

Grafting of industrial cellulose pulp using the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ redox system as initiator

László Zara*, József Erdélyi, Zoltán Hell, Éva Borbély, and István Rusznák

ABSTRACT: The iron(II)/hydrogen peroxide redox system was studied to initiate the grafting of industrial cellulose pulp with vinyl acetate monomer. The parameters of the copolymerization reaction (reagents ratio, pH, temperature, reaction, and pulping time) were investigated and their effects are discussed.

KEYWORDS: Cellulose, copolymerization, (EVA) polymers, hydrogen peroxide, iron, parameters, pulps, redox reactions.

The chemical modification of cellulose by grafting copolymerization has generated interest among researchers because few comonomer molecules change significantly and advantageously a number of characteristics of the original natural polymer. Thus, new areas of the application might be opened for the modified cellulose-type materials.

Being a polymer itself, cellulose can be copolymerized only with block or grafting procedures. The block copolymerization of cellulose essentially modifies its physical structure, and therefore cannot be used. A graft copolymer is a system comprised of a backbone material to which a second polymer is attached at intervals along the chain. The pulp cellulose modified by grafting copolymerization does not change its fibrous structure, which is very advantageous for further use.

Most of the grafting copolymerization examined so far (1) describes

the use of cotton or regenerated cellulose as the substrate, generally in the form of papers or fibers. There are few papers about the grafting of cellulose pulp used in the paper industry (2).

Recently we examined the grafting of industrial celluloses with vinyl monomers initiated with cerium(IV) salts (3). Unfortunately, these salts are very expensive and can be used only for grafting of bleached celluloses.

It is known (1, 4) that the iron(II)/ H_2O_2 redox system can also be used to initiate the grafting of cellulose. The results on the grafting of industrial cellulose pulp with vinyl acetate is reported in this paper.

Role of Fe^{2+} ions in the grafting process

It is also known (5, 6) that slightly oxidized cellulose pulp adsorbs metal ions from their aqueous solution.

This process can be described by the following equation (5):



where RCOOH is a carboxyl group of cellulose while M^+ is the appropriate metal ion. The ion exchange adsorption of the metal ions by the pulp depends on the proportion of the carboxyl groups in cellulose, on the concentration of the metal ions in the solution and on the pH of the mixture (7).

The adsorption plays a very important role in the grafting of cellulose. If the fibers were transferred from the solution of the iron(II) salt to the initiator-monomer mixture without washing, 6–7 times more monomer reacted in homopolymerization than in grafting (3). If the Fe^{2+} ions are bound to the carboxyl group of the cellulose molecule, the migration of the OH radicals, formed in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, is retarded in the solution so the proportion of homopolymers decreases in the grafted system (8).

Effect of monomer concentration on grafting efficiency (Table I)

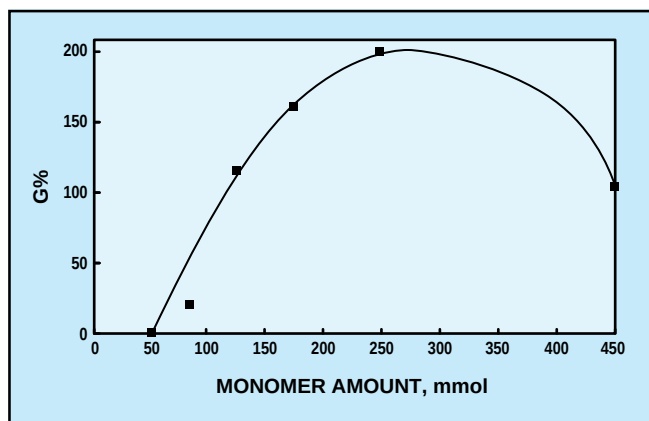
The applicability of grafted copolymers in the paper industry depends strongly on the percent grafting (increase in mass in percent, G%) reached. If this G% is too small, the properties of the paper are not improved sufficiently; if it is too big,

Zara is a student, Erdelyi and Borbély are professor and assistant professor, respectively, Dept. of Paper Industries, Technical College for Light Industry, H-1036 Budapest, Doberdo U. 6, Hungary. Hell and Rusznák are assistant professor and professor, respectively, Dept. of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest, P.O.B. 91, Hungary.

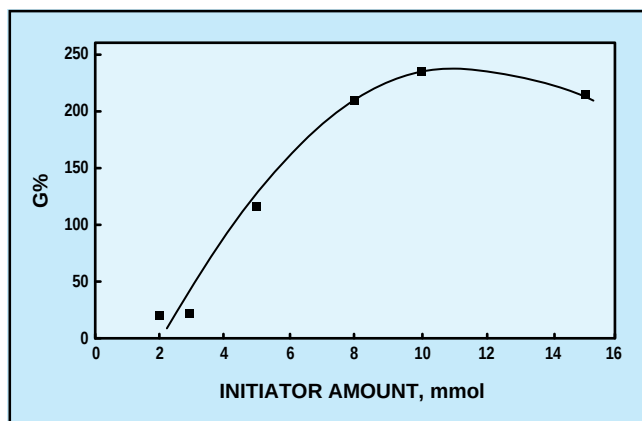
*Present address: Dept. of Plastics and Rubber Technology, Technical University of Budapest, H-1521 Budapest, P.O.B. 91, Hungary.

Cellulose Grafting

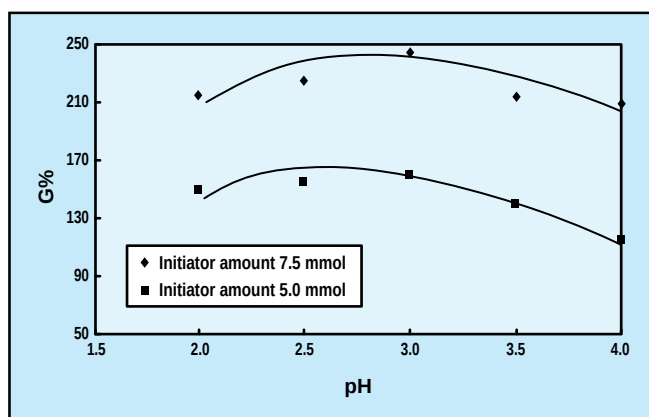
1. Effect of monomer amount on G%



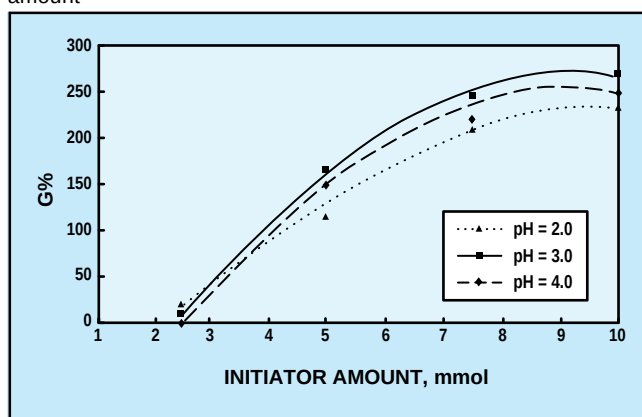
2. Effect of initiator amount on G%



3. Effect of pH on G%



4. Effect of initiator amount and pH on G% at 0.125 mol monomer amount



I. Effect of the monomer amount on G%.

Monomer amount, mol	0.450	0.250	0.175	0.125	0.085	0.050
G%	105	200	160	115	20	0

the pulp becomes unsuitable for papermaking.

G% depends, first of all, on the applied monomer concentration. The change in G% as the function of the monomer amount at a fixed initiator amount is shown by a curve with a maximum peak (Fig. 1). This maximum occurred because over a given concentration the homopolymerization became the preferred reaction among the concurrent reactions. The homopolymer precipitates onto the wall of the reaction vessel in the form of small oily drops. These drops can be observed also on the prepared product. These samples were unsuitable for further exami-

nation. The homopolymer content of some of the samples grafted at and below the optimal concentration was examined with an extraction method described earlier (9) and found to be 10–15%. Because this amount of homopolymer does not affect disadvantageously neither the papermaking properties nor the properties of the resulting paper, this maximum 15% homopolymer content is included in G% in this paper.

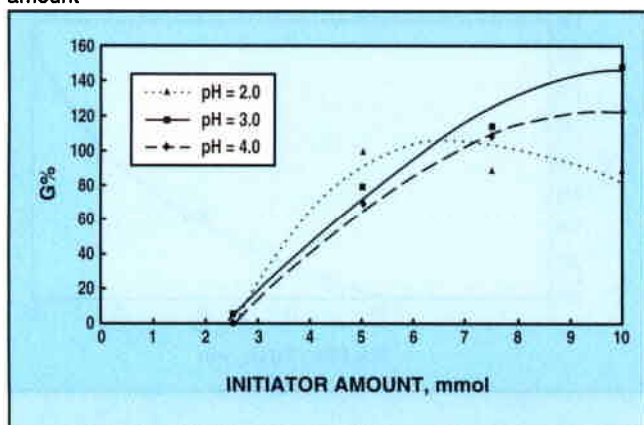
Effect of H₂O₂ concentration on G%

In the aqueous solution of H₂O₂ and vinyl acetate mixture, the fast copo-

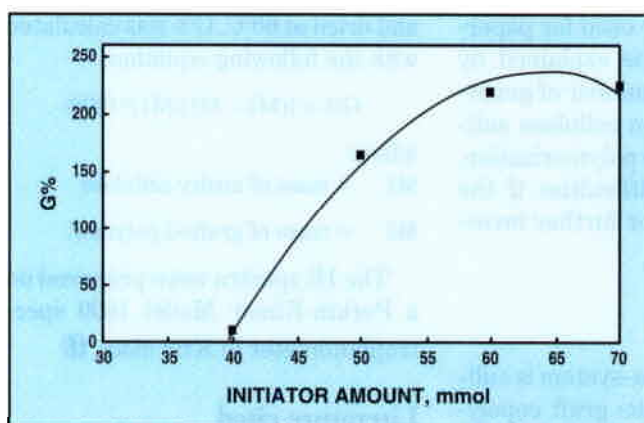
lymerization is initiated by the ·OH radicals formed in the interaction of Fe²⁺ ions and H₂O₂. The mechanism of the formation of these radicals was described by Haber and Weiss (10, 11). The hydroxyl radical is the first to be formed in the reaction of H₂O₂ and Fe²⁺. This radical can initiate the copolymerization or react in a chain process with hydrogen peroxide forming the hydroperoxyl radical which, in the presence of the suitable reactant H₂O₂, decomposes to form the hydroxyl radical again. This mechanism can be described by the following equations:



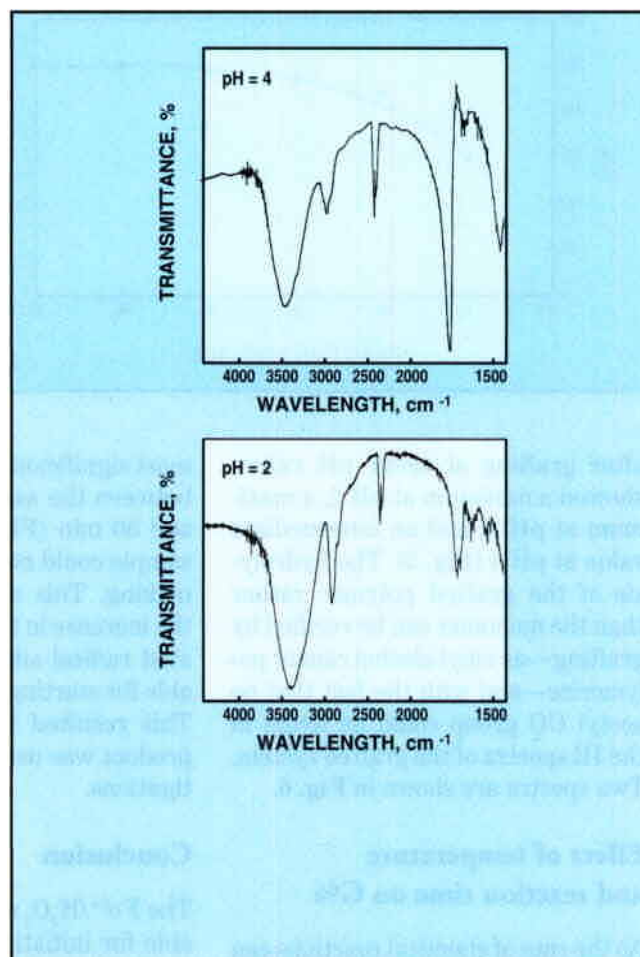
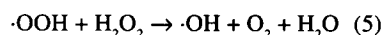
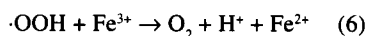
5. Effect of initiator amount and pH on G% at 0.085 mol monomer amount



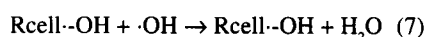
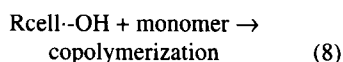
7. Effect of temperature on G%



6. IR spectra of the grafted system



In the presence of cellulose pulp, the $\cdot\text{OH}$ radicals create active centers by abstracting an active hydrogen from the backbone polymer chain, producing a free-radical site capable of initiating copolymerization. This mechanism can be described by Eqs. 7 and 8 (12, 13):



According to this mechanism, grafting occurs simultaneously with the formation of only a small amount

of homopolymer. The $\cdot\text{OH}$ radicals can also initiate the homopolymerization of the monomer, but the growing poly(vinyl)acetate radicals can remove hydrogen radicals from the cellulose backbone at which site vinyl polymerization is initiated. As to the effect of the initiator concentration at the optimal (0.125 mol) monomer amount, G% has decreased over a value of 10.0 mmol (Fig. 2). This tendency can be explained by Eqs. 4 and 6.

Above a critical value of the initiator concentration the amount of OH radicals formed diminishes according to Eqs. 3, 4, and 6, published by Misra *et al.* (9). This, of course, decreases the G% value.

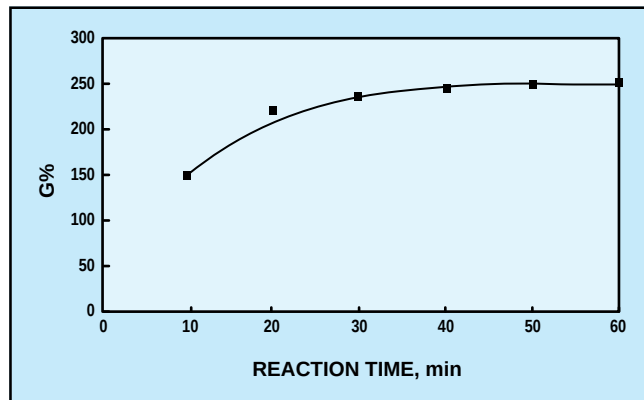
It is known that the binding of Fe^{2+} ions to cellulose pulp depends on the pH of the system (7). If the amount of the adsorbed iron ions is

too high, G% increases during the grafting but the product became yellowish. If, however, the amount of the fixed ions is too small the efficiency of grafting diminishes. At optimal monomer and initiator concentrations, maximum G% could be achieved at pH 3, as shown in Fig. 3.

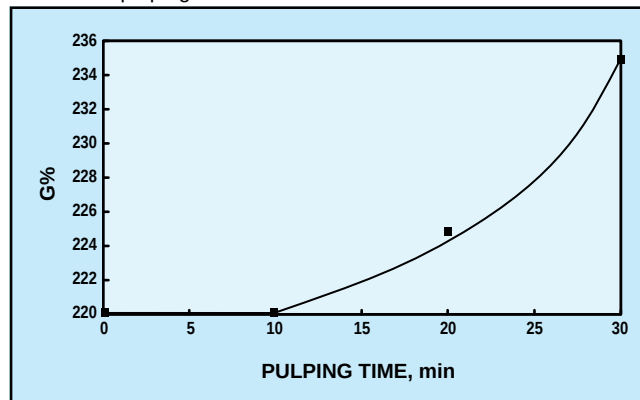
The acidification of the system is advantageous in preventing the yellowing of the product, but at low pH values the poly(vinyl acetate) chains can hydrolyze. The effect of different pHs and initiator concentrations on G% at the values of optimal and lower monomer concentrations is shown in Figs. 4 and 5. So we can establish the minimal monomer concentration at which the hydrolysis has not yet adversely affected G%.

The experimental values are in good agreement with the theoretical considerations. The increase in mass

8. Effect of reaction time on G%



9. Effect of pulping time on G%



after grafting at acidic pH values showed a minimum at pH 2, a maximum at pH 3, and an intermediate value at pH 4 (Fig. 5). The hydrolysis of the grafted polymer rather than the monomer can be verified by grafting—as vinyl alcohol cannot polymerize—and with the fact that no acetyl CO group could be found in the IR spectra of the grafted system. Two spectra are shown in Fig. 6.

Effect of temperature and reaction time on G%

As the rate of chemical reactions can be regulated with variation of temperature, experiments indicated that an increase in temperature had a very strong effect on G% (Fig. 7). At 40°C, there was practically no reaction. Increase in the temperature increased G% dramatically, but the difference between 60 and 70°C was only a few percent. This latter can be explained by the low boiling point (72.3°C) of the monomer. From these results, 60°C can be proposed for the optimal grafting temperature of this system.

As to the time dependence of the grafting reaction, G% increased rapidly in the first 20 min of the process. Longer durations did not significantly improve the efficiency of grafting (Fig. 8).

Grafting copolymerization occurred on the surface of the pulp, so the efficiency of grafting depends strongly on this surface. Increasing the pulping time increased G%. The

most significant difference occurred between the samples pulped for 20 and 30 min (Fig. 9), but the latter sample could not be used for papermaking. This can be explained by the increase in the number of generated radical sites on cellulose suitable for starting the polymerization. This resulted in difficulties if the product was used for further investigations.

Conclusion

The $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ redox-system is suitable for initiating the graft copolymerization of cellulose pulp with vinyl acetate monomer. The parameters for most efficient grafting could be optimized as far as its papermaking suitability is concerned.

Experimental

Vinyl acetate and Mohr-salt were purchased from E. Merck (Darmstadt).

General grafting procedure

Two grams of airdry bleached sulfite pulp cellulose was treated with 100 mL aqueous $6.5 \times 10^{-3} \text{ mol/dm}^3$ $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ solution for 20 min. Sulfuric acid was added to the system to set the appropriate pH, then distilled water was added to the mixture to reach the required total volume of 400 mL. At the appropriate temperature first H_2O_2 was added to the solution dropwise followed by the addition of the monomer into the mix-

ture under vigorous stirring. After 50-min copolymerization the suspension was filtered, washed with water and dried at 60°C. G% was calculated with the following equation:

$$\text{G\%} = \frac{(\text{M}_2 - \text{M}_1)}{\text{M}_1} \times 100\%$$

where

M1 = mass of airdry cellulose

M2 = mass of grafted polymer.

The IR spectra were prepared on a Perkin-Elmer Model 1600 spectrophotometer in KBr discs. 

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