NOTES

Highly Water-Absorptive Cellulose by Postdecrystallization

INTRODUCTION

In an earlier study,[1-3] detailed grafting methods that lead to highly rubberlike elasticity in the case of cellulosic fibers were discussed. A more recent study[4] demonstrated that highly elastic cellulosic fibers could be achieved by a postdecrystallization technique applied to the inelastic grafted fiber. In the present paper, details of rendering cellulosic-based substrates highly water adsorbent will be discussed.

EXPERIMENTAL

A continuous filament, semidull rayon was used in this work. Also, a cellulose film obtained from Sylvania (0.02 mm) was used in the film-grafting study. In both cases, the samples were degassed under a 10^{-6} mmHg vacuum and then irradiated in a cobalt-60 gamma irradiator. Following irradiation, a previously degassed monomer solution was introduced into the sample tube, and the grafting reaction was allowed to proceed for various time periods. After grafting, the samples were extracted in methanol, and the percent graft determined on the basis of the original dry weight of the sample.

Water sorption isotherms were determined by suspending the sample from a sensitive quartz spring (1 mm extension/1 mg load) in a thermostatted vacuum chamber. After evacuation, water vapor was turned into the chamber, and the sample was allowed to equilibrate at that humidity.

Determination of the water absorption under liquid conditions was accomplished in the case of fiber by centrifuging the sample for 1 hr at 600 rpm after it had equilibrated with liquid water. The centrifuge tube had a fine mesh strainer stepped away from the botton of the tube to allow excess water to drain away from the sample. Also, the centrifuge tube was sealed to assure 100% relative humidity in order to prevent desorption of water by the sample. The cellophane samples were simply blotted after soaking in liquid water.

RESULTS AND DISCUSSION

Typical preirradiation grafting curves for the grafting of acrylic acid to cellophane film and rayon are shown in Figures 1 and 2, respectively. The shape of the grafting-time curve shown in Figure

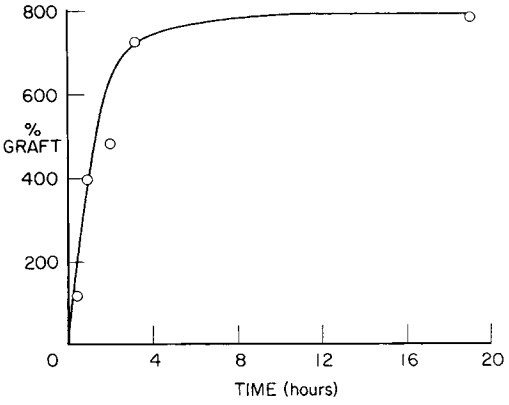

Fig. 1. Preirradiation grafting of 70% acrylic acid to cellophane film (0.02 mm) at 45°C. All samples irradiated to 4.0 megarads.

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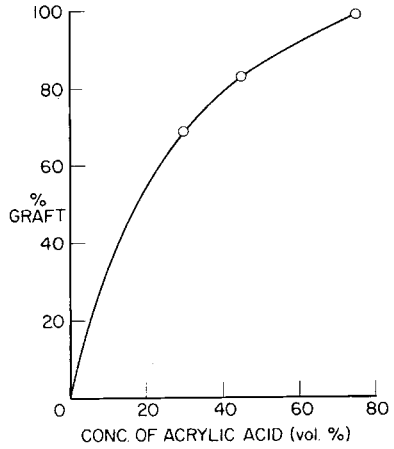

Fig. 2. Preirradiation grafting of acrylic acid to rayon as a function of monomer concentration in water at 45°C. All samples irradiated to 4.0 megarads with grafting times of 24 hr.

1 is not unexpected and has been discussed in detail elsewhere.[2] The effect of monomer concentration shown in Figure 2 is for a reaction time of 24 hr.

In a separate set of experiments, selected grafting levels for both the grafted rayon and cellophane were examined for the water sorption behavior at 25°C, and the results are summarized in Figures 3 and 4. Although there are slight differences in the water absorption behavior, in the case of the grafted samples the magnitude of these increases are small, especially at low humidities. However, if these grafted samples are subjected to a postdecrystallization in 70% aqueous zinc chloride, followed by a thorough water wash, the samples then absorb more than 3000% water with liquid water. The corresponding sorption isotherms for the postdecrystallized samples for rayon and cellophane are also shown in Figures 3 and 4, respectively. It is interesting to note that at the lower water activities the samples do not absorb in such a relatively dramatic fashion as found at water saturation.

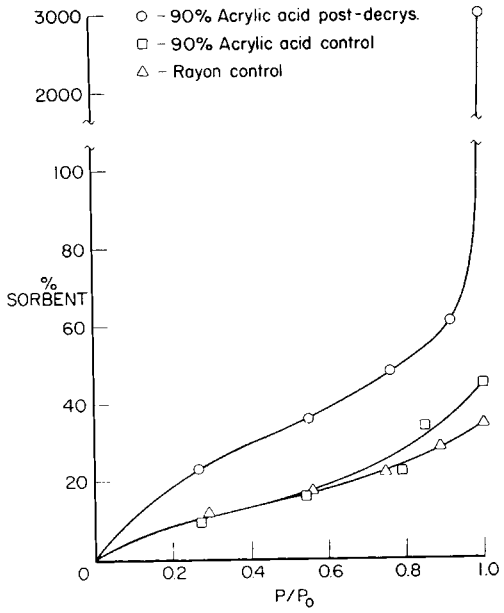

Fig. 3. Water sorption isotherms for acrylic acid-grafted rayon (semidull) at 25°C.

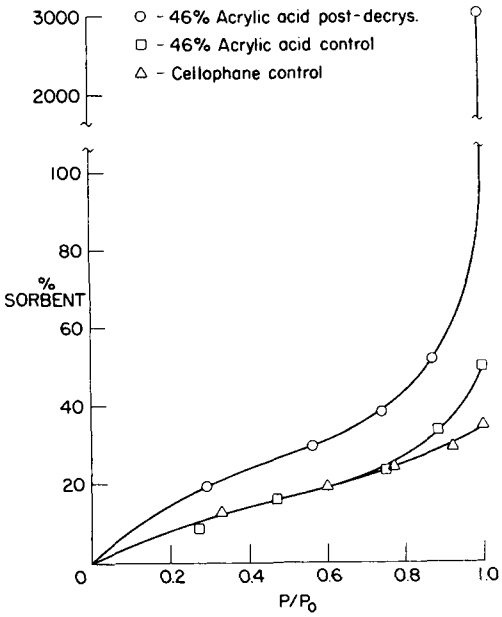

Fig. 4. Water sorption isotherms for acrylic acid-grafted cellophane (Sylvania) at 25°C.

The ability of the postdecrystallized sample to absorb high percentages of water relative to the nondecrystallized grafted substrate is presumably due to the less restrained swelling possible when the crystalline regions are dissolved, i.e., decrystallized. The presence of the grafted side chains prevents the sample from completely dissolving in the cellulosic solvent. Removal of the decrystallizing agent allows the cellulose chains to recrystallize, but normal crystallization of the cellulose chains is now hindered by the presence of the grafted polyacrylic acid side chains. As a consequence, the postdecrystallized grafted substrate can now swell more freely when rewet, restrained only by any newly formed crystalline regions and crosslinks that might occur during the grafting process, as shown schematically in Figure 5.

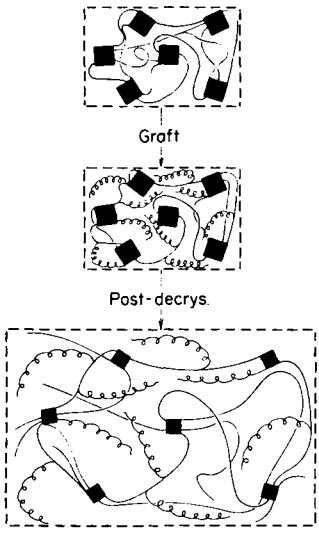

Fig. 5. Schematic representation of postdecrystallization of irradiation grafted cellulose (solid blocks represent crystalline regions).

Although work to date has been applied mainly to cellulosic systems, these modification techniques should, in principle, apply as well to synthetic polymers, and work along these lines is currently in progress and will be reported in due course. Any method of grafting is effective in this process, although radiation has been explored in more detail. Other methods and the results obtained are described in ref. 5.

References

1. J. L. Williams, D. K. Woods, V. T. Stannett, L. G. Roldan, S. B. Sello, and C. V. Stevens, *Text. Res. J.*, **43**, 205 (1973).
2. J. L. Williams, D. K. Woods, V. T. Stannett, S. D. Sello, and C. V. Stevens, *J. Appl. Radiat. Isotopes*, **26**, 159 (1975).
3. J. L. Williams, D. K. Woods, V. T. Stannett, S. B. Sello, and C. V. Stevens, *J. Appl. Radiat. Isotopes*, **26**, 169 (1975).
4. J. L. Williams and V. T. Stannett, *Polym. Lett.*, **10**, 665 (1972).
5. J. L. Williams and V. T. Stannett, U. S. Pat. 4,036, 588, July 19, 1977.

J. L. WILLIAMS
V. T. STANNETT

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607

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