Radiation Grafting of Vinyl Monomers onto Wood Pulp Cellulose. II

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Synopsis

The effect of radiation dose rate and beating time on the mutual radiation grafting of styrene to unbleached and bleached kraft wood pulp was studied. Companion studies on the effect of beating time, peroxidation grafting, and order of monomer addition on the preirradiation graft copolymerization of acrylamide and diethylaminoethyl methacrylate were conducted on bleached wood pulp. The grafting rate of styrene increased with dose rate, but the kinetics suggests a significant diffusional resistance to the observed grafting rate. The per cent graft measured at fixed grafting conditions decreased markedly as pulp beating (effected prior to grafting) was increased. It is suggested that the decrease in grafting with beating is due to an increase in the accessibility and swelling of the beaten fibers. Dimethylaminoethyl methacrylate appeared to inhibit the grafting of acrylamide, and double grafting had to be used to graft both hydrophilic polymers to the pulp. The mechanical properties of high-yield pulp and groundwood were improved by the addition of the grafted pulps. The double grafts appeared to show promise as fibrous beaten additives for dry strength improvement. The styrene-grafted pulps were found not to respond at all to the beating process.

INTRODUCTION

Graft polymerization onto cellulose and its derivatives has been investigated in great detail. An excellent and complete review of the whole field of grafting onto polysaccharides has recently been published by Arthur.[1] Grafting to wood pulp has been less studied than to purer forms of cellulose but has received increasing attention in recent years in attempts to improve the properties of paper by this technique. A review of this work has recently been presented by Phillips et al.[2] Earlier studies in these laboratories with the radiation grafting of styrene[3-5] and with acrylamide[5] have now been extended to another monomer, N-dimethylaminoethyl methacrylate, and to its copolymers with acrylamide and to double grafts with both homopolymers. Acrylamide was chosen because it is known to improve the strength of paper[5,6] through its high hydrogen-bonding capacity. With high-yield pulps and with groundwood, however, it is not so effective,[5] It was thought that a cationic polymer such as N-dimethylaminoethyl methacrylate might provide a better partial ionic bonding with the ligno-sulfonates and other lignin moieties in the wood pulp. Such a possibility has been

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discussed in detail by Linke[7] for the case of polymeric dry-strength additives for papers. Combinations of both monomers could therefore in principle lead to excellent dry-strength properties, even with high-yield pulps.

In addition to studies of the new monomer system, the specific effect of beating has been investigated in some detail. Beating is a mechanical treatment of wood pulp used routinely in the paper industry which defibrillates, masticates, and severs the pulp fibers. This seemingly straightforward process is, in fact, highly complex and results in dramatic improvements in the mechanical properties of the resultant paper such as bursting strength, tensile strength, folding endurance, and smoothness. These effects result from morphologic changes in the fiber structure rather than from chemical modifications.

The effect of beating time and total radiation dose on the rates of grafting were studied with preirradiation, peroxide, and mutual grafting techniques. The grafting of the individual monomers and monomer mixtures was also investigated and compared with grafting each monomer in sequence.

EXPERIMENTAL

Materials

Wood Pulp Specimens. Unbleached kraft pulp was graciously supplied by the Wood and Paper Science Department of the School of Forest Resources at the North Carolina State University in Raleigh, North Carolina. Groundwood pulp was prepared from southern pine. The high-yield unbleached kraft softwood pulp contained 20.8% lignin.

The bleached kraft pulp was prepared from blends of southern pine kraft pulp and hardwood kraft pulps reacting with chlorine dioxide following an alkali wash. The bleaching process was completed by extensive washing with water. The resultant lignin concentration was reduced close to zero by this technique.

Monomers. Styrene monomer was obtained from the Eastman Chemical Company and was distilled in a packed column to remove inhibitor and water, then stored under vacuum in a refrigerator and redistilled prior to use.

Acrylamide, also obtained from the Eastman Chemical Company, was recrystallized from acetone before use. The N-dimethylaminoethyl methacrylate was obtained from the Rohm and Haas Company and was stabilized with methyl hydroquinone. It was purified by passing the monomer through a column of Amberlyst A27 ion-exchange resin.

Graft Copolymerization

Mutual Irradiation Grafting. The pulp and monomer were added to the solvents in an ampoule which was connected to a high-vacuum manifold. Four freeze–thaw cycles under 10^{-5} mm Hg served to degas the ampoule

contents.   The ampoules were subsequently sealed, with the contents frozen.

The thawed and warmed ampoules were irradiated for controlled times and at controlled rates at room temperature.

For very large pulp samples, the pulp was degassed separately and the degassed monomer and solvents were introduced to the pulp through a breakseal.

Immediately after irradiation, the sealed tubes were opened and the pulp mass was extracted in a Soxhlet apparatus for 24 hr with benzene (for the styrene grafts) or water (for the acrylamide and N-dimethylaminoethyl methacrylate grafts).   The samples were then dried for 24 hr at 60°C and 10^{-3} mm Hg: the per cent graft was calculated as the weight gain consequent to grafting divided by the original dry weight of pulp.

Preirradiation Grafting.   Pulp samples were degassed for 24 hr at 10^{-5} mm Hg in glass ampoules fitted with breakseals.   After sealing, the ampoules were irradiated to the desired dose and then resealed to the vacuum manifold.   The previously degassed monomer (acrylamide or N-dimethylaminoethyl methacrylate) and solvent were introduced to the pulp through a breakseal, then the ampoules were kept for 24 hr at 25°C while submerged in a water bath.

Immediately after the reaction period, the sealed tubes were opened and the pulp mass was extracted with water in a Soxhlet apparatus for 24 hr. The samples were then dried for 24 hr at 60°C and 10^{-3} mm Hg; the per cent graft was calculated as the weight gain divided by the original dry weight of pulp.

Peroxide Grafting.   The pulp samples were irradiated in air in an open beaker.   They were then placed in an ampoule, degassed, and treated exactly as with the preirradiation method described above.

Pulp Beating.   The pulp was introduced to a PFI Beater Mill, and beating was effected for a controlled time period.   Both beaten elements rotate counterclockwise against the beater house wall during the actual beating.   Consequent to beating, the pulp was washed into a disintegrator, the water level adjusted to 2 liters, and the disintegration or defibrillation carried out for 25 min (3100 revolutions).

Determination of the Canadian Freeness Number of Grafted and Ungrafted Pulp.   The Canadian Freeness Number (Tappi Procedure T227-M-50) is a measure of the resistance to water drainage of a pulp sample. A known volume of pulp in 2 liters of aqueous suspension was drained through a screen plate.   The pulp deposits on the screen plate, providing a resistance to drainage.   The volume of filtrate collected from the downstream side of the screen plate is recorded as the Canadian Freeness Number.

Mechanical Testing.   The mechanical properties of handsheets prepared according to Tappi Procedure T 205M-58 were determined.   Tappi Test T 404 ts-66 was used to measure the tensile breaking strength, T 403 ts-63 was used to determine Bursting strength, and the folding endurance was measured according to T 511 su-69.

RESULTS AND DISCUSSION

Styrene Grafting

The data presented in Figure 1 summarize the effect of time, proportional to total dose, on the grafting yields onto unbleached, unbeaten kraft pulp. The results are quite similar to and consistent with the earlier data of Lepoutre et al.[3] and Oraby et al.[4] for a similar grafting recipe involving styrene, dioxane, and water, but with different pulps. Rather classical kinetics are found in the early stages of grafting, with the initial reaction rates proportional to the square root of the dose rate. At longer reaction times, the rate tends to decrease, presumably because of the decreasing accessibility of the fibers to the grafting process. Such results have been observed and discussed also with the cellulose acetate-styrene grafting system.[8]
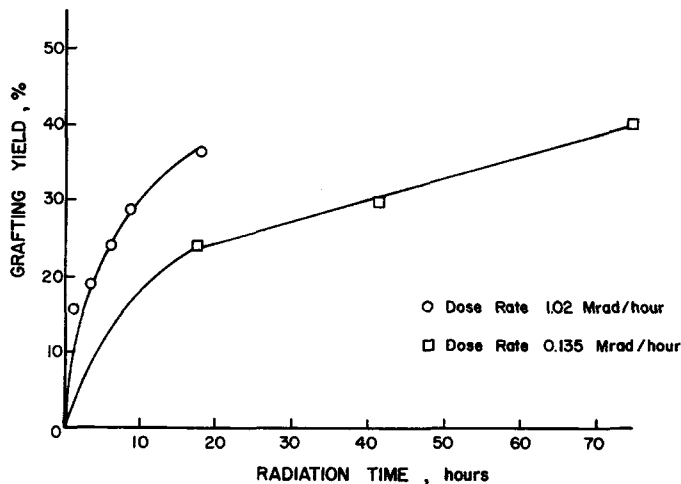

Fig. 1. Effect of irradiation time on grafting of styrene to unbleached unbeaten kraft pulp. Mutual grafting at 30°C in 33% sytrene, 66% dioxane, and 1% water.

The effect of beating was studied briefly, and a reduction in grafting was found to occur. This rather unexpected result was studied in more detail with bleached kraft pulp since the unbleached pulp could not be grafted with the hydrophilic monomers to be studied later. The results of beating on the grafting yield with a fixed recipe and total dose is presented in Figure 2. Initially, the grafting had little effect, but increased beating decreased the grafting yield considerably; and at 12 min of beating, the yield had dropped to less than one half the value for the unbeaten pulp. Similar results were found with the two hydrophilic monomers studied. The effect of beating will be discussed below.
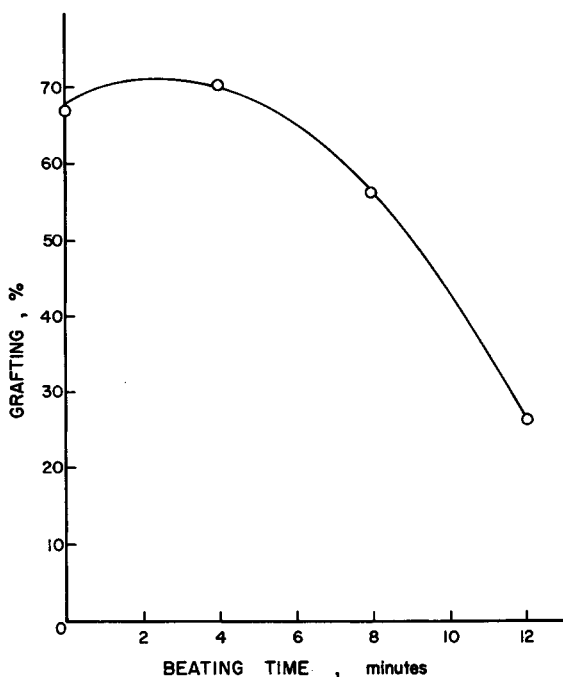
Fig. 2. Effect of beating on grafting of styrene to bleached kraft pulp. Mutual grafting at 30°C in 33% styrene, 66% dioxane, and 1% water. Dose rate 0.83 Mrads/hr.

Grafting of N-Dimethylaminoethyl Methacrylate and Acrylamide to Pulp

Both hydrophilic monomers polymerize rapidly with radiation, making the mutual method of grafting difficult as excessive homopolymer is formed. The studies tended therefore to be restricted to the preirradiation or peroxide method. An extensive study of the grafting of acrylamide to pulp has recently been published.[5] In this work, the study has been extended to the effects of beating on the grafting yields. Initially, the mutual grafting of N-dimethylaminoethyl methacrylate to bleached kraft pulp was studied, with the results shown in Figure 3. The rapid initial rate to a plateau grafting yield of about 20% is probably due to a rapid saturation of the grafting volumes available and is quite reminiscent of the styrene–cellulose acetate system described in an earlier publication.[8] All the subsequent work was carried out using the preirradiation in vacuum (trapped radical) technique with this monomer.

The data of Figure 4 show the grafting yields obtained from mixtures of acrylamide and N-dimethylaminoethyl methacrylate reacted with bleached pulp which has been beaten for 6 min. Although the grafting of pure N-dimethylaminoethyl methacrylate is inherently much slower than the grafting of acrylamide, the grafting yields of the mixtures are much lower
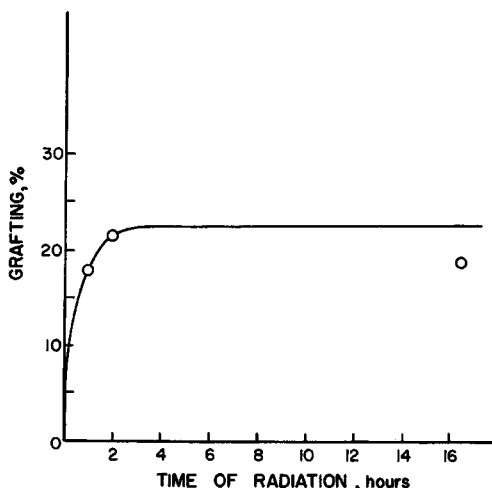
Fig. 3. Effect of irradiation time on grafting of dimethylaminoethyl methacrylate to bleached kraft pulp.   Mutual grafting at 30°C with 20% monomer in 90:10 water: ethanol.

than one would expect if there were no interaction between the monomers. Apparently, the presence of N-dimethylaminoethyl methacrylate significantly inhibits the rate of acrylamide grafting; consequently, the extent of grafting drops sharply as N-dimethylaminoethyl methacrylate is introduced to the grafting mixture.   The reasons are not clear; it could be due to unfavorable reactivity ratios, or to complexing and solubility factors.   More work would be needed to elucidate the reasons for this unexpected behavior.

In contrast, the prior grafting of 82% acrylamide to bleached pulp apparently has no rate-limiting effect on the subsequent grafting of N-dimethylaminoethyl methacrylate to the acrylamide–wood pulp graft copolymer.   Moreover, the data of Figure 5 suggest that there is no diffusional contribution to the observed grafting kinetics of N-dimethylaminoethyl methacryiate to the acrylamide pulp graft.   The incremental grafting was not only extensive but was linear in reaction time, suggesting ready access of monomer to very stable growth centers.   Since the pulp contained 45% of grafted polyacrylamide, it is likely that much of the N-dimethylaminoethyl methacrylate was grafted to polyacrylamide as well as to cellulose.

The effect of beating on the preirradiation grafting of acrylamide at two radiation doses and of N-dimethylaminoethyl methacrylate is shown in Figure 6.   An example of peroxide grafting of acrylamide is also included. All the curves have the same form, and the per cent graft decreases rapidly with beating.   The shape of the curves is different from the results obtained with the same pulp with styrene by the mutual irradiation method.

In the preirradiation process, the grafting takes place by reaction of the trapped radicals with the monomer after the monomer solution is admitted to the irradiated wood pulp.   This process competes with the rapid re-
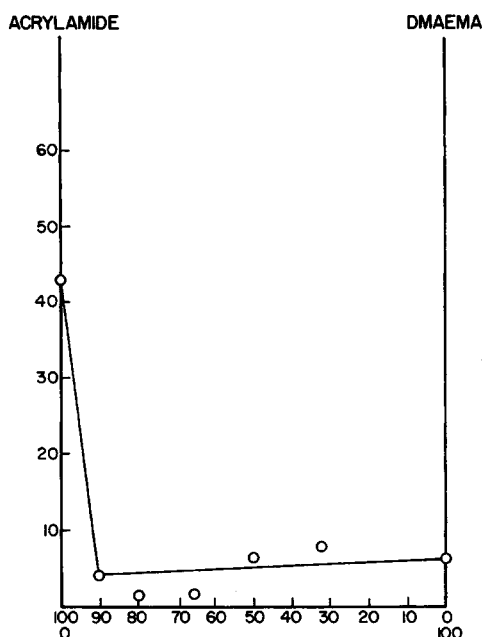
Fig. 4. Effect of monomer composition on preirradiation grafting of acrylamide and dimethylaminoethyl methacrylate (DMAEMA) to bleached kraft pulp (beaten for 6 min). Dose 2.5 Mrads. Grafting solution, 20% monomers in 90:10 water:ethanol. Temperature, 30°C.

combination of the trapped radicals as the swelling agent, water in this case, which is a necessary component of the monomer solution, enters the fibers. Beating increases the surface area and decreases the diameter of the pulp fibers enormously; and this would seem to offer a reasonable explanation of the decrease in grafting since the rapid swelling would lead to a rapid recombination of the radicals before the larger monomer molecules could reach them. It is interesting that the pulp which received a higher dose and presumably contained a larger concentration of trapped radicals grafted less after beating, although the yield was higher with the unbeaten pulp. This is perhaps due to the initial faster decay of the radicals before and during the addition of monomer, possibly due to radiation damage to the beaten pulp. More experiments would need to be conducted, however, to clarify the reasons for this phenomenon.

Peroxide grafting is always less efficient than preirradiation grafting under vacuum; and, in practice, the grafting is accomplished by the breakdown of the cellulose peroxy compounds and by radicals trapped in rather inaccessible regions of the fibers which consequently do not react with the oxygen during the irradiation. In any case, the yield of grafted radicals is lower when the irradiation is carried out in air. An interesting discussion of these and other effects is contained in a recent paper by Arthur et al.[10] The slower production of radicals and lower population in the case of per-
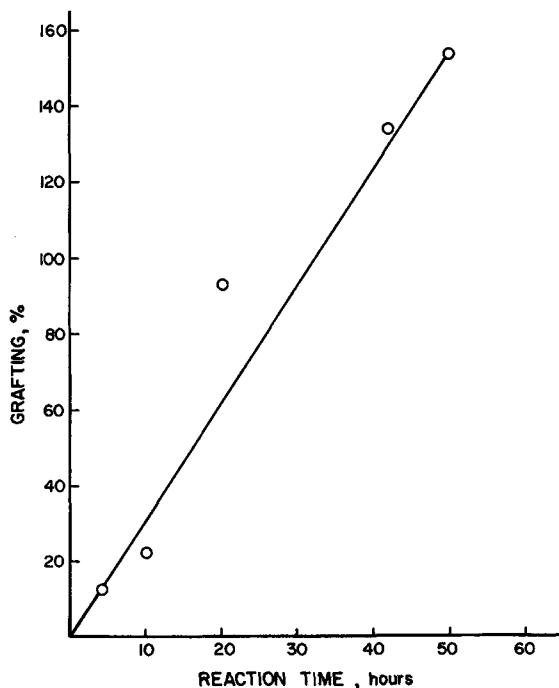
Fig. 5. Effect of reaction time at 30°C on grafting yield of dimethylaminoethyl methacrylate to bleached kraft pulp previously grafted with 82% acrylamide. Preirradiation, 2.5 Mrads in 20% monomer in 90:10 water:ethanol.

oxide grafting could lead to a more favorable competition of grafting, with termination as the fibers swell. This would be reflected in the similar but lesser effect of beating with this grafting technique. In both cases, the release of the small quantities of phenolic materials from the lignin by the beating could also be responsible, since such compounds are known to inhibit grafting significantly.[5] The bleached kraft, however, was essentially lignin free, although tiny amounts undoubtedly were still present in the fiber.

The explanation in the case of styrene (Fig. 2) may be more complicated, since it is known that lignin does not inhibit with the mutual method with styrene. Also, the initial beating causes a small increase in the grafting yield. The mutual method continuously produces radicals during the irradiation; and the fibers are already in a swollen state, quite different from the conditions prevailing with the preirradiation and peroxide methods. It is suggested, however, that the combination of the rate of supply of monomer and the radical termination rate determines the grafting yield. This combination is well known to produce maxima in the grafting yield-versus-monomer concentration curves, as has been well demonstrated, for example, for the cellulose acetate–styrene system.[8] The initial beating would remove the remaining primary cell walls and generally make the pulp more accessible to monomer, causing a small increase initially. Fur-
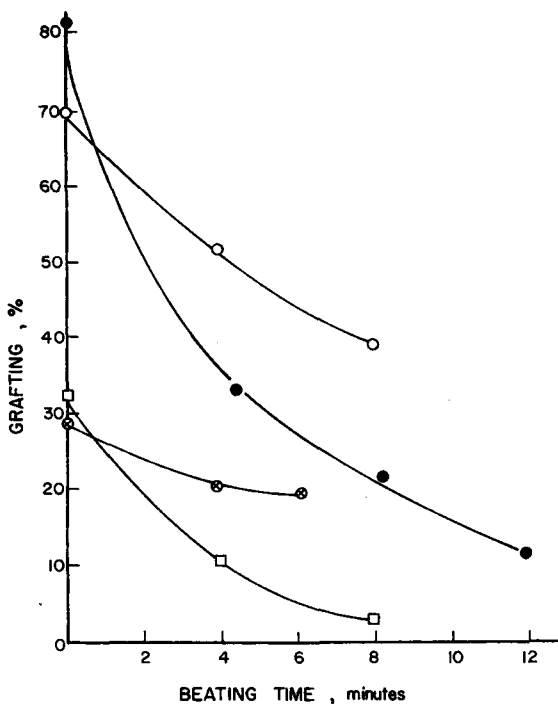
Fig. 6. Effect of beating on grafting of acrylamide and dimethylaminoethyl methacrylate to bleached kraft pulp. Preirradiation of 20% monomer (in 90:10 water: ethanol): (O) acrylamide, 2.5 Mrads; (●) acrylamide, 5.0 Mrads; (□) dimethylaminoethyl methacrylate, 2.5 Mrads; (⊗) acrylamide, 2.5 Mrads, peroxidation technique.

ther beating, however, reduces the size of the pulp fibers and renders them somewhat more swollen, and termination becomes faster whereas the rate of supply of monomer may be essentially the same.

These explanations all appear to be quite reasonable; the negative effect of beating on the grafting yield is not perhaps so strange as initially thought. In this connection, it must be pointed out that beating increases the equilibrium water sorption of the fibers only slightly; it does, however, increase the held water content, i.e., the so-called water of hydration and the swelling and compliance of the pulp fibers. The monomer solution would be held also in the voids, cavities, and capillaries of the pulp matt (as with the water of hydration) where polymerization would also take place. Much of such polymer would be virtually unextractable and would be included in the grafting yields itself.

Mechanical Properties of the Graft Copolymers

In a previous paper,[5] it was shown that acrylamide-grafted pulp led to remarkable improvements in the strength of high-yield unbleached kraft pulps by blending. The improvements were far greater, for example, then by blending with a strong long-fibered, ungrafted bleached kraft pulp. This was true even with pulps containing 20.8% lignin, although the per

cent improvements were less than with higher-yield pulps. Groundwood pulp, however, did not respond in the same way, and far greater improvements were found by blending with the ungrafted bleached kraft pulp used with the other high-yield pulp studies. Groundwood has also been found not to respond to the addition of a polyacrylamide dry-strength additive.[9] It was thought that such pulps were too lignaceous to respond to a simple hydrogen-bonding additive and that a cationic polymer of N-dimethyl-aminoethyl methacrylate or perhaps a copolymer or co-grafted pulp with acrylamide would be more successful. An interesting discussion of this kind of thinking has been presented by Linke.[7] A series of experiments were therefore conducted with grafts to bleached kraft pulp of N-dimethyl-aminoethyl methacrylate (22.7% graft) with acrylamide alone (58% graft) and a double graft of acrylamide (82% graft) followed by N-dimethyl-aminoethyl methacrylate (40% graft based on the original pulp).

Both grafts were blended with a very high-yield pulp (20.8% lignin content) and with a groundwood pulp. Blending was accomplished by mixing a 10% aqueous slurry in a Waring Blendor for 3200 revolutions. Handsheets were then formed at a pH of 4.5 and tested according to Tappi standard methods as outlined in the experimental section.

The more highly (double) grafted pulp was blended with the pulps at a lower proportion, 30%, than the lower per cent single graft, which was tested at 50% grafted pulp content. This brought the N-dimethylamino-ethyl methacrylate content to roughly the same proportions in the overall pulp blend. The effect of the blending on the strength properties of the resulting paper is summarized for the high-yield pulp in Table I and for groundwood in Table II.

TABLE I
Effect of Blending Grafted Pulps with High-Yield (20.8% Lignin)
Pulp on Mechanical Strength Properties

Blend[a]	Tensile strength, lbs/in	Elongation, %	Bursting strength, psi
100 High-yield pulp (HYP)	5.0	1.8	5.4
50:50 A HYP	5.8	3.0	6.7
50:50 C HYP	9.0	2.7	22.0
50:50 BKP HYP	8.0	1.8	18.2
70:30 B HYP	3.4	<1.5	5.7
70:30 C HYP	6.0	3.0	17.8
70:30 BKP HYP	5.8	1.5	15.2

[a] Blends: A, 22.7% N-dimethylaminoethyl methacrylate; B, 58.0% acrylamide; C, double-grafted 82% acrylamide with 40% N-dimethylaminoethyl methacrylate, both based on the original pulp weight.

TABLE II
Effect of Blending Grafted Pulps with Groundwood Pulp on
Mechanical Strength Properties

Blend[a]	Tensile strength, lbs/in	Elongation, %	Bursting strength, psi
100 groundwood pulp (GWP)	5.3	2.2	8.8
50:50 A GWP	15.5	3.0	22.3
50:50 C GWP	8.3	2.2	22.0
50:50 BKP GWP	18.9	3.0	27.2
70:30 B GWP	14.0	2.0	14.2
70:30 C GWP	8.3	2.2	16.1
70:30 BKP GWP	16.9	5.0	17.9

[a] Blends: A, 22.7% N-dimethylaminoethyl methacrylate; B, 58.0% acrylamide; C, double-grafted 82% acrylamide with 40% N-dimethylaminoethyl methacrylate, both based on the original pulp weight.

Considering first the results obtained with the high-yield (20.8% lignin content) pulp, it is clear that the cationic-grafted pulps did indeed impart greater strength to the paper. The double grafts, in fact, gave better results than by blending with strong long-fibered bleached kraft pulp. The differences were not great, however, between the two fibrous additives and probably not sufficient to justify the extra costs involved. In contrast, pulp grafted only with polyacrylamide did not give much, if any, improvement in strength to the paper.

The results obtained with the groundwood pulp were rather different. In no case did the grafted pulps give higher strength than the same amount of blended, bleached kraft pulp. In every case, however, the grafted pulps did impart higher strength properties to the paper made with pure groundwood pulp. The simple cationic graft gave rather better improvements in strength than did the double-grafted pulp. The straight polyacrylamide graft also conferred good strength improvements to the groundwood, but not as good as the simple cationic-grafted pulp.

In summary, the idea of using polycationic-type grafts for the improvement of the strength of high-yield and groundwood pulps was shown to be valid. The double grafts, in particular, seemed to be potentially interesting grafted pulps for strength improvement. Considering that no special attempts were made to optimize the results, the approach may be considered highly encouraging, and further work in this field is clearly warranted.

Finally, attempts were made to beat the styrene-grafted pulp. As can be seen in Figure 7, no reduction in freeness could be achieved. Also,
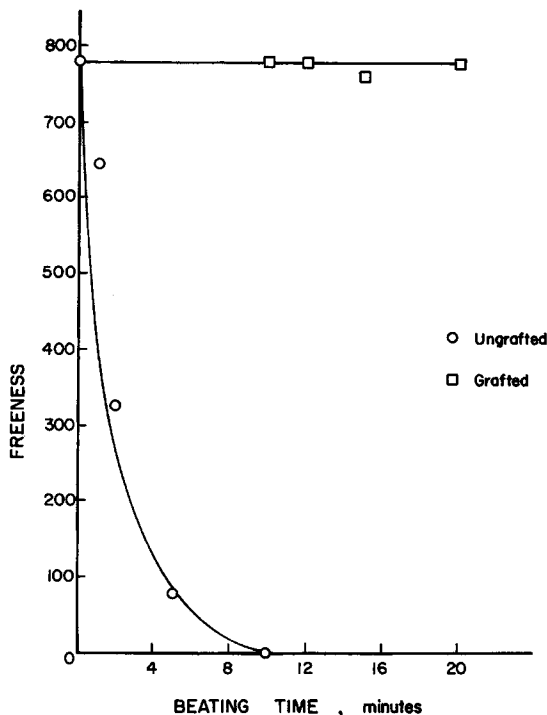
Fig. 7. Effect of beating: freeness curves for unbleached kraft pulp. Ungrafted and 51% styrene-grafted pulp.

sheets formed from the pulp were extremely weak, as would be exptected. Apparently the grafted styrene effectively prevented the defibrillation process even though the equilibrium swelling in water is only reduced by about 20% based on the original pulp weight. It is clear that the grafting should therefore be carried out on the paper itself with hydrophobic polymer grafts.

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