The Xanthate Method of Grafting. X. Grafting of Acrylamide onto Very-High-Yield Chemithermomechanical Birch and Aspen Pulps

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Synopsis

Hardwood pulp (birch: Betula Papyfera Marsh, and aspen: Populus Tremolides Michx) has been copolymerizeed with acrylamide using the xanthate grafting method. Grafting has been initiated using a redox system of ferrous ion and hydrogen peroxide. The effect of operating conditions on grafting parameters was also investigated. The factors studied were initial pH, time, and concentrations of hydrogen peroxide and acrylamide. When birch was used as a substrate, grafting parameters were as follows: grafting efficiency 82%, degree of conversion 35%, and polymer loading 60%. In the case of aspen, the maximum level of grafting efficiency, i.e., 87%, was reached with a polymer loading of 60%. Nevertheless, as in the case of birch, the conversion reached a rather low-level reading, i.e., 50%. Finally, some mechanical properties of paper sheets obtained through grafted pulps (dry and wet breaking lengths, dimensional stability, modulus, and extension at break) are compared to those of standard paper sheets.

INTRODUCTION

The xanthate method of grafting has been successfully applied for grafting low lignin pulps,[2] high-yield pulps,[3,4] as well as mechanical[5] and thermomechanical pulps.[6,7] The pulps, in the above-mentioned studies, were softwood pulps (spruce and balsam fir). Little research has been done, however, on hardwood pulp. Young[8] found that grafting efficiencies of aspen could reach about 50% for both styrene and acrylonitrile used as initial monomers. Kokta et al.[9] showed that in optimized grafting conditions grafting efficiency reached almost 100% in the case of acrylonitrile grafting on aspen pulp at a 80% level of conversion. In the case of styrene grafting, it has been shown[10] that, by optimizing the xanthate grafting method, a conversion of 97% could be reached at roughly a 80% grafting efficiency level.

The first objective of the present study is to optimize grafting parameters for aspen and birch with the help of acrylamide as a monomer.

For softwood pulps in general, papermaking properties could be inhanced by grafting acrylamide in low-strength pulp (as in high-yield and mechanical pulps).[8] Hardwood fibers, therefore, which are shorter and less compressible than those of softwood, usually produces mechanically weaker pulps. Logically, mechanical properties of hardwood pulp paper sheets should be improved by acrylamide grafting because of an increase in hydrogen bonding.

The second objective of this study is to verify the effect of acrylamide grafting on paper properties.

Journal of Applied Polymer Science, Vol. 34, 2517–2526 (1987)
 CCC 0021-8995/87/072517-10$04.00

TABLE I
Typical Experimental Conditions

Experimental condition →	• 4.5 g pulp • Birch (CTMP) • Aspen (CMP) • 9.09 g acrylamide • 1.5 g H_2O_2 • 5.5 pH • 150 min • 25°C

RESULTS AND DISCUSSION

The experimental conditions (see Table I) in this study are similar to those described in previous papers.[9,10] Grafting parameters were as follows:

Polymer loading (%): $(A - B)/B \times 100$

Grafting efficiency (%): $(A - B)/(D - B) \times 100$

Degree of conversion (%): $(D - B)/C \times 100$

where A is the weight of the product after copolymerization and extraction, B the weight of the pulp, C the weight of the monomer charged, and D the weight of the product after copolymerization.

Effect of Operating Conditions on Grafting Efficiency, Conversion, and Loading

In one of our previous studies[11] dealing with the optimization of the xanthate method, it was found that the variables with the most influence on grafting values were the following: concentration of sodium hydroxide during mercerization; concentration of hydrogen peroxide; time; monomer concentration; initial pH and concentration of ferrous ammonium sulphate. In the present study, most of the above-mentioned variables were examined for acrylamide when applied to birch or aspen in the form of chemithermomechanical pulp.

Dependence of Grafting on Initial pH (Figs. 1 and 2)

Optimum grafting values appear between pH 6–7 birch and pH 6–8 for aspen. Absolute values of grafting efficiencies are the same for both species (80%).

Values of grafting efficiencies for acrylamide compare well to those found for acrylonitrile (79.5%) (Ref. 9).

As far as conversion is concerned, pH 4–8 seems to be the optimal level. As in the case of grafting efficiency, very acidic conditions (pH 1–2) decrease drastically the final value of conversion. This behavior is in accordance with other previous studies.[9,10] The major difference between acrylamide and other monomers previously described lies in the lower absolute level (1/2) of

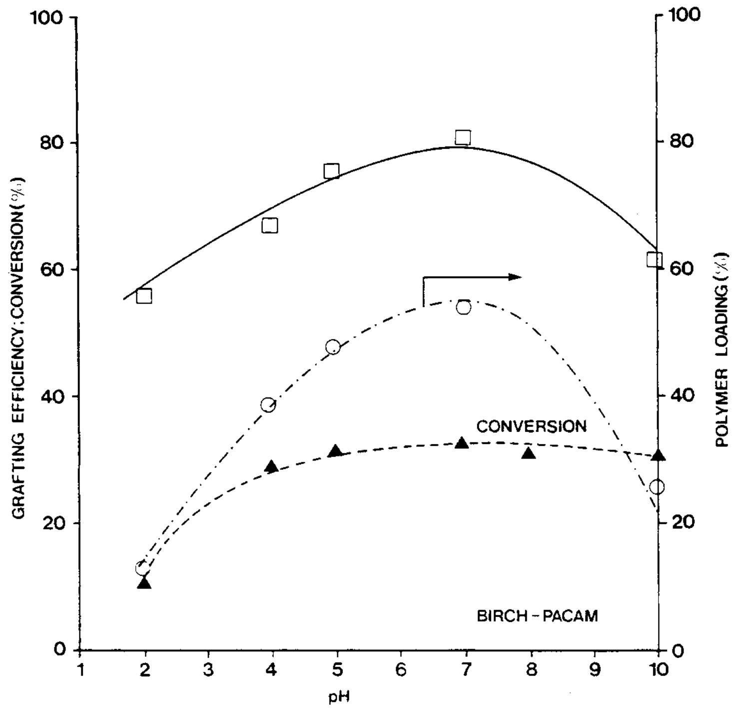


Fig. 1. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on pH; fiber, birch.

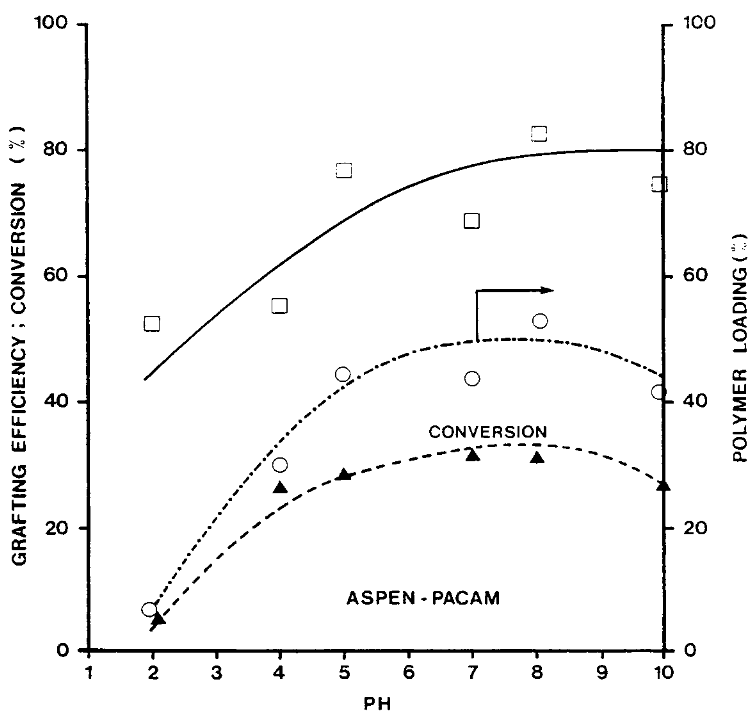
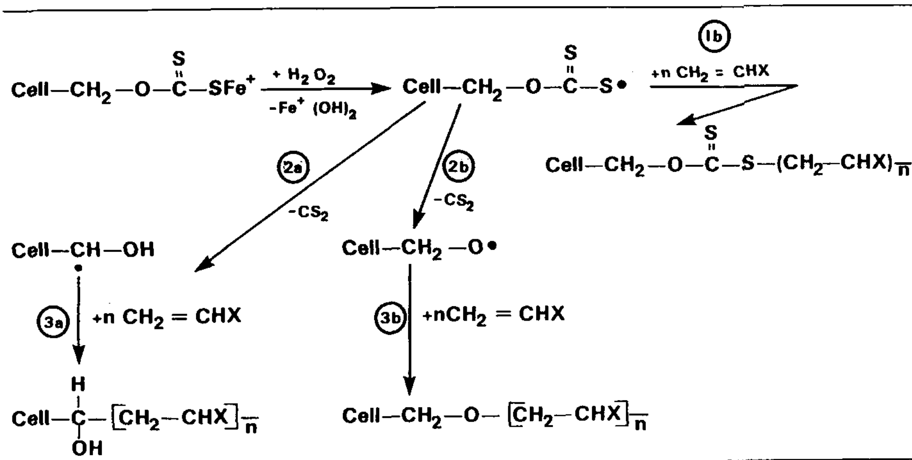


Fig. 2. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on pH; fiber, aspen.

TABLE II
Activation of Cellulose Xanthate by Hydrogen Peroxide



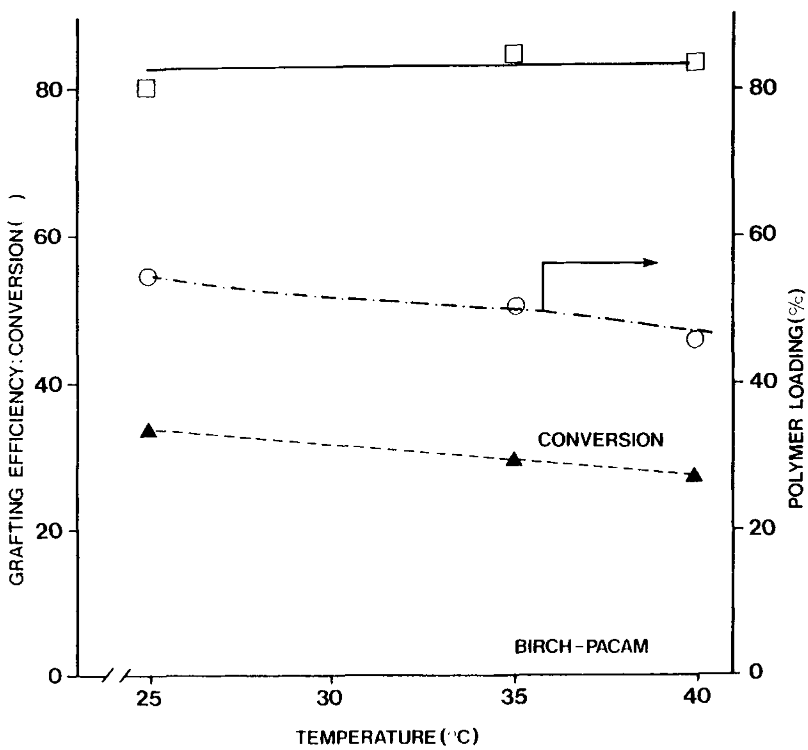


Fig. 3. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on temperature; fiber, birch.

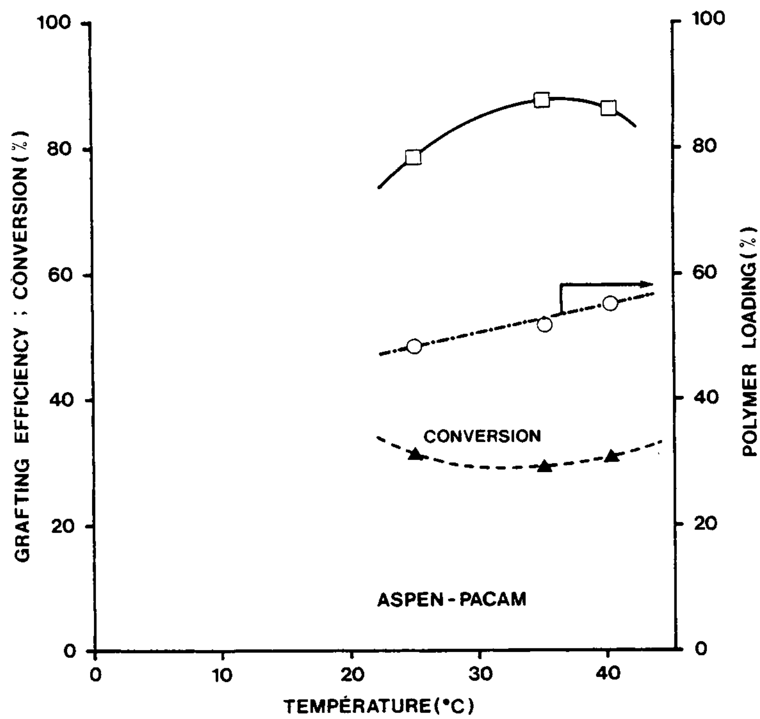


Fig. 4. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on temperature; fiber, aspen.

conversion. In our opinion, this difference could be partially explained by some solubility of a lower molecular fraction of polyacrylamide during the extraction stage.

The reaction mechanism of grafting and the importance of pH have been discussed in previous papers.[9,10] Generally, the pH region from 5 to 7 corresponds to optimal conditions in which the ferrous ion stays absorbed on partial cellulose xanthate and on other ion exchange group present (see Table II). This presence on cellulose is necessary in order to initiate grafting or copolymerization near the fibers and, therefore, decrease or eliminate homopolymerization.

Dependence of Grafting on Temperature (Figs. 3 and 4)

In general, temperature (from 25 to 40°C) has an almost negligible effect on grafting efficiency and conversion in the case of birch. There results are consistent with our previous studies.[9] In the case of aspen, 30°C seems to provide the best grafting efficiency above the 80% level.

Dependence of Grafting on Hydrogen Peroxide (Figs. 5 and 6)

In the time period studied, there was no significant change of grafting efficiency or conversion due to the increase in the amount of hydrogen peroxide from about 1 to 4 g (4.65–18.6 g/L).

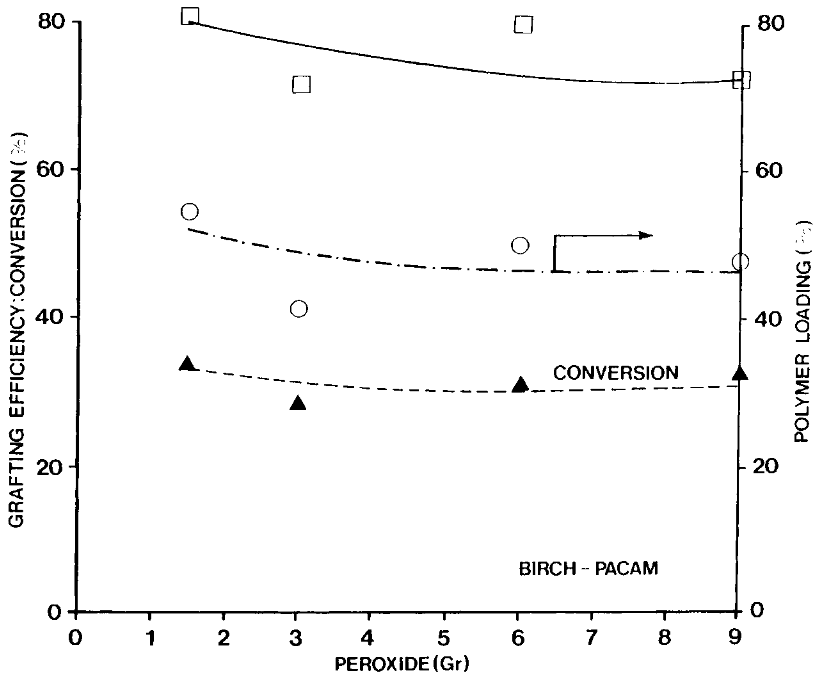


Fig. 5. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○), on quantity of hydrogen peroxide; fiber, birch.

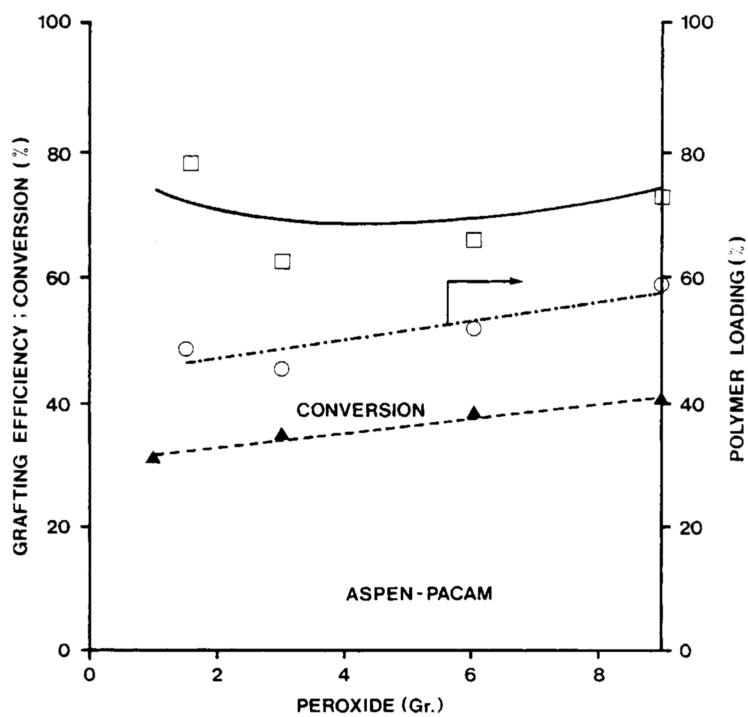


Fig. 6. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on quantity of hydrogen peroxide; fiber, aspen.

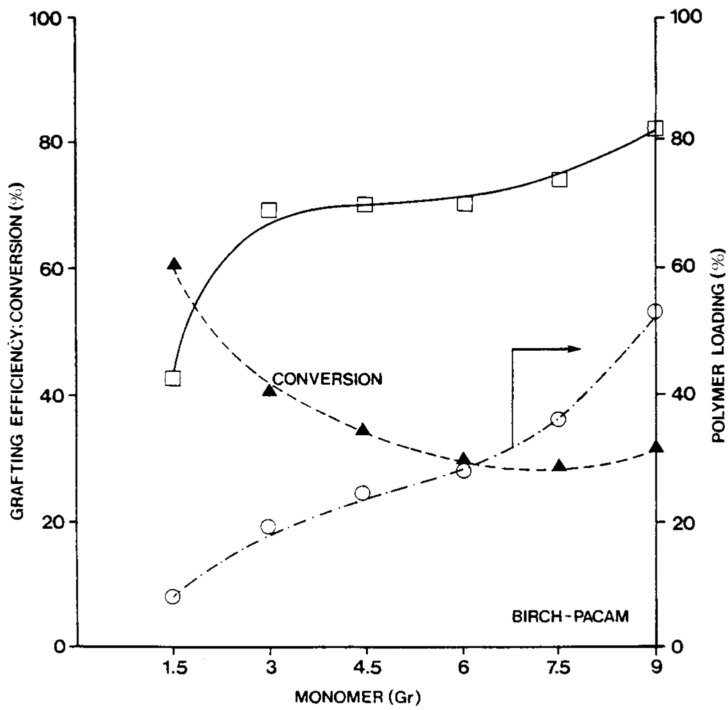


Fig. 7. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on quantity of monomer; fiber, birch.

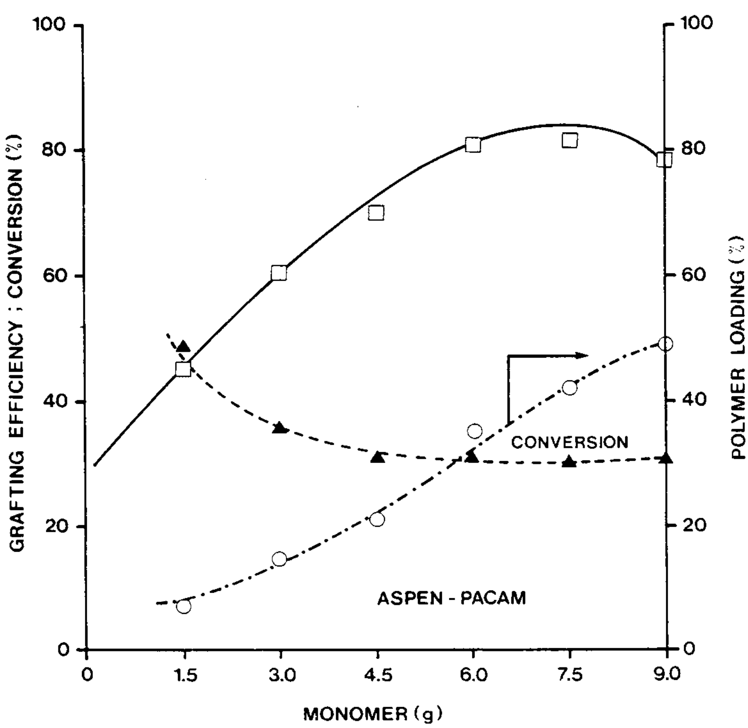


Fig. 8. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on quantity of monomer; fiber, aspen.

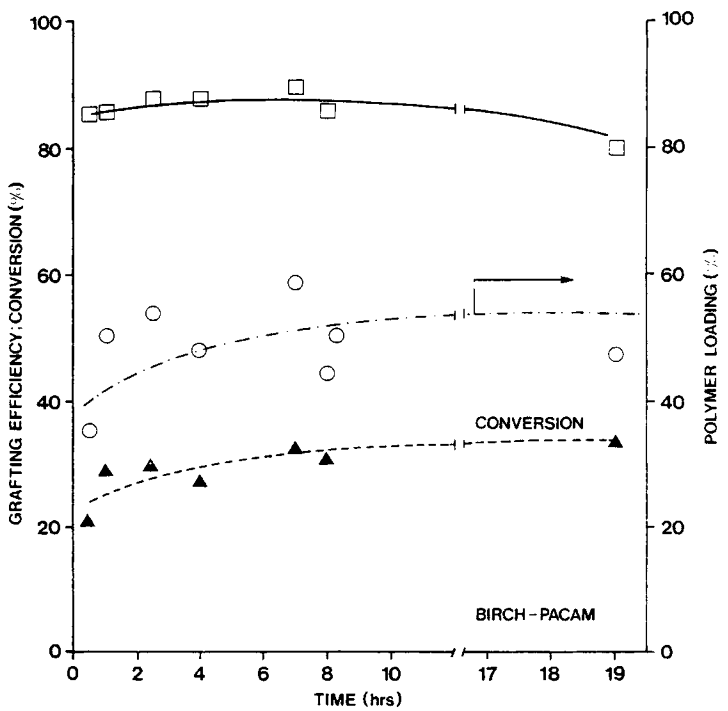


Fig. 9. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on time; fiber, birch.

Dependence of Grafting on Monomer Quantity (Figs. 7 and 8)

For both pulps, the conversion is highest when there is a low amount of monomer (or a high pulp/monomer ratio 4.5/1.5 = 3). When the ratio reaches 3, conversion equals 60% for birch, and 50% for aspen. The conversion decreases with an increase in the amount of monomer present, and then stays constant when the pulp/monomer ratio equals 1.

Grafting efficiency increases constantly in the case of aspen up to the pulp/monomer ratio equal to 0.75 when it reaches 83%. In the case of birch, grafting efficiency reaches its maximum level when the ratio roughly equals 1.5.

These differences between aspen and birch emphasize the complex balance which exists near grafted fibers which influence copolymerization.

Dependence of Grafting on Time (Figs. 9 and 10)

For both pulps, there is a rapid copolymerization during the first 15 min of reaction, and then the rate of polymerization becomes very slow and rather constant.

The results are quite similar to the ones obtained for styrene and acrylonitrile grafting.[10] The only significant difference has to do with the initial speed of copolymerization which is the highest for acrylamide.

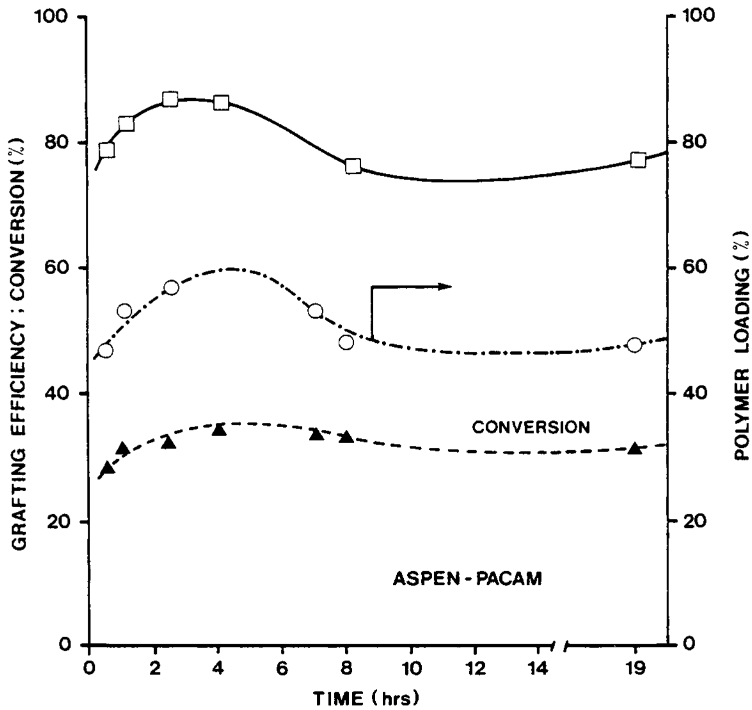


Fig. 10. Dependence of conversion (▲), grafting efficiency (□), and polymer loading (○) on time; fiber, aspen.

Optimal Conditions of Grafting

It has been shown that the xanthate method of grafting could be successfully applied to modify very-high-yield pulps of aspen or birch using acrylamide as a monomer.

Consider that grafting efficiency is the most important parameter in grafting, the conditions described in Table III would lead to 80 or 85% grafting efficiencies for birch or aspen respectively.

TABLE III
Summary of Optimal Grafting Conditions

Pulp	Birch (CTMP), yield: 90%	Aspen (CMP) yield: 90%
Monomer	0.5	0.7
H_2O_2	2–3 g/L	2 g/L
Initial pH	5.5	7
Monomer	Acrylamide	Acrylamide
Time	2.5 h	2 h
Temperature	25°C	35°C
NaOH	0.75*N*	0.75*N*
$(NH_4)_2FeSO_4$	150 mL 0.004%	150 mL 0.004%
Conversion	35%	35%
Grafting efficiency	80%	85%

TABLE IV
Paper Properties Improvement for Grafted CTMP of Aspen and Birch

Birch (%)		Aspen (%)	TMP[a] (*) Spruce/pine (%)
	Dry State		
+19	Burst index	+32	+10
+37	Breaking length	+48	+29
+49	Modulus, Young	+85	
+11	Breaking energy	+16	
	Wet State		
+900	Burst index	+850	
+82	Tear index	+110	
+3300	Breaking length	+2000	+500
+117	Elongation	+90	+183
+11600	Breaking Energy	+3300	
+450	Modulus, Young	+900	

[a] Bohuslav V. Kokta, Lisandro Araneda, and Claude Daneault, *Polym. Eng. Sci.*, **24**(12), 950 (1984).

Paper Property Improvement for Grafted CTMP of Aspen and Birch[1]

As expected, the grafting of acrylamide leads to the improvement of paper sheet properties especially in wet state. A summary of property improvement appears in Table IV.

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Received December 12, 1986
Accepted March 16, 1987