Polymer Bulletin 20, 137–141 (1988)

Polymer Bulletin

Grafting of vinyl monomers onto wood fibers initiated by peroxidation

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Summary

The oxidation of chemithermomechanical (aspen) pulp with ruthenium tetroxide followed by peroxidation with hydrogen peroxide was performed to study the graft copolymerization of methacrylic acid, epoxypropyl acrylate and epoxypropyl methacrylate. For epoxy monomers, lower pH (i.e. <5) is more favorable due to the participation of the epoxy group in the grafting reaction in acidic medium. Moreover, the grafting of epoxy monomers appeared more efficient than methacrylic acid.

Introduction

Direct oxidation of the cellulose backbone by chemical means, e.g. by ozone or by H_2O_2 with the formation of peroxides, or carbonyl, or carboxyl groups, is well known(1-4). An alternative method of oxidation of cellulose using ruthenium tetroxide has scarcely been studied (5,6). Daneault, Kokta and Cheradame(6) extensively studied the grafting of acrylamide and acrylonitrile onto bleached Kraft softwood pulp using this method. They also compared the results with the xanthate method of grafting and showed that the latter method provided better results with acrylonitrile, while the reverse was observed with acrylamides. In the present study, the effect of certain parameters, e.g. pH, reaction time and concentration of monomer on grafting parameters of methacrylic acid (MAA), epoxypropyl acrylate (EPA) and epoxypropyl methacrylate (EPMA) onto non bleached chemithermomechanical pulp (CTMP) of hardwood aspen, has been investigated.

Experimental

Materials

Non bleached chemithermomechanical pulp (CTMP) aspen was used as the substrate. Preparation and properties of the pulps were discussed elsewhere(7).

The monomers, methacrylic acid (MAA), epoxypropyl acrylate (EPA) and epoxypropyl methacrylate (EPMA) were supplied by Polyscience Inc., USA. The monomers and other chemicals employed in this study were used as supplied by manufacturers.

Method

The oxidation (5,6) of pulps was carried out by the treatment of 10 g of pulps with a 150 ml solution of NaOCl (0,5% of Cl_2) containing 10 mg of $RuCl_3$ (1 mg/g of pulp) at ambient temperature and with occasional agitation, for 60 min. The resulting oxidized pulps were allowed to react with a mixture of 40 ml of concentrated H_2SO_4 and 200 ml of H_2O_2 (35%) at 25°C for 3 hours. The pulps were washed thoroughly with distilled water at 4°C.

The dry peroxidized pulp was presoaked with a mixture of 50 ml of distilled water, 0,9 g of Tween 80 and 10/20 g of monomer and, after 15 minutes, 350 ml of ferrous ammonium sulfate solution (0,001 M) was added. The initial pH of the mixture was adjusted to 3/5 (with 0,1 N H_2SO_4) and stirred gently. The temperature of the reaction was maintained at 60 + 0,5°C. The reaction was allowed to proceed for 60 minutes or 90 minutes. The polymerization mixture was finally filtered and washed with water. The polymerized pulps were dried at 50°C for 4 h. The homopolymer of methacrylic acid was removed after boiling with water for 8 hours, while the homopolymers of other monomers were removed by Soxhlet extraction with acetone for the same number of hours.

Grafting parameters were calculated as follows: polymer loading, %: [(A-B)/(B)]x100; grafting efficiency, %: [(A-B)/(D-B)]x100; degree of conversion, %: [(D-B)/(C)]x100, where A is the weight of the product after copolymerization and extraction; B the weight of pulp; C the weight of monomer charged; and D the weight of the product after copolymerization.

Results and Discussion

It is well known that pH plays an important role in graft copolymerization. In order to find out the effect of pH, the graft copolymerization of EPA and EPMA was carried out at pH 3 and 5. The results are shown in Table 1.

The reaction time of the two sets of experiments is also simultaneously varied, e.g. 60 minutes and 90 minutes. It is worth while to mention that Daneault, Kokta and Cheradame(6) studied the effect of reaction time for the grafting of acrylamide using the same initiator method. They reported that rapid polymerization takes place during the first 15 minutes of the reaction and, after about 30 minutes, the system was no longer active. Furthermore, there is only a

Table 1

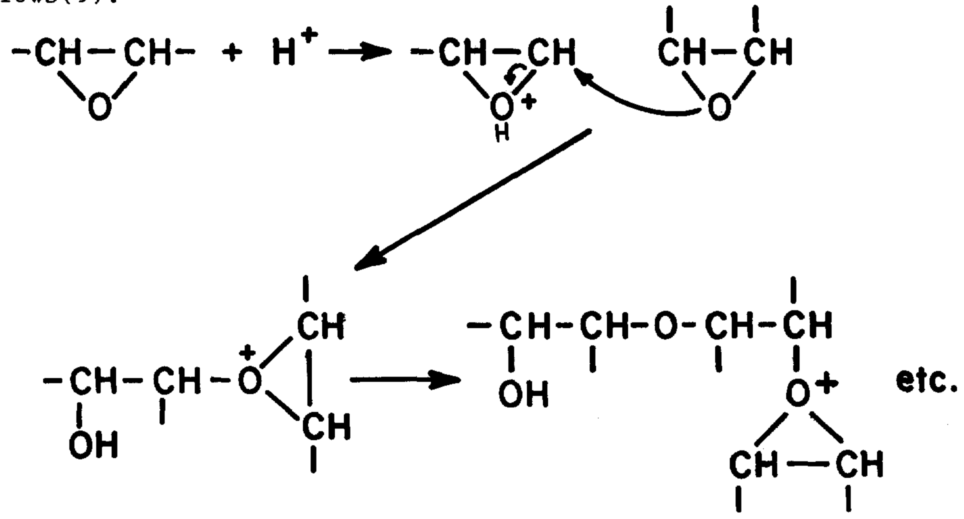
Effects of pH, reaction time and nature of monomer on grafting

Nature of the monomer	pH	Reaction time (min)	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
Epoxypropyl acrylate (EPA)	3	90	39,0	98,1	39,8
	5	60	42,7	98,1	21,8
Epoxypropyl methacrylate (EPMA)	3	90	81,3	94,4	86,1
	5	60	68,6	95,5	71,8

Reaction conditions: Cellulose peroxide, 10 g (oven-dry weight); monomers, 10 g; temperature, 60°C.

negligible difference between grafting parameters under two reaction times, e.g. 60 minutes and 90 minutes.

Thus, avoiding the contribution of yield for 30 minutes difference between the two sets of reactions and if only the effect of pH is considered, one finds that grafting efficiency is not modified with the change in pH (Table 1). But, when we consider the degree of conversion, one easily observes that the degree of conversion decreases at a higher pH level. Again, considering the polymer loading, one can say the same trend is followed for EPMA. Unfortunately, for EPA, the polymer loading at pH 5 is only slightly above that at pH 3. The optimum pH range for other monomers undergoing the same initiation (6) (or another initiation' (8) is 5-7. The polymer loading and degree of conversion should increase with pH from 3 to 5. The anomalous results in the present case can be explained by the reactivity of the epoxy group om a stronger acidic medium. It is believed that in the presence of a strong acid, the epoxy group can polymerize as follows(9).



The pH range 5-7, which is known(10) as being the most favorable one for maximum adsorption of ferrous ions onto the functional group, is a common phenomena for all sorts of vinyl groups. But the reactivity of the epoxy group to accept another epoxy group is enhanced at lower pH (i.e. in a stronger acidic medium). The competition of the two pH dependant reverse reactions may lead to slightly higher polymer loading, % of EPA at pH 5.

Again from the same table, if one compares the results of two monomers, it is clear that grafting efficiency of EPA is higher than EPMA. It is quite natural, because grafting efficiency decreases with the increase of branching of the acrylate monomers(11). This decreased reactivity of the acrylate radicals may be due to the steric and polar effects. Polymer loading and the degree of conversion are higher in the case of EPMA. In this context, it is worthwhile to note the explanation of Varma et al.(12) according to which since acrylate has more branched chains, e.g. methyl methacrylate, offers a relatively stable polymer radical compared to the more reactive methacrylate.

Table 11 shows the effect of the amount of monomer on grafting parameters of methacrylic acid.

Table 11

Effects of the monomer concentration and nature of monomer on grafting

Nature of the monomer	Ratio of monomer:pulp	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
Methacrylic acid (MAA)	1:1	12,2	58,7	20,7
	2:1	34.8	72,2	24.1
Epoxypropyl acrylate (EPA)	2:1	110.5	98,7	56,0
Eproxypropyl methacrylate (EPMA)	2:1	173.5	97,7	88.3

Reaction conditions: Cellulose peroxide, 10 g (oven-dry weight); monomers, 10 g and 20 g; pH, 3; reaction time, 60 min; temperature, 60°C.

All grafting parameters increase with the rise in the monomer and polymer ratio from 1:1 to 2:1. At a higher monomer concentration level, grafting parameters increase due to the gel effect, which is more pronounced at higher monomer concentrations. The formation of a complex between the initiator, cellulose and the monomer cannot be ruled out(13). The larger the concentration of monomer, the more favored will be the formation of a complex which will trigger the grafting process.

Grafting parameters of EPA and EPMA at a higher monomer level, polymer ratio, e.g. 2:1, and under identical experimental conditions as that of MAA, appear in Table 11. It is obvious from this table that EPMA shows the best results while EPA leads MAA in as much as polymer loading and conversion are concerned. This is quite consistent with the previous discussion according to which methacrylic acid without the epoxy group provides inferior results. In addition, this supports the suggestion that the epoxy group takes part in the grafting reaction. Incidentally, Harris and Arthur(14,15) studied the grafting of EPMA onto cotton fibers using a photo induced method and showed that grafting of such monomer was very efficient. It is therefore recommended to select a monomer with a epoxy group.

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Accepted June 9, 1988 K