

Absorption of Water by Graft Copolymers of Cotton with Methyl Methacrylate Using High-Resolution NMR

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Synopsis

Graft cotton fibers containing poly(methyl methacrylate) were initiated by ultraviolet radiation. High-resolution NMR was used to study the nature of water absorption by these graft copolymers and also by mixtures of cotton fibers with the corresponding homopolymers. Results obtained help in investigating the structure of the copolymers and to differentiate, in a simple way, between true graft copolymers and mechanical mixtures or coated fibers.

INTRODUCTION

High-resolution NMR spectroscopy was used to study the nature of water adsorbed on cellulose¹ and cellulose graft copolymers.² For copolymers, the change of the width at half-value of the spectrum ($\nu_{1/2}$) with water content or with per cent grafting was found to be related to the composition and structure of the substance depending on the type of cellulose and polymer used, method of initiation, length, position, and number of grafts.

High values of $\nu_{1/2}$ indicate high affinity of water molecules to cellulosic materials. This water is called bound water, where water molecules are supposed to be strongly attached to unbound hydroxyl groups, preferably in the amorphous regions of the fiber. However, low values of $\nu_{1/2}$ indicate the presence of free water.

Graft copolymerization reactions are also supposed to take place on the surface of the fibers starting in these regions. The hydrophobic components introduced replace the adsorption centers leading to a decrease in the hydrophilicity of the fibers and a change in the nature of the adsorbed water.

Grafting reactions usually lead to copolymer mixed with the corresponding homopolymer and unreacted cellulose molecules. Due to experimental difficulties, molecular graft copolymers are very rare,³ which makes it difficult to correlate the change in properties only to grafting effect.

In the present study, graft copolymers of Iraqi cotton fibers with PMMA were prepared and freed from the homopolymers in the usual way. Mechanical mixtures containing cotton fibers and the mentioned homopolymer were also prepared. A comparative study of the nature of water absorption by both systems

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using high-resolution NMR may help in investigating the composition and structure of these graft copolymers and differentiating between true copolymers and mechanical mixtures or coated fibers.

EXPERIMENTAL

Graft copolymers of Iraqi cotton fibers with PMMA were prepared using UV initiation. Special experimental conditions of concentration, temperature, wavelength region, atmosphere, and time of irradiation were chosen to get copolymers having definite extent of grafting (%), molecular weight, and number of grafted chains⁴ as shown in Table I.

The products were extracted by acetone to constant weight in order to exclude homopolymer. The per cent grafting of the graft copolymer was directly determined from the increase in weight. Grafted copolymer was treated with 72% sulfuric acid and the poly(MMA) of the grafts was isolated. The degree of polymerization (D.P.) of grafts was determined from the viscosity of the acetone solution at 25°C. The D.P. of irradiated and nonirradiated cotton fibers was determined from the viscosity of Cu/ammonia solution at 25°C. Its average value was found to be 1800.

Mechanical mixtures were prepared by soaking the cotton fibers in solutions of homopolymers extracted from the first reaction systems. The fibers were then filtered off and dried to constant weight:

$$\text{mixing (\%)} = \frac{\text{increase in weight}}{\text{original weight}} \times 100$$

Samples containing 0% to 165% were prepared from each graft copolymer and mixture, and packed closely in sample tubes. The absorption curve for each sample was obtained by measuring the high-resolution NMR absorption spectrum, the width at half-value ($\nu^{1/2}$).

A Varian A60D NMR spectrometer was used at 25°C, using a filter band width 4 HZ, R.F. field 0.5 G, sweep time 50 sec, sweep width 500 HZ, sweep offset 78 HZ, and spectrum amplitude 80.

Microscopic studies of the fibers were carried out using an Orthoplan Lietz-Wetzler polarizing microscope with an average magnification power of 3600.

TABLE I
Reaction Conditions and Description of Samples*

Irradiation time, hr	Temp., °C	Amount of cotton, g	Atmosphere	Grafting, %	\bar{M}_w of grafts $\times 10^{-4}$	No. of grafts, moles per mole cell
2	50	0.25	N ₂	15.0	16.00	0.27
4	50	0.25	N ₂	50.0	48.00	0.30
6	40	0.50	vacuum	77.5	13.80	1.64
6	50	0.50	vacuum	101.2	74.00	0.39
6	60	0.50	N ₂	165.0	135.00	0.35

* 2.5-ml fractions of monomer were added to wet cotton samples and irradiated in Pyrex glass tubes. A mercury discharge lamp (Gallenkamp LH-530) was used as UV source.

RESULTS AND DISCUSSION

Figure 1 shows the general shape of the NMR spectra of cotton samples having increasing water content (%). In general, a decrease in the width at half-value ($\nu_{1/2}$) is observed with increasing water content.

From Figure 2, it is clear that both purified and UV-irradiated fibers have the same nature of water absorption. This curve can be easily divided into two parts of different slopes. The first part, showing a rapid decrease in $\nu_{1/2}$, corresponds to bound water strongly attached to the molecules of cellulose. The second part, showing a small or zero change in $\nu_{1/2}$, corresponds to free water. It is interesting to observe that the position of the point of inflection between the two curves depends upon the type and hydrophilicity of different cellulosic materials. For Iraqi absorbent cotton fibers, this point lies at about 50-60% water content.

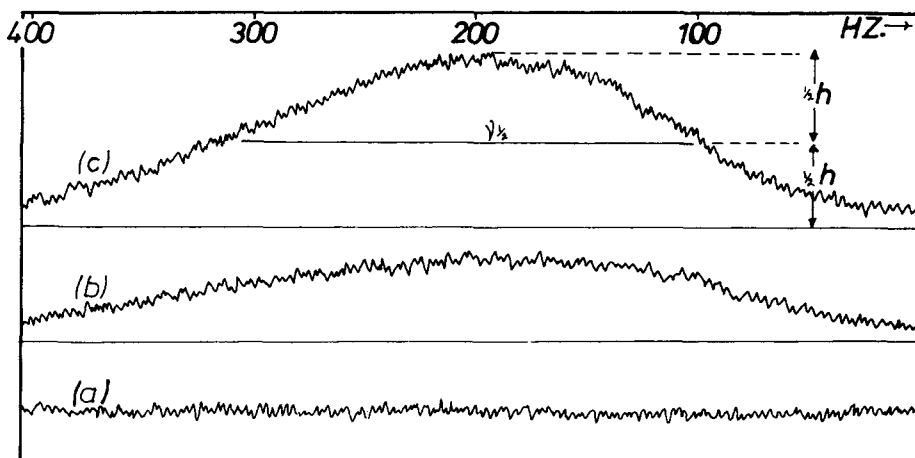


Fig. 1. NMR spectra of cotton samples showing change of the width at half-value with water content: (a) dry fibers; (b) 30% water; (c) 60% water.

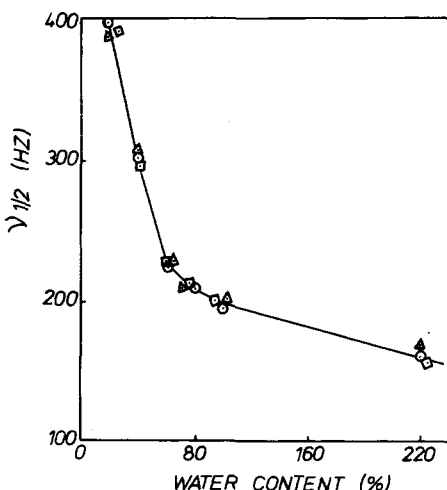


Fig. 2. Relationship between width at half-value and water content for cotton fibers: (○) native; (□) purified; (△) irradiated (24 hr).

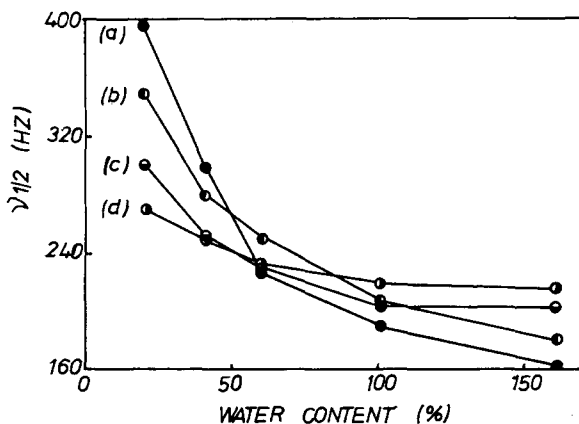


Fig. 3. Relationship between width at half-value and water content for cellulose-PMMA graft copolymers. Per cent grafting: (a) 0%; (b) 15%; (c) 40%; (d) 100%.

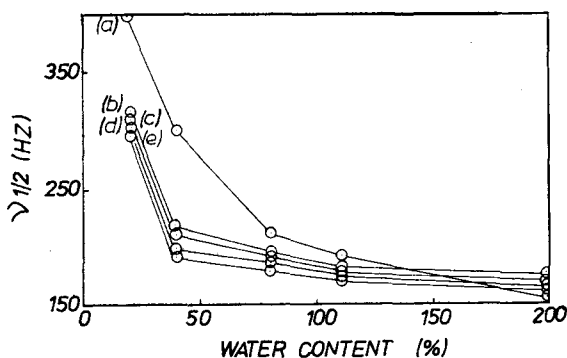


Fig. 4. Relationship between width at half-value and water content for mixtures of cellulose and PMMA having different PMMA %: (a) 0%; (b) 25%; (c) 50%; (d) 100%; (e) 165%.

Figures 3 and 4 show the change of $\nu_{1/2}$ with water content (%) for cellulose-PMMA graft copolymers and mechanical mixtures. For graft copolymers and mechanical mixtures, the general shape of the curves is almost the same. However, for graft copolymers (Fig. 3), the part of the curve corresponding to bound water is found to change its slope toward that for free water as the % graft increases. At 100% grafted, the two parts of the curve have almost the same slope, indicating minimal hydrophilicity. This decreased hydrophilicity is in good agreement with the assumption that the hydrophobic grafts, chemically bonded to the cellulose molecules, replace the adsorption active centers in the amorphous regions. Water absorbed in this case is of the second type, i.e., free water.

On the other hand, such behavior is not observed in the case of mechanical mixtures (Fig. 4). From the figure, a certain drop in $\nu_{1/2}$ is seen as a result of mixing. This drop may be attributed to the shielding effect caused by the homopolymer layer coating the fibers. Increasing the homopolymer percentage in the mixtures shows no considerable effect on the nature of water absorption, and the fibers behave as if they were pure cotton.

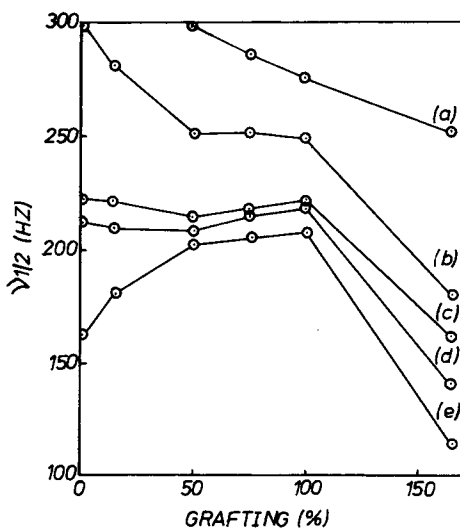


Fig. 5. Relationship between width at half-value and the grafting % of cellulose-PMMA graft copolymers having different water contents: (a) 20%; (b) 40%; (c) 60%; (d) 100%; (e) 165% water.

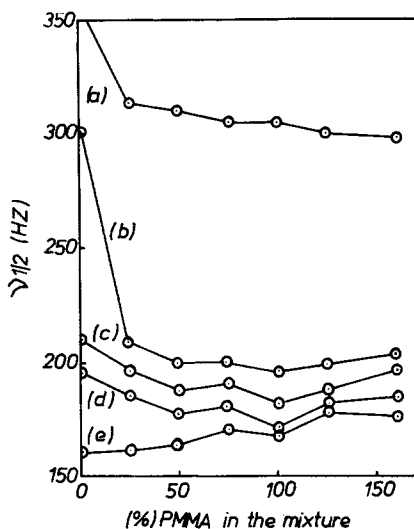


Fig. 6. Relationship between width at half-value and homopolymer % for cellulose-PMMA mixtures at different water contents: (a) 20%; (b) 40%; (c) 80%; (d) 120%; (e) 200% water.

On this basis, for any graft copolymerization reaction, a comparative study of the dependence of $\nu_{1/2}$ on water content with those for mixtures of different composition can be helpful in investigating the structure of the product and telling whether it is true graft copolymer or just a mechanical mixture of two homopolymers.

Differentiation between copolymers and mixtures can also be done by studying the change in $\nu_{1/2}$ with per cent grafting and per cent mixing. Figures 5 and 6 show that the behavior of copolymers and mixtures differs indicative of different

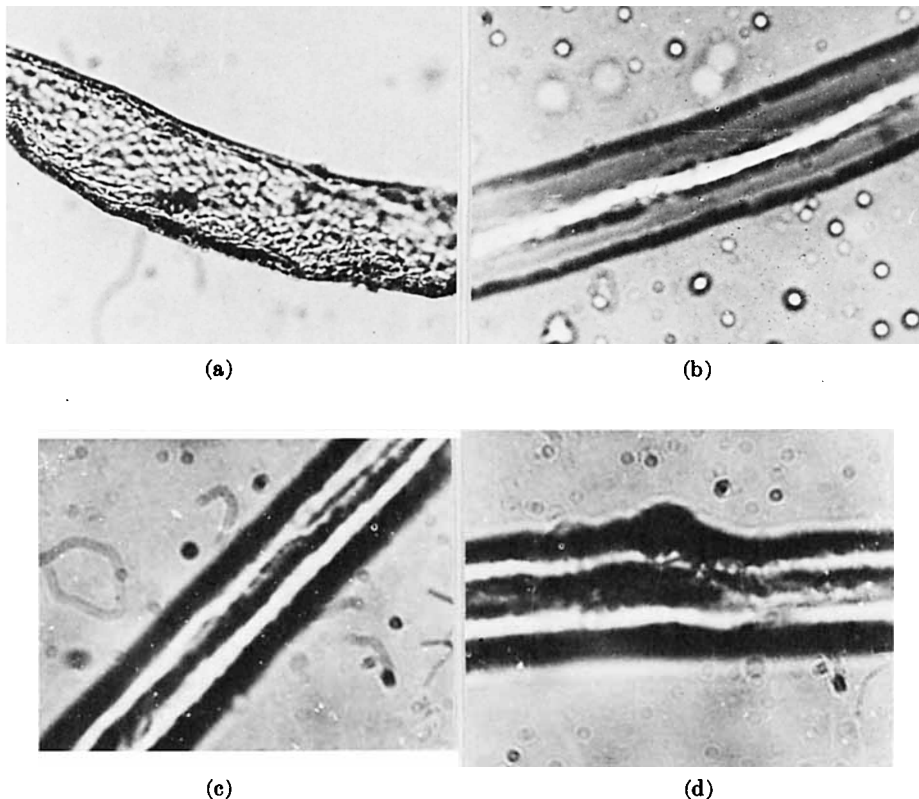


Fig. 7. Photomicrographs of PMMA graft cotton fibers (magnification $\times 600$): (a) pure cotton (alkaline treated); (b) 50%; (c) 101.2%; (d) 165% grafted.

manner of water absorption. From the figures it can be seen clearly that for graft copolymers the hydrophilicity of the fibers depends upon the per cent grafting, while in the case of mixtures it is not changed by per cent mixing if the last exceeds a certain value.

The fact that the water binding power does not relate linearly with the per cent grafting (Fig. 5) could be attributed to the structure of graft cotton.

It is difficult to explain clearly the exact reason for the maximum observed on Figure 5e. It may be related, however, to the superficial nature of the grafting reaction in its first stage, which leads to the formation of grafted polymer on the surface of the fiber.

At this stage, grafting preferentially attacks the rough structure of cellulose fibers, which has not enough power to restrict the motion of neighboring water molecules. This is known as the covering effect² and is supposed to be the reason for the increased water-binding power in the first stage of grafting.

With progress of the polymerization reaction, the location of the grafting sites proceeds on the inside of the fiber. This leads to a considerable drop in its hydrophilicity causing the observed decrease in $\nu_{1/2}$ values. Such maxima have also been observed in copolymers of PMMA and commercial dissolving sulfite pulp.²

The amplitude and position of these maxima are directly related to the method of initiation used besides the structure and homogeneity of graft copolymers formed.

Photomicrographs of cotton fibers having increased per cent grafted are shown in Figure 7. From the figure, it is clear that the grafted polymer layer which appears opaque to the plane-polarized light starts to be formed on the surface of the fiber and then proceeds on the inside causing a considerable increase in its cross-sectional area. This is in good agreement with the aforementioned explanation.

Negishi and Nakamura⁵ reported that the hydrophilicity of cellulose fibers or fabrics treated with HCHO and then grafted with butyl acrylate is not affected by the grafted polymer. In our opinion, and on the basis of the previous discussion, this needs more study. It could be explained by assuming that grafting did not take place at all under their conditions and that the product was a mixture of crosslinked cellulose fibers with insoluble PBA homopolymer.

From the reported results, we conclude that it is probably possible to differentiate between graft copolymers and mechanical mixtures or coated fibers by comparing the nature of water absorption at different water content values or different degrees of grafting or mixing. We also conclude that UV initiation used under our experimental conditions leads to the formation of graft copolymers. However, the effect of unreacted cellulose molecules is not yet clear and needs more study.

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