A Comparison of the Properties of Ceric Ion and Preirradiated Acrylic Acid Grafts to Rayon Fibers

Dedicated to the Memory of the late Professor Ichiro Sakurada

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(Received January 19, 1987)

ABSTRACT: Acrylic acid has been grafted to rayon filaments using both the high energy radiation and ceric ion methods. By using preirradiation and a pretreatment of the cellulose with the ceric salt, homopolymer was reduced to acceptable amounts. A number of properties have been measured on the treated controls without monomer and on the grafted samples. These included tenacities, elongations, initial moduli and work to rupture. The moisture regains and water retention values were also determined. Considering the tensile properties, the pretreatments resulted in a drop in the values except for the initial moduli. Ceric ion initiation produced more degradation than the preirradiation treatment. This was attributed to the additional acidic and oxidative effects in the case of the former method. Grafting with both methods of initiation led to an initial improvement of properties over the treated control values. As the degree of grafting increased, however, the values decreased. In all cases ceric ion gave somewhat lower properties compared with preirradiation. The moisture regains and water retention values showed some rather minor differences between the two types of grafting. Explanations of the various behavior patterns are presented.

KEY WORDS Ceric-Ion / Preirradiation / Grafting / Cellulose / Acrylic Acid / Properties / Sorbency / Tensiles /

Graft copolymerization was first consciously studied in the early nineteen fifties and was immediately extended to cellulose and its derivatives. A large number of methods have been developed over the years for the synthesis of cellulose graft copolymers. These have been well reviewed in the monograph of Hebeish and Guthrie.¹ There is no doubt however that two methods have dominated the field. These are the use of high energy radiation and of ceric ion oxidation to generate free radicals on the cellulose substrate. Contact with the chosen monomer, under a variety of conditions, then leads to excellent yields of graft copolymer.

Acrylic acid-cellulose grafts are of particular interest because of their potential value as

super water absorbents, for ion exchange and a variety of other uses. Acrylic acid is, however, a difficult monomer to graft since it tends to generate large quantities of homopolymer with both methods of initiation. However, the preirradiation method of grafting^{1,2} reduces them to almost zero. The ceric ion method has also been modified³⁻⁵ to yield acceptable amounts of homopolymer. The procedure involves a pretreatment in which the rayon is soaked in the ceric ammonium sulfate solution. This is followed by rinsing in a 90:10 toluene-methanol solution to remove excess ceric salt. The acrylic acid monomer is then added in toluene solution. The hydrated ceric ion has very limited solubility and diffusion into the organic phase essentially preventing

homopolymerization. The monomer solution acts as a reservoir feeding the moist pretreated rayon as grafting proceeds. Grafting yields of up to 65% could be obtained in this way with less than 5% of homopolymer. There have been very few studies comparing the two methods from the point of view of the properties at similar degrees of grafting. This paper will present such a study with a rayon monofilament as the substrate and acrylic acid as the monomer.

EXPERIMENTAL

Material

50 denier rayon monofilaments, approximately 90 μm in diameter and with a roughly circular cross section crenulated were used. These were obtained without added finishes from the American Enka Company.

Acrylic acid (Fisher Scientific Company) was distilled twice before use. All other reagents were from the same supplier and were not further purified.

Experimental Procedure

The preirradiation method used has been described in detail elsewhere.² The samples of rayon were irradiated with 4.0 mrad. at 25°C at a dose rate of 0.16 mrad. per hour under vacuum in a cobalt-60 source. A 75% acrylic acid aqueous solution, previously degassed was then introduced through a break seal. The assemblies were held in a thermostat at 40°C for various times to vary the amount of grafting. The samples were removed, washed in methanol and dried in a vacuum oven. The increase in weight was recorded as the percent "graft." A grafting level of more than 160% could be obtained by this procedure.

The ceric ion method has also been described in detail.⁴ The rayon samples were pretreated for two hours with 0.1 *N* ceric ammonium sulfate solution in 1 *N* sulfuric acid, rinsed with a 10–90 methanol–toluene solution and dried with an air gun. The samples

were then treated under nitrogen with a 1 *N* acrylic acid solution in toluene for various times to yield different percent grafts. They were then washed in methanol, 1 *N* H_2SO_4 , 1 *N* NaOH and water. Percent grafting was expressed as the increase in weight after drying over the initial weight $\times 100$.

Properties

Tensile tests were performed on the rayon monofilament conditioned at 21°C and 65% relative humidity. An Instron Model 1123 coupled with a Microcon I was used with a gage length of 25 mm and a crosshead speed of 10 mm min^{-1} .

Typically 10 specimens were tested and the tensile properties, namely breaking tenacity, elongation at break, initial modulus and toughness were automatically calculated by the computer.

Wet tests were performed after soaking for 5 min in water containing 0.1% Triton X-100 as a nonionic wetting agent.

The linear density was measured using a vibroscope, Insko Co. ASTM procedure D1577 and expressed as denier (grams per 9000 meters length).

Moisture regain values were measured by drying the samples at 50°C for 12 h in a Stabil Therm laboratory oven, weighing, conditioning for 24 h in a standard atmosphere of 21°C and 65% relative humidity, and reweighing.

Water retention values (WRV) were determined by soaking the fibers in distilled water for one hour followed by centrifuging at 1200 grams force for 30 minutes and weighing. The samples were then dried for 24 h at 50°C and reweighed.

The conditioned or the wet weights minus the dry weights divided by the dry weights $\times 100$ were recorded as the moisture regains or the WRV's respectively.

Table I. Tensile properties of grafted samples including the initial values and treated controls

Grafting method	Dry tenacity at break/ g.p.d.		Dry elongation at break/ %		Dry initial modulus/ g.p.d.	
	Ceric	Radiation	Ceric	Radiation	Ceric	Radiation
Initial values	1.93	1.93	31.9	31.9	33.9	33.9
Treated controls	0.59	1.16	2.09	22.3	42.9	22.0
20% graft	1.33	1.57	28.5	31.8	22.2	29.9
40% graft	0.96	1.28	21.1	31.1	21.1	26.3
60% graft	0.69	1.11	7.8	28.1	20.9	24.8

Table I. (continued)

Grafting method	Dry work of rupture/ g.p.d. $\times 10^2$		Wet tenacity at break/ g.p.d.		Wet elongation at break/ %	
	Ceric	Radiation	Ceric	Radiation	Ceric	Radiation
Initial values	82.3	82.3	1.28	1.28	25.5	25.5
Treated controls	0.90	49.4	0.34	0.77	5.38	17.8
20% graft	36.6	55.0	0.57	0.79	32.7	30.8
40% graft	33.1	42.0	0.27	0.48	37.3	33.5
60% graft	4.8	35.0	0.10	0.32	18.9	35.0

RESULTS AND DISCUSSION

Tensile Properties

The tenacity and elongation at break, the initial modulus and the work of rupture were measured as described in the experimental section on both dry and wet samples. The results are presented in Table I for the dry fibers and the tenacity and elongations at break for the wet samples. The initial modulus and the work of rupture values for the wet specimens are not reported due to their small magnitudes.

The values corresponding to the untreated samples, those subjected to the grafting procedure but without monomer, *i.e.*, treated controls, and those corresponding to the 20, 40, and 60% grafts are presented. The latter were taken from the smoothed out property *versus* percent grafting curves. The controls in the case of the radiation samples were taken proportionally from a previous study on similar

rayon monofilaments.

Considering first the treated controls these are most interesting. The tenacities, elongations at break and the works to rupture are severely reduced by the procedure without monomer in the case of the ceric ion method. This is presumably due to the extended acid treatment, plus, perhaps, radical attack and oxidation. As mentioned earlier, the fibers were soaked for 2 h in the ceric ion solution containing 1 *N* sulfuric acid, washed in a toluene-methanol mixture and following grafting, again washed in sodium hydroxide and sulfuric acid solutions and, finally with water.

The preirradiation method also caused reductions in the tensile properties of the treated controls but to a much lesser degree, *e.g.*, 40% reduction compared with 69.5% for tenacity, and 30% reduction compared with 93.4% for the elongation. The latter was found to be particularly low with the ceric ion fibers. Radiation is also known to degrade the cel-

lulose molecules but since only a simple water and methanol wash was used no further degradation was expected from the procedure. The wet tenacities and elongations at break of the treated controls display a similar pattern of behavior but, again, the effects are much less with the radiation treatment.

Curiously the dry initial modulus of the ceric treated control is similar to the initial value falling within the limits of the standard deviation. This suggests that within the limits of the small strain, the stiffness of the fiber is not much affected by the procedure.

The effects of grafting on the dry tensile properties will now be considered. The values at 20% or less are equal or greater than the treated controls but decrease steadily as grafting proceeds further. Compared with the initial values, however, there is a rather sharp drop. The radiation grafted samples all have considerably higher values than those produced by the ceric ion method. Most of the degradation with both methods probably takes place before grafting begins. Presumably the lower amounts of graft copolymer reinforce the weakened structure. Larger amounts are known to disrupt the crystallinity and structure in general causing the observed decrease in the tensile properties.

The wet tenacities at break show similar tendencies as the dry values. The corresponding elongations however increase on grafting and remain high. This can be attributed to the plasticizing effect of the water on the acrylic acid grafted rayon structure. The same effect is also responsible for the lower tenacity values compared with the dry fibers.

Other Properties of the Grafted Fibers

The denier or the linear density and the diameters of the grafted fibers increased with grafting as would be expected. There were no discernable differences between the values of the ceric and the preirradiation grafted fibers.

A number of structural features were also examined.⁵ These included crystalline orien-

tation, crystallinity, molecular orientation and surface morphology, as given by wide angle X-ray diffraction, optical microscopy and scanning electron microscopy (SEM) respectively. A separate paper⁶ discussing these results in detail will be published.⁶ These investigations did show clearly, however, that a greater disruption and degradation of the rayon fibers was caused by the ceric ion method of grafting. These results reinforced the effects of the initial treatment, without monomer, and grafting on the tensile properties discussed in this paper. The SEM studies also revealed that surface grafting was more prevalent with the ceric ion process.

The moisture regains and the water retention values, WRV's were also measured. The results are shown in Figures 1 and 2 for the regains and Figure 3 for the WRV's. The moisture regains decrease somewhat for the unmodified grafts. A reasonable explanation is that the sorption of water is, within the experimental error slightly restricted by the consolidation of the structure by the free acid grafts particularly at the low, 65% relative humidity exposure and after drying. The results are, however, rather unexpected and the regain of such systems at higher RH's would be worth exploring.

Post Graft Decrystallization

It has been shown previously^{2,7,8} that decrystallizing acrylic and methacrylic acid graft copolymers of cellulose and transforming into the sodium salts led to a dramatic increase in both moisture regains and the WRV's. The decrystallizing can be achieved by treatment with a cellulose solvent or strong swelling agent followed by removing, *e.g.* by washing. 70% zinc chloride solution is very effective for many grafts but in the case of the acid grafts hot sodium hydroxide solution was also nearly as useful. A sequential treatment with ZnCl_2 followed by hot NaOH solution was the most effective. A full description and discussion of the decrystallization technique

Figure 1. Moisture regain of the ceric grafted rayon fibers before and after decrystallization with NaOH.

Figure 2. Moisture regain of the radiation grafted rayon fibers before and after decrystallization with NaOH.

Figure 3. Water retention values of ceric and radiation grafted rayon before and after decrystallization with NaOH.

and its effect on the water sorption and retention properties may be found in references 2, 7, and 8.

In this work only hot NaOH treatments were studied. After exploring various conditions a 10% solution at 50°C for one hour was selected as the standard procedure. The effect of this treatment on the moisture regains are included in Figures 1 and 2. There is a considerable increase in the regains with both methods of grafting. The ceric ion grafts are somewhat higher in keeping with the greater disruption of the structure compared with radiation indicated by the tensile and other properties discussed earlier in this paper. The ceric ion samples show regains which tend to level off at higher percent grafting in contrast to the radiation samples which continue to increase at a higher rate as grafting proceeds. The latter would be expected as the grafting is comparatively uniform with preirradiation. As the structure becomes more disrupted, the swelling restraints to the sorption by osmotic forces weaken and a greater increase would take place. The ceric ion method with its bulky initiating entity tends to localize grafting on and closer to the surfaces, as clearly indicated by examination of surfaces under SEM. This, in spite of the degradation effects, could lead to a gradual decrease in sorption as a function of grafting due to restraints imposed presumably by the relatively ungrafted core. Further work would be needed to confirm these suggestions and/or to elucidate other reasons for the differences in behavior.

The WRV's presented in Figure 3 show, within the scatter of the results, rather similar behavior with both techniques used. The water retentions included substantial surface effects which compensate for the rather minor differences in the regain. Detailed discussions of this subject may be found in a recent monograph on the subject.⁹

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