NMR Study of Adsorbed Water on Acrylic Acid-Grafted and Methacrylic Acid-Grafted Cellulose

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Synopsis

The water-adsorbing properties of cellulose samples which had been graft copolymerized with hydrophilic vinyl monomers using ceric salt as an initiator were investigated by means of the width of the high-resolution NMR absorption spectrum, water retention, and moisture regain of the samples. In the change of the width at half-value of the spectrum with per cent grafting, a maximum value followed by a minimum value was observed on samples both grafted with acrylic acid and methacrylic acid. Thus, the effect of grafting on the water-adsorbing properties appeared not to be simple. Though no special change in the water retention by grafting was observed, the per cent grafting dependence on the moisture regain in high relative humidity showed a peculiar and definite relation. The per cent grafting giving maximum moisture regain was about 8% and 18% for acrylic acid and methacrylic acid, respectively, and this agreed very well with the minimum widths at half-value. The change in the glass transition temperature of the sample–water system caused by grafting is also described.

INTRODUCTION

As for graft copolymers in which hydrophobic vinyl monomers are grafted on inherently hydrophilic cellulose, interesting relations[1] have been found between structure and water-adsorbing properties. On the other hand, it is expected that the water-adsorbing property of cellulose is greatly affected by grafting hydrophilic vinyl monomers onto cellulose. Graft copolymerization[2–7] of such monomers onto cellulose in various initiation systems have been carried out. The structures of nylon 66 film grafted with acrylic acid and acrylamide and cellulose grafted with acrylamide were examined by Jeffries et al.[8] and by Simionescu and Oprea,[9] respectively. Leeder and Pratt[10] investigated the effect of hydrophilic vinyl polymers on the water absorption in wool–polymer systems. In our previous study,[11] it has been found that among several initiators, ceric salt was most effective in the graft copolymerization of this type of vinyl monomers. It is not difficult to attain several decades on per cent grafting, but a relatively long reaction time is needed because of the extremely slow initiation reaction. It seems that the structure of the graft copolymer

of this type has not been thoroughly clarified yet and that many unsolved problems might exist in the interaction of the polymers with water.

In the present study, in order to determine the nature of bonding between these graft copolymers and water, cellulose samples were prepared by grafting with acrylic acid and methacrylic acid up to about 50% grafting using ceric salt as an initiator; and the width at half-value of the high-resolution NMR absorption spectrum of adsorbed water and its relation with the water retention and moisture regain were investigated.

EXPERIMENTAL

Preparation of Grafted Samples

Commercial dissolving sulfite pulp was used as cellulose sample, and acrylic acid (AA) and methacrylic acid (MA) as vinyl monomers. Graft copolymerization was carried out in a system initiated by ceric salt under nitrogen. Copolymerization conditions were fixed almost identical to those of the previous study.[11] Namely, a known concentration of ceric ammonium nitrate was added to the system containing 5.0 g cellulose, 25 ml monomer, 300 ml distilled water, and 100 ml 0.1*N* nitric acid to make the salt concentration equal 10 mmole/l. in the system. Polymerization times ranged from 10 min to 8 hr. Polymerization temperatures were 20°C and 45°C for AA and MA, respectively. Polymerized products were extracted with hot water for 10–15 hr to remove homopolymers. The weight increment by grafting based on cellulose was indicated as per cent grafting.

Width at Half-Value of NMR Absorption Spectrum

Samples containing 5% to 30% water were prepared for each graft copolymer and packed closely in sample tubes. The high-resolution NMR absorption spectrum was measured by using a JEOL NMR spectrometer Model TNM-C-60HL with its accessories for varying temperature under the following conditions: resonance frequency, 60 Mc; sweep rate, 90 ppm/2.5 min; RF level, 40 db; sample temperature, −60°C to 90°C. The width at half-value of the spectrum was indicated as $\nu_{1/2}$.

Water Retention Value (WRV)[12]

After immersing the sample in water for 24 hr, it was filtered to form a mat, which was dehydrated with a centrifugal force of 3000 G for 15 min. The moisture remaining in the samples was expressed as percentage of the oven-dried weight.

Moisture Regain

The values of each sample at relative humidities of 66% and 93% were obtained by placing dried samples over saturated aqueous solutions of sodium nitrite and ammonium phosphate, respectively, at 20°C for one week.

RESULTS AND DISCUSSION

Hydrophilic Nature of Grafted Cellulose

Figure 1 shows the change in WRV. It was observed that the WRV of the graft copolymers increased with the introduction of AA and MA. Inasmuch as the grafted chains themselves have a good solubility in water if split off from the trunk cellulose, the water-retaining property of samples is expected to increase with increase in per cent grafting. As a result, a remarkable effect was observed for AA, whereas the effect was very small for MA. Considering such a large difference between monomers, it is assumed that fairly complicated factors are at play in the phenomenon of water adsorption in polymers.

Figure 2 gives the relation between the width at half-value and the water content of AA-grafted cellulose. As seen in the figure, two straight lines are drawn for each grafted samples, and the slope, the position, and the inflection point of these straight lines are peculiar to each sample. Similar relations were obtained for MA-grafted cellulose, and the width at half-value was possible to be estimated for samples with various per cent grafting at any given water content.

The relation between the width at half-value and the per cent grafting of AA-grafted cellulose is shown in Figure 3 for water contents of 10% and 15%. It is remarkable that for any water content of the samples, the maximum and the minimum of the width at half-value were observed at about 5% and 8% grafting, respectively. This phenomenon supposedly indicates a special interaction between grafted cellulose and water which appeared as the per cent grafting approached those values. As seen in Figure 4, the same tendency was also observed for MA-grafted cellulose;

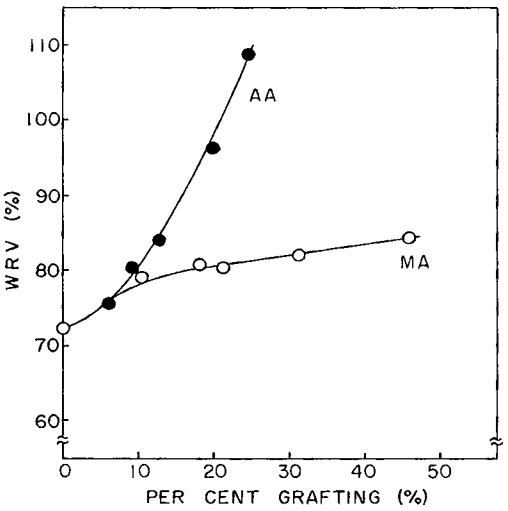

Fig. 1. Water retention value of grafted copolymer.

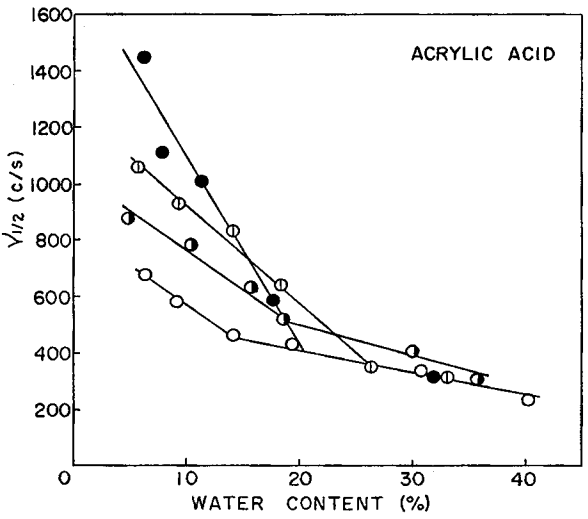

Fig. 2. Relation between width at half-value and water content in AA-grafted samples. Per cent grafting: (○) 0%; (◑) 4.9%; (◑) 11.4%; (●) 28.0%. Sample temperature, 24°C.

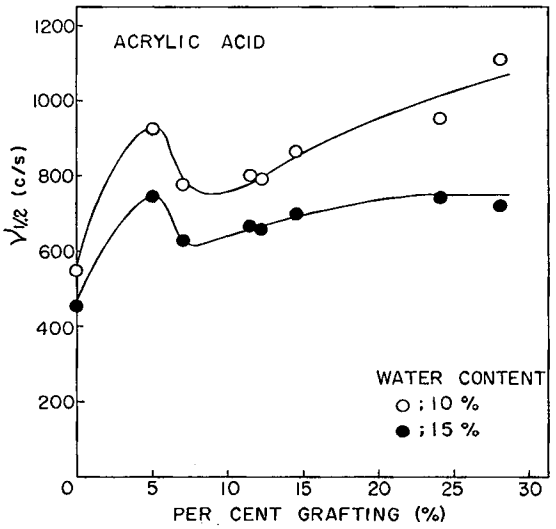

Fig. 3. Relation between width at half-value and per cent grafting in AA-grafted samples compared at certain water contents.

and, in this case, the maximum of the width at half-value was observed at about 8% grafting and the minimum at about 18%.

As the water-adsorbing property of polymers is also characterized by the moisture regain of samples, relations between the value and the per cent grafting were obtained and are shown in Figure 5. At a relative humidity of 66%, the moisture regain of grafted samples was observed to

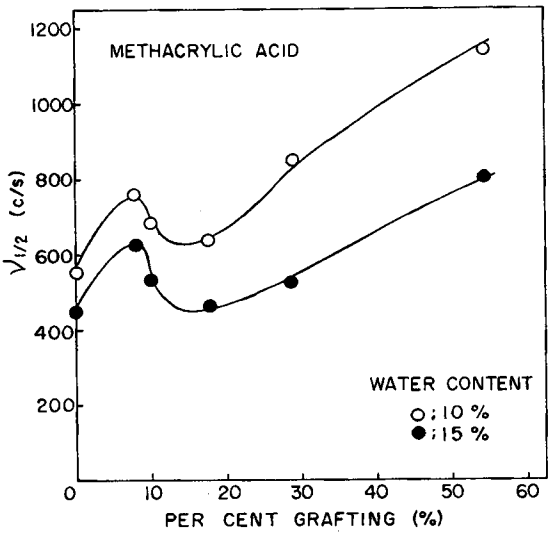

Fig. 4. Relation between width at half-value and per cent grafting in MA-grafted samples compared at certain water contents.

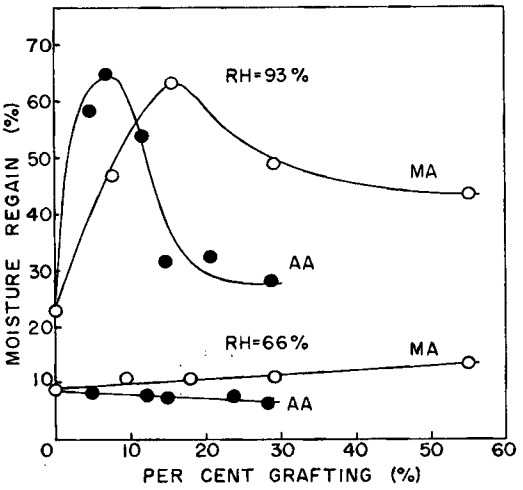

Fig. 5. Moisture regain of grafted copolymer.

be independent of the per cent grafting, and the difference between monomers was very small. However, at a relative humidity of 93%, a peculiar and definite relation was obtained in that the maximum moisture regain was attained at a certain per cent grafting. The values were 8% and 18% for AA- and MA-grafted cellulose, respectively. These values happened to agree well with the per cent grafting at which the width at half-value became minimum for both grafted celluloses described above. This agreement is very definite and interesting.

Although any per cent grafting characterizing the increase in WRV of samples by grafting was not found, a per cent grafting specifying the width of the NMR absorption spectrum as well as the moisture regain at a high humidity were found to exist. The reasons for these could be interpreted as follows. WRV reflects a rather macroscopic change in the structure of fibers, whereas width at half-value or moisture regain is thought to detect microscopic changes in structure more sensitively. In the process of graft copolymerization, the surface, the microvoids, and the amorphous regions of the cellulose fibers are gradually filled with hydrophilic polymer, and the maximum hydrophilic property of the whole system is determined by the constitution of trunk and grafted polymers. Naturally, the per cent grafting corresponding to this point depends on the polymer to be introduced. Water in this system is also thought to behave in a particular manner. As the width at half-value can be considered as an index of differential energy of binding, i.e., force of binding between water and cellulose in the system,[13] it is thought to be possible to indicate the state of protons in bound water by the width of the NMR absorption spectrum. The experimental results indicated that the adsorption energy of water became minimum in a sample with the per cent grafting at which the maximum moisture regain was obtained. It seems that such information on the water-binding property of the samples has an important significance in the examination of the hydrophilic polymer-grafted cellulose.

Glass Transition Temperature of Grafted Cellulose

According to the previous paper,[14] the temperature dependence of the width at half-value was examined for the samples with various water contents. Figure 6 shows the results for ungrafted cellulose samples. The relations of width at half-value temperature are represented by two straight lines for each water-containing sample, and the temperature at the intersection of these lines, namely, the critical temperature of the water-containing polmer system (T_c, designated as glass transition temperature according to the previous paper[14]), can be read from the figure. It is possible to obtain the relation between these temperatures and the water content of the samples. Similar relations were obtained for AA-grafted samples with a per cent 6.9% grafting and are shown in Figure 7. In these samples, a remarkable difference was observed in their properties toward water as compared with those of ungrafted samples; namely, the force of water binding in a lower range of water content was maintained high, even at higher temperature. However, the dependence of T_c on the water content hardly differed between the grafted and ungrafted samples.

The above results are summarized in Figure 8. It was observed that the water content dependence of the glass transition temperature of the grafted cellulose–water system was hardly affected by grafting up to about 7%. However, as for the samples with 28% grafting, the moisture regain was almost the same as that of ungrafted sample, but a definite increase in the glass transition temperature was observed if the comparison

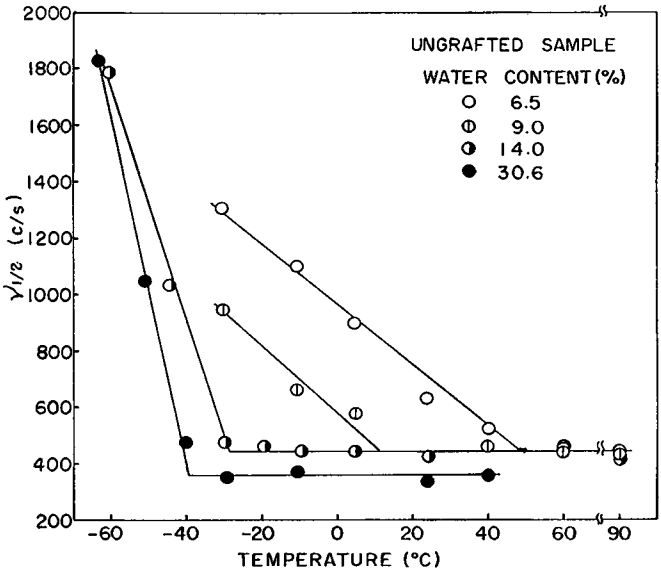

Fig. 6. Relation between width at half-value and temperature in ungrafted samples with various water contents.

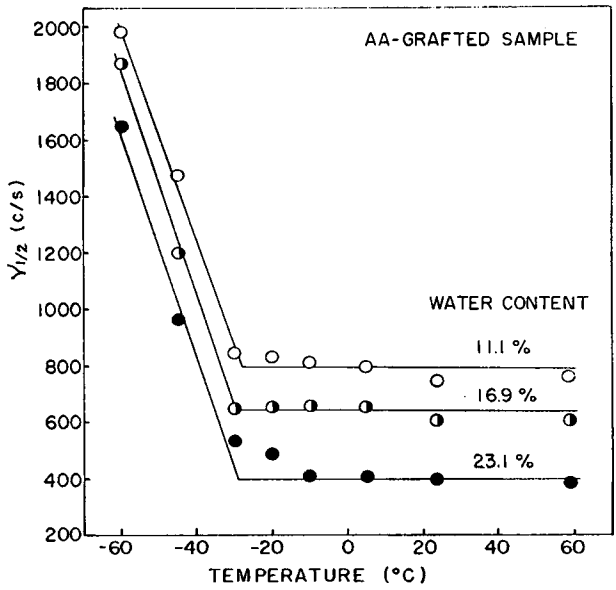

Fig. 7. Relation between width at half-value and temperature in AA-grafted samples with various water contents.

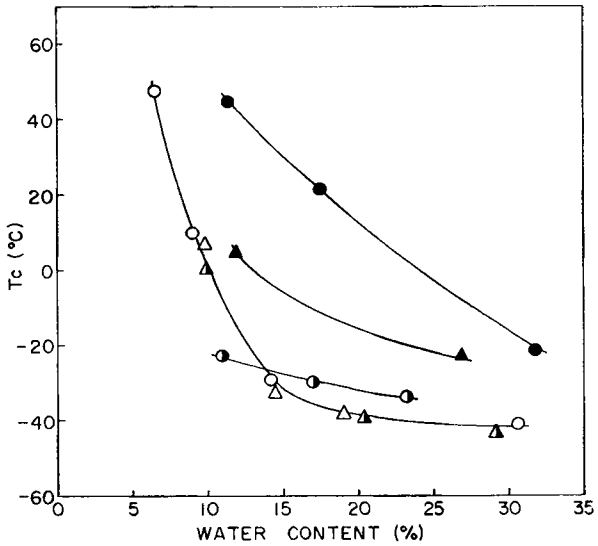

Fig. 8. Relation between T_c and water content. Per cent grafting of AA-grafted sample: (○) 0%; (◑) 6.9%; (●) 28.0%; Per cent grafting of MA-grafted sample: (△) 17.9%; (▲) 28.9%; (▲) 54.8%.

was carried out at the same water content. In Figure 8, the results for MA-grafted cellulose are also shown. For the samples with grafting of below 30%, no difference from ungrafted cellulose was observed in these relations. The increase in glass transition temperature was first observed at 50% grafting. The different effect of these monomers on the shift in glass transition temperature can be easily assumed by examining the changes in moisture regain and the force of water-binding of cellulose samples by graft copolymerization.

Thus, the grafting of relatively small amounts of hydrophilic monomer sensitively increases the force of water binding of cellulose samples at a water content lower than 15%. However, the grafting has a small effect on the glass transition temperature of the cellulose–water system, and the effect of increasing the temperature first appears at a per cent grafting more than several decades, depending on the monomer.

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