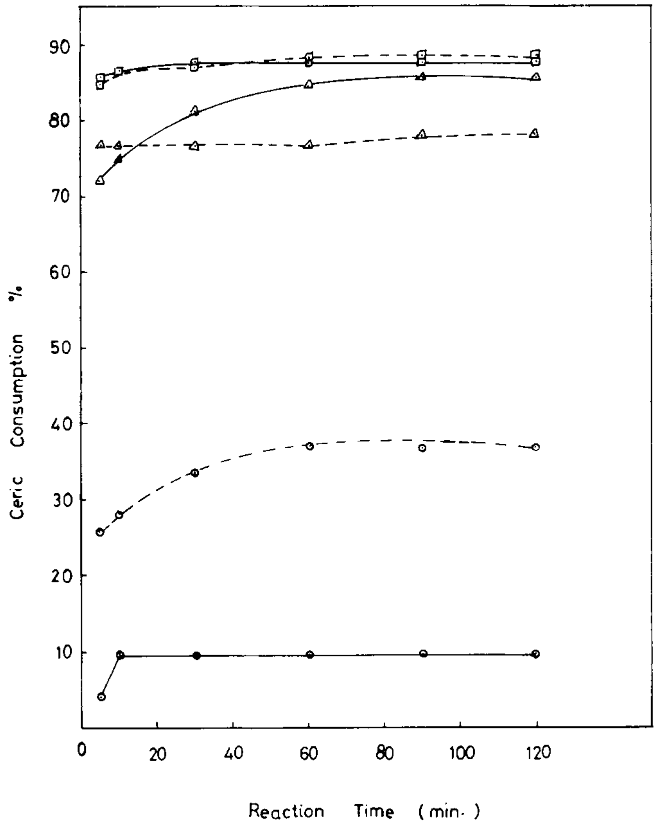

Fig. 6. Effect of ceric concentration on Ce(IV) consumption during grafting of bagasse pulp: (⊙) 0.002*M*; (△) 0.01*M*; (⊡) 0.02*M*; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1 g.; (—), unbeaten pulp; (---), beaten pulp.

paper sheets than the original pulp. Thus, the density of paper sheets as well as their strength properties were strongly decreased as the polymer loading of the fibers increased. Also a large decrease in the water retention value of the grafted sample was observed comparatively to that of sheets made of pulp without grafting. It is observed that the moisture regain of the grafted samples

TABLE III
Effect of Beating Degree on Ceric Consumption during Grafting of Pulps[a]

	Ce(IV) consumption, %							
	Bagasse pulp				Wood pulp			
	Beating degree, °SR:							
Reaction time, min	Unbeaten	30	50	70	Unbeaten	30	50	70
5	72.00	78.03	76.57	76.57	72.00	74.85	77.82	79.26
10	75.00	79.49	76.57	76.03	74.00	75.61	77.82	79.26
30	81.25	79.49	76.57	76.49	78.50	76.26	77.82	79.26
60	84.50	79.49	76.57	76.49	82.25	79.09	79.26	79.26
90	85.50	79.49	78.03	78.03	84.00	79.09	79.26	80.69
120	85.50	79.49	78.03	78.03	84.00	79.09	79.26	80.69

[a] CAN concentration, 0.01*M*; AN, 1 g; cellulose, 1 g; liquor ratio 50:1; Temperature, 50°C.

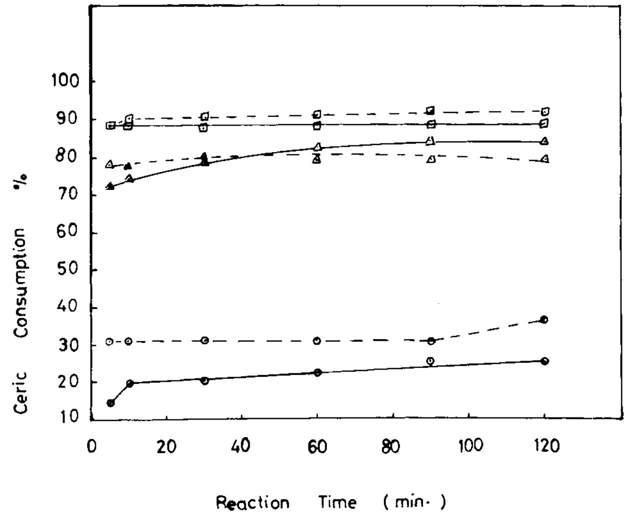

Fig. 7. Effect of ceric concentration on Ce(IV) consumption during grafting of wood pulp: (⊙) 0.002*M*; (△) 0.01*M*; (⊡) 0.02*M*; temp., 50°C; liquor ratio, 50:1; AN, 1 g.; cellulose, 1 g.; (—), unbeaten; (- - -), beaten pulp.

showed approximately the same trend as the WRV of the samples (Table IV). It should be pointed out that lowering of WRV of the pulp after grafting resulted in a greater dimensional stability of the paper.[14] It is noticed that the ungrafted pulp was beaten faster than the grafted pulp samples. Thus, the beating time increased from 6 to 36 min as the polymer loading of the pulp was increased from 0% to 13%. This may be attributed to the more porous structure of ungrafted pulps, i.e., the beatability of the pulp is inversely proportional to the degree of grafting. Opposite results were obtained in the case of wood pulp, since grafting of AN onto wood pulp resulted in an initial improvement in the tearing resistance and fold number of produced sheets, followed by a decline in the strength at higher polymer content. The behavior of tearing resistance related to the density of the paper sheets, since the tearing resistance is inversely proportional to density.[15] Moreover, the beatability of wood pulp was improved by grafting. Table IV shows a great decrease in the time of beating of wood pulp from about

TABLE IV
Paper Properties of Grafted Pulps[a]

Sample	Bagasse pulp			Wood pulp		
Polymer loading, %	—	0.56	13.00	—	1.15	8.14
Time of beating, min	6	22.5	36	48.4	35	30
°SR	30	30	30	50	50	50
Density, g/cm³	0.7546	0.5850	0.5572	0.8469	0.7713	0.7127
Breaking length, m	6533	2150	2094	6380	5659	4247
Burst factor	37.77	17.30	—	45.91	38.02	17.98
Tear factor	3.38	1.56	1.86	4.65	5.03	2.44
Double fold	83	20	—	209	256	9
WRV, %	542.46	167.40	165.82	453.23	396.38	308.04
Moisture regain, %	7.16	6.72	3.89	6.35	7.20	6.67

[a] CAN concentration, 0.01*M*; AN, 1 g; cellulose, 1 g; liquor ratio 50:1; temperature, 50°C; time, 60 min.

48 min to 30 min as the polymer load increased from 0% to 8%. The WRV of wood pulp follows nearly the same trend as bagasse pulp.

Effect of Introducing of Acetyl Group before Grafting of AN onto Pulps on the Physical Properties of Produced Paper Sheets

The strength properties of acetylated grafted pulps are given in Table V. It is clear that changing the chemical structure of cellulose by acetylation before grafting of AN had a bad effect on the strength properties of bagasse pulp. The breaking length greatly decreased from 2150 m to 871 m, the tearing resistance slightly decreased from 1.6 to 1.5, and the bursting strength and fold number were greatly decreased. It is also seen that grafting of pulp after introducing acetyl groups resulted in a pulp which needed less time for beating than that required for pulp grafted without acetylation. On the other hand, wood pulp behaved differently. Thus, grafting of acetylated wood pulp caused a great improvement in the strength properties compared to those of grafted pulp without acetylation. The breaking length increased by 21.64% whereas the burst factor was increased by 91.05%. Also a considerable increase in the tearing resistance and folding indurance of wood pulp was observed. Thus, introducing of acetyl groups onto pulp before grafting led to 78.28% and 115% increases in the tear factor and fold number, respectively.

Influence of Beating of Pulp before Grafting of AN onto Pulps on the Physical Properties of the Paper Sheets

In order to indicate the effect of beating of the pulp before grafting on its physical properties, the bagasse and wood pulps grafted in the unbeaten state were then beaten up to 50°SR while the pulps treated in the beaten state, 50°SR, were once taken directly for sheet making and once rebeaten up nearly to the starting (°SR) freeness. The results are given in Table VI. In case of beaten grafted bagasse paper pulp, the breaking length and tearing resistance increased by 5.69% and 36.01%, respectively, with increasing the polymer loading from 0.27% to 1.83%. It it clear that beating before grafting delivered pulp which possessed higher strength properties, at lower °SR, than that beaten after

TABLE V
Paper Properties of Acetylated Grafted Pulps

Sample	Bagasse pulp		Wood pulp	
State of pulp	Unacetylated	Acetylated[a]	Unacetylated	Acetylated[a]
Polymer loading, %	0.5969	0.43	8.14	7.58
Time of beating, min	22.5	20	30	24.3
°SR	30	30	50	50
Density, g/cm^3	0.585	0.6013	0.7127	0.7065
Breaking length, m	2150	871	4247	5166
Burst factor	17.30	—	17.98	34.35
Tear factor	1.56	1.50	2.44	4.35
Double fold	20	—	9	14
WRV, %	167.4	205.47	308.04	206

[a] Bagasse and wood pulps were acetylated to 8.8% and 10.98% acetyl content respectively before grafting.

TABLE VI
Effect of Beating before Grafting of Pulps on the Physical Properties of Paper Sheets

Sample State of pulp	Bagasse pulp Unbeaten[a]		Beaten before grafting[b]		Re-beaten[c]	Wood pulp Un-beaten[a]	Beaten before grafting[b]		Re-beaten[c]
Beating time, min	30.4	19.2	16	16	16 + 13	35	48.4	48.4	48.4 + 13
°SR of grafted pulps	50	30	30	30	45	50	46.5	45	46
Polymer loading, %	0.597	0.597	0.566	1.828	0.566	2.28	2.41	15.06	2.41
Density, g/cm^3	0.725	0.530	0.984	0.817	0.692	0.771	0.743	0.672	0.592
Breaking length, m	385	1575	4089	4331	2547	5659	5330	4349	2745
Burst factor	26.80	14.00	33.44	31.56	7.02	38.02	22.69	29.48	13.72
Tear factor	1.95	1.41	3.11	4.23	1.50	5.03	4.49	3.82	2.74
Double fold	48	10	100	59	—	256	110	53	8
WRV, %	174.4	165.2	296.4	333.0	375.0	496.4	332.6	280.1	204.7

[a] The pulp was beaten after grafting.
[b] The pulp was beaten before grafting up to 50°SR.
[c] The pulp was beaten before grafting up to 50°SR, then it was beaten again after grafting nearly to the original freeness value.

grafting. This is due to the fact that the beating increases fiber surface area and leads to more interfiber bonding during sheet formation and thus raises paper strength. It is obvious that grafting of AN onto beaten bagasse pulp reduced the °SR and WRV from 50 to 31 and from 542.46% to 296.38%, respectively. Also the beating time of pulp up to 50°SR before grafting was 16 min while beating the pulp after grafting needed much more time, 30.4 min, and did not lead to higher strength, i.e., beating of the pulp before grafting significantly reduced the time of beating. It can be seen that the rebeating process decreased the strength properties of pulp, but increased the WRV (Table VI).

Wood pulp was found to behave differently than bagasse pulp. Therefore, beating before grafting did not result in an improvement in strength properties, i.e., on grafting of beaten wood pulp, its °SR and its strength properties were decreased considerably. Rebeating of the pulp up to nearly the initial °SR resulted in an additional decrease in the strength properties.

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