The Xanthate Method of Grafting. XII. Effect of Operating Conditions on the Grafting of Vinyl Monomers onto Wood Pulp

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Synopsis

The present paper examines the influence of various reaction parameters (e.g., pH, type, and concentration of peroxide, reaction time, oxygen as well as reaction medium) on the graft copolymerization of methacrylic acid, butyl methacrylate, epoxypropyl acrylate, and epoxypropyl methacrylate onto chemithermomechanical pulps, initiated by the xanthate method. The optimum concentration of H_2O_2 changes with the monomer used. Among the peroxides investigated, H_2O_2 offered the best performance. Oxygen and organic solvents, e.g., acetone and vegetable oil, inhabited grafting reaction. In addition, epoxy monomers showed better results compared to other monomers; this may be due to the participation of epoxy groups in the polymerization reaction.

INTRODUCTION

The xanthate method of grafting has already been acknowledged as one of the most practical methods of introducing thermoplastics into cellulosics.[1-4] Similar to other chemical-induced methods, the xanthate method of graft copolymerization is influenced by experimental conditions,[5-10] e.g., pH, concentration of hydrogen peroxide and monomer, reaction temperature and time, etc. A variety of monomers have been grafted into cellulosics, but the grafting of epoxy monomers is known to be very efficient.[11,12] Unfortunately, the detailed study of these monomers is very limited.

In the present investigation, various factors, for example, pH, reaction time, type and concentration of peroxide, influence of oxygen and additives on the grafting of epoxy monomers [e.g., epoxypropyl acrylate and epoxypropyl methacrylate onto chemithermomechanical pulp (hardwood-aspen)], have been examined. In order to compare the grafting ability of epoxy monomers, two other monomers, e.g., methacrylic acid and butyl methacrylate, were also used.

EXPERIMENTAL

Materials

Pulp. Chemithermomechanical pulp (CTMP), hardwood-aspen (Populus Tremuloides Michx) was used as the substrate. The pulp was prepared in a Sund Defibrator: temperature, 126°C; retention time, 5 min; pressure, 0.12

MPa; refining energy, 5.26 MJ/kg; Na_2SO_3, 5%; NaOH, 5%; pH, 12.9. The properties of such fibers are: yield, 92%; lignin, 17.9%; average fiber length, 0.75 mm; drainage index, 119; breaking length, 4.46 km; tear index, 7.2 mN m^2/g.

Monomer. Butyl acrylate (BA; Eastman Chemical Grade) was distilled in a column filled with copper rings. The center cut was collected and stored in a refrigerator. Other monomers, e.g., methacrylic acid (MAA), epoxypropyl acrylate (EPA), and epoxypropyl methacrylate (EPMA) (supplied by Polysciences Inc.) as well as all other reagents, were employed as supplied by the manufacturers.

Method

Generally, 4.54-g pulps (oven-dried weight and corrected for solubility in 0.75N NaOH) were partially mercurized at 25°C for 45 min in 150 mL 0.75N NaOH. The resulting pulps were filtered, washed, and kept under CS_2 vapor for 2 h at 25°C. After the xanthation was over, the pulps were washed with 300 mL of acidified distilled water (pH, 4.5), followed by an ion exchange for 2 min in 250 mL solution of 0.006% ferrous ammonium sulfate and finally washing with 300 mL of distilled water (pH, 6.5).

For copolymerization, the pulps were impregnated in a solution of surfactant (Tween-80), 0.9 g (or 1/10 of monomer weight), distilled water, 212 mL (or an equivalent amount of water additive or only an additive, e.g., acetone) for 15 min, and then a few drops of 0.1N H_2SO_4 (to adjust the pH 4.5 or 7.0) and H_2O_2 (concd, 30%) or other peroxides, 6 g/L (unless specified) were added. In most of the cases, dissolved air of the mixture was displaced by N_2 and the reaction was allowed to proceed at 25°C for 1.5, or 19 h. After the desired time had elapsed, the resulting polymerization mixtures were filtered and washed with water. The polymerization became complete by treating the products with 1% $K_2S_2O_5$ solution for 5 min and, finally, washed and dried in an oven (60°C) for 24 h.

The homopolymer of methacrylic acid was removed by boiling in water for 8 h, while the homopolymers of other monomers were removed by Soxhlet extraction with acetone during the same amount of time. The grafting parameters were calculated as follows: polymer loading (%), $[(A - B)/(B)] \times 100$, grafting efficiency (%), $[(A - B)/(D - B)] \times 100$, and degree of conversion (%), $[(D - B)/(C)] \times 100$, where A is the weight of the product after copolymerization and extraction, B the weight of pulp C the weight of the monomer charged, and D the weight of the product after copolymerization.

RESULTS AND DISCUSSION

The parameters of graft copolymerization induced by the xanthate method are sensitive to initial pH in the reaction medium. The optimum pH also varies according to the nature of the monomer, e.g., for methacrylic acid[6] it is ~ 1,0, while for other monomers[8,9] it generally varies from 5 to 7. In order to investigate the effect of pH on grafting parameters of acrylate monomers, e.g., butyl methacrylate, epoxypropyl acrylate, and epoxypropyl methacrylate, the grafting reaction was carried out at pH 4.5 and 7. The results of the experiment are illustrated in Table I. Most of the grafting parameters, except

TABLE I
Effect of Initial pH on Grafting Parameters[a]

	Grafting parameters[b]								
pH	Butyl methacrylate (BMA)			Epoxypropyl acrylate (EPA)			Epoxypropyl methacrylate (EPMA)		
	X	Y	Z	X	Y	Z	X	Y	Z
4.5	127.0	66.7	94.3	163.7	99.2	81.7	152.3	97.0	77.8
7.0	119.8	64.2	92.4	141.2	99.6	70.3	122.8	98.5	61.6

[a] Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; H_2O_2, 6 g/L; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

[b] X = polymer loading (%); Y = grafting efficiency (%); Z = degree of conversion (%).

grafting efficiency of EPA and EPMA, decreased with the increase in pH from 4.5 to 7. During other experiments, the pH was maintained at 4.5.

The results presented in Figures 1–4 show the effect of H_2O_2 on the grafting parameters of MAA, BMA, EPA, and EPMA, respectively. Figure 1 shows that both polymer loading and degree of conversion increase at the beginning (i.e., up to 12 g/L) along with that of the H_2O_2 concentration, and then decrease. Grafting efficiency, for its part, remains constant. This observation is quite consistent with what was observed by El-Rafie et al.[6] during the grafting of the same monomer onto cotton fabric. At a lower concentration level of H_2O_2, the hydroxyl free radicals (produced by the reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot$) were mainly utilized to initiate a grafting reaction through the formation of cellulose macroradicals. But, at relatively higher concentrations, the hydroxyl free radicals also took part in termination and/or oxidation to inactive growing grafting chains.[7]

Once again, when one examines Figures 2–4, one sees that the grafting efficiencies of other monomers are more or less constant, much in the same way as MAA. Polymer loading decreases considerably, while the degree of conversion decreases to a small extent accompanied by an increment in the
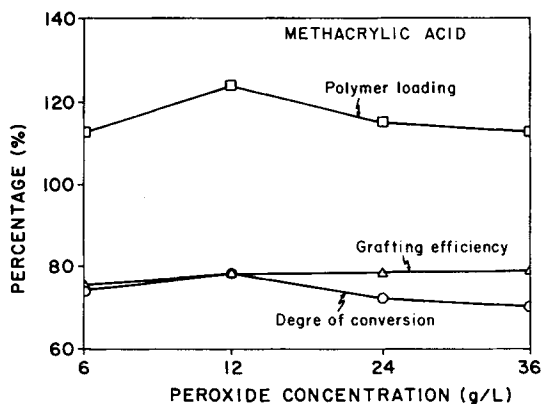

Fig. 1. Effect of the hydrogen peroxide concentration on grafting parameters of methacrylic acid. Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; F.A.S., 0.006%; time, 19 h; temperature, 25°C.
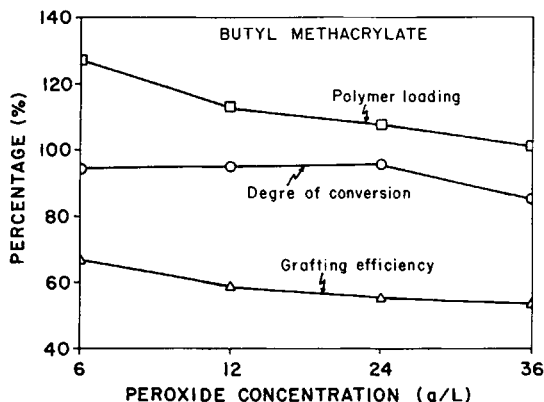
Fig. 2.   Effect of the hydrogen peroxide concentration on grafting parameters of butyl methacrylate. Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

concentration of H_2O_2. Daneault and Kokta[13] reported similar results for the grafting of methyl methacrylate onto the same substrate. In the present case, the difference in optimum H_2O_2 concentration to show the maxima of grafting parameters of monomers can be explained by the higher solubility of MAA in an aqueous medium compared to less solubility of hydrophobic monomers, such as BMA, EPA, and EPMA. The optimum concentration of H_2O_2 was believed to be 6 g/L.

Table II presents a comparative study of different organic peroxides, e.g., di-t-butyl, benzoyl, and lauroyl with H_2O_2 when EPMA was used as a monomer. It is obvious from the table that most of the organic peroxides show inferior results compared to H_2O_2. This can be explained by the fact that H_2O_2 is highly soluble while the peroxides are not. In order to justify this statement, one of the organic peroxides, e.g., lauroyl, was transformed into a solution by preparing an emulsion. Emulsion was reached by heating the peroxide with an emulsifier, Tween 80, and water. The results of this experi-
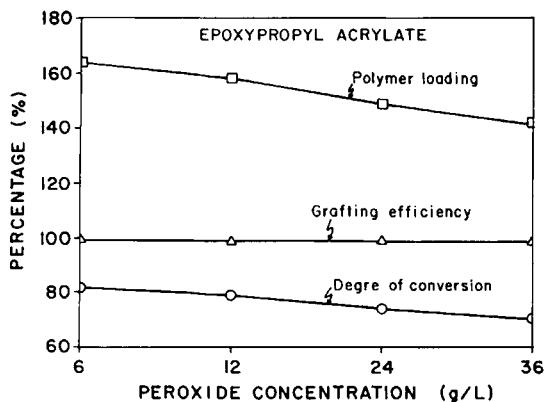

Fig. 3.   Effect of the hydrogen peroxide concentration on grafting parameters of epoxypropyl acrylate. Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; F.A.S., 0.006%; time, 19 h; temperature, 25°C.
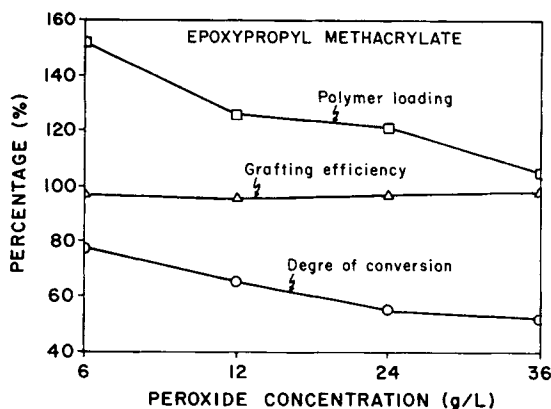
Fig. 4. Effect of the hydrogen peroxide concentration on grafting parameters of epoxypropyl methacrylate. Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

ment also appear in Table II. By using peroxy emulsion, all of the grafting parameters are improved, e.g., polymer loading from 116.0% to 138.1%, grafting efficiency from 82.7% to 90.0% and degree of conversion from 69.5% 76.4%. Furthermore, the decomposition of organic peroxide used to generate free radical centers at such a low temperature, such as 25°C, is not efficient in comparison to H_2O_2.

Table III illustrates the grafting parameters of MAA, EPA, and EPMA, when reaction time was varied (1.5 and 19 h). There was a slight rise in the grafting parameters associated with the reaction time. In fact, the difference is negligible compared to the time difference between 1.5 and 19 h. There is enough evidence[8,9] that rapid polymerization takes place during the first 2 h of reaction. Then, the rate of polymerization initiated by the xanthate method either increases to a small extent or settles to a rather constant level.

From Tables I and III as well as from Figures 1–4, if one compares the grafting parameters of epoxy monomers to those of other monomers, it clearly appears that the former type of monomers provides superior results. Better performance of epoxy monomers can be explained by the fact that epoxy

TABLE II
Effect of the Nature of Peroxide on Grafting Parameters of Epoxypropyl Methacrylate (EPMA)[a]

Nature of the peroxide	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
Hydrogen	152.3	97.0	77.8
Di-t-butyl	110.9	96.0	57.2
Benzoyl	130.7	79.9	1.0
Lauroyl	116.0	82.7	69.5
Lauroyl-emulsion	138.1	90.0	76.4

[a] Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; peroxide, 6 g/L; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

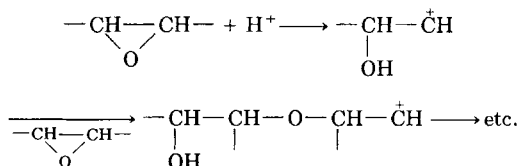| Reaction time (h) | Grafting parameters[b] | | | | | | | | |
	Methacrylic acid (MAA)			Epoxypropyl acrylate (EPA)			Epoxypropyl methacrylate (EPMA)		
	X	Y	Z	X	Y	Z	X	Y	Z
1.5^c	108.8	82.8	65.1	142.7	99.1	71.3			
19.0^c	112.6	75.1	74.2	163.7	99.2	81.7			
1.5^d							101.3	97.4	50.7
19.0^d							105.6	98.8	52.9

[a] Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; F.A.S., 0.006%; temperature, 25°C.
[b] X = polymer loading (%); Y = grafting efficiency; Z = degree of conversion (%).
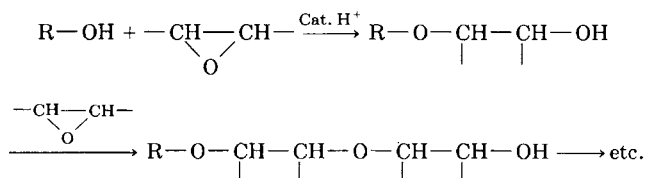[c] H_2O_2, 6 g/L.
[d] H_2O_2, 36 g/L.

groups in an acidic medium can polymerize as follows[14]:

$$-CH\overset{\diagdown O \diagup}{-}CH- + H^+ \longrightarrow -CH-\overset{+}{C}H \atop OH$$

$$\xrightarrow[-CH\overset{\diagdown O \diagup}{-}CH-]{} -CH-CH-O-CH-\overset{+}{C}H \longrightarrow etc. \atop \quad OH$$

In addition, the copolymerization of epoxy groups with an OH group in the presence of an acid catalyst cannot be ruled out.[15] As a result, OH groups of cellulose and lignin molecules of nonbleached wood fibers can react with the epoxy group in the following way:

$$R-OH + -CH\overset{\diagdown O \diagup}{-}CH- \xrightarrow{Cat.\ H^+} R-O-CH-CH-OH$$

$$\xrightarrow[-CH\overset{\diagdown O \diagup}{-}CH-]{} R-O-CH-CH-O-CH-CH-OH \longrightarrow etc.$$

where R—OH represents cellulose or lignin molecules. Due to the possibility for the epoxy groups (aside from vinyl groups) to participate in the polymerization reaction, epoxy monomers show better results compared to ordinary monomers.

Similar to the effect of pH, the dissolved gas in the grafting medium plays an interim role in controlling the grafting parameters.[5,10] Unlike other initiator systems, the hypothesis according to which a special (inert) atmosphere is required in the xanthate method is true only for certain monomers, while, for others, the presence of O_2 either does not hamper the polymerization at all or accelerates it. The effect of O_2 on the grafting parameters of EPMA is shown in Table IV; the grafting reaction was conducted in the presence of air and in a nitrogen atmosphere. It is observed from the table that polymerization reaction is enhanced tremendously: For example, polymer loading, from 2.2% to 105.6%; grafting efficiency, from 47.5% to 98.8%; degree of conversion, from

TABLE IV
Effect of Oxygen on Grafting Parameters of Epoxypropyl Methacrylate (EPMA)[a]

Nature of gas	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
Air	2.2	47.5	2.5
Nitrogen	105.6	98.8	52.9

[a] Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; H_2O_2, 36 g/L; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

TABLE V
Effect of Additions on Grafting Parameters of Epoxypropyl Methacrylate (EPMA)[a]

Solvent	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
Water	152.3	97.0	77.8
Water + vegetable oil (4.0 g/L)	128.9	90.8	70.3
Acetone	6.9	83.8	4.1

[a] Reaction conditions: pulp, 4.54 g; monomer, 9.08 g; pH, 4.5; H_2O_2, 6 g/L; F.A.S., 0.006%; time, 19 h; temperature, 25°C.

2.5% to 52.9%, when a nitrogen atmosphere is used. This observation is in good agreement with what was reported by Hornof et al.[5] for other monomers, e.g., acrylamide and methacrylic acid. In order to get an appreciable amount of graft copolymer, dissolved air in the reaction medium for the entire study was displaced by pursing with nitrogen gas.

Solvents, especially organic ones, sometimes constitute a useful media for graft copolymerization.[4,8,16] Table V shows the comparative data of epoxypropyl methacrylate, when three different reaction media, e.g., water, water + vegetable oil (4 g/L), and acetone, were used. It is obvious that all grafting parameters were reduced symmetrically when vegetable oil was added to water. On the other hand, a drastic reduction in polymer loading and degree of conversion was recorded when water was completely replaced by acetone. The chain transfer caused by these solvents might be the cause of such a shrrp decrease in grafting parameters. Hornof et al.[8] also studied the effect of different solvents, e.g., acetone and alcohols from methanol to t-butanol, on the grafting of acrylinitrile onto wood pulp using the xanthate method. Our result is consistent with their observations. Therefore, the use of solvents, such as vegetable oil or acetone other than water, is not at all beneficial so far as the xanthate method is concerned.

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