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The Xanthate Method of Grafting. III. Effect of Lignin Content on the Graftability of Wood Pulp*

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Synopsis

Several commercial wood pulps of different chemical origin and with various lignin content were copolymerized with acrylonitrile using the xanthate grafting process. A number of experiments were carried out to evaluate the effects exerted by the residual lignin and by other wood components on the grafting reaction. The results obtained show that graft copolymers can be prepared in good yields with pulps containing as much as 23% lignin. With the aim to investigate the effect of lignin in more detail, two series of pulps were prepared by delignification of a crude sulfite pulp and a crude Kraft pulp to different levels of lignin content. Sodium chlorite was used as a bleaching agent. Copolymerization results obtained with these pulps indicate some fundamental differences in behavior between sulfite and Kraft pulps. In both cases, the copolymerization is afflicted by a short inhibition period whose duration, however, does not depend on the lignin content in the pulp.

INTRODUCTION

The rising cost of wood as a raw material combined with equally rising costs of chemical pulping processes bring about increasing demands for a more complete utilization of this resource. Chemical pulping processes normally utilize some 50–60% of the wood, and further losses of the material are incurred as a result of bleaching processes. The remaining ~50% is only partially recovered as byproducts; the rest is often burned or discarded, with obvious environmental consequences.

The voluminous literature devoted to grafting of synthetic polymers onto pure cellulose is only poorly matched by papers, studying the same reactions on raw cellulosic or wood-based materials as grafting substrates. This is easy to explain: the grafting reactions being inherently complex by themselves, an introduction of additional unknowns by using primary materials of a variable and often unknown structure is undesirable if the mechanistic and kinetic parameters of the grafting reaction are to be properly evaluated. From a more practical point of view, however, these are the materials which stand to benefit the most from a modification by high polymers. Unfortunately, the corresponding literature shows clearly that, in most cases, grafting reactions of raw cellulosic

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materials do not parallel those taking place when using pure cellulosic pulps or cellulose itself.[1,2]

The xanthate method of grafting, discovered by Faessinger and Conte,[3] appears to offer considerable advantages over other grafting processes, such as a relatively low cost and availability of the starting material and no need for expensive chemicals or inert atmosphere. While the original patents list lignin-containing wood products among the possible substrates for grafting, a later paper by Brickman[4] of the same research group indicated that the method has been employed predominantly with high α-cellulose materials such as cotton cellulose and rayon. Similarly, both Dimov and Pavlov[5] and Kokta and Valade[6] used relatively pure cellulosic materials in their investigations of the xanthate grafting method.

The results published by Stannett and co-workers[1] and by Erdelyi[2] have left little doubt about the profound effect exerted on grafting by the residual components in unbleached or partially bleached pulps. The present study aims at establishing the feasibility of grafting crude pulps with the help of the xanthate process and at determining to what extent the presence of lignin and of other residual wood components affects the grafting reaction.

EXPERIMENTAL

Materials

The commercial pulps used in this work have been supplied by the Consolidated-Bathurst Research Center, Grand-Mère, Québec. With the exception of the kraft semibleached pulp, which has been supplied by Division Waygamack of the same Company. The pulps were used as received, without any purification or chemical treatment. The three bleached pulps, supplied under the form of air-dry sheets, were disintegrated by hand before the mercerisation step.

Acrylonitrile (monomer) was purified by distillation. The central cut was collected and stored in the refrigerator.

All other reagents used in this work were employed as supplied by the manufacturers.

Delignification of Pulps

Sodium chlorite was used as the bleaching agent at pH 4. The concentrations of chlorite required to obtain a given degree of delignification were determined by preliminary experiments.

In a bleaching operation, the required quantity of pulp was disintegrated and placed into a polyethylene bag. The calculated amount of sodium chloride dissolved in water was subsequently added and the mixture was homogenized by trituration. The pH was then adjusted to 4 with sulfuric acid, and the mixture was once again homogenized and the pH readjusted if necesssary. The bag was placed in a controlled-temperature bath maintained at 50°C for a desired period of time. After bleaching, the pulp was filtered off, thoroughly washed, and then subjected to alkaline extraction by sodium hydroxide (1% by weight in respect to dry pulp) at 80°C during 1 hr. The extracted pulp was thoroughly washed until the disappearance of alkaline reaction and then filtered to approximately 20% of dryness. All pulps were preserved in a refrigerator.

The pulps prepared by this procedure as well as the commercial pulps have been characterized by standard methods of the Canadian Pulp and Paper Association (CPPA-Technical Section).

Copolymerization

A detailed account of pulp preconditioning and of the copolymerization procedure has been given in previous publications.[6,7] All experiments presented in this paper have been carried out with 4.5 g pulp (oven-dry weight) and 9.09 g monomer.

The grafting parameters used to characterize the products are defined as follows:

$$\text{total conversion, \%} = (D - B)/C \times 100$$
$$\text{polymer loading, \%} = (A - B)/B \times 100$$
$$\text{grafting efficiency, \%} = (A - B)/(D - B) \times 100$$

where A is weight of products after copolymerization and extraction; B is weight of pulp (oven-dry, corrected for solubility in NaOH solution); C is weight of monomer charged; and D is weight of products after copolymerization.

RESULTS AND DISCUSSION

Grafting onto Commercial Pulps

Table I shows the properties of commercial pulps used for copolymerization. Copolymerization results obtained with reaction times of 1 hr and 18 hr are summarized in Tables II and III, respectively.

It is evident that the character of pulp used produces an important effect on the copolymerization reaction. It is also evident, however, that the xanthate method can be employed, with good yields, for the grafting of any commercial pulp used in this work. According to the data shown in Table II, the kraft unbleached (or partially bleached) pulps seem to give a considerably poorer grafting efficiency than the other pulps. Conversely, the bleached kraft pulps show the best grafting efficiency results at 1 hr of reaction time. This might indicate that the thiolignin present in unbleached (or semibleached) kraft pulps has a particularly deleterious effect on the polymerization reaction. This sugges-

TABLE I
Properties of Commercial Pulps Used for Graft Copolymerization

Pulp	Lignin content, %	CED viscosity, cps	Solubility in NaOH,[a] %
Bisulfite, high yield	23.2	5.2[b]	6.65
Sulfite, low yield	7.5	23.7[b]	2.96
Kraft, unbleached	4.5	24.2	6.00
Kraft, semibleached	0.8	12.7	3.50
Kraft, bleached, softwood I	<0.05	15.3	1.87
Kraft, bleached, softwood II	<0.05	19.3	2.00
Kraft, bleached, hardwood	<0.05	16.4	6.25

[a] 4.5 g pulp (oven dry) in 150 ml of 0.75N NaOH (45 min).
[b] Limited solubility in cupriethylenediamine (CED).

TABLE II

Dependence of Graftability on Pulp Type at 60 min of Reaction Time

Sample	Pulp	Degree of xanthation γ	Total conversion, %	Polymer loading, %	Grafting efficiency, %
70	Bisulfite, high yield	6.5	23.2	37.1	74.1
88	Sulfite, low yield	5.3	38.6	69.1	86.0
87	Kraft, unbleached	4.8	39.9	50.9	56.9
49	Kraft, semibleached	5.0	39.9	51.9	61.6
69	Kraft, bleached, softwood I	4.2	35.1	62.8	83.4
62	Kraft, bleached, softwood II	4.2	38.6	75.1	96.1
66	Kraft, bleached, hardwood	5.2	33.0	64.9	91.4

TABLE III

Dependence of Graftability on Pulp Type at 18 Hr of Reaction Time

Sample	Pulp	Degree of xanthation γ	Total conversion, %	Polymer loading, %	Grafting efficiency, %
40	Bisulfite, high yield	6.5	80.1	127.2	75.1
41	Sulfite, low yield	5.3	84.5	88.2	60.1
86	Kraft, unbleached	4.8	81.9	93.9	53.4
28	Kraft, semibleached	5.0	87.0	112.3	59.9
34	Kraft, bleached, softwood I	4.2	65.0	70.1	52.4
35	Kraft, bleached, softwood I	4.2	67.3	73.9	53.4
39	Kraft, bleached, softwood II	4.2	69.3	62.8	45.0
38	Kraft, bleached, hardwood	5.2	71.3	92.8	61.8
23	Kraft, semibleached, plus 1 g sodium lignosulfonate	5.0	34.4	59.8	81.8

tion seems quite reasonable considering the fact that —SH groups are known to be effective chain transfer agents and retarders of radical polymerizations. The bisulfite and sulfite pulps, on the other hand, show a better graftability than their kraft counterparts. This comes as a surprise in view of the fact that an addition of lignosulfonates to the reaction mixture has effectively reduced the total conversion to polymer (see last row in Table III). However, a higher grafting efficiency is observed in the presence of the lignosulfonate. It seems probable that the presence of water-soluble lignosulfonates added to the reaction mixture decreases especially the formation of homopolymer, although it also has a negative effect on the copolymerization. The heterogeneous lignosulfonates present in the pulp, on the other hand, do not seem to have a significant effect on the reaction.

The results shown in Table III were obtained with 18-hr polymerization time. The mostly lower grafting efficiency values found here reflect most likely the increased proportion of homopolymer formed at later stages of the reaction, when xanthate groups are no longer available to initiate the copolymerization. The rate of decomposition of xanthate groups depends, above all, on the pH of the reaction mixture. While the initial pH of the reaction mixture was in all experiments adjusted to 5, a rapid drop in pH ensued immediately in the early stages of the reaction. In Figure 1, the pH of the reaction mixture is plotted against time separately for the individual pulps. One observes that pH decreases most rapidly in the case of bleached pulps. In the case of unbleached and

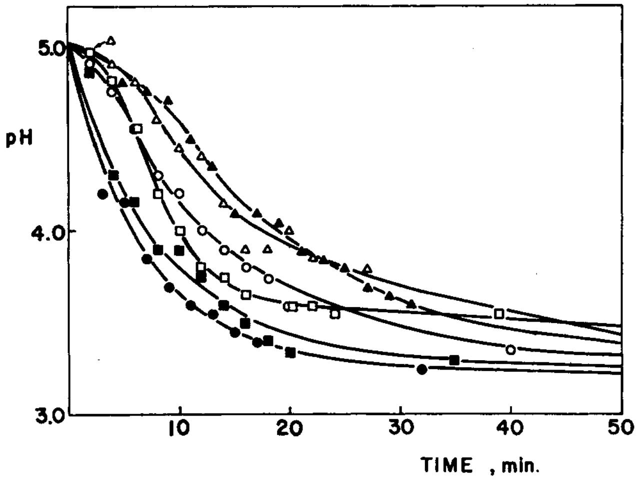

Fig. 1. Variation of pH with copolymerization time and pulp type: (○) high-yield bisulfite; (△) low-yield sulfite; (□) bleached kraft, hardwood; (▲) semibleached kraft; (●) bleached kraft, softwood I; (■) bleached kraft, softwood II.

semibleached pulps, the pH drop is considerably slower. It is difficult to correlate the grafting efficiency results shown in Tables II and III with the pH decrease without a good knowledge of the processes which take place in the system. It would appear that the bleached pulps, in particular, undergo a fast copolymerization immediately after H_2O_2 is added. This initial reaction produces mainly graft copolymer. Due to low pH, xanthate groups disappear rapidly and large amounts of homopolymer are formed at later stages of the reaction, bringing down the overall grafting efficiency. This scheme, however, does not explain the behavior of the lignin-containing pulps. For example, the grafting efficiencies for semibleached kraft, unbleached kraft, and bisulfite pulps do not change when going from 1 hr to 18 hr of polymerization, regardless of the fact that the pH has already stabilized at ~3 at the end of the first hour of polymerization and that total conversion doubles in the following 17-hr period. It appears, hence, that in these cases the homopolymer–copolymer ratio does not vary throughout the reaction period and that it depends solely on the character of pulp and on reaction conditions. This conclusion is in agreement with previous results obtained by these authors with semibleached Kraft pulp (7).

Tables II and III also list the degree of xanthation of each pulp determined by an iodometric titration method. The degree of xanthation varies slightly from one pulp to another and is generally higher in the case of unbleached pulps. This may reflect the higher content of hemicellulose in such pulps (including the bleached hardwood pulp). However, no direct correlation can be discerned between the degree of xanthation and the grafting results.

Effect of Residual Lignin on Grafting

The results presented in the foregoing paragraph give a strong indication that the residual lignin in pulp (as well as other pulp components such as the hemicellulose) may exert a marked influence on its graftability. Apart from the radiation-induced graft copolymerizations carried out by Stannett and coworkers,[1] very little information on this subject is available in the literature.

TABLE IV
Properties of Sulfite Pulps Bleached by Sodium Chlorite[a]

Sample	Sodium chlorite, %[b]	Lignin content, %	Copper index	CED viscosity, cps
SL-0	0	7.0	2.6	26.5
SL-4	1	5.6	2.2	42.7
SL-3	3	4.4	2.1	47.3
SL-2	7	2.4	2.1	52.6
SL-1	12	1.6	1.8	51.3

[a] Low-yield sulfite pulp (see Table I, second row) used as starting material.
[a] Weight percentage in reference to the weight of dry pulp.

TABLE V
Properties of Kraft Pulps Bleached by Sodium Chlorite[a]

Sample	Sodium chlorite, %[b]	Lignin content, %	Copper index	CED viscosity, cps
KW-0	0	4.4	1.00	26.2
KW-4	1.5	3.2	0.95	24.3
KW-3	3.5	2.8	0.93	25.3
KW-2	8	1.0	0.51	24.7
KW-1	10	0.6	0.37	25.8

[a] Unbleached kraft pulp (see Table I, third row) used as starting material.
[b] Weight percentage in reference to the weight of dry pulp.

The only comprehensive study of pulp graftability in dependence on its lignin content, using acrylonitrile as the monomer, has been published by Erdélyi.[2] In his work, a series of pulps having different lignin content was prepared by the sulfate cooking process and by subsequent bleaching with sodium hypochlorite. The resulting pulps were subjected to grafting with acrylonitrile as monomer and cerium nitrate as initiator. The grafting results obtained with copolymerization times between 5 and 90 min showed clearly that the degree of delignification has a significant effect on copolymerization results. In particular, the presence of lignin in the pulp led to a drop in polymer loading and brought about prolonged inhibition periods at higher lignin contents (>1%). On the basis of his results, Erdélyi affirmed that it was not practically feasible to graft pulps containing over 1.6% lignin.

The results shown in Tables II and III indicate that the xanthate grafting process is capable of producing graft copolymers with pulps having a lignin content as high as 23%. It thus appeared of interest to pursue this study further. For that purpose, two series of pulps were prepared: the first based on the sulfite (low yield) pulp (see Table I, second row), the other on the unbleached kraft pulp (see Table I, third row). In both cases, the original pulp was bleached with four different concentrations of sodium chlorite to prepare pulps with decreasing lignin content. Sodium chlorite was selected as the bleaching agent in order to minimize cellulose degradation. The resulting pulps were characterized by standard methods, and their properties are listed in Tables IV and V for sulfite and kraft pulps, respectively. It is evident that the objective of bleaching has been reached. The lignin content of the pulps is evenly distributed

TABLE VI

Sulfite Pulp Graftability as a Function of Lignin Content at 30 Min of Reaction Time

Sample	Lignin content, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %
SL0-2	7.0	12.2	23.7	93.7
SL4-2	5.6	13.9	27.3	95.1
SL3-2	4.4	12.9	21.1	78.8
SL2-2	2.4	22.2	36.2	79.3
SL1-2	1.6	12.1	19.0	75.5

TABLE VII

Sulfite Pulp Graftability as a Function of Lignin Content at 60 min of Reaction Time

Sample	Lignin content, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Copolymer molecular weight $\bar{M}_v$
SL0-1	7.0	28.2	47.6	81.8	17,500
SL4-1	5.6	28.5	53.6	90.7	26,500
SL3-1	4.4	34.1	60.9	86.3	41,000
SL2-1	2.4	34.1	54.9	78.0	28,600
SL1-1	1.6	34.7	56.7	78.6	65,500

TABLE VIII

Kraft Pulp Graftability as a Function of Lignin Content at 30 Min of Reaction Time

Sample	Lignin content, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %
KW0-2	4.4	17.4	28.4	79.5
KW4-2	3.2	12.4	19.2	70.1
KW3-2	2.8	7.0	13.5	92.6
KW2-2	1.0	6.8	11.0	77.7
KW1-2	0.6	7.3	13.9	90.8

over the interval limited by zero on one side and by the lignin content of the original pulp on the other. On the other hand, almost no change of CED viscosity is observed regardless of the degree of delignification. (Pulps SL-0 and SL-4 show lower CED viscosities; this is caused by the imperfect solubility of these high-lignin pulps in CED.) This indicates that cellulose was not seriously attacked by the chlorite under the reaction conditions used.

Before discussing the grafting results summarized in Tables VI, VII, VIII, and IX, it is perhaps useful to make some explanatory comments regarding the accuracy of grafting efficiency data. These data have been obtained by the extraction of copolymerization products with dimethylformamide. The extractions were performed under vacuum during 12 hr. This time has been previously established as sufficient to carry the extraction to completion. It is believed, however, that even after this period there will still be some polymer which will remain occluded in the cellulose matrix. In respect to this possible source of error, extraction results referring to products characterized by a very low polymer loading (results compiled in Tables VI and VIII, in particular) should be looked

TABLE IX
Kraft Pulp Graftability as a Function of Lignin Content at 60 Min of Reaction Time

Sample	Lignin content, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Copolymer molecular weight $\bar{M}_v$
KW0-1	4.4	44.3	59.1	65.0	22,000
KW4-1	3.2	37.7	54.8	70.9	16,500
KW3-1	2.8	19.8	30.8	75.3	10,000
KW2-1	1.0	21.7	35.0	77.6	3,500
KW1-1	0.6	23.7	39.1	79.1	19,000

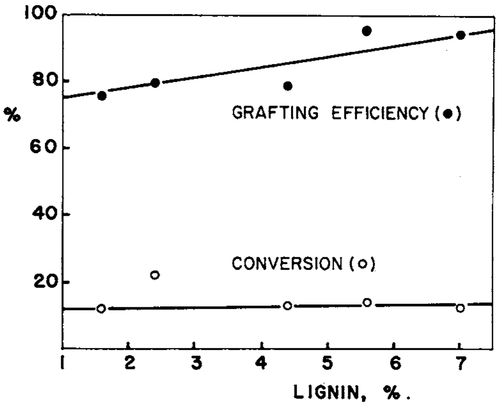

Fig. 2. Effect of lignin content on graftability of sulfite pulp at 30 min of reaction time.

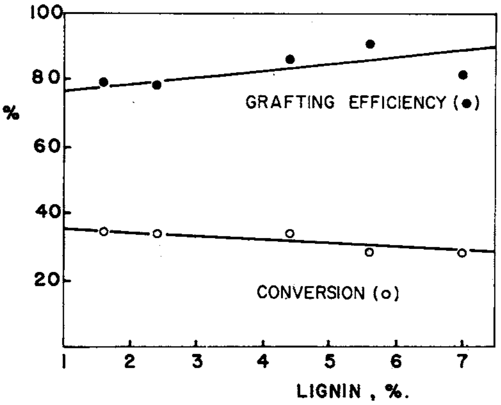

Fig. 3. Effect of lignin content on graftability of sulfite pulp at 60 min of reaction time.

upon with extreme caution. However, the data obtained are believed to be sufficiently accurate to enable one to discern the general trends of the dependence of copolymerization parameters on the degree of pulp delignification.

Let us first discuss the copolymerization behavior of the sulfite pulps. It is evident from Tables VI and VII and from Figures 2 and 3 that, in the absence of other effects, the lignin present in the pulp does not act as an inhibitor of the copolymerization reaction. Moreover, it should be noted that while the total conversion shows almost no dependence on lignin content at 30 min of reaction

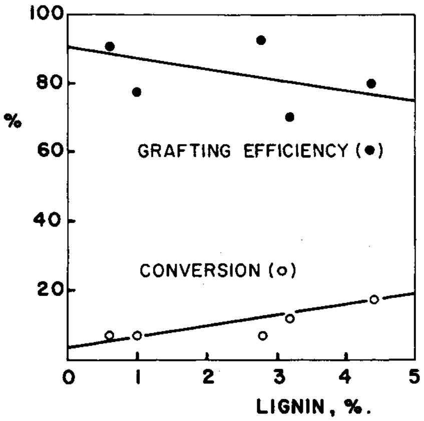

Fig. 4. Effect of lignin content on graftability of kraft pulp at 30 min of reaction time.

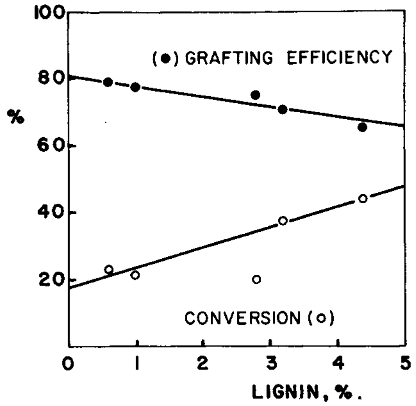

Fig. 5. Effect of lignin content on graftability of kraft pulp at 60 min of reaction time.

time and drops slightly with growing lignin content at 60 min of reaction time, the parameter of grafting efficiency has a tendency to increase in both cases with rising lignin content. This in turn results in an increased polymer loading.

A different behavior is found in the case of the kraft pulps. The grafting results are summarized in Tables VIII and IX and are plotted against lignin content in Figures 4 and 5. Although the experimental scatter is considerable in these experiments (especially those with 30 min of reaction time), the results seem to indicate that for both reaction times, total conversion rises with increasing lignin content; while grafting efficiency tends to decrease at the same time. The experimental scatter is particularly obvious in Figure 4, but the general trend mentioned above is still apparent. It should be noted at this point that, while an attempt was made in Figures 2, 3, 4, and 5 to combine each individual set of points with straight lines, there is no reason to believe that the dependence of total conversion or grafting efficiency on lignin content is linear. These straight lines should thus be looked upon only as visual aids without any special significance.

One notices also that the grafting results obtained with pulps SL-0 and KW-0 (the first members of the two series, which have not been subjected to bleaching) are not identical with the results obtained when using the correspond-

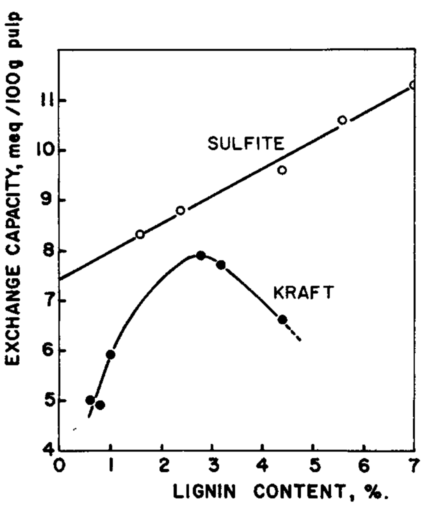

Fig. 6. Dependence of cation exchange capacity on lignin content in sulfite and kraft pulps.

ing crude commercial pulps (samples 88 and 87 in Table II). This is perhaps not surprising: prior to delignification, the crude pulps were thoroughly disintegrated and washed. At this stage, the samples SL-0 and KW-0 were withdrawn and their analysis showed a decrease in lignin content of 0.5% in the case of the sulfite pulp and 0.1% in the case of the kraft pulp, as compared with the two original pulps. Furthermore, the disintegration process considerably enlarges the specific surface of the pulp. This factor has been shown previously[8] to have a significant effect on the grafting reaction; this can probably explain the higher grafting efficiency after disintegration.

The last columns of Tables VII and IX list the molecular weights of polyacrylonitrile copolymerized with pulp. There does not seem to be any well-defined dependence of copolymer molecular weight on the degree of delignification. The application of the acetolysis method[9] of polymer isolation was rendered difficult by the presence of lignin and only low-concentrated solutions were obtained even after repeated extractions of the residue with dimethylformamide. Perhaps the only conclusion that can be made is that, in all the cases, the copolymer molecular weight is sufficiently low to bring about an effective modification of the pulp.

Insofar as the grafting efficiency values reported in this paper may seem rather low in some cases, it is important to note that the amount of homopolymer formed can be reduced to very low levels by a simple increase in H_2O_2 concentration. This has been amply demonstrated in a previous work.[7] The present system enables one to observe more clearly the relationship between the degree of delignification and grafting efficiency.

There is another point which warrants further discussion. Delignification is evidently not the only change undergone by the pulp during its exposure to sodium chlorite and during the following alkaline extraction. Another important change which takes place is a decrease in hemicellulose content. Also the content of reducing functions in the pulp varies in dependence on the degree of bleaching, especially in the case of kraft pulps. This is clearly demonstrated by the copper index data listed in Tables IV and V. All these changes may have an

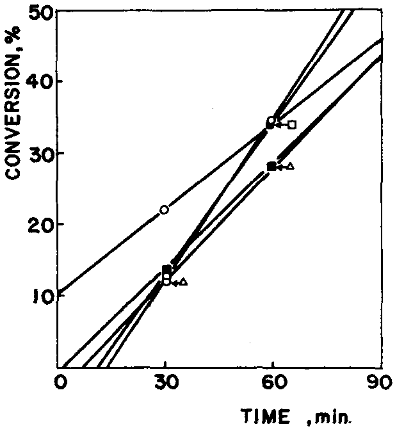

Fig. 7. Dependence of total conversion to polymer on reaction time and on lignin content in sulfite pulps. Per cent lignin: (○) 1.6%; (●) 2.4%; (□) 4.4%; (■) 5.6%; (△) 7.0%.

effect on the grafting reaction. The possible influence of hemicellulose content on the degree of xanthation has been already mentioned in the chapter dealing with commercial pulps.

The variations in the cation exchange capacity of the individual pulps may also be of importance. As a part of the pulp prepolymerization treatment, the xanthated pulp is steeped in a dilute solution of ferrous ammonium sulfate. The number of ferrous ions retained by the pulp depends on its exchange capacity. Although the overall exchange capacity of a xanthated pulp will depend, to a great extent, on the degree of thiocarbonation, it appeared interesting to find out the contribution of exchanging functions existing in the pulp before xanthation. To this effect, the exchange capacities of pulps SL and KW have been determined by the sodium bicarbonate absorption method (Tappi T237 su-63). The results obtained are plotted against lignin content in Figure 6. It is evident that the two types of pulp behave quite differently. In the case of sulfite pulps, the exchange capacity increases linearly with rising lignin content, presumably due to the increasing content of sulfonic groups. The kraft pulps, on the other hand, show a maximum exchange capacity at about 3% lignin content, and its absolute value is generally lower than in the sulfite series. Considering a degree of xanthation $\gamma \doteq 5$, this brings about an additional exchange capacity of approximately 30 meq/100 g due to thiocarbonate groups. It is therefore evident that, especially in the case of sulfite pulps, the original exchange capacity contributes significantly to the overall capacity and may thus have an effect on the copolymerization reaction.

The two total conversion results obtained with each pulp (30 and 60 min of reaction) are not sufficient for an accurate evaluation of inhibition periods, but it is possible to make a qualitative estimate. In Figures 7 and 8, the total conversion data are plotted against time for sulfite and kraft pulps, respectively, and each pair of points is connected by a straight line. The intercepts of these straight lines with the abscissa give a rough estimate of the inhibition periods afflicting the graft copolymerization. One observes that while inhibition periods of 10–20 min are found in almost all the cases, the reaction rate thereafter is not affected, to a large extent, by the content of lignin in the pulp. This behavior is

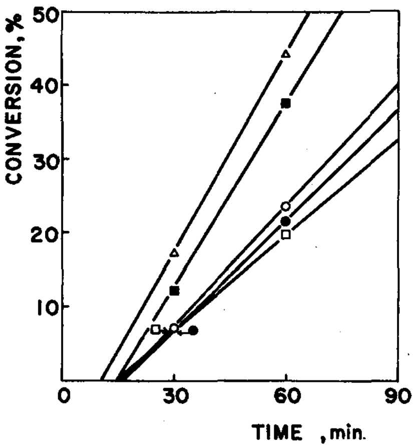

Fig. 8. Dependence of total conversion to polymer on reaction time and on lignin content in kraft pulps. Per cent lignin: (○) 0.6%; (●) 1.0%; (□) 2.8%; (■) 3.2%; (△) 4.4%.

quite different from that encountered by Erdélyi[2] in his system using ceric nitrate as initiator. He observed an almost complete absence of inhibition periods at low lignin contents (<1%), but their duration increased very rapidly with rising lignin content. A 4.7% level of lignin rendered the pulp almost ungraftable. From a comparison of Erdélyi's results and those shown in the present article, it would appear that the xanthate method lends itself more readily to the grafting of high-lignin pulps than the ceric-ion process.

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