

## The Xanthate Method of Grafting. V. Graftability of Mechanical Pulp

V. HORNOF, B. V. KOKTA, and J. L. VALADE, *Groupe de Recherche en Pâtes et Papiers, Département de l'Ingénierie, Université du Québec à Trois-Rivières, Trois-Rivières, Quebec, Canada*

### Synopsis

Softwood mechanical pulp was copolymerized with acrylonitrile using the xanthate redox grafting process. Experiments carried out under different reaction conditions (temperature,  $H_2O_2$ , concentration, pH, reaction time) showed that mechanical pulp is less apt to form graft copolymers than chemical pulps. In most cases, long inhibition periods were observed, and the product formed thereafter contained large quantities of homopolymer. It was not possible to raise grafting efficiency by increasing the concentration of hydrogen peroxide. A series of experiments with pulps having different particle size showed a moderate increase in total conversion to polymer with decreasing mean fiber length. The latter, however, produced little influence on the copolymer/homopolymer ratio.

### INTRODUCTION

Pulps of paper-making quality are commercially produced by chemical processes, which remove a large part of the lignin present in wood or other raw materials used. It is a well-known fact that lignin in pulp fibers is responsible for poorer sheet properties and as a consequence, the use of groundwood or refiner mechanical pulp in paper manufacture is confined to low-quality papers where strength and color properties are not critical. This is rather unfortunate when one considers the disadvantages of chemical pulping. First, a large part of the primary material is either completely lost or only partly recovered as by-products; secondly, the costs of pollution abatement rank among the highest in chemical industry and many pulp and paper companies simply cannot afford the necessary installations. These problems are being tackled by the industry in different ways. For example, the whole-tree utilization concept is to extend the available raw material base. Pulp mills are being built in isolated areas where pollution standards are less stringent. High-yield pulping processes are being widely used.

The ultimate in pulping yield, however, is mechanical pulp. Here, pulp is manufactured by simply disintegrating the wood into fibers by a mechanical process such as stone grinding (groundwood) or disk refining (refiner pulp). It must be noted that the properties of mechanical pulp (in particular its strength, brightness, and uniformity) do not even come near to those of chemical pulps. The only notable exception is the thermomechanical pulp, which is expected to replace some lower-grade chemical pulps.

It is generally believed that the poor strength properties of mechanical pulp are due to the presence of lignin—a hydrophobic material whose effect is to diminish the strength of interfiber bonds. While in wood lignin represents the resin component of a fiber–resin reinforced composite system, the disintegrated or chemically degraded lignin in pulped wood prevents hydrogen bonds from being established during sheet formation and thus has a negative effect on sheet strength. Furthermore, the reactive groups present in lignin result in poor chemical stability of produced paper.

Chemical modification of mechanical pulp to improve its physical properties and to remove some of its deficiencies is indeed a tempting possibility, despite the relatively high cost of such a treatment compared to the low cost of the starting material. A feasible way of introducing groups capable of modifying the fiber-bonding characteristics of pulp is offered by the process of graft copolymerization. A suitable choice of monomers enables one to graft chains with a different degree of hydrophilicity, which in turn will allow or disallow the formation of hydrogen bonds, affecting sheet strength. Most work on grafting, however, has been devoted to rather pure forms of cellulose mainly in the textile field. A notable exception represents the work of Stannett and co-workers.<sup>1,2</sup> Their results have shown that a hydrophilic graft, viz., polyacrylamide, was capable of improving mechanical properties of paper, while hydrophobic grafts resulted in a reduction of sheet properties.

Sakata and co-workers<sup>3</sup> studied the grafting of styrene onto woody fibers by direct irradiation with x-rays as well as by a pretreatment with peracetic acid. They determined the ratios of polymer grafted to cellulose and polymer grafted to lignin and investigated the molecular weight distributions of the grafts. In another study,<sup>4</sup> they succeeded in grafting N-methylolacrylamide onto woody fibers and cellulosic pulps. Under identical reaction conditions, however, the degree of grafting observed was 10–20 times lower for woody fibers than for a Kraft pulp.

Zoldners and co-workers<sup>5</sup> investigated the chain-transfer grafting of wood and of various lignin derivatives prepared therefrom with styrene. In the case of the wood itself, the reactions produced mostly homopolymers; the highest grafting efficiency of about 50% was recorded with methylated lignins whose phenolic functions had been blocked.

The present authors have been studying the xanthate grafting process<sup>6</sup> for some time.<sup>7,8</sup> Two recent articles deal with the effect of lignin on grafting in the particular cases of Kraft and sulfite<sup>9</sup> and bisulfite high-yield<sup>10</sup> pulps. As a result of those experiments, it appeared that the xanthate process is better adapted to use with lignin-containing pulps than either the radiation or the ceric-ion grafting methods. The present work is a continuation of the previous studies.

## RESULTS AND DISCUSSION

In order to compare the grafting behavior of mechanical pulp with other pulps studied previously, several sets of experiments were carried out to find out the effect of various reaction conditions on polymer formation and on the copolymer–homopolymer ratio. These experiments were carried out under conditions comparable with those used in the grafting of chemical pulps with acrylonitrile

as the monomer. The results obtained with some of the commercially produced chemical pulps are shown in Table I. It is evident that all of the pulps tested undergo grafting, although some with better yields than others. In particular, the pulps produced by any of the two sulfite processes show comparatively low homopolymer levels. On the other hand, Kraft pulps show very high grafting efficiencies at 60 min of reaction time which drop considerably in samples at 18 hr of reaction time.<sup>9</sup>

Let us now have a look at the grafting results obtained with mechanical pulp as the substrate. The experiments compiled in the lower half of Table II were performed under the same conditions as those shown in Table I (including the concentration of H<sub>2</sub>O<sub>2</sub>). It is evident that in this case the reaction starts much

TABLE I  
Grafting on Different Commercial Pulps<sup>a</sup>

Pulp	Lignin content, %	Time, hr	Total conversion, %	Grafting efficiency, %
Bisulfite, high yield	23.2	1	23.2	74.1
		18	80.1	75.1
Sulfite, low yield	7.5	1	38.6	86.0
		18	84.5	60.1
Kraft, unbleached	4.5	1	39.9	56.9
		18	81.9	53.4
Kraft, bleached (softwood)	0.05	1	35.1	83.4
		18	65.0	52.4
Kraft, bleached (hardwood)	0.05	1	33.0	91.4
		18	71.3	61.8

<sup>a</sup> Conditions: pulp, 4.5 g (oven-dry weight); monomer (acrylonitrile), 9.0 g; initial pH, 5.0 ± 0.1; temperature, 25°C.

TABLE II  
Dependence of Grafting on Reaction Time<sup>a</sup>

Time, min	H <sub>2</sub> O <sub>2</sub> , g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
60	0.6	3.4	—	—
120	0.6	5.3	—	—
240	0.6	13.1	24.9	94.6
360	0.6	28.1	31.4	55.5
1200	0.6	52.8	36.8	34.7
60	1.5	6.2	—	—
120	1.5	18.1	19.7	54.2
240	1.5	56.7	41.9	36.8
360	1.5	69.5	56.6	40.5
1200	1.5	67.8	76.8	56.4

<sup>a</sup> Conditions: pulp, 4.5 g (oven-dry weight); monomer (acrylonitrile), 9.0 g; initial pH, 5.0 ± 0.1; temperature, 25°C.

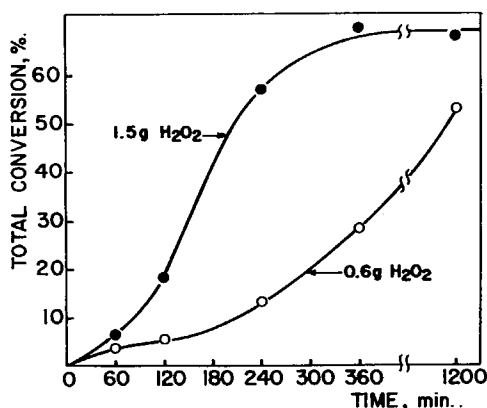


Fig. 1. Dependence of total conversion to polymer on time and on peroxide concentration.

more slowly than with any of the chemical pulps. For example, the bisulfite high-yield pulp gives 23.2% conversion, and the sulfite low-yield pulp gives 38.6% conversion at 60 min of reaction time, whereas the mechanical pulp shows a conversion just slightly over 6%. It would thus appear that the nondegraded form of lignin present in mechanical pulp affects adversely both the copolymerization and homopolymerization reactions and that this effect is stronger than that of the partially degraded lignins in chemical pulp. Model compound studies carried out by Straforelli<sup>11</sup> as well as by Stannett and co-workers<sup>12</sup> have indeed shown that some of the phenolic structures in lignin do cause inhibition and/or retardation of polymerization. Such effects become of special importance in the presence of oxygen or oxidants, since the products of lignin oxidation (quinones) readily scavenge radicals. The present authors have observed long induction periods in similar copolymerisation using bisulfite high-yield pulp partially bleached with sodium chlorite.<sup>10</sup> In that case, the longest induction period was observed at approximately 15% lignin content while the original pulp (23% of lignin) showed a graftability almost equal to that of bleached pulps. The

TABLE III  
Dependence of Grafting on the Concentration of Hydrogen Peroxide<sup>a</sup>

H <sub>2</sub> O <sub>2</sub> , g	Time, min	Temperature, °C	Total conversion, %	Polymer loading, %	Grafting efficiency, %
0.60	60	25	3.4	—	—
3.00	60	25	5.1	—	—
6.00	60	25	19.2	86.2	33.3
0.12	240	40	5.0	—	—
0.30	240	40	23.1	16.6	35.7
0.60	240	40	49.9	35.0	34.9
0.60	240	25	13.1	24.9	94.6
1.20	240	25	37.5	35.2	46.7
1.50	240	25	56.7	41.9	36.8
0.60	1200	25	52.8	36.8	34.7
1.50	1200	25	67.8	76.8	56.4

<sup>a</sup>Conditions: pulp, 4.5 g (oven-dry weight); monomer (acrylonitrile), 9.0 g; initial pH, 5.0 ± 0.1.

presence of oxidized, reaction-inhibiting lignin structures in partially bleached pulps could be a possible explanation. Similarly, oxidized lignin structures are no doubt formed in the reaction mixture containing mechanical pulp and hydrogen peroxide.

The results shown in the upper half of Table II were obtained with a lower concentration of peroxide. There is barely any reaction up to almost 3 hr of reaction time; the conversion curve then turns up. It is interesting to note that while at 4 hr of reaction time there is a difference of 43.6% in conversion for the two concentrations of  $H_2O_2$ , the respective difference at 20 hr of reaction time is only 15.0%. After the expiration of the initial induction period, the reaction proceeds to fairly high conversions even at the low  $H_2O_2$  concentration. This gives evidence that the peroxide is not completely exhausted by reactions with lignin. The conversion curves for both concentrations of  $H_2O_2$  are plotted in Figure 1.

TABLE IV  
Dependence of Grafting on Initial pH<sup>a</sup>

pH initial	pH final	H <sub>2</sub> O <sub>2</sub> , g	Time, min	Total conversion, %	Polymer loading, %	Grafting efficiency, %
1.0	1.0	0.6	60	2.6	—	—
2.0	2.0	0.6	60	41.2	12.4	15.0
3.0	3.0	0.6	60	40.1	14.2	17.6
5.0	4.1	0.6	60	3.4	—	—
4.0	3.2	1.5	180	26.3	18.6	35.1
5.0	3.3	1.5	180	32.9	25.3	38.3
6.0	3.7	1.5	180	17.7	24.4	68.5
9.0	3.8	1.5	180	19.4	28.0	71.9

<sup>a</sup>Conditions: pulp, 4.5 g (oven-dry weight); monomer (acrylonitrile), 9.0 g; temperature, 25° C.

TABLE V  
Grafting of Mechanical Pulp with Different Monomers and Their Mixtures<sup>a</sup>

Acrylamide	Monomer, g		Total conversion, %	Polymer loading, %	Grafting efficiency, %
	Acrylonitrile	Styrene			
25.0	—	—	9.6	3.4	33.3
—	25.0	—	78.8	39.3	49.2
—	—	25.0	86.8	61.9	70.5
—	12.5	—	83.2	24.7	58.7
—	—	12.5	84.0	24.7	58.1
—	6.0	—	75.0	10.9	60.0
—	—	6.0	78.3	9.3	48.9
—	12.5	12.5	80.4	42.9	52.7
—	6.0	6.0	91.7	27.1	60.9
12.5	12.5	—	60.8	2.4	3.9
12.5	—	12.5	38.0	26.3	68.4
8.3	8.3	8.3	68.0	27.1	39.4

<sup>a</sup>Conditions: pulp, 25 g (oven-dry weight); hydrogen peroxide, 6 g; surfactant (Tween-40), 2 g; water, 500 ml; initial pH, 7.0 ± 0.2; reaction time, 20 hr at room temperature.

It was observed in a previous study<sup>8</sup> using a Kraft semibleached pulp that increasing the concentration of  $H_2O_2$  in the reaction mixture had a favorable effect on the copolymer/homopolymer ratio. The formation of homopolymers was almost eliminated at a sufficiently high concentration of  $H_2O_2$ . This is, however, not the case when mechanical pulp serves as the grafting substrate. It is readily observed from the results shown in Table III that, in most cases, the grafting efficiency does not exceed 50% and is frequently as low as 30–40%. This is considerably less than the results observed for chemical pulps (Table I). The data corresponding to three different reaction times and to two temperatures indicate no direct increase of grafting efficiency with  $H_2O_2$  concentration. The very high grafting efficiency observed in one particular experiment (0.60 g  $H_2O_2$ , 240 min, 20°C) cannot be explained satisfactorily. It is likely that this high value is due to poor extractibility of that particular sample (homopolymer remains occluded). The extraction method of determining the homopolymer–copolymer ratio involves rather large errors at low total conversions. For this reason, grafting efficiency and polymer loading corresponding to conversions lower than 10% are not shown.

Perhaps the most important factor having effect on both total conversion and grafting efficiency is the initial pH of the reaction mixture. This is confirmed by the results compiled in Table IV. Two series of results are shown: one at low pH values (1–5) with a lower  $H_2O_2$  concentration (0.6 g) and shorter reaction time (60 min), and the other at higher pH range (4–9) with an increased  $H_2O_2$  concentration (1.5 g) and longer reaction time (180 min). It is evident that while the fastest reaction occurs at pH 2–3, it is mostly homopolymerization which takes place. Similar results have been obtained in a previous work with Kraft semibleached pulp.<sup>8</sup> On the other hand, Dimov and Pavlov<sup>13</sup> reported best

TABLE VI  
Dependence of Grafting on Mean Fiber Length<sup>a</sup>

Pulp no.	$E$ , <sup>b</sup> hp. day/ air-dry ton	Mean fiber length, $\mu$	Monomer, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
2	46	1950	25.0	58.0	37.0	62.1
			12.5	65.6	19.3	57.3
3	52	1600	25.0	72.4	44.6	59.7
			12.5	74.4	21.1	54.8
4	57	1360	25.0	74.4	44.5	58.6
			12.5	72.0	22.4	50.0
5	66	925	25.0	79.6	48.2	59.3
			12.5	76.8	23.2	59.4
6	87	540	25.0	78.8	39.3	49.2
			12.5	83.2	24.7	58.7
7	95	460	25.0	82.4	41.7	49.0
			12.5	81.6	21.9	52.0
8	100	330	25.0	86.0	52.6	46.7
			12.5	85.6	53.3	23.6

<sup>a</sup>Conditions: pulp, 25 g (oven-dry weight); hydrogen peroxide, 6 g; surfactant (Tween-40), 2 g; water, 500 ml; initial pH, 7.0  $\pm$  0.2; reaction time, 20 hr at room temperature.

<sup>b</sup> $E$ , cumulative refining energy.

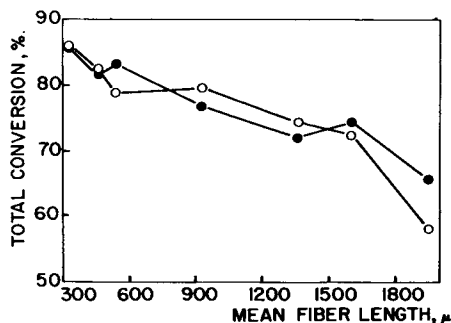


Fig. 2. Dependence of total conversion to polymer on mean fiber length: (O) monomer:pulp = 1:1; (●) monomer:pulp = 1:2.

grafting at pH 1–2 in their system using bleached cotton calico as a grafting substrate. A possible explanation for this discordance is the large difference in the degree of xanthation used ( $\gamma \approx 40$ –50 in the work of Dimov and Pavlov;  $\gamma \approx 5$  in the present work) as well as the different character of the substrate.

The second series of results shown in Table IV indicates a maximum conversion at pH 5. As far as the grafting efficiency is concerned, it increases with rising initial pH. The effect of initial pH still remains unclear. While the initial pH is in fact maintained in the reaction mixture only for a very short time period and is subject to a rapid decrease to a final pH of about 3.0–3.5, it seems to have a decisive effect on the copolymerization and in particular on the copolymer–homopolymer ratio. However, attempts to gain a better insight into this question by using buffered reaction mixtures have been unsuccessful.

Table V summarizes copolymerization results obtained with acrylamide, acrylonitrile, and styrene alone and in mixtures. These experiments were carried out under conditions different from those used in the preceding parts of this work (see Table V). With both acrylonitrile and styrene as well as with their mixtures, good conversions were obtained with the grafting efficiency ranging from 50–70%. The addition of acrylamide to styrene or acrylonitrile leads to lower conversion and/or lower grafting efficiency. In the case of pure acrylamide, there was almost no reaction; this, however, could be considerably improved by carefully purging the system with nitrogen.<sup>11</sup> In a particular experiment using a Kraft semi-bleached pulp, polymer loading increased from 11.9% to 44.2% when using an inert nitrogen atmosphere.<sup>14</sup>

Physical strength tests performed on the above-mentioned materials showed mostly a deterioration of properties in respect to the original pulp. This deterioration was the most serious in the case of the folding endurance test. Oxidation of the pulp by hydrogen peroxide is considered to be the most important factor. Attempts are being made to reduce the oxidation effects by carrying out the reaction under milder reaction conditions and using shorter reaction times.

The reactivity of pulp fibers toward graft copolymerization depends on the character of the fibers and, in particular, on their active surface. The following series of experiments was carried out with mechanical pulps prepared by disk refining at different total refining energies. The pulps prepared were characterized by their mean fiber length and subjected to graft copolymerization with acrylonitrile at two different pulp:monomer ratios. The results are presented

in Table VI. It is evident that the total conversion to polymer increases steadily with decreasing fiber length (Fig. 2). This appears to be accompanied, however, by a slight decrease in grafting efficiency. The pulp:monomer ratio does not seem to have an important effect on the grafting parameters.

## CONCLUSIONS

Mechanical pulp was found to behave differently vis-a-vis the xanthate grafting reaction than chemical pulps. In most cases, lower conversions and higher homopolymer contents are observed than in comparable polymerizations involving chemical pulps. It was not possible to increase grafting efficiency by employing a higher concentration of hydrogen peroxide. Decreasing mean fiber length resulted in increased total formation of polymer but reduced grafting efficiency.

## EXPERIMENTAL

### Materials

The pulps used in this work were prepared from white spruce chips in a 12-in. Bauer disc refiner using different refining energies. Except for the first fraction, which was too coarse for carrying out any meaningful experiments, the pulps are listed in Table VI and their characteristic properties shown. All experiments summarized in Tables II, III, IV, and V have employed the pulp #6 as a grafting substrate.

Acrylonitrile and styrene (Eastman Chemicals) were purified by distillation; the central cut was collected and stored in a refrigerator in dark bottles. All the other chemicals employed in this work were used such as supplied by the manufacturers.

### Copolymerization

The experimental conditions employed in this work differ for the results shown in Tables II, III, and IV and those compiled in Tables V and VI. While the former experiments were carried out under the same conditions as used in the previous work,<sup>7-9</sup> the latter were done with a larger amount of pulp and higher pulp concentration. The conditions were as follows: pulp,  $25.0 \pm 0.1$  g (oven-dry weight); mercerization, 30 min in  $0.5M$   $N_aOH$ ; xanthation, 3 hr in the atmosphere of  $CS_2$  vapors; ion exchange, 2 min in 350 ml of  $0.06M$   $(NH_4)_2Fe(SO_4)_2$ .

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