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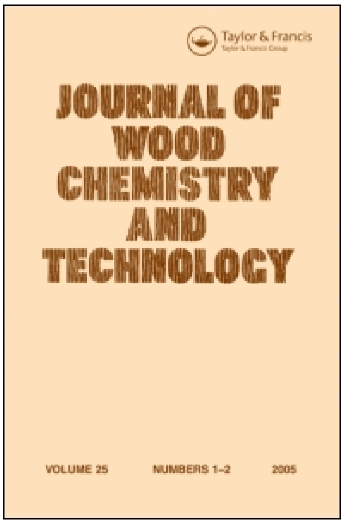

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GRAFT PULPING IN ORGANOSOLV SYSTEMS

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Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

It has been previously demonstrated that free radicals are produced in the delignification of wood. These free radicals can be utilized to initiate grafting of vinyl polymers to the wood pulp. This simultaneous delignification and graft copolymerization has been referred to as graft pulping. The grafting of a variety of vinyl monomers to aspen wood pulp in alcohol-based solvent pulping has been evaluated in this study. Variables evaluated included cooking conditions, catalysts and two-stage pulping. The analysis of the reaction is complicated due to effects of the vinyl monomers on the delignification process and losses of wood during the extraction sequences. Although only low levels of polymer loading were obtained when single monomers were added to the pulping solvent, much better results were obtained using a binary monomer system of acrylonitrile(AN) and styrene(ST). At a monomer addition level of 10% (1.75% AN, 8.25% ST) to the aqueous ethanol solvent, a 14.6% polymer loading was achieved with the majority of the graft as polystyrene (88%). The use of a two-stage pulping sequence improved the polymer loading of polyacrylonitrile but not polystyrene. Lignin was the primary site of grafting.

INTRODUCTION

There has been a considerable amount of literature published over the last 25 years on grafting of synthetic vinyl polymers to isolated wood polymers, especially for modification of cellulose (1-3). A variety of methods have been utilized to generate the free radicals necessary to initiate the polymerization reaction including, ultraviolet and gamma radiation, homolytic chemical decomposition of peroxides and oxidation-reduction systems involving metal ions. In 1966, Kleinert (4) demonstrated that free radicals are formed during the pulping reaction with wood. These radicals can be used to initiate copolymerization of vinyl monomers with lignocellulosic fibers.

The grafting of wood fibers concurrent with the pulping of wood was first introduced by von Krause _et al_. (5, 6) and referred to as "graft pulping". When 12.5% styrene (based on liquor volume) was added to neutral sulphite pulping media, a total yield of 115% was obtained. After the removal of homopolymer, the yield of grafted pulp was 85% (based on O.D. wood). The polymer loading was 16% and the polymer conversion and grafting efficiency were 68% and 34%, respectively. It was discovered that the polystyrene was grafted entirely to the lignin fraction and that there was a linear correlation between the grafted pulp yield and the acid insoluble material derived from the pulp. An experiment using the more hydrophilic monomer, acrylic acid surprisingly exhibited a yield that was lower than that obtained with styrene. It was assumed that acrylic acid was an active pulping agent. Polysaccharide degradation was accompanied by a reduction in the strength properties of the pulp.

The advantages of the graft pulping process are: a) pulping and graft copolymerization can be done in one step, thus utilizing woody biomass more efficiently, b) expense of intermediate isolation and purification steps can be avoided, c) potential for production of both modified cellulose and lignin, and d) wide range of products possible depending on the choice of monomer.

Although no direct evidence for free radical formation in solvent systems has been provided, it was felt that organosolv pulping systems developed in recent years should be compatible with graft copolymerization conditions; therefore, we explored the potential of graft pulping in an alcohol solvent-based pulping process (7). We selected the alcohol system developed by Professor Sarkanen over 10 years ago (7, 8). It was demonstrated that a 1:1 ethanol/water mixture offered the best pulping media for aspen chips and that the Lewis acid, $AlCl_3$ was an effective catalyst.

Free radical formation in organosolv pulping was also studied by Kleinert (9). These free radicals can be used advantageously for graft copolymerization. If a Lewis acid, such as $AlCl_3$, is used as a catalyst in aqueous alcohol pulping, this compound may also influence the vinyl monomer polymerization. Generally speaking, so called "graft pulping" involves three major chemical reactions simultaneously: a) delignification, b) grafting of vinyl monomer onto the substrate, and c) homopolymerization.

The aim of this investigation was to determine the optimum reaction and cooking conditions for the delignification and grafting processes leading to the most efficient wood and monomer utilization.

RESULTS AND DISCUSSION

There are many variables that can be explored in graft pulping of vinyl monomers. Those that were evaluated in this investigation include the effects of vinyl monomers, organosolv cooking conditions, catalysts and two-stage pulping.

Effects of Monomers

As noted in the literature, different monomers can show quite different reactivity in grafting reactions, depending on the experimental conditions (1). The ability of a monomer to polymerize in the pulping system will also vary according to type and concentration. As shown in Figure 1, high yields were obtained from the graft pulping reaction. The unextracted yield (see experimental section) obtained with isoprene (I) and styrene monomers (ST) was higher than that obtained with acrylonitrile (AN) and methyl methacrylate (MMA). After extraction, the yield was approximately 2 to 5% higher with these four monomers compared to the yield from the control cook. The weight increase of polyacrylonitrile, PAN-grafted pulp (at 15% monomer concentration) was 2.1%. Based on the nitrogen content, the weight increase includes 1.3% grafted PAN, with the balance as the increase in substrate yield. The reactivity of a monomer in graft copolymerization is a function of resonance stability, energy stability, and steric hindrance (1).

The presence of the acrylamide monomer slowed down the pulping progress. A higher pulping temperature and a longer cooking time were necessary to obtain a pulp

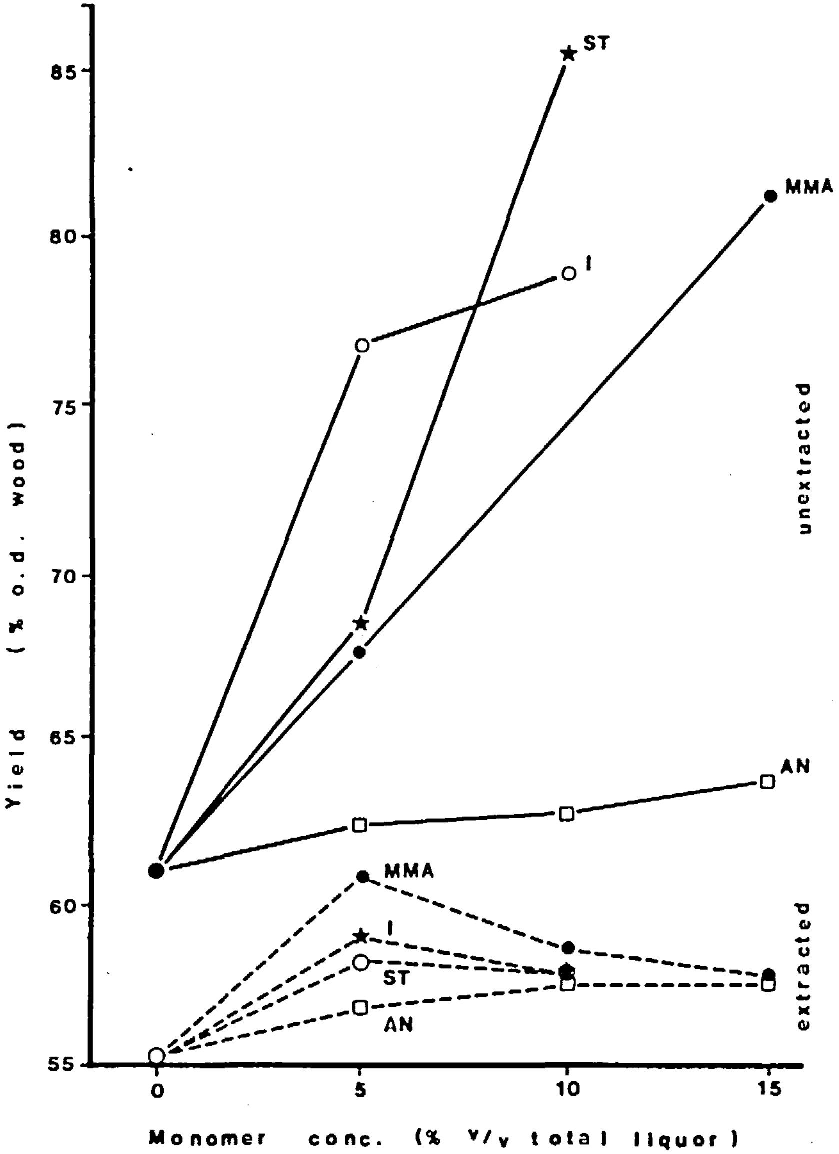


Figure 1. The effects of monomer type and monomer concentration on the yield from graft pulping. (——): unextracted yield, and (---): extracted yield.

TABLE 1

The Effect of Substitution and Concentration of Styrene On Graft Pulping.

Yield (%)	Styrene 5%	Styrene 10%	Chlorostyrene 5%	Chlorostyrene 10%	Methylstyrene 5%
Unextracted	68.3	85.5	79.8	124.6	78.8
Extracted	58.2	57.7	58.0	63.3	59.6

Cooking conditions: standard, temperature/time 100°C (58 min.) 150°C (90 min.).

which could be easily defiberized when using acrylamide (120 min. at 165°C with a programmed temperature rise, PTR, see experimental section). With the other monomers a good chemical pulp was produced in 60 min. at 165°C (with PTR). Cooking times longer than 120 minutes decreased the yield. Obviously there is a complex interaction of pulping and grafting reactions which depends on both the monomer type and concentration.

Vinyl monomer reactivity is also affected by the type of attached substituent. For example, either electron withdrawing or donating groups can alter the extent of reaction. Styrene bearing an electron withdrawing group such as p-chlorostyrene, or an electron donating group such as in methylstyrene behaves differently in graft pulping as shown in Table 1. Both substituted monomers increase the unextracted and grafted yields. The weight increase is more pronounced if a higher concentration of monomer is added to the system.

The Effect of Cooking Conditions

Variables which require evaluation for grafting under pulping conditions are pulping temperature, catalyst, solvent, time and liquor-to-wood ratio. The effect of maximum cooking temperature and acrylonitrile monomer concentration on the graft pulping of aspen is shown in Figure 2. The lower maximum pulping temperature gives both higher unextracted and extracted yields. The lower yield at higher temperature is ascribed to more extensive delignification. Therefore, less lignocellulosic material is present in the grafted pulp at higher pulping temperatures. The higher temperature (T165°C) also caused greater formation of homopolymer.

As already discussed, aluminum chloride was added to the graft pulping system as a pulping catalyst. Concentrations higher than 0.02 M decreased both the unextracted and the extracted yield. It appears that the yield loss with increasing concentration of catalyst was due to increased loss of woody material as a result of enhanced delignification, rather than decreased polymerization of styrene.

In the ethanol-water system, the highest yield was obtained at a 40/60 ethanol-water composition (55.5% extracted yield). However, variations between 50/50 to 80/20 ethanol-water composition did not produce large differences (3.4%). When methanol was substituted for ethanol as the aqueous pulping solvent a higher yield of grafted pulp (extracted) was obtained with 10% ST (59.2% vs. 52.7%). Propanol and butanol did not act as pulping agents in the presence of the monomers.

The effect of cooking time on graft pulping was evaluated for two monomers, chlorostyrene and acryloni-

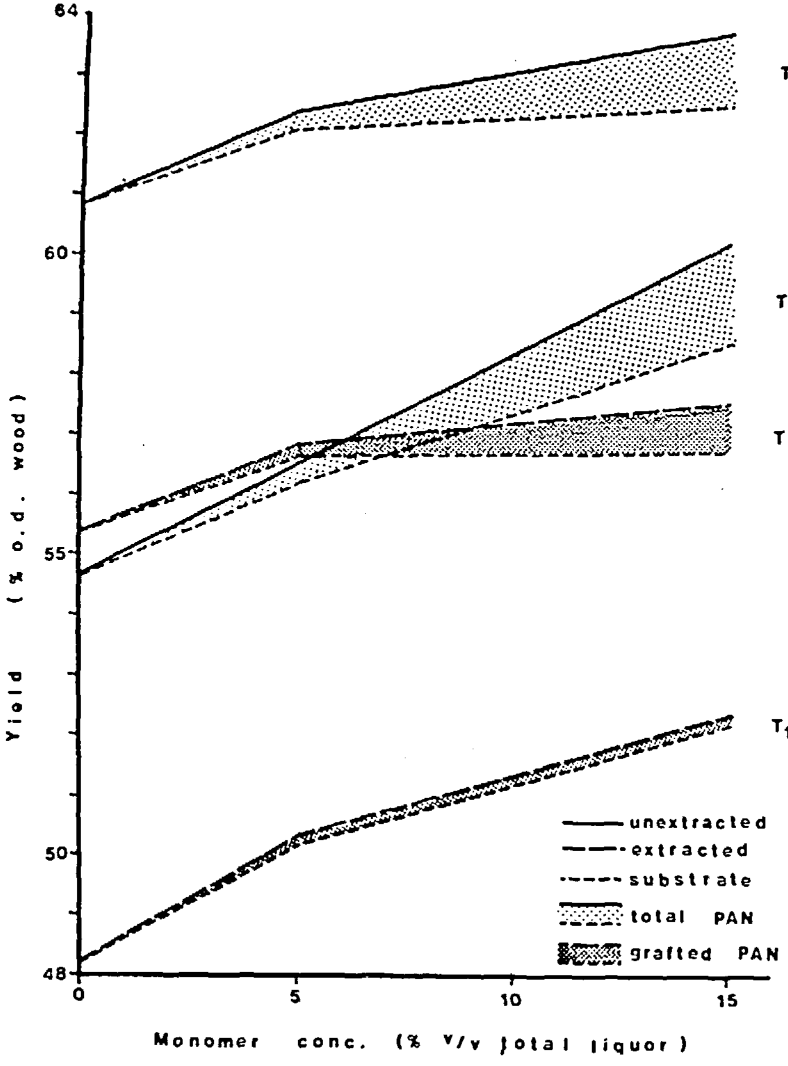


Figure 2. The effects of maximum pulping temperature with different monomer concentrations. Cooking conditions: standard, temperature/time 100°C (58 min), 150°C (90 min), or 100°C (68 min), 165°C (60 min).

trile. Longer cooking time benefited somewhat the chlorostyrene polymerization but reduced the yields with acrylonitrile. The grafted yield for chlorostyrene reached a maximum after about 100 minutes at the maximum pulping temperature (extracted yield at: 90 min. = 58.0%, 100 min. = 64.7%). Prolonged cooking time decreased the extracted yield a small amount probably because the delignification of the substrate proceeded after the grafting was maximized.

A series of experiments employing two variables simultaneously, i.e., cooking time (5 levels) and acrylonitrile concentration (4 levels) gave the results illustrated in Figure 3. Longer cooking time decreased the yields; but higher monomer concentrations enhanced the yields. Monomer concentrations exhibited a linear correlation with the unextracted and extracted yields. Analysis of variance for these experiments was performed and the statistical analysis for both unextracted and extracted yields indicated that the cooking time is more important than the acrylonitrile concentration to maximize yield.

Based on the nitrogen content, the maximum polymer loading of acrylonitrile was only 1.1%. The maximum value was obtained by employing a high acrylonitrile concentration and a relatively short cooking time (10% AN, 55 min. at 180°C).

The liquor-to-wood ratio is known to have a significant effect on the extent of delignification in organosolv pulping (7, 8). Therefore, this variable was also investigated for graft pulping. Cooking at higher liquor-to-wood ratios increased the unextracted yield but did not affect the grafted yield with styrene and acrylonitrile monomers. In other words, decreasing the

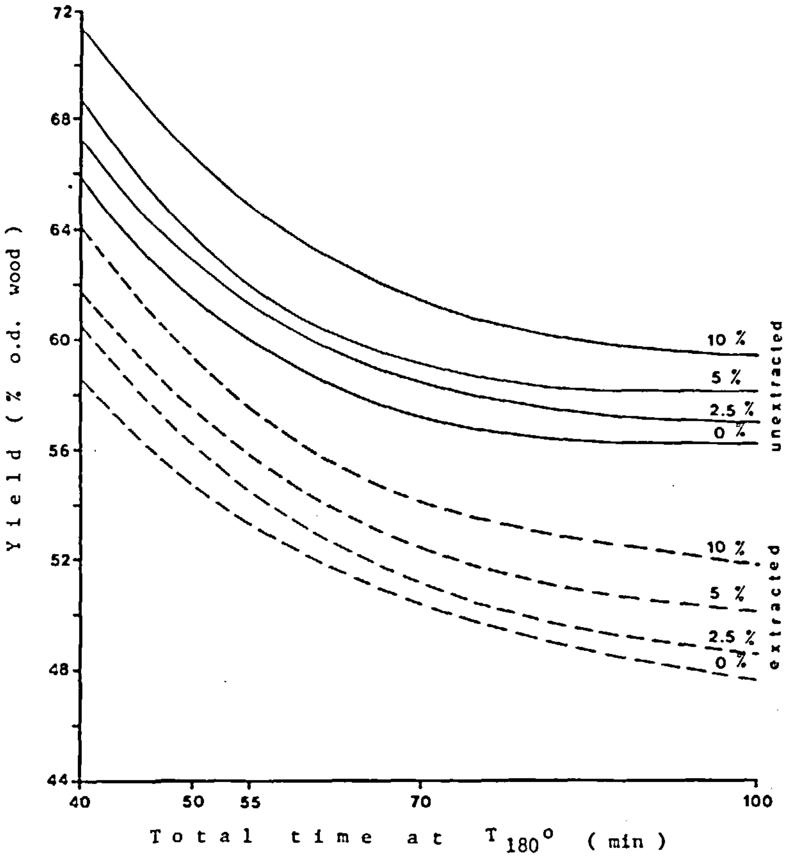


Figure 3. The effects of cooking time and acrylonitrile concentration on the yield from graft pulping. Cooking conditions: presoaked in aqueous methanol containing $AlCl_3$, drained, added with a fresh solvent and monomer prior to cooking, pulping temperature 180°C.

amount of substrate in the system is advantageous for homopolymerization, decreasing the efficiency of grafting. Total polymer conversion exhibited a decreasing trend with decreasing amounts of substrate.

Binary Monomer System

A synergistic effect on grafting of cellulose with an acrylontrile-styrene monomer combination has been reported in previous work (10). The polymerization of acrylonitrile is enhanced in a binary organosolv system, as shown in Figure 4. The grafted PAN was estimated by nitrogen analysis and, if solvent soluble material from the control pulp is assumed to be constant (7%), the content of total polystyrene can also be estimated (see experimental section). In addition, if there is no change in the weight of substrate at the various monomer compositions, the amount of grafted polystyrene can also be estimated. Under these assumptions, the highest total polymer conversion is observed with a 5% AN + 5% ST composition, with the major contribution from polystyrene. However, the highest total polymer loading is given by a composition of 1.75% AN + 8.25% ST.

Grafting parameters derived from Figure 4 are summarized in Table 2. The synergistic effect of a binary monomer system is clearly present in graft pulping. Additional combinations might prove even more viable for graft pulping.

The binary monomer effect can be explained in terms of copolymerization kinetics by the marked preference that the two monomers, acrylonitrile and styrene, have for each other. The reactivity ratios cited in the literature for acrylonitrile and styrene are 0.02 and 0.47, respectively, at 65°C; however, the reaction ratios are approximately reversed in the solvent system used in this investigation (11).

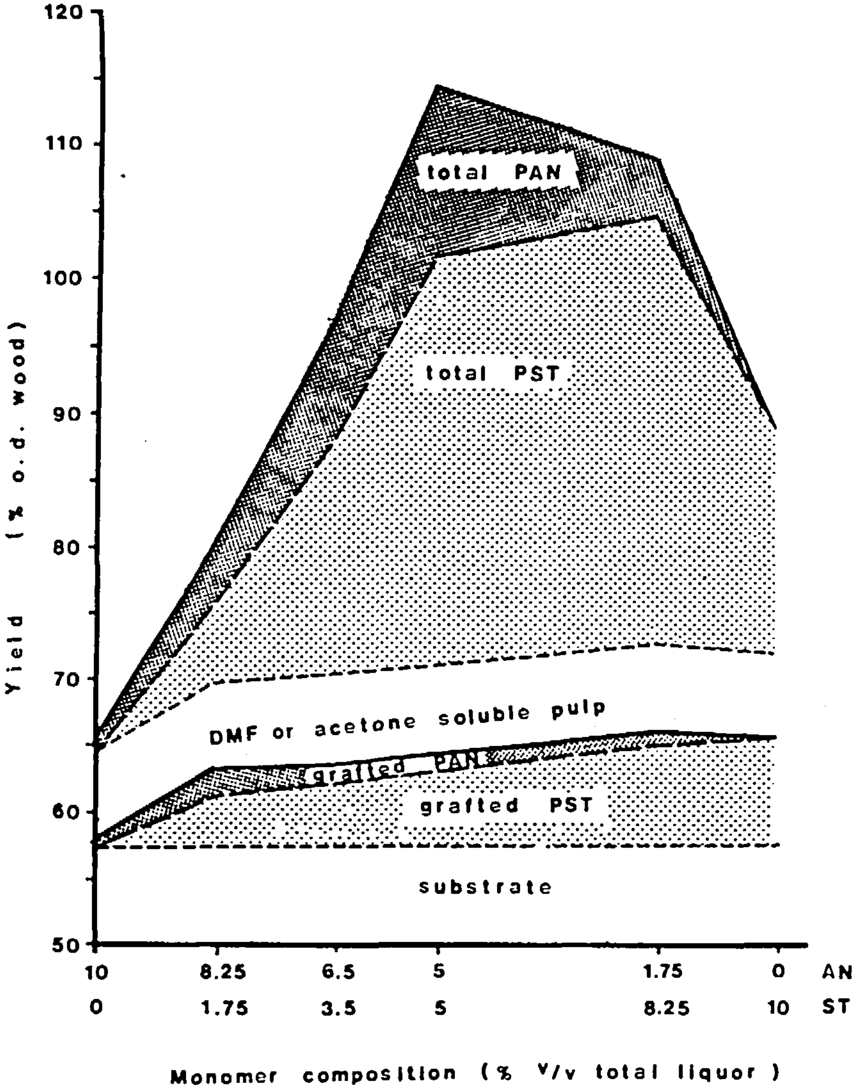


Figure 4. Characteristics of grafted pulps with acrylonitrile + styrene combination. Cooking conditions: methanol/water 1/1, .005 M $AlCl_3$, L/W ratio 10/1, temperature/time 100°C (90 min) 180°C (50 min).

TABLE 2

Grafting Parameters of Acrylonitrile-Styrene-Wood Copolymerization in Pulping System.

AN,%	10	8.25	6.5	5.0	1.75	0
ST,%	0	1.75	3.5	5.0	8.25	10
Total	10	10.00	10.0	10.0	10.00	10
Polymer conversion, %						
PAN	1.0	11.5	21.8	31.8	10.5	0
PST	0	37.7	55.0	56.1	41.0	18.6
Total	1.0	49.2	76.8	87.9	51.5	18.6
Polymer loading, %						
PAN	.6	2.2	2.6	2.5	1.7	0
PST	0	7.5	7.6	9.6	12.9	13.1
Total	.6	9.7	10.2	11.1	14.6	13.1
Grafting efficiency, %						
PAN	45	27	17	8	24	0
PST	0	72	25	18	24	45

Two Stage Pulping

Another alternative considered viable for graft pulping is a two-stage graft pulping process. The supposition is that the first stage causes partial delignification to expose the fibers for enhanced grafting in the second stage. Additional initiators can also be added for improved grafting.

The approach utilized for two stage pulping was as follows: In the first stage, the wood chips were pulped with PTR in an aqueous solvent and aluminum chloride. After a period of time, the vessel was discharged, and the pulp was washed with water; then fresh solvent, monomer and initiator were added for the second stage cook. The second stage was performed directly at pulping temperature. For application of Fenton's

TABLE 3

Comparison of Yields From One- and Two-Stage Graft Pulping.

Pulping	Styrene		Acrylonitrile		Me-methacrylate	
	unext.	ext.	unext.	ext.	unext.	ext.
One stage	97.5	64.4	88.1	59.3	102.0	59.8
Two stage (Fenton reagent)	69.0	63.3	96.6	63.0	89.6	60.2

Cooking conditions: standard, temperature/time 100°C (58 min.), 150°C (90 min.), 10% monomer concentration. Two stage cooking conditions: first stage cooking is standard, temperature/time 100°C (58 min.), 150°C (60 min.); second stage cooking with 6% monomer, H_2O solvent, temperature/time 150°C (85 min.).

reagent initiator (iron (II)-ions and hydrogen peroxide), iron was added in the first stage, and the hydrogen peroxide was added to the second stage. To increase the solubility of iron, a small amount of hydrochloric acid was added to the pulping medium.

Compared to one stage pulping, a two-stage process gave higher yields and more grafting with acrylonitrile; but similar or reduced grafting for styrene (Table 3). With acrylonitrile monomer, the unextracted yield was 96.6% and the extracted yield 63.6% in the two-stage process catalyzed with Fenton's reagent. The swollen substrate and the removal of a fraction of the lignin in the first stage obviously enhanced the polymerization and grafting of acrylonitrile to the pulp. The detrimental effect on styrene grafting indicates the preferential reaction of this monomer with lignin.

The use of aqueous methanol in the first stage gave improved grafting over that obtained with aqueous ethanol (Table 4). The methanol solvent system was used

TABLE 4

Alcohol Effects on Yields in the First Stage of Two-Stage Graft Pulping With Different Monomers

Monomer(s)	Methanol/water 1/1		Ethanol/water 1/1	
	unext.	ext.	unext.	ext.
Styrene	73.4	65.6	69.0	63.3
Methyl methacrylate	87.4	67.5	89.6	60.2
3% AN + 3% ST	86.8	66.9	87.5	63.7
Acrylonitrile	97.9	67.8	96.6	63.0
Grafting parameters:				
Total conversion, %	66.6		67.3	
Polymer loading, %	8.3		5.4	
Grafting efficiency, %	15.3		9.1	

Cooking conditions: first stage: .01 M $AlCl_3$, .01 M $FeCl_2$, temperature/time 100°C (58 min), 150°C (60 min); second stage: H_2O solvent, .6% (based on the total liquor) H_2O_2 3%, temperature/time: 150°C (85 min).

to further evaluate the effect of the delignification on grafting of acrylonitrile in the two-stage system.

In a two-stage graft pulping system, the degree of delignification can be controlled in the first stage. The characterization parameters of the products obtained after the second stage appear to be correlated with the effects on the substrate in the first stage. In Figure 5 it is shown that as delignification of the substrate proceeds the polymer conversion steadily decreases. This phenomenon can be interpreted as the participation of lignin in the graft polymerization of acrylonitrile by acting as a substrate and/or through creation of free radicals during removal.

Maintaining a high lignin content in the first stage, the grafting in the second stage was performed at three different temperatures, 150°, 165° and 180°C. The

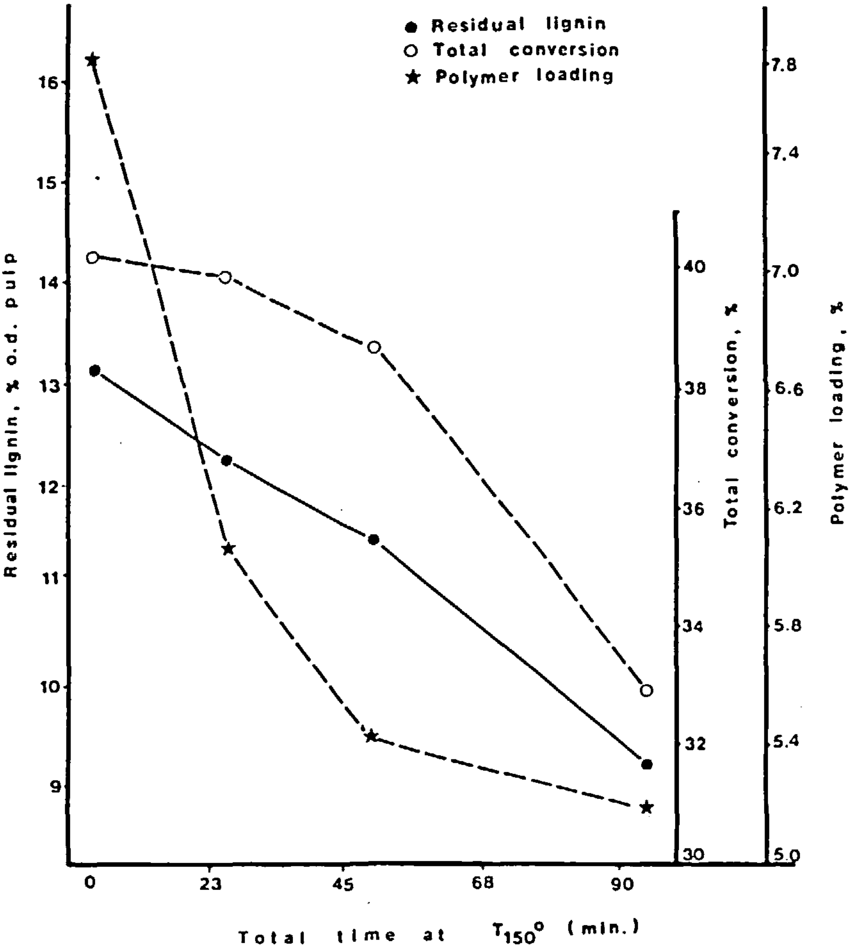


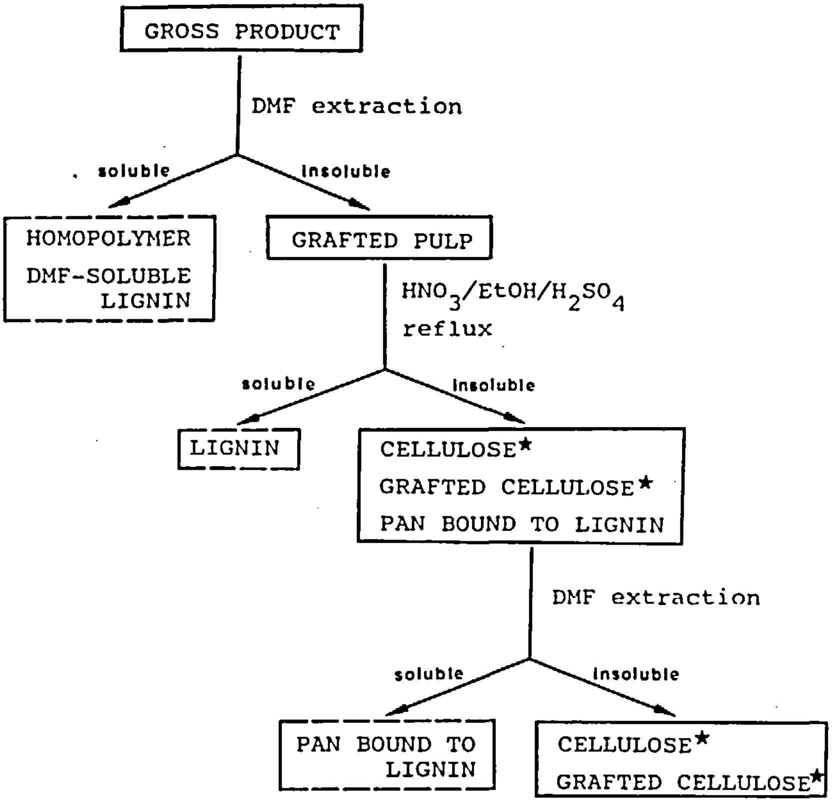
Figure 5. Correlation between the degree of delignification in the first stage and total conversion and polymer loading in the products thereafter. Cooking conditions: first stage: aqueous methanol, .005 M $AlCl_3$, and .01 M $FeCl_2$, temperature/time 100°C (58 min), 150°C (designated time); second stage: 10% acrylonitrile, H_2O_2, water solvent, temperature/time 150°C (85 min).

highest extracted and unextracted yield were achieved at the lowest temperature. The highest polymer loading was obtained by cooking at 165°C for a short time. The effect of treatment time was again confirmed in these series of experiments. The longer the cooking time, the lower the yield. Longer cooking time increased the homopolymer formation, but decreased grafting.

Grafting Sites in the Graft Pulping System

It is probable that the grafting is with both polysaccharides and lignin in the woody biomass. The extractives were not considered important for grafting since they are generally present in small quantities. The effect of extractives would be particularly negligible with a two-stage process.

Following the component fractionation scheme given in Figure 6, one can construct a material balance to evaluate the distribution of grafting sites in the pulp. Based on analyses by gravimetric, Kjeldahl nitrogen and solubility in 72% sulfuric acid, the grafting distribution analysis of pulp-g-PAN obtained by a two-stage process is shown in Figure 7 (conditions given in Figure 5). From the acid insoluble material in the last step of fractionation, it was found that 30% of PAN is grafted to polysaccharide fraction, and 70% grafted on the lignin fraction. Considering the lower lignin content in the pulp compared to the polysaccharide content, it is obvious that lignin has higher graftability (polymer loading 25%) than the polysaccharides (polymer loading 3%). The infrared spectrum of the grafted polysaccharide fraction exhibited a peak near 2400 cm^{-1}, indicative of a nitrile group.



★ hemicellulose may also present in this fraction

Figure 6. Scheme of fractionation of the grafted pulp for grafting site determination.

A similar method using acetone extraction (except nitrogen analysis) was conducted to determine the grafting distribution of polystyrene on a pulp produced with styrene monomer under the same conditions. Based on this analysis, 58% of the grafted polystyrene was on the polysaccharide fraction and the balance of 42% on

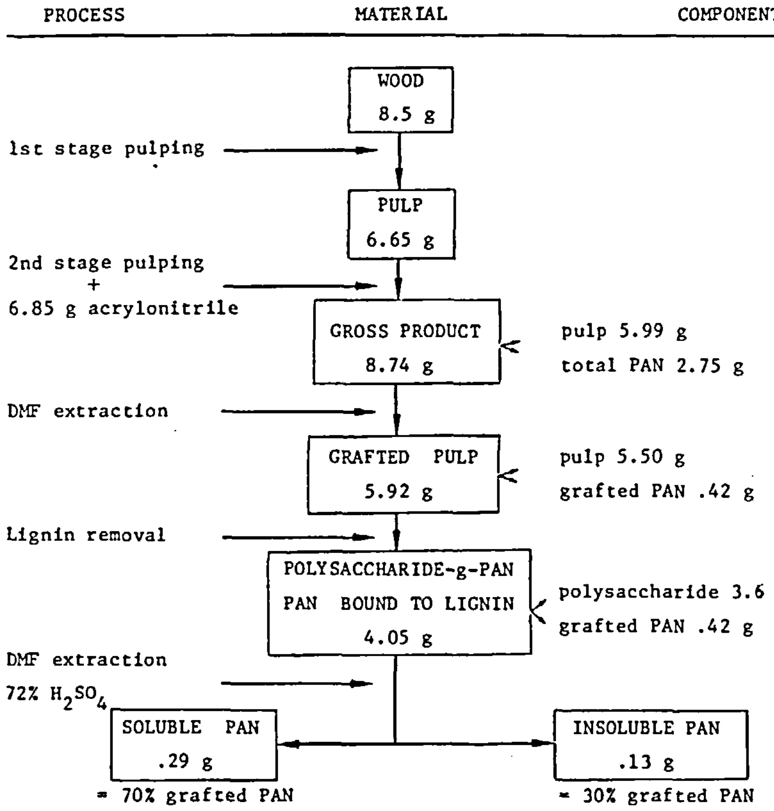


Figure 7. Grafting distribution in pulp-g-PAN obtained by a two-stage process.

the lignin component. Based on the weight of each component, polymer loading on the polysaccharide fraction was 8% and polymer loading on the lignin fraction was 77%. This evidence supports the view that lignin is more reactive to the grafting reaction than the polysaccharide.

CONCLUSIONS

Several aspects of graft pulping have been investigated. Grafting in the alcohol pulping system varied depending on the monomers and reaction conditions. In a graft pulping system, two major reactions are operating simultaneously, i.e., polymerization (homopolymerization and graft copolymerization) and delignification or the pulping reaction. During the progress of graft pulping, one reaction may promote or interfere with the other.

Free radical formation during organosolv pulping was indicated by the evidence of grafting. However, the concentration of free radicals may not be adequate to polymerize the entire monomer present in the pulping medium. A considerable amount of the monomer charged into the system remained unconverted. With acrylonitrile grafting, polymer loading was less than 1%, and the polymer conversion was less than 3%. In a binary monomer system, acrylonitrile considerably improved styrene grafting to the pulp, to almost 15% polymer loading.

A two-stage graft pulping process was also evaluated. The first stage provided a superior swollen state of the substrate with partial removal of the lignin. A co-catalyst such as ferrous ion (in the case of Fenton's reagent) was added in the first pulping stage, with hydrogen peroxide introduced in the second stage. The polymerization process was performed in the second stage. A polymer loading of 8.5% was obtained with acrylonitrile under these conditions.

Lignin demonstrates a higher graftability than the polysaccharide fraction. This fact indicates that in the progress of pulping, a major portion of the free radicals are probably produced from lignin fragmentation rather than degradation of the hemicellulose or polysaccharide fractions. This result is in good agreement with previous investigations.

Kleinert (9) recognized the levelling off of the free radical concentration in lignocellulosic materials after pulping 25 minutes with a rapid temperature rise to 180°C. This explains the rapid polymerization of the vinyl monomers in the first 30 minutes of the graft pulping reaction noted in this investigation. Homopolymerization was still progressing after 30 minutes reaction time, but grafting usually had already reached a maximum. The overall yield decreased with prolonged reaction times, as a result of the pulping reaction alone. The soluble grafted lignin from the pulping reaction was not characterized in this investigation. Further optimization of reaction conditions and characterization of the products is necessary.

EXPERIMENTAL

Raw Materials

Aspen (*Populus tremuloides* Michx.) air dried chips (1.5 x .6 x .3 cm) were used for all trials. After removal of inhibitors the vinyl monomers were distilled prior to use. The vinyl monomers were as follows: styrene (ST), p-chlorostyrene, p-methylstyrene, methyl methacrylate (MMA), acrylonitrile (AN), isoprene (I), acrylamide (AM). Acrylamide was used without further purification.

Pulping

Graft pulping was carried out in small laboratory scale bombs (100 ml capacity). The total liquid volume added in the bomb was 85 ml. Wood chips were loaded into the vessel and a stainless steel screen was positioned to keep the wood below the liquid surface. The other ingredients were mixed thoroughly prior to loading to ensure homogeneity of the solution. The percentage of the monomer is based on the total volume of cooking liquor. Depending on the type of vinyl monomer and the monomer concentration, a surfactant (Tween 80) was added to the solution. Cooks without monomer were performed as controls. The vessel was tightly sealed and immersed in an oil bath. At the end of the cook, the vessel was quenched in water. The wood and liquor were defiberized in a blender for 20 seconds. The pulp was then filtered, washed with water, dried, and weighed.

Two different time/temperature treatments were carried out in the experiments:

a) The cook with a Programmed Temperature Rise (PTR). This method employed immersion of the vessel into the bath at 100°C. The temperature was increased gradually to a maximum pulping temperature. Then, the pulping was extended at the steady temperature. The notation used to describe the temperature/time profiles are: $T_1(t_1)$ $T_2(t_2)$,

where T_1 denotes initial bath temperature (°C)

T_2 denotes maximum pulping temperature (°C)

t_1 denotes time to reach T_2 (min)

t_2 denotes time at the maximum temperature (min).

b) Direct cook at maximum pulping temperature, with the parameters described as T (t),
where T denotes maximum pulping temperature (°C)
t denotes time at maximum pulping temperature (min).

The standard cook was as follows: ethanol/water (1/1), .01 M $AlCl_3$, liquor to wood ratio 10/1, and PTR.

Grafting Analysis

The yield after the cooking process is termed unextracted yield. This includes carbohydrates (grafted and ungrafted), lignin (grafted and ungrafted), minor amounts of extractives, and homopolymer. The waste liquor was not characterized but may have contained soluble grafted oligomers of lignin in addition to degraded lignin. Homopolymer was removed from the pulp by extraction into an appropriate solvent (acetone for styrene, methyl methacrylate and isoprene; DMF for acrylonitrile; and hot water for acrylamide). The product after extraction, defined as extracted yield, was considered to be only grafted pulp. The material removed by extraction consisted of homopolymer, soluble lignin, minor amounts of extractives, some degraded polysaccharides and probably some low molecular weight grafted oligomers. Calculations were based on the oven-dry state of the wood chips.

The yield of cooks without monomer addition apparently cannot be used as a basis for evaluating grafting parameters. The presence of vinyl monomer in the pulping media has an effect on the delignification process. However, the measurement of the three grafting parameters is important for the characterization of monomer polymerization and the determination of apparent grafting levels. Thus, in graft pulping, precise determination of the extent of grafting must be obtained indirectly using the side chain functional group of the synthetic polymer as a monitor.

Pulp-g-PAN

The pulps before and after homopolymer extraction were subjected to Kjeldahl nitrogen analysis. The PAN content is defined as the weight of PAN divided by oven-dry wood. Correction was made for the nitrogen content of the untreated wood (0.06%). Conversion factors based on nitrogen loss were applied to determine the PAN content of the products.

The calculated PAN content in the sample was then used to derive:

a) Unextracted substrate = unextracted pulp yield - PAN content of unextracted pulp

b) Extracted substrate = extracted pulp yield - PAN content of extracted pulp

c) Polymer loading =

$$\frac{\text{PAN content of extracted pulp} \times 100\%}{\text{extracted substrate}}$$

d) Total conversion =

$$\frac{\text{PAN content of unext'd pulp} \times \text{wt.of wood} \times 100\%}{\text{wt.of monomer charged}}$$

e) Grafting efficiency =

$$\frac{\text{PAN content of extracted pulp} \times 100\%}{\text{PAN content of unextracted pulp}}$$

Fractionation of the components in the pulp-g-PAN was carried out according to the scheme in Figure 7.

From the grafted product, the lignin component was dissolved in boiling HNO_3/EtOH, containing a small amount of sulfuric acid. The PAN previously bound to lignin was subsequently removed by DMF extraction. The remaining insoluble material was considered to be the grafted cellulose, although the product may also contain some grafted hemicellulose.

Pulp-g-PST and Pulp-g-PMMA

Polystyrene and polymethyl methacrylate are resistant to acids, therefore, lignin can be isolated through the Klason method with 72% H_2SO_4 (a small amount of acid soluble lignin may be dissolved in the solution). However, due to the difficulties in separation of PST or PMMA from the lignin, the total acid insoluble material was used in these cases to characterize the grafted pulps.

ACKNOWLEDGEMENTS

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