Activating Pulp toward Acetylation by Chemical or Mechanical Means

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

Synopsis

Activation of pulps during acetylation, by prior mechanical or chemical treatment, has been investigated. The effect of degree of beating on the acetylation rate of wood and bagasse pulps has been studied. It is found that the acetylation rate of pulps increases when the degree of beating of pulps is increased to a definite degree, after which it slows down. The maximum reactivity of bagasse pulp is obtained at 50°SR, while that of wood pulp is observed at 30°SR. The effect of grafting of acrylonitrile onto bagasse and wood pulps on their reactivity during acetylation has been also studied. The results indicate that grafting of acrylonitrile onto pulps has a favorable effect on their acetylation rate. This is dependent on the degree of grafting as well as the origin of pulp fibers. The most suitable method of activation during acetylation reaction is dependent on the origin of the pulp. The reactivity of bagasse pulp during acetylation is influenced more by beating of pulp, prior to the reaction, than by the grafting of acrylonitrile onto pulp. On the other hand, the acetylation reaction of wood pulp is activated by grafting rather than by beating. Also the effect of the activation process, mechanical or chemical, on the strength properties of the paper sheets produced from acetylated pulps has been investigated. Chemical activation of wood pulp prior to acetylation resulted in pulp with slightly higher strength properties than that activated by mechanical means. But, in the case of bagasse pulp, mechanical activation resulted in a pulp with strength superior to that produced by chemical activation.

INTRODUCTION

Reactivity of cellulose during acetylation depends mainly on its origin as well as the pretreatment of cellulose. The acetylation rate of sulfite viscose or linseed cellulose decreased by mercerization, heating, or drying at 150°C, but increased by prior hydrolysis.[1] Acetylation of cotton cellulose was rapid and acetylation of linseed cellulose was very slow. Also the preliminary mercerization[2] of cotton cellulose and wood pulp led to an increase in the content of loose fractions and a decrease in the acetylation rate. On the other hand, their hydrolysis led to an increase in the acetylation rate. The grafting of acrylonitrile, onto cotton linter, bleached sulfite dissolving pulp and prehydrolyzed beech sulfate pulp, was done to activate the cellulosic material during acetylation.[3,4] The acetylation capacity of the products, especially those from sulfite pulp, increased as the degree of grafting increased. The reactivity of pulps to acetylation[5–7] declines after beating to a definite degree (17–46°SR), whereas their reactivity increases in the 46–70 freeness range.

Strength properties of paper sheets made from acetylated pulp differ according to the acetyl content of the pulp.[8,9]

The purpose of the present investigation was to study the effect of beating on acetylation rate of pulps and also to study the effect of grafting of acrylonitrile onto pulps on their reactivity during acetylation. Another objective of this work

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was to evaluate the strength properties of paper sheets obtained from acetylated pulps.

EXPERIMENTAL

Materials

Pulp preparation: Unbleached commercial bagasse pulp provided by Edfo Mill, Egypt, was used in this study. The pulp was bleached by applaying 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, and 909 DP. Also commercial bleached birch sulfate pulp of 85% α-cellulose, DP, SCAN C_{15}, 1045, was used as a reference. The pulp samples were beaten in a Jokro mill to a different degrees (30–70°SR) to study the effect of the beating degree of the pulp on its acetylation rate.

Glacial acetic acid, acetic unhydride, and perchloric acid as catalyst, were used for acetylation process.

Ceric ammonium nitrate (CAN), BDH reagent grade, aqueus solution containing concentrated nitric acid, 1%, was used after standardization with ferrous sulfate.[10]

Freshly distilled acrylonitrile (AN) was used.

Methods

Acetylation process: It was carried out as follows: The wet pulp samples were introduced into a flask containing glacial acetic acid for 5 min and then were squeezed. This step was repeated three times to replace the water present in the samples by acetic acid. Then the samples were activated with glacial acetic acid containing traces of acetic anhydride (100 mL acid containing 0.5 mL anhydride) for 5 min at 80°C using liquor ratio of 20:1 (based on pulp weight). The samples were then squeezed thoroughly. The activated samples were acetylated using a mixture of glacial acetic acid: acetic anhydride (100:50), in presence of perchloric acid (1 mL/L acetic acid) as a catalyst. The reaction temperature was 25°C, the liquor ratio was 30:1 (based on pulp), and the reaction was carried out for different time intervals (0.25–5 min). After the required time, water was added to the samples to stop the reaction, and the samples were then washed with distilled water (till free from acid). The samples were stabilized by successive treatment with hot water and finally dried at room temperature. The acetyle content, expressed as combined acetic acid %, was determined according to a method described by Genung.[11]

Graft copolymerization: Grafting of acrylonitrile (AN) onto pulps 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 the water-swollen pulp sample was immediately introduced into the flask. The liquor ratio was 50:1 and the reaction temperature was 50°C. 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 the Standard Kjeldahl procedures.[12]

Papermaking and testing: Acetylated wood and bagasse pulps were beaten up to 30°SR using Jokro mill. In another series of experiments the acetylation reaction was carried out on wet pulp samples which were first beaten up to 30°SR.

Also, acetylation was carried out on wet samples which were first grafted with AN. Hand sheets were made from the above pulp samples according to the Swedish Standard Method (SCA). The strength properties of the prepared sheets were tested according to Tappi Standard Method.

RESULTS AND DISCUSSION

In this work one method of acetylation was used and two methods of activation, mechanical or chemical, were used prior to the acetylation process. In the first method of activation, the pulp was activated by beating up to different degrees of freeness. The effect of the beating degree of bagasse and wood pulps on their rate of acetylation and on the properties of the produced pulps has been investigated. In the second activation method, the pulp was activated by grafting with acrylonitrile (AN). The effect of grafting of AN onto bagasse and wood pulps on their acetylation rate as well as on the strength properties of the resulting pulps has also been studied.

Influence of the Degree of Beating on the Acetylation Rate of Pulps

Figures 1 and 2 represent the rate of acetylation of wood and bagasse pulps beaten to different degrees of freeness (30–70°SR). For comparison the rate

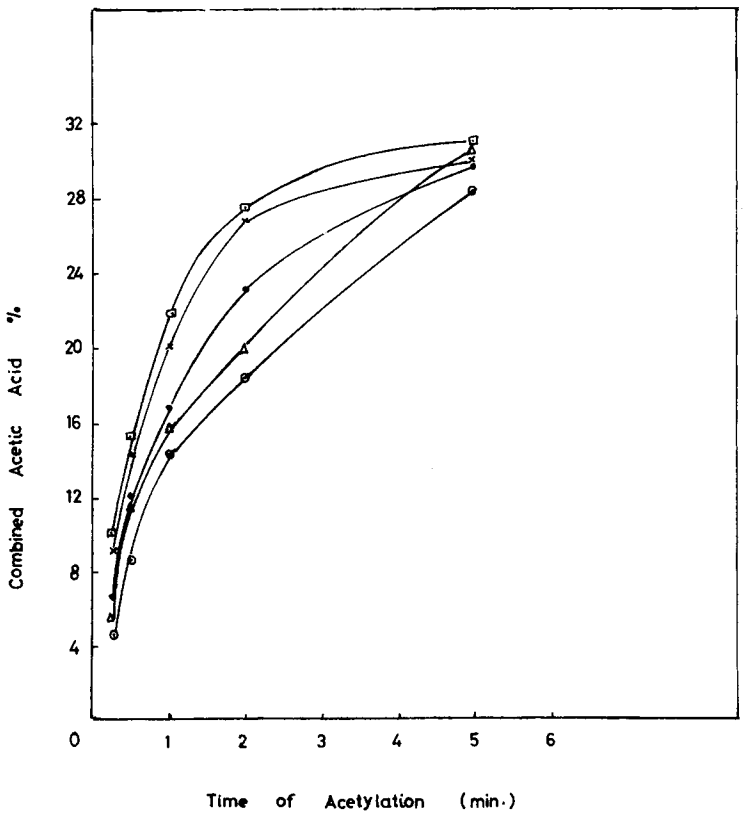

Fig. 1. Acetylation rate of beaten bagasse pulp: (⊙) unbeaten; (△) pulp of 30°SR; (⊡) pulp of 50°SR; (×) pulp of 60°SR; (●) pulp of 70°SR.

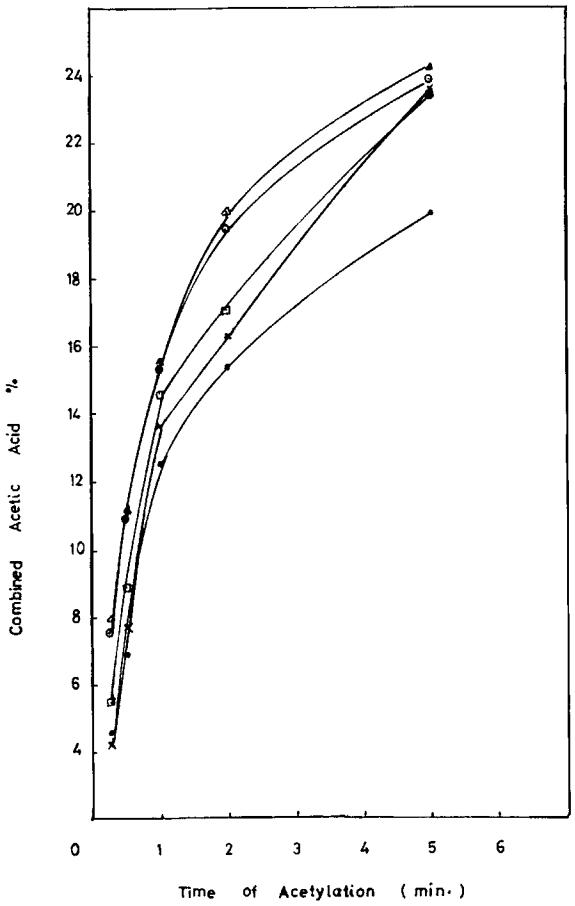

Fig. 2. Acetylation rate of beaten wood pulp: (⊙) unbeaten; (△) pulp of 30°SR; (⊡) pulp of 50°SR; (×) pulp of 60°SR; (●) pulp of 70°SR.

of acetylation of unbeaten pulps is also shown in the figures. From the figures, it can be seen that different combined acetic acid contents of wood and bagasse pulps, beaten or unbeaten, were obtained by changing the time of acetylation, in the range studied. It is obvious from both pulps that the acetylation reaction proceeds very fast, especially in the earlier stages of the reaction. This holds true for both beaten and unbeaten pulps. The acetylation reaction is affected by the rate of diffusion, the rate of swelling, and the rate of the acetylation reaction itself. But the reaction is governed by the rate of diffusion of the acetylating agent more than by the chemical reaction itself. Therefore, the combined acetic acid content of unbeaten wood pulp increased rapidly in the early stage of acetylation as compared to that of unbeaten bagasse pulp; i.e., 7.5% acetyle content of wood pulp was reached after reaction for 0.25 min, while the acetyle content of unbeaten bagasse pulp acetylated for the same reaction time was only 4.8%. The compact structure of cellulose in the case of bagasse pulp would account for this. Hence, the diffusion of acetylation liquor inside the bagasse pulp fibers would be very difficult in early stage of reaction, and the reaction is only

achieved in the outer layer of cellulose of bagasse pulp. The diffusion of reaction mixture through all the fibers needs more time. Direct support for this interpretation can be found in increasing the combined acetic acid content of bagasse pulp by increasing the time of acetylation to 5 min, showing a much higher acetyl content (28.5%) than that of wood pulp (23.9) acetylated for the same time of reaction. A similar trend is also observed with respect to the beaten pulps up to 30°SR. Opposite results are obtained on beating the pulps up to more than the above degree. Where the acetyl content of beaten (50–70°SR) bagasse pulp is much higher than that of wood pulp beaten to a corresponding degree of freenesss. This is found to be true over all the reaction time, in the range studied. This is due to the fact that beating of bagasse pulp resulted in a more of an increase in its external surface area than that of wood pulp.

The effect of beating degree of pulps on their acetyl content is shown in Figure 3. The reactivity of pulps during acetylation is favorably influenced by increasing the beating degree. It is apparent that increasing the freeness value of bagasse pulp to a definite degree accompanied by an increase in its acetyl content; i.e., the reactivity of bagasse pulp toward acetylation increased when the beating degree of the pulp increased from the unbeaten state (11°SR) to 30°SR. An additional increase in its reactivity is observed with increasing its freeness range, reaching an optimum value at 50°SR. Then its reactivity tends

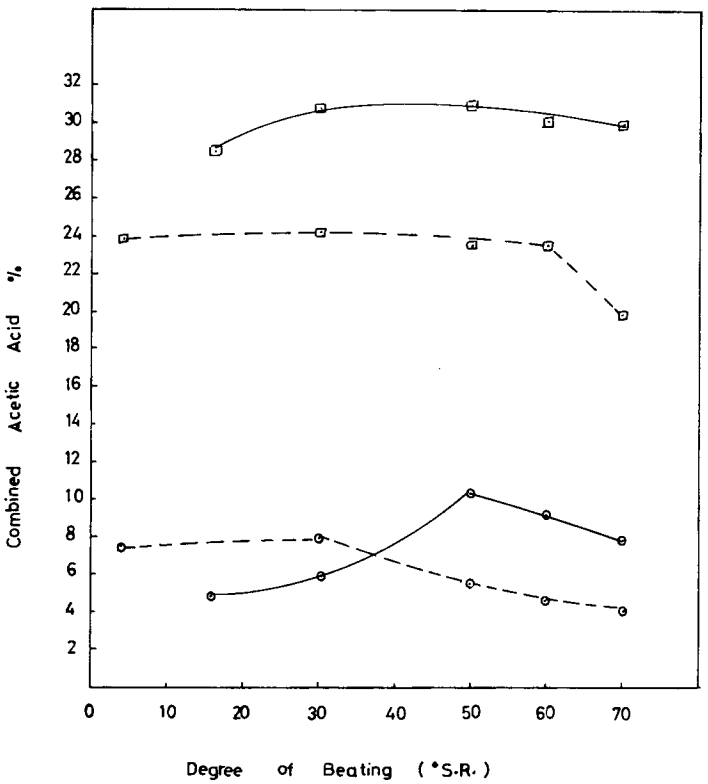

Fig. 3. Effect of degree of beating on acetylation rate of bagasse and wood pulps: (⊙) acetylation time 0.25 min; (⊡) acetylation time 5 min; (—) bagasse pulp; (- - -) wood pulp.

to decrease by increasing the freeness value from 50 to 70°SR, but still higher than the reactivity of the unbeaten pulp. This is manifested by its higher acetyl content than that of unbeaten pulp. The acetyl content of 0.25-min acetylated beaten pulp (30°SR) amounts to 5.67%. Increasing the freeness value of bagasse pulp to 50°SR is accompanied by an increase in its acetyl content (10.26%). A further increase of freeness to 70°SR causes a drop in its acetyl content to 7.83%, while that of the unbeaten pulp treated for the same time amounts only to 4.83%; i.e., 0.25-min acetylation of beaten pulp up to 30°SR results in a 17.39% increase in the acetyl content over that obtained in case of unbeaten pulp treated for the same time. A further increase in the freeness value from 30 to 50°SR results in a large additional increase (80.95%) in the acetyl content while at a freeness above 50°SR there is a gradual drop in the acetyl content of the pulp, which is still higher than that of unbeaten pulp. This is attributed to the fact that the surface area of the fibers is much increased by beating; thus a higher amount of acetylating mixture can penetrate through the capillary structure of the fiber, resulting in a higher degree of substitution within a much shorter time than with unbeaten pulp. The above discussion is true for the pulp treated for different times, 0.25–5 min (Fig. 3). However, the additional increase observed in the acetyl content by increasing the freeness value of the pulp from 30 to 50°SR is much greater in the early stage of reaction, 0.25-min acetylation, than that obtained in the latter stage, 5-min reaction.

From Figure 3 the behavior of beaten wood pulp toward acetylation can be also seen. It shows that the wood pulp behaves similarly to bagasse pulp, i.e., its reactivity increases when the degree of beating of the pulp increases to a definite degree. However, the reactivity of bagasse pulp is much higher than that of wood pulp, and the maximum reactivity of wood pulp is observed at 30°SR. Increasing the freeness value from 30 to 70°SR results in a great decrease in the acetyl content of the 0.25-min acetylated beaten pulp from 7.95% to 4.2% which is lower than that of the original unbeaten, 9°SR, pulp (7.53%). The same observation is found for wood pulp treated for all times of reaction studied in this work.

Paper Sheets from Beaten Acetylated Pulp

Two lots of unbeaten bagasse pulp were used; one with an acetyl content of 4.8% and the second with a higher acetyl content, 14.6%. Also two unbeaten wood pulp samples with 7.53% and 15.40% acetyl content were prepared. Paper sheets were made from these samples, after beating up to 30°SR, and their strength properties were measured. In another series of experiments the pulps were first beaten up to 30°SR, and then acetylated to a value corresponding nearly to the acetyl content of the above samples. The results are shown in Table I. From this table it is clear that all strength properties of paper sheets made from wood and bagasse pulps with low combined acetic acid contents are higher than those made from sample with a higher acetyl content. This can be attributed to the fact that the acetylation reaction is strongly exothermic, causing degradation, as well as acetylation, which causes a reduction of paper strength in addition to a reduction caused by blocking off some of the reactive hydroxyls of cellulose by strong acetylation, resulting in a decrease in the cohesion of the fibers. The amount of this degradation is controlled by the origin of cellulosic fibers.

TABLE I
Paper Properties of Beaten Acetylated Pulps

	Bagasse pulp				Wood pulp			
	Unbeaten (beating after acetylation)		Beaten (beating before acetylation)		Unbeaten (beating after acetylation)		Beaten (beating before acetylation)	
Time of beating to 30° SR (min):	8.5	21	6	6	17.53	21	35.8	35.8
°SR of acetylated pulp	11	11	23	14.5	9	9	29	28
Density (g/cm^3)	0.6652	0.6669	0.5644	0.4664	0.7576	0.6944	0.6378	0.5695
Breaking length (m)	2724	1486	2118	781	4710	3254	2811	1222
Burst factor	17.74	—	6.08	—	30.65	17.43	17.94	6.40
Tear factor	2.68	1.61	3.04	2.73	4.46	2.77	7.2	3.84
Doublefold	4	—	3	—	85	3	8	4

Therefore, the amount of degradation occurring by increasing the acetyl content of wood pulp is lower than that of bagasse pulp. The decrease in strength properties of paper as its acetyl content is increased is also attributed to progressive replacement of the hydroxyl groups by the hydrophobic acetyl groups; thus the opportunity for interfiber hydrogen-bonding formation and swelling of the fibers in water is decreased. The above discussion is true for paper sheets obtained from pulps beaten before or after acetylation.

The beating time of the pulp is dependent on the degree of substitution. It is clear from Table I that, as the degree of substitution increases the time of beating of the pulp to a given degree increases and, consequently, its strength properties decrease.

By comparing the strength properties of the sheets obtained from pulps beaten after acetylation with those of pulps beaten before the reaction, we can notice that the strength properties of the former pulp are higher, except tearing resistance, than those of the latter one. This increase in mechanical properties of pulps beaten after acetylation is attributed to the opening of the micellar structure of the fibers by the introduction of acetyl groups. A looser structure is thus produced, which favors the development of external surface on beating. On the other hand, the decrease in physical strength properties of the paper obtained from pulp beaten before acetylation is attributed to progressive replacement of the hydroxyl groups by the hydrophobic acetyl groups, which decrease the swelling of the fibers in water as well as having less of a chance of favoring the external surface area of the fibers, which is responsible for increasing the accessibility of the hydroxyl groups to hydration and increasing the bonding capacity between the hydroxyl groups of the adjacent fiber surfaces as the water is removed on drying the paper. Wood and bagasse pulps behave similarly in this respect. Also, the reduction of strength properties of beaten acetylated pulps due to decreasing their freeness value occurs during the reaction (Table I).

It is evident that acetylation to higher degree of substitution resulting in a reduction of paper strength due to the decrease in the DP[13] occurs simultaneously with acetylation of the pulp, in addition to the reduction caused by introducing acetyl groups. Therefore, it is necessary to adjust the maximum limit of acetyl content which is to be reached, after which strength properties deteriorate. Also it is evident that the beating of pulps after acetylation is better than when carrying out the beating process before acetylation.

Effect of Graft Copolymerization on Acetylation Rate of the Pulps

Activation of fibers was affected by graft copolymerization of AN prior to acetylation. Samples of two different polymer loads were prepared from both bagasse (3% and 13%) and wood (1.19% and 9.8%) pulps. Acetylation reaction was carried out on the above samples for a different reaction times, 0.25–5 min. The results are shown in Figures 4–6. Figure 4 shows that the acetylation reaction of bagasse pulp is characterized by an initial fast rate followed by a slower one. However, the initial fast rate observed with grafted samples is significantly higher than that of the ungrafted ones. It is seen that increasing the polymer load of bagasse pulp from 0% to 3% is accompanied by an increase in its acetyl content. This is observed with samples acetylated for 0.25–2 min, while, with respect to the sample treated for more than 2 min, there was a drop in its acetyl

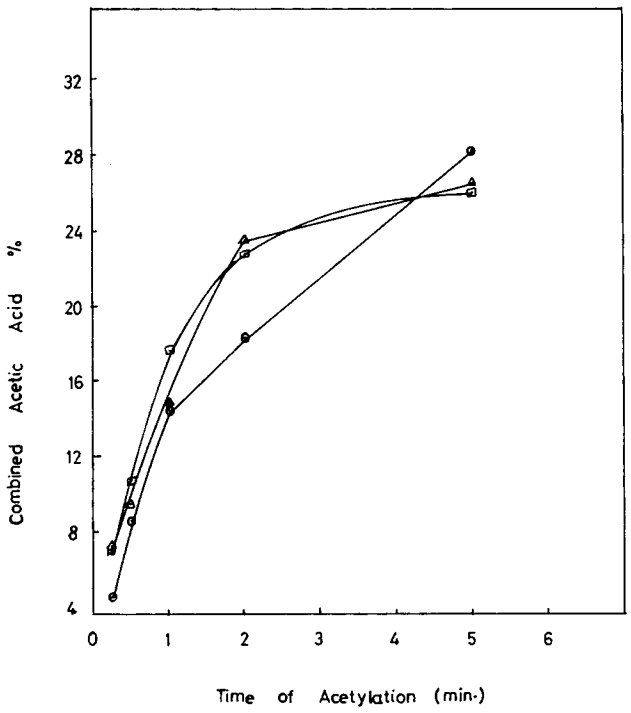

Fig. 4. Acetylation rate of grafted bagasse pulp: (⊙) ungrafted; (△) pulp with 3% polymer load; (⊟) pulp with 13% polymer load.

content. A further increase in the polymer load of the pulp from 3% to 13% results in an additional increase in the acetyl content of samples acetylated for 0.25–1 min, while the acetyl content of the pulp decreases on proceeding the acetylation reaction more than 1 min (Figure 3).

The effect of grafting of AN onto wood pulp on its rate of acetylation may be realized from Figure 5. It is apparent that the rate of acetylation is influenced by increasing the polymer load. It is obvious that the rate of acetylation of grafted wood pulp with low polymer load, 1.19%, is significantly higher than that of the ungrafted sample. Opposite results are obtained for pulp with a higher polymer load, 9.8%. This implies that further modification of wood pulp by grafting reduces its susceptibility toward acetylation.

As shown in Figure 6, the increasing of the polymer load of wood pulp from 0% to 1.19% results in an increase in its acetylation rate by 33.86%, 11.93%, for 0.25-min and 5-min acetylated samples, resp.; i.e., the rate of acetylation was rapid in the early stage of reaction. The acetylation rate of the pulp strongly drops by additional increase in its polymer load. The maximum rate of acetylation was obtained with a pulp samples having a low polymer value, 1.19%. Activation of the pulp fibers by grafting of AN prior to acetylation is probably due to the creation of more inner surfaces within the fibers.

In order to investigate the most suitable method of activation of pulp during acetylation, chemical and mechanical activation have been compared. The acetylation rate has studied with respect to the combined acetic acid content. The results are given in Table II. As shown in this table, the activation process depends on the origin of the pulp fibers. Bagasse pulp can be more activated

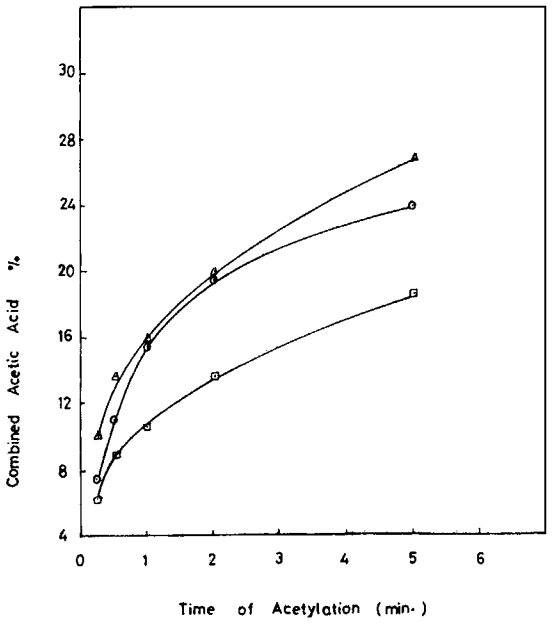

Fig. 5. Acetylation rate of grafted wood pulp: (⊙) ungrafted; (△) pulp with 1.19% polymer load; (⊡) pulp with 9.8% polymer load.

by beating, mechanical activation of pulp prior to acetylation, rather than by grafting of AN onto pulp. Acetylation of beaten samples, for instance, for 0.25 min, produces pulp which has a combined acetic acid content of 10.26%, while acetylation, for the same time, of a grafted sample results in a pulp which has only 7.54% acetyl content. This is due to the increase in the external surface area by beating, which is responsible for penetration of the acetylating mixture through the fibers.

On the other hand, chemical activation of wood pulp is more convenient than

TABLE II
Effect of Activation Process on Acetylation Rate of Pulps

Time of acetylation (min)	Bagasse pulp			Wood pulp		
	—	Chemical[a]	Mechanical[b]	—	Chemical[c]	Mechanical[d]
	Acetyl content (%)					
0.25	4.83	7.54	10.26	7.53	10.08	7.96
0.5	8.78	10.98	15.44	10.98	13.63	11.19
1	14.60	17.86	21.92	15.36	15.81	15.38
2	18.59	23.02	27.53	19.46	19.87	19.93
5	28.49	26.25	30.96	23.88	26.73	24.16

[a] The pulp is grafted prior to acetylation to 13% polymer load.
[b] The pulp is beaten up to 50°SR prior to acetylation.
[c] The pulp is grafted prior to acetylation to 1.19% polymer load.
[d] The pulp is beaten up to 30°SR prior to acetylation.

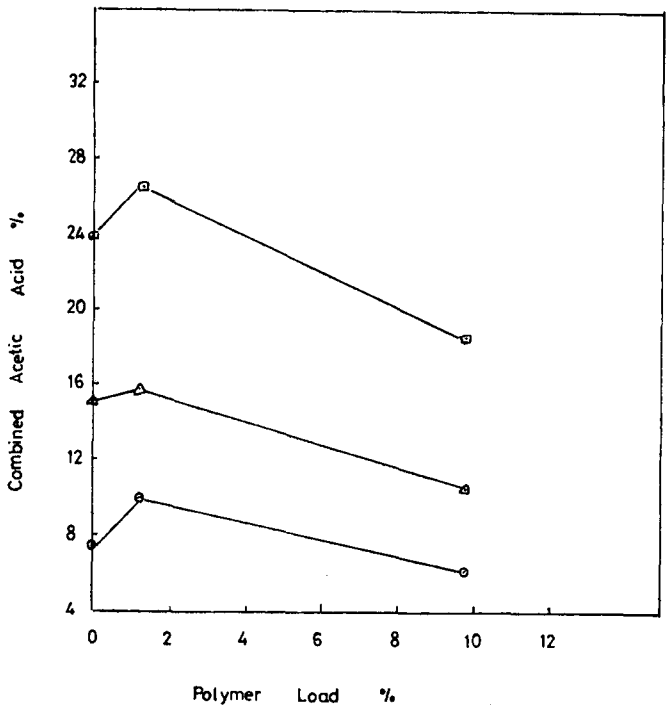

Fig. 6. Effect of degree of grafting on acetylation rate of wood pulp: (⊙) acetylation for 0.25 min.; (△) acetylation for 1 min; (⊡) acetylation for 5 min.

the mechanical activation. It is interesting to note that the acetylation rate of grafted wood pulp is faster than that of beaten pulp (Table II).

Paper Sheets from Grafted Acetylated Pulps

The influence of chemical activation of cellulosic fibers, prior to acetylation by grafting of acrylonitrile onto pulps, on their strength properties is studied. Two bagasse pulp samples of 3% and 13% polymer loads were prepared by grafting of AN onto pulp at 50°C for 5 min and 60 min, resp., by using CAN as initiator. Also grafted wood pulp samples were prepared, with 1.19% and 9.8%

TABLE III
Paper Properties of Grafted Acetylated Pulps

	Bagasse pulp				Wood pulp			
Polymer load (%)	—	—	3	13	—	—	1.19	9.80
Acetyl content (%)	4.83	14.60	9.56	10.98	7.53	15.36	10.08	10.51
Time of beating up to 30° SR (min)	8.5	18	15	27	17.6	16	15	22
Density (g/cm^3)	0.665	0.667	0.667	0.5026	0.758	0.694	0.790	0.659
Breaking length (m)	2724	1486	1830	—	4710	3254	4354	848
Burst factor	17.74	—	1.87	—	30.65	17.43	31.74	—
Tear factor	2.68	1.61	1.50	1.50	4.46	2.77	2.94	1.36
Doublefold	4	—	—	—	85	2.5	115	—

polymer loads, by carrying out the reaction for 5 min and 90 min, resp. Acetylated samples, with practically the same combined acetic acid content, about 10%, were prepared from the above grafted pulps. The paper sheets were made from these samples, and their strength properties were measured. The results are shown in Table III. It can be seen that not only increasing the acetyl content of pulps but also the activation process influenced their strength properties. Acetylated pulps with different contents of polymer loads and nearly the same acetyl content showed great differences in strength properties. The decrease in the physical strength properties of the paper prepared from grafted acetylated pulp, as the polymer load increased, is attributed to the decreasing in the interfiber hydrogen bonding of the fibers by increasing the polymer load. It should be pointed out that wood and bagasse pulps behave similarly in this respect. Also, it is clear from Table III that, as the polymer load of the pulp increases, the time of beating up to the same °SR increases; consequently, the strength properties decrease. As the polymer load of bagasse pulp increased from 3% to 13%, the beating time up to 30°SR increases from 15 min to 27 min. This is owing to the decrease in the porous structure of pulp by grafting.

It can be concluded that the reactivity of pulps to acetylation increases by beating to a definite degree (11–50°SR and 9–30°SR in case of bagasse and wood pulps, resp.), whereas their reactivity decreases in the 50–70 and 30–70 freeness range, resp. The results obtained in this work agree with those found in the literature[5–7] which report that the reactivity of pulps to acetylation declines after beating to a definite degree. The only difference is found in the range in which the reduction of reactivity occurs.

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