

Graft Copolymerization of Acrylic Acid onto Cellulose: Effects of Pretreatments and Crosslinking Agent

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ABSTRACT: The graft copolymerization of acrylic acid (AA) and 2-acrylamido 2-methylpropane sulfonic acid (AASO₃H) onto cellulose, in the presence or absence of crosslinking agent *N,N'*-methylene bisacrylamide (NMBA), by using different concentrations of ceric ammonium nitrate (CAN) initiator in aqueous nitric acid solution at either 5 or 30°C was investigated. To investigate the effect of pretreatment of cellulose on the copolymerization, before some grafting reactions cellulose was pretreated with either 2 or 20 wt % NaOH solutions or heated in distilled water/aqueous nitric acid ($2.5 \times 10^{-3} M$) at 55°C. To determine how the excess of initiator affects the grafting and homopolymerization, separate reactions were carried out by removing the excess of ceric ions by filtration of the mixture of initiator solution and cellulose before the monomer addition. Extraction-purified products were characterized by grafting percentage and equilibrium swelling capacity. Pretreatment of cellulose with NaOH solutions decreased the grafting percentage of copolymers. In the case of AA–AASO₃H mixtures, nonpretreated cellulose gave a higher grafting percentage than NaOH-pretreated cellulose. Filtration also lowered the grafting of AA on the cellulose in the cases of pretreatment with either water or nitric acid. Copolymers with the highest grafting percentage (64.8%) and equilibrium swelling value (105 g H₂O/g copolymer) were obtained in grafting reactions carried out in the presence of NMBA at 5°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2267–2272, 2001

Key words: cellulose; graft copolymerization; acrylic acid; 2-acrylamido 2-methylpropane sulfonic acid; *N,N'*-methylene bisacrylamide

INTRODUCTION

Cellulose is cheap, renewable, biodegradable, and is the most abundant organic raw material in the world. Research on cellulose graft copolymers, produced by copolymerization of various vinyl monomers onto cellulose and their applications, has been carried out for the past several decades.^{1,2} Depending on the chemical structure of the monomer grafted onto cellulose, graft copoly-

mers gain new properties such as, hydrophilic or hydrophobic character, improved elasticity, water absorption, ion-exchange capabilities,^{3,4} and heat resistance.^{2,5–8} These copolymers are finding applications for water treatment in the textile industry, for reclaiming ions of precious metals, and for personal care products such as infant diapers and feminine hygiene products.^{2,10,11} In the graft copolymerization of vinyl monomers onto cellulose, radical sites are generated on the cellulose backbone either by various chemical initiators or by radiation. After Mino and Kaizerman¹² grafted various vinyl monomers such as acrylamide, acrylonitrile, and methyl methacrylate onto poly(vinyl alcohol) by using Ce⁴⁺ initiator, various vinyl

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monomers were grafted onto cellulose by direct oxidation with this initiator.^{13–15} Among the various redox-type initiators, Ce^{4+} has gained great importance because of its high grafting efficiency.¹⁶ In the grafting of vinyl monomers onto cellulose by Ce^{4+} initiator, the mechanism of the initiation reaction is highly complex. In the initial step of the reaction, a complex between cellulose and Ce^{4+} ions, which is followed by the oxidation of cellulose,^{2,17–20} is formed. Hydrogen abstraction from a carbon atom-carrying hydroxyl group is also considered to be a likely mechanism in the initiation of graft copolymer formation.¹² Guzman et al.^{21,22} observed that graft yield and graft efficiency increased and homopolymer formation decreased when the excess of Ce^{4+} initiator was removed in grafting of mixtures of vinyl acetate–methyl acrylate monomers onto cellulose by filtration after a given contact time of cellulose and Ce^{4+} initiator. Fanta et al.^{23,24} showed that the water absorption capacity of acrylonitrile + 2-acrylamido 2-methyl propane sulfonic acid-grafted starch increased fivefold in the grafting of acrylonitrile containing 1–10 mol % 2-acrylamido 2-methyl propane sulfonic acid.

Because many graft copolymerization reactions of cellulose are carried out in aqueous and heterogeneous media, and because the intercrystalline swelling of cellulose by water occurs mainly on the accessible or amorphous regions of cellulose, the diffusion of monomer and the grafting reaction is probably restricted to these regions.^{1,2} The grafting efficiency can be increased by increasing the ratio of cellulose/monomer either by swelling the cellulose before the reaction or by performing the grafting reaction in a medium in which cellulose swells. Therefore, Okieimen²⁵ and Stannet et al.^{26,27} decrystallized the graft copolymers by treatment with 70 wt % $ZnCl_2$ solution, after grafting of acrylic acid onto cellophane and rayon by γ -radiation of ^{60}Co . These investigators also observed that the decrystallization of graft copolymers with $ZnCl_2$ solution alone was not enough to improve the absorbency of graft copolymers and decrystallization of the copolymer must be carried out in both $ZnCl_2$ solution and NaOH solution.

In this work, we examined the influence of pretreatment of cellulose, removal of excess Ce^{4+} initiator, and the presence of comonomer AASO₃H and crosslinking agent NMBA on some properties of polyacrylic acid-grafted cellulose copolymers. For some reactions, cellulose was pretreated with NaOH solutions at room tempera-

ture before the grafting of monomers AA, AASO₃H, and AA containing 1–10 mol % AASO₃H. The copolymerization experiments in which the excess of initiator was removed by filtration after a given contact time of cellulose and CAN in aqueous solution were performed to investigate the effect of removal of excess initiator. For the investigation of the effects of the structure of the grafted polymer to the properties of graft products, NMBA was used as a crosslinking agent. The effect of the presence of the crosslinking agent NMBA was also investigated in some copolymerization reactions.

EXPERIMENTAL

Chemicals

NMBA, CAN, AASO₃H, nitric acid, dioxane, acetone (Merck, Darmstadt, Germany) and cellulose (Sigma, St. Louis, MO) were used as received. AA monomer was distilled under vacuum and stored at $-8^{\circ}C$ until it was used. Bidistilled and vacuum-degassed water was employed in copolymerization reactions. Nitrogen was purified by passing it through a freshly prepared alkaline pyrogallol solution.

Pretreatment Procedures for Cellulose

The following pretreatment procedures of cellulose were carried out to increase the reactivity of its crystalline regions and to decrease the formation of homopolymer during reaction, before the grafting.

- Cellulose was stirred in NaOH solutions (either 2 or 20 wt %) at room temperature, 24 or 2 h, respectively, and then washed with hydrochloric acid solution (1 wt %) and distilled water.
- Cellulose was stirred in distilled water or aqueous nitric acid ($2.5 \times 10^{-3} M$) for 1 h at $55^{\circ}C$.
- To reduce the homopolymer formation during the copolymerization, cellulose was heated in distilled water/aqueous nitric acid up to $55^{\circ}C$ by stirring, and then kept at that temperature for 1 h. The mixture was cooled to $30^{\circ}C$ and then CAN was added. After stirring 15 min by a magnetic stirrer, the excess of CAN was removed by filtration from the reaction mixture.

Graft Copolymerization

Cellulose (4 g, pretreated or nonpretreated) was added to 320 mL of HNO_3 solution ($2.5\text{--}17.5 \times 10^{-3} \text{ M}$) in a three-necked flask, then stirred and purged by passing nitrogen for 30 min. CAN ($2\text{--}4 \times 10^{-3} \text{ M}$) and monomers in various concentrations of AA ($0.21\text{--}1.25 \text{ M}$); AA + AASO_3H (0.85 M , containing 1–10 mol % AASO_3H); AASO_3H (0.85 M); and NMBA (0.05–0.1 wt % according to AA monomer) were added into the reaction mixture. The grafting reaction was carried out in a N_2 atmosphere at 5 or 30°C for 5.5 or 3 h, respectively. Then, the reaction was stopped by addition of hydroquinone. The graft copolymer and homopolymer mixture were separated by adding acetone into the reaction medium. The solution was filtered and the precipitated product was washed with acetone, then dried. Dried homopolymer and graft copolymer mixtures were subjected to extraction with dioxane in a Soxhlet apparatus for 40 h to remove the homopolymer.

Analysis Methods

Grafting Percentage Determination²⁸

The grafting percentage was determined by a titration method. The graft copolymer in a 0.1N NaBr solution was titrated with a solution of 0.1N NaOH in the presence of phenolphthalein indicator and calculated from the following equation:

$$\text{Grafting percentage (\%)} = \frac{m_1}{m_2} \times 100$$

where m_1 is the weight of poly(acrylic acid) grafted onto cellulose (in g) and m_2 is the weight of the original cellulose (in g).

Equilibrium Swelling Capacity Determination²⁹

The Na form of graft copolymer obtained by titration of graft copolymer with 0.1N NaOH solution was subjected to swelling by holding it in distilled water at room temperature until equilibrium was reached. Equilibrium swelling values of graft copolymers were determined gravimetrically according to the following equation:

$$\text{Equilibrium swelling value} = \frac{w_3 - w_4}{w_4} \quad (\text{g H}_2\text{O/g copolymer})$$

where w_3 is the weight of the swelled graft copolymer (in g) and w_4 is the weight of the initial graft copolymer (in g).

RESULTS AND DISCUSSION

Figure 1 summarizes the effects of pretreatment procedures applied to cellulose with either 2 or 20 wt % NaOH solutions on the grafting of AA, AA + AASO_3H , and AASO_3H monomers. As seen from the curves in Figure 1, the highest grafting percentages were obtained by grafting of AA or AASO_3H alone and their mixture to nonpretreated cellulose. Therefore, pretreatment of cellulose with different concentrations of NaOH solutions made no improvement on grafting percentages of copolymers. The presence of 10 mol % AASO_3H monomer in the monomer mixture increased the grafting percentage approximately twofold compared to that by grafting of AA alone onto nonpretreated cellulose. Also these pretreatment procedures did not considerably affect the equilibrium swelling capacities of copolymer products.

The grafting percentages of copolymers prepared after pretreatment at 55°C with either distilled water or nitric acid followed by polymerization either after filtration or without filtration of excess CAN initiator are given in Figure 2. Higher values of grafting percentages were obtained without removal of excess CAN initiator. As is known,^{12,13} radical sites on cellulose back-

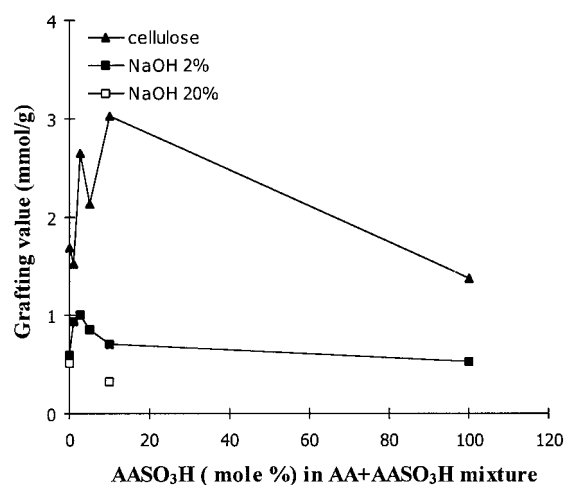


Figure 1 Effect of the pretreatment of cellulose with NaOH solution on the grafting percentage (AA + AASO_3H : 0.85 M ; CAN/HNO_3 : $4.10^{-3} \text{ M}/7.5 \times 10^{-3} \text{ M}$, 30°C , 3 h).

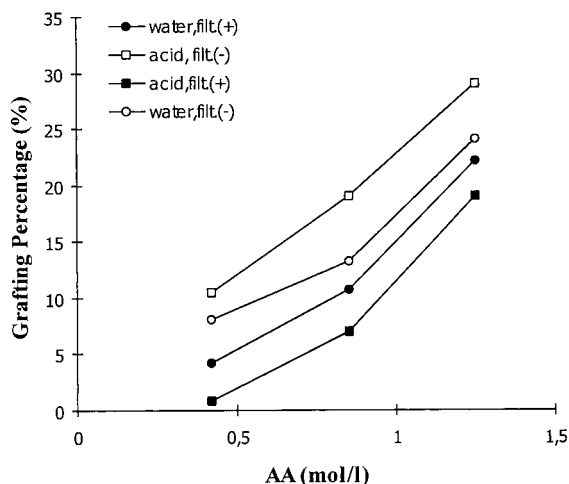


Figure 2 Effect of the removal of the excess initiator after the pretreatment of cellulose in water or aqueous nitric acid ($2.5 \times 10^{-3} M$) on the grafting percentage (CAN/HNO₃: $4.10^{-3} M/2.5 \times 10^{-3} M$, 30°C, 3 h).

bone occur when cellulose and initiator come into contact in the solution. In the grafting reactions without removal of excess initiator, initiator molecules dissolved in the reaction medium continue to form new radical sites on cellulose, leading to higher grafting percentages. In addition to that, homopolymer formation, leading to problems in the purification of copolymer, increased during the copolymerization reaction.

The equilibrium swelling values and grafting percentages of copolymers, as shown in Figure 3, indicate that grafting percentage has little effect

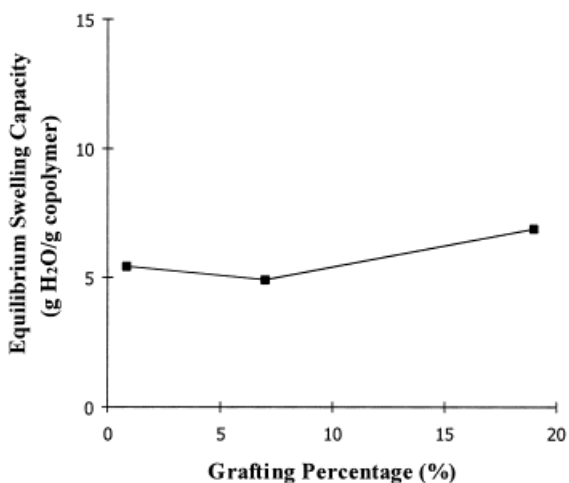


Figure 3 Variation of the equilibrium swelling capacities with the grafting percentages of the copolymer products indicated in Figure 2.

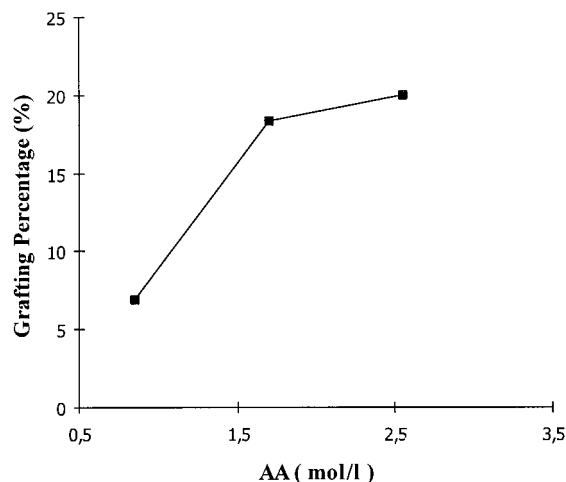


Figure 4 Effect of the monomer concentration on the grafting percentage in the grafting of AA onto nonpretreated cellulose (CAN/HNO₃: $4.10^{-3} M/2.5 \times 10^{-3} M$, 30°C, 3 h).

on the swelling of the polymer. This was also observed in our previous work.³⁰ Polymers having similar grafting percentages but prepared at different temperatures could show very different equilibrium swelling properties. The effect of monomer concentration on the grafting percentage is shown in Figure 4 and indicates a rapid increase in grafting percentage with AA concentration up to 0.85M, which is followed by a region with reduced rate. Because the formation of homopolymers at this high AA concentration increases, the complete removal of homopolymers from graft copolymers becomes difficult because of the high viscosity of the reaction mixture, leading to errors in the determination of grafting percentage. Therefore, working with more concentrated AA solutions was not considered.

The influence of temperature on grafting can be seen in Figure 5. The grafting percentages of copolymers obtained at 5°C for 5.5 h and 30°C for 3 h are about the same. Because the cellulose was heated in aqueous nitric acid before the grafting in these experiments, the equilibrium swelling values of these copolymers are not high, probably as a result of the change in the molecular structure of cellulose during the pretreatment procedure. Variations of grafting percentages and equilibrium swelling values of copolymers obtained from the grafting reaction of AA monomers onto nonpretreated cellulose in the presence of the crosslinking agent NMBA are shown in Figures 6 and 7. As expected,³¹ the presence of the crosslinking agent NMBA generally improved the

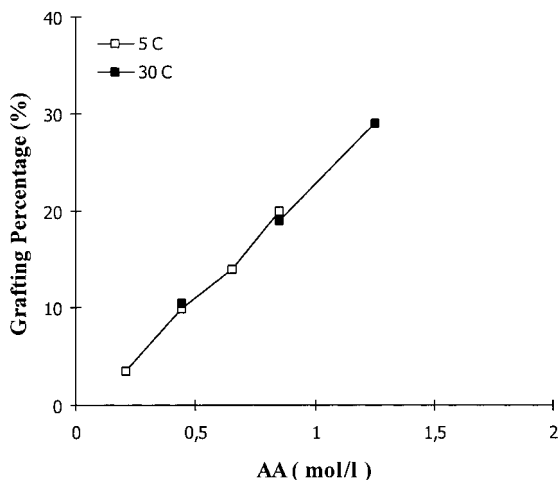


Figure 5 Effect of the grafting temperature on the grafting percentage in the grafting of AA onto cellulose pretreated with aqueous nitric acid (CAN/HNO₃: 4.10⁻³ M/2.5 × 10⁻³ M; 30°C, 3 h; 5°C, 5.5 h).

grafting percentages and values of equilibrium swelling capacity.

CONCLUSIONS

Before the grafting reaction:

1. Pretreatment of cellulose with NaOH solution did not increase the grafting percentage but, contrary to expectations, de-

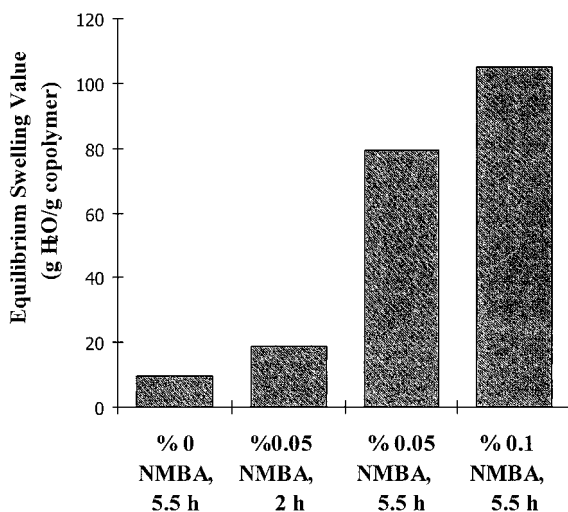


Figure 6 Effect of the crosslinking agent NMBA on the equilibrium swelling capacity in the grafting of AA onto nonpretreated cellulose (CAN/HNO₃: 2.10⁻³ M/17.5 × 10⁻³ M; AA: 0.85M, 5°C).

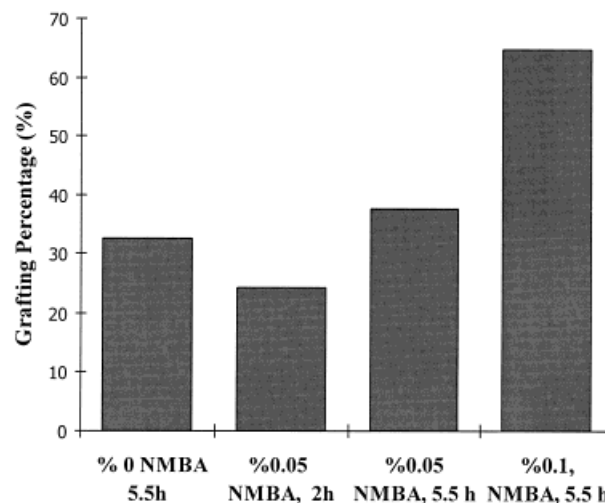


Figure 7 Effect of the crosslinking agent NMBA on the grafting percentage in the grafting of AA onto nonpretreated cellulose (CAN/HNO₃: 2.10⁻³ M/17.5 × 10⁻³ M; AA: 0.85M, 5°C).

creased it. Moreover, pretreatment of cellulose had no improvement on the equilibrium swelling capacities of polymers.

2. In a comparison of pretreatments with either distilled water or aqueous nitric acid, heating in nitric acid, without filtration of the excess of CAN initiator, provided higher grafting.
3. Copolymer products with the higher grafting percentages were obtained with nonpretreated cellulose when the excess of CAN initiator was not removed.

In grafting reactions:

1. Higher AA concentrations gave higher grafting percentages.
2. In the grafting of AA onto nonpretreated cellulose, low-temperature (5°C), longer reaction times gave the same grafting percentages as those at 30°C, shorter reaction times.

The grafting percentage and equilibrium swelling capacity increased both with the presence and with the increase in the concentration of NMBA in monomer mixtures.

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