

pulps that comprise most paper furnishes and give us an array of properties beyond those available from each type individually.

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LITERATURE CITED

- Bagby, M. O., Clark, T. F., Cunningham, R. L., Tallent, W. H., "Non-Wood Plant Fiber Pulping—Progress Report No. 3", Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1972, p 6.
- Baker, F. L., Princen, L. H., "Encyclopedia of Polymer Science and Technology", Vol. 15, Wiley, New York, N.Y., 1971, p 498.
- Baker, F. L., Princen, L. H., *J. Microsc. (Oxford)* **102**, 393 (1975).
- Cathirgamu, T., Manokeran, P., "Non-Wood Plant Fiber Pulping—Progress Report No. 6", Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1975, p 35.
- Clark, T. F., Bagby, M. O., Cunningham, R. L., Touzinsky, G. F., Tallent, W. H., "Non-Wood Fiber Pulping—Progress Report No. 2", Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1971a, p 267.
- Clark, T. F., Cunningham, R. L., Wolff, I. A., *Tappi* **54**, 63 (1971b).
- Clark, T. F., Nelson, G. H., Nieschlag, H. J., Wolff, I. A., *Tappi* **45**, 780 (1962).
- Clark, T. F., Uhr, S. C., Wolff, I. A., *Tappi* **50**, 52A (1967).
- Clark, T. F., Wolff, I. A., *Tappi* **45**, 786 (1962).
- Clark, T. F., Wolff, I. A., *Tappi* **48**, 381 (1965).
- Cunningham, R. L., Clark, T. F., Kwolek, W. F., Wolff, I. A., Jones, Q., *Tappi* **53**, 1697 (1970).
- Jeyasingam, T., *Pap. Trade J.* **158**(46), 28 (1974).
- Moore, C. A., Trotter, W. K., Corkern, R. S., Bagby, M. O., *Tappi* **59**, 117 (1976).
- Nagasawa, T., Yamamoto, H., *Ippta VII (C.N.)*, i (1970).
- Nieschlag, H. J., Nelson, G. H., Wolff, I. A., *Tappi* **44**, 515 (1961).
- Parham, R. A., *Tappi* **58**, 138 (1975).
- Touzinsky, G. F., Clark, T. F., Tallent, W. H., "Non-Wood Plant Fiber Pulping—Progress Report No. 3", Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1972, p 25.
- Touzinsky, G. F., Clark, T. F., Tallent, W. H., Kwolek, W. F., "Non-Wood Plant Fiber Pulping—Progress Report No. 4", Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1973, p 49.

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Modification of High-Yield Pulp Fibers by the Xanthate Method

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A series of high lignin content pulps has been graft copolymerized with acrylonitrile, styrene, and acrylamide by the xanthate method. The degree of conversion of monomer to polymer and percent grafted polymer were much lower for modification reactions with mechanical pulps (stone groundwood, thermomechanical) than with chemical (kraft, oxygen) and semichemical (neutral sulfite semichemical) pulps. The amount of grafted polymer appears to be correlated with the lignin content of the pulp. Enhanced levels of grafting for high-yield kraft and thermomechanical pulps can be realized when binary mixtures of monomers are used in the reaction media. Differences in reactivity and surface properties of the pulp fibers are discussed in relation to the modification reactions.

Methods for chemical modification of pulp fibers are being investigated as part of a continuing research program on the structure and bonding of flexible fiber composites at the University of Wisconsin. Such composites include both synthetic papers and nonwoven fabrics and represent a fiber end-use of increasing importance. The further penetration of pulp products into nonwoven markets will be substantially influenced by fiber characteristics and bonding considerations and in turn will be appreciably affected by the chemical composition of the fiber. It would be highly desirable if the modification reactions were applicable to pulp fibers of high lignin contents. This not

only would increase potential yields and lower costs, but would also avoid some of the pollution problems associated with waste lignins from pulping and bleaching.

One widely studied technique of fiber modification is the grafting of vinyl monomers to cellulosic fibers (Phillips et al., 1972; Stannett, 1970; Stannett and Hopfenberg, 1970). However, the overwhelming majority of research has been on grafting rather pure forms of cellulose and, indeed, most grafting reactions are not amenable to lignin-containing cellulose fibers. Recently, however, several investigators have reported methods for modification of high-yield fibers (Rånby and Hatakeyama, 1975; Hornof et al., 1975a, 1976). Hornof et al. (1975a,b) have utilized a technique involving xanthation of the cellulose fiber prior to the formation of the free radicals. The method takes advantage of the capability of cellulose xanthates to form a redox couple with a suitable agent. The essential re-

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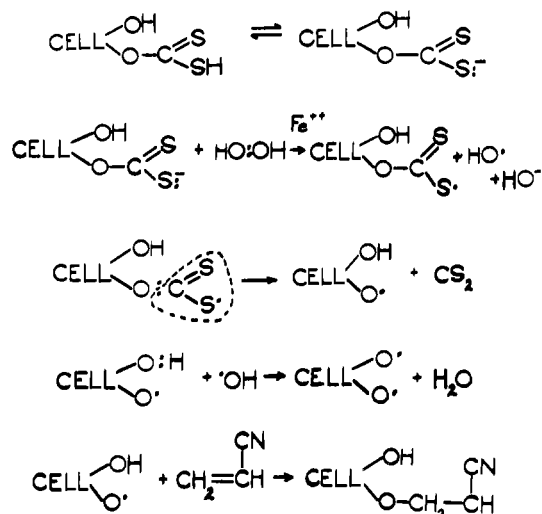


Figure 1. Reaction mechanism proposed by Dimov and Pavlov (1969) for graft copolymerization of cellulose (CELL) by the xanthate method; reproduced with the permission of the *Journal of Polymer Science*.

Table I. Properties of Pulps Used for Graft Copolymerization

Pulp	Lignin content, %	Exptl losses, %	Deg of xanthation γ^a
Chemical			
Kraft	8.3	5.7	14.6
Oxygen	2.5	2.3	11.2
Semichemical			
NSSC	13.0	2.3	13.8
Mechanical			
TM	26.5	6.3	12.9
Stone	28.0	4.9	13.4

^a γ = number of xanthate groups per 100 units of glucose.

actions that probably occur in the system were proposed by Dimov and Pavlov (1969) and are shown in Figure 1.

Hornof et al. (1975a, 1976) found that the presence of lignin in both kraft and bisulfite fibers did not substantially retard the grafting reaction, and in some cases it was found that the lignin actually improved graftability. Copolymer molecular weights were reported normally in the range of 17 000 to 30 000 with a high-yield kraft pulp. The utility of this technique for grafting of high-yield pulps prepared by chemical, semichemical, and mechanical methods is shown in the work reported in this paper.

EXPERIMENTAL SECTION

Materials. The pulps used in this investigation were supplied through the USDA Forest Products Laboratory, Madison, Wis., and included softwood kraft (douglas fir) and oxygen (southern pine), hardwood neutral sulfite semichemical (aspen), and softwood stone groundwood (balsam fir), and thermomechanical (balsam fir). The Klason lignin determinations were performed by the analytical laboratory at the Forest Products Laboratory and are given in Table I.

Acrylonitrile and styrene were treated with sodium hydroxide to remove inhibitors and distilled prior to use. Acrylamide was used without further purification. The additional chemicals were as described by Kokta and Valade (1972) except Tween-80 was used as a surfactant.

Methods. A procedure similar to the one described by Kokta and Valade (1972) and Hornof et al. (1975a,b) was used in this investigation. The cellulose xanthate was prepared by mercerizing never-dried pulp in diluted so-

dium hydroxide (0.75 M) solution at 25 °C for 45 min, pressed to 1.5–2 times the original weight, and then placed in an evacuated vacuum desiccator over carbon disulfide at 25 °C for 2 h. The product was washed with distilled water until the wash was no longer yellow. The washed product was dipped for 2 min in 300 mL of a 0.004% solution of ferrous ammonium sulfate, then filtered and washed again with distilled water. The ion-exchanged xanthate was then transferred to a three-necked flask equipped with a condenser to prevent loss of monomer. The flask had been previously filled with water, surfactant (0.5 part per 10 parts of monomer), and monomer. After a 15-min presoaking, 5 g of 30% hydrogen peroxide was added, the pH adjusted to 6 (with 0.1 N H₂SO₄), and the start of copolymerization recorded. The mixture was gently shaken periodically at room temperature. After the desired time, the resulting polymerization mixture was filtered and washed with an excess of water, and the copolymers were dried at 50 °C for 48 h and at 30 °C under vacuum for 8 h.

The degree of xanthation of the pulp obtained by using this procedure was determined by a modified iodometric titration method (Hornof et al., 1975b). The results are reported in terms of γ , the number of xanthate groups per 100 units of glucose. However, γ can only be considered as an approximation of the actual degree of xanthation since the hemicelluloses and lignin are also xanthated in the procedure. Corrections for lignin content (cf. Table I) are considered valid since lignin is not expected to contribute significantly to the overall level of xanthation.

The apparent level of grafting and polymer loading was determined by Soxhlet extraction with the appropriate solvent (acetone for styrene, *N,N*-dimethylformamide for acrylonitrile, and hot water for acrylamide). In the case of binary monomer mixtures, the extractions were performed with both of the corresponding solvents as described above. Hornof and co-workers (1975b) carried out similar extractions under vacuum to minimize degradation; this additional feature was omitted to ensure more complete removal of possible occluded homopolymer through enhanced swelling at the higher extraction temperatures. For calculation purposes, the dried weight of the pulp was used after being corrected for losses in the mercerization step (cf. Table I).

The grafting parameters are defined as follows: total conversion, % = $(D - B)/C \times 100$; polymer loading, % = $(A - B)/B \times 100$; grafting efficiency, % = $(A - B)/(D - B) \times 100$, where *A* is the weight of products after copolymerization and extraction, *B* is the weight of pulp (oven dry, corrected for solubility in NaOH solution), *C* is the weight of monomer charged, and *D* is the weight of products after copolymerization.

RESULTS AND DISCUSSION

The properties of the chemical, semichemical, and mechanically produced pulps are shown in Table I. A range of Klason lignin contents is exhibited with the oxygen pulp having the lowest (2.5%) and the stone groundwood the highest (25.0%). However, oxygen pulps are high in the acid-soluble lignin component which is not included in Klason determination (Karna and Sarkanen, 1976; Swan, 1965). Thus, it is probable that the oxygen pulp contains a somewhat higher lignin content than noted in Table I. A control run was carried out on each pulp sample, and the experimental losses incurred are also reported in the table. The majority of the loss results from the sodium hydroxide treatment prior to the xanthation reaction. The degree of xanthation, corrected for lignin content, is relatively consistent considering the varied

Table II. Effect of Pulp Type and Time of Treatment on Grafting of Acrylonitrile

Pulp		Total conversion, %	Polymer loading, %	Grafting efficiency, %
Chemical				
Kraft	1 h	61.9	99.2	72.5
	18 h	87.3	104.5	67.7
Oxygen	1 h	57.8	64.8	65.8
	18 h	81.9	100.4	66.7
Semichemical				
NSSC	1 h	47.1	45.1	52.9
	18 h	81.0	76.5	52.3
Mechanical				
TM	1 h	13.5	19.7	71.3
	18 h	43.8	45.5	56.7
Stone	1 h	16.1	25.7	76.4
	18 h	35.6	27.6	48.1

history of the pulp samples, and all fall in the range of $\gamma = 11.2$ – 14.6 .

A comparison of the grafting results for the chemical, semichemical, and mechanical pulps is shown in Table II. The chemical pulps (kraft and oxygen) exhibited the highest total conversion and polymer loading while the mechanical pulps (thermomechanical or TM and stone groundwood) showed the poorest results according to these two parameters. However, the grafting results for the mechanical pulps by this method are far superior to other methods of grafting. With the ceric ion technique (Kulkarni and Mehta, 1968), for example, essentially no grafting can be obtained with lignin-containing materials. The grafting results with the semichemical pulp (neutral sulfite semichemical, NSSC) were in between the chemical and mechanical pulps in terms of total conversion and polymer loading.

The most obvious cause for the noted differences is the influence of lignin on the grafting reaction. From the data presented in Tables I and II, the polymer loading for the various pulps can be ascertained as a function of Klason lignin content. There is a definite tendency at both 1 h and 18 h reaction times toward decreased polymer loading with increasing lignin content. This trend represents an overall summarization of the effect of lignin on the grafting reaction for the pulps, which had varied chemical histories. The treatments in the chemical and semichemical pulping undoubtedly alter the lignin in the process of delignification. Therefore, the higher polymer loading noted at the lower lignin contents probably represents both the effect of a modified lignin as well as the decreased lignin content. Although lignin may participate in the grafting reaction (Sakata et al., 1972) it also acts as a reactive transfer agent giving more stable and less reactive radicals (Hornof et al., 1976). This latter effect is probably the major factor resulting in decreased grafting levels with lignin-containing materials.

Hornof et al. (1975a, 1976) have found that with some chemical pulps a larger amount of lignin has a favorable effect on the polymer loading. These investigators studied the grafting reaction on chemical pulps successively delignified with sodium chlorite. In acid media, chlorite gives a variety of reactive species including chlorine dioxide, chlorous acid, hypochlorous acid, and chlorine (Chang and Allan, 1971), all of which modify the lignin, and to some extent the carbohydrates, in the delignification reaction. Thus it is difficult to interpret results based only on lignin content of the pulp fibers. As noted by Hornof et al. (1976), the degree to which lignin interfaces with the grafting reaction varies from one pulp to another and is largely dependent on the chemical history of the sample.

Table III. Grafting of Styrene to Chemical and Mechanical Pulps

Pulp	Total conversion, %	Polymer loading, %	Grafting efficiency, %
Chemical (Kraft)	21.7	32.4	74.6
Semichemical (NSSC)	16.9	18.8	55.5
Mechanical (TM)	3.8	2.4	31.9

Table IV. Grafting of Acrylamide to Chemical and Mechanical Pulps

Pulp	Total conversion, %	Polymer loading, %	Grafting efficiency, %
Chemical (Kraft)	29.3	39.6	76.6
Semichemical (NSSC)	32.1	52.5	90.5
Mechanical (TM)	9.0	14.2	89.0

More importantly, this indicates that by proper pretreatment of the pulp, it should be possible to enhance the amount of grafting which can be obtained.

The effect of time of treatment is shown for the three classes of pulps in Table II. The chemical and semichemical pulps show similar behavior, with both the percent total conversion and polymer loading increasing dramatically at 18 h reaction time while the grafting efficiency remains relatively constant. These results are consistent with those of Hornof et al. (1975b) who found that the percent total conversion for a semibleached kraft pulp increased up to 8 h reaction time and remained relatively constant thereafter, while the grafting efficiency did not vary up to 18 h reaction time.

Similar to the chemical and semichemical pulps, the TM and stone groundwood pulps exhibited an increase in the percent conversion after 18 h reaction time and the polymer loading increased, though not significantly with the stone groundwood sample. The grafting efficiency, however, decreased dramatically after the longer (18 h) reaction time. It appears that the grafting polymerization in the case of the mechanical pulps is not diffusion related. The reaction probably occurs predominantly at the surface of the mechanical pulp fibers as compared with the chemical and semichemical pulps, the latter two of which would have a more porous surface structure related to the chemical removal of lignin from the lignocellulosic gel in the pulping reaction.

Rånby (1975), in a study of methyl methacrylate grafting to groundwood pulp using an acetic acid–hydrogen peroxide initiator, found that improved efficiencies could be obtained by extraction of the groundwood pulp with alcohol–benzene (1:2) solutions which removed the so-called “resins”. This investigator also found that the extraction reduced the initial inhibition period he noted in mechanical pulp grafting. This suggests that extractive type material may be an additional cause of lowered grafting parameters with mechanical pulps.

Grafting of Styrene and Acrylamide. The parameters for grafting of styrene to kraft, NSSC, and thermomechanical pulps are shown in Table III. Both the total conversion and polymer loading are considerably less for the three pulp samples when using the styrene than

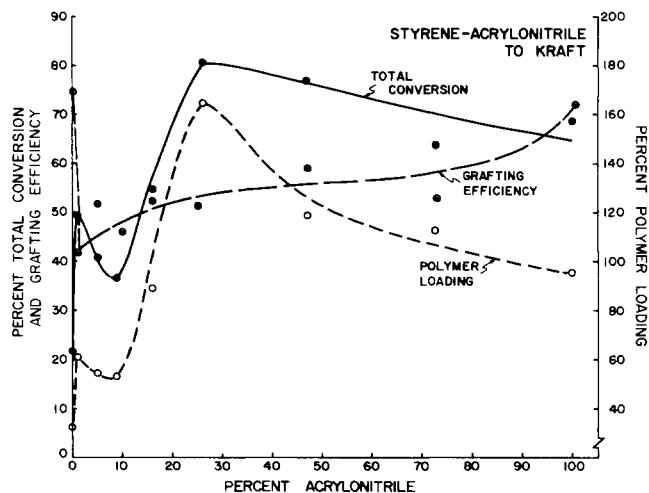


Figure 2. Grafting of styrene-acrylonitrile onto high-yield kraft pulp.

with the acrylonitrile monomer. This most likely reflects the difference in affinity of the two monomers for cellulose. Acrylonitrile as an electron acceptor would be expected to have a much higher affinity for the cellulose component of the pulp sample.

The results of grafting acrylamide to the three pulps are shown in Table IV. The kraft and TM pulps show percent total conversion and polymer loading of acrylamide in between the results obtained with acrylonitrile and styrene monomers. The NSSC pulp, however, exhibits the higher percent polymer loading with the acrylamide monomer. Since this monomer has the highest hydrogen bonding capability, it is probable that the acrylamide interacts with the sulfonate groups present in the NSSC pulp during the initial phase of the reaction. Some amount of sulfonated lignin is undoubtedly situated at the surface of the NSSC pulp fiber (Michell et al., 1965), and the enhanced wetting characteristics of NSSC pulp fibers (Young, 1977) and the high bonding strength of sulfite fibers (Hartler and Mohlin, 1975) have been attributed to the presence of such modified lignin. The high grafting efficiency (90.5%) obtained when grafting acrylamide to NSSC pulp fibers is in accord with these postulations. The high grafting efficiency (89.0%) obtained for grafting TM pulp with acrylamide is, however, not explainable on this basis though TM pulp fibers show a somewhat surprisingly high wettability (Young, 1977).

The level of grafting of polymer to the fibers is considerably lower using the styrene monomer, and it would be desirable if increased polymer loadings could be obtained preferably in shorter reaction times with these high-yield pulps. One method of enhancing the grafting reaction is the use of binary mixtures of monomers. Thus, Sakurada et al. (1963) by radiation grafting to rayon and Kokta and Valade (1972) by xanthate grafting to bleached kraft pulp demonstrated that dramatic increases in the amount of grafting can be obtained by using mixtures of styrene-acrylonitrile, styrene-acrylamide, or combinations with butadiene. Similar synergistic effects have been noted in this investigation using styrene-acrylonitrile and styrene-acrylamide binary monomer mixtures for grafting to high lignin content kraft fibers by the xanthate method as shown in Figures 2 and 3. Both the total conversion and the polymer loading were increased above the levels of grafting for either of the single monomers. The two maxima shown in the curves in Figures 2 and 3 possibly represent two distinct effects of binary polymerizations. The initial sharp increase in polymer loading related to small percentages of either acrylonitrile or acrylamide in

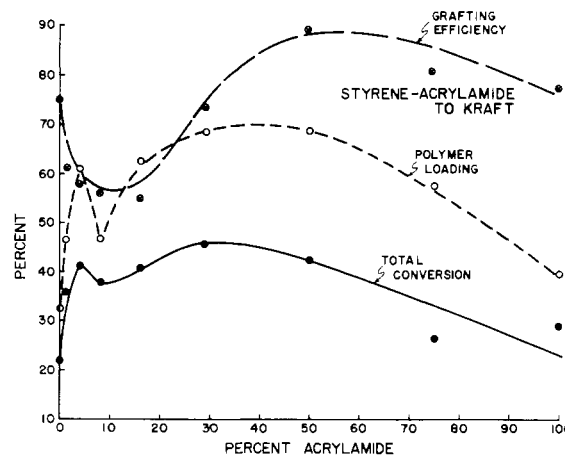


Figure 3. Grafting of styrene-acrylamide onto high-yield kraft pulp.

the reaction media may result from a "seeding" effect caused by localized swelling of the cellulose matrix similar to the phenomenon noted as "popcorn polymerization" by earlier investigators using binary mixtures with butadiene (Miller and Perizzolo, 1955). Increased amounts of the monomers (acrylonitrile and acrylamide) apparently upset the cellulose gel-radical complex, and a different mechanism becomes applicable. At higher percentages of acrylonitrile and acrylamide with styrene, the seeding effect is lost and generalized enhanced swelling of cellulose caused by the polar monomers takes predominance. Kokta and Valade (1972) have explained this effect as the result of a complex balance between the concentrations of comonomers in close proximity to the cellulose fibers, the reactivity of the resulting cellulose-polymer radicals, and the ratios between rates of propagation and termination.

Rapson and Kvasnika (1963) similarly studied the effects of binary monomer mixtures but on the grafting of cellulose triacetate with γ radiation. These investigators noted, for example, that styrene when used alone grafted readily onto cellulose triacetate but even small amounts of acrylonitrile added to this system decreased the amount of styrene grafted to nearly zero. These results were interpreted as leaving little doubt that the presence of hydroxyl groups in cellulose and the associated swelling effects of water are extremely important in grafting reactions. Although such an interpretation is valid, the mechanism of grafting with binary monomer mixtures is probably more complex and dependent on the specific types of monomers utilized in the reaction.

The grafting efficiency using the styrene-acrylonitrile binary monomer mixture with kraft pulp (Figure 2) was lower than the efficiency obtained with a single monomer (either styrene or acrylonitrile). However, with the styrene-acrylamide monomer mixture (Figure 3) there was a decrease in efficiency at low levels of acrylamide in the mixture but moderately enhanced efficiency near equal parts of the two monomers. The slight efficiency enhancement is most likely related to the polar nature of this monomer which results in strong affinity for the hydrophilic cellulose, as previously discussed.

Figure 4 shows grafting results for thermomechanical pulp using the styrene-acrylonitrile binary monomer mixture. Enhanced polymer loading and total conversion are also realized with this pulp sample. Increases in the grafting parameters are of even more importance in the case of mechanical pulps since the initial grafting levels are much lower than with chemical and semichemical pulps using single monomer systems. The grafting efficiency

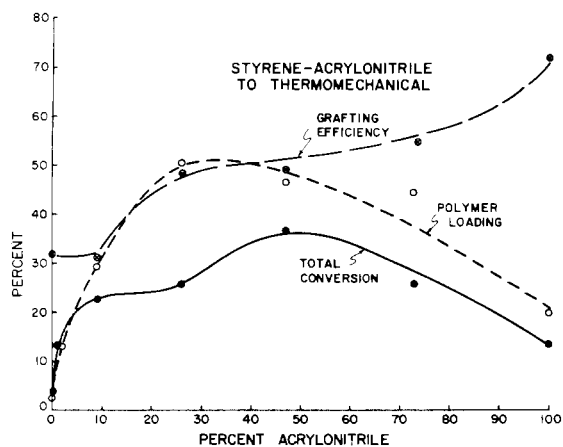


Figure 4. Grafting of styrene-acrylonitrile onto thermomechanical pulp.

follows a similar pattern to that shown for grafting of the same binary mixture to kraft pulp (Figure 2). Only minor increases in graft copolymerization were noted when using the styrene-acrylamide binary monomer mixture with the TM pulp.

Earlier investigators have found that enhanced levels of grafting can also be realized by addition of certain organic solvents. Quéré et al. (1973) have found that the presence of *tert*-butyl alcohol or acetone considerably improved grafting efficiency with acrylamide monomer (ceric ion), and Sakurada et al. (1963) reported that addition of methanol enhanced styrene grafting to cellulose (γ radiation). Hornof et al. (1975b) in contrast noted decreased monomer conversion and polymer loading when grafting in the presence of similar organic solvents using the xanthate method on kraft pulp, though these latter investigators did note enhanced grafting efficiencies with certain solvents.

It was surmised that with the high lignin content pulps used in this study lignin solvents might aid swellability of the lignocellulosic gel in water and, thereby, enhance the grafting reaction. Schuerch (1952) has published a listing of the most favorable lignin solvents related to their solubility parameters, and several of these were selected to determine their effect on grafting of high-yield kraft pulp by the xanthate method. The solvents, dioxane and methyl Cellosolve, were used in a 1:1 mixture with water, and the results are shown in Table V. In both cases the total conversion and polymer loading were drastically reduced with the high-yield kraft pulp and the grafting efficiency showed little change. Thus, there is no advantage to using organic solvents for grafting high-yield pulps by the xanthate method.

CONCLUSIONS

The utility of the xanthate method for modifying high-yield chemical, semichemical, and mechanical pulps has been demonstrated. This method is one of the few techniques available for grafting mechanical pulps, and even further enhancement of grafting levels can be realized by using binary monomer mixtures. In general, the presence of lignin is detrimental to the grafting reaction, though the chemical history of the pulp samples also appears to strongly influence the graft copolymerization.

Table V. Effect of Lignin Solvents on Grafting of Kraft Pulp^a

Reaction medium	Total conversion, %	Polymer loading, %	Grafting efficiency, %
Water	75.2	83.6	64.5
Dioxane	14.5	16.4	64.0
Methyl Cellosolve	21.8	23.6	60.7

^a Acrylonitrile monomer, 10.9 g H₂O₂ (30%).

Such results indicate that it should be possible to enhance grafting of high-yield pulps by premodification of the lignin in the sample.

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LITERATURE CITED

- Chang, H.-M., Allan, G. G., in "Lignins, Occurrence, Formation, Structure and Reactions", Sarkanen, K. V., Ludwig, C. H., Ed., Wiley, New York, N.Y., 1971, p 433.
- Dimov, K., Pavlov, P., *J. Polym. Sci.* **7**, 2775 (1969).
- Hartler, N., Mohlin, U.-B., *Sven. Papperstidn.* **78**, 295 (1975).
- Hornof, V., Kokta, B. V., Valade, J. L., *J. Appl. Polym. Sci.* **19**, 1573 (1975a).
- Hornof, V., Kokta, B. V., Valade, J. L., *J. Appl. Polym. Sci.* **19**, 545 (1975b).
- Hornof, V., Kokta, B. V., Valade, J. L., *J. Appl. Polym. Sci.* **20**, 1543 (1976).
- Karna, J. H., Sarkanen, K. V., College of Forest Resources, University of Washington, Seattle, 1976, unpublished results.
- Kokta, B. V., Valade, J. L., *Tappi* **55**, 366 (1972).
- Kulkarni, A. Y., Mehta, P. C., *J. Appl. Polym. Sci.*, **12**, 1321 (1968).
- Michell, A. J., Watson, A. J., Higgins, H. G., *Tappi* **48**, 520 (1965).
- Miller, G. H., Perizzolo, A. F., *J. Polym. Sci.* **18**, 411 (1955).
- Phillips, R. B., Quéré, J., Guioy, G., Stannett, V. T., *Tappi* **55**, 858 (1972).
- Quéré, J., Phillips, R. B., Guioy, G., paper presented at the Fourth Canadian Wood Chemistry Symposium, July 1973, Quebec City, Quebec, Canada.
- Rånby, B., Hatakeyama, H., *Cellul. Chem. Technol.* **9**, 583 (1975).
- Rapson, W. H., Kvasnicka, E., *Tappi* **46**, 662 (1963).
- Sakata, I., Miyata, N., Senju, R., *J. Jpn. Wood Res. Soc.* **18**, 593 (1972).
- Sakurada, I., Akada, T., Hatakeyama, S., Kimura, F., *J. Polym. Sci., Part C* **4**, 1233 (1963).
- Schuerch, C., *J. Am. Chem. Soc.* **74**, 5061 (1952).
- Stannett, V. J., *J. Polym. Sci., Macromol. Rev.* **4**, 1177 (1970).
- Stannett, V. J., Hopfenberg, H. B., "Cellulose and Cellulose Derivatives", Vol. 5, Part 5, Wiley, New York, N.Y., 1970, p 907.
- Swan, B., *Sven. Papperstidn.* **68**, 791 (1965).
- Young, R. A., *Wood Fiber*, in press (1977).

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