Radiation-Induced Graft Copolymerization of Methyl Methacrylate on Natural and Modified Wool. II. Sorption Behavior

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Synopsis

The water vapor sorption-desorption isotherms of graft copolymers of methyl methacrylate with natural and chemically modified wool (i.e., oxidized, reduced, methylated, and crosslinked) has been investigated. As a result of graft copolymerization a reduction in water absorption was observed. The results have also been analysed in the light of Hailwood–Horrobin equations.

INTRODUCTION

Adsorption and desorption isotherms of wool showing considerable hysteresis at 25°C were first reported for seven types of wool in 1930.[1] The effect of temperature and the drying conditions on the amount of water adsorbed and the extent of hysteresis between the adsorption and desorption curves was investigated by Goodings[2] and Speakman et al.[3-5] The reduction of wool causes little change in the sorption behavior,[6,7] but reduction followed by alkylation of the sulphydryl groups causes significant changes which depend on the extent of reduction and the alkylation procedure.[6] Kinetics of sorption of water has also been investigated for the wool-water system.[8-10]

Nicholls and Speakman[11] have reported the adsorption of primary alcohols by wool and have inferred that, the fraction of the wool which is accessible to the adsorbate decreases with increasing size of the exploratory molecule. By applying the Hailwood-Horrobin analysis they[12] have tried to find out the crystalline/amorphous ratio of the keratin fibers. Recently, Watt et al.[13] have worked on the sorption properties of the graft copolymers of wool with acrylic acid, acrylamide, and acrylonitrile. The adsorption of water increases with the grafting of polyacrylamide and polyacrylic acid on wool, whereas the grafting of polystyrene reduced the water sorption considerably.[14]

The present paper deals with the sorption behavior of the graft copolymers of natural and modified wool with methyl methacrylate. A literature survey has revealed that such investigations have not been reported.

EXPERIMENTAL

Malpura wool of Indian origin was purified by soxhlet extraction with petroleum ether for 24 hr, followed by repeated washing with distilled water and then drying in air. The clean natural wool was modified chemically by oxidation (hydrogen peroxide), reduction (sodium bisulphite), methylation (methyl sulphate and sodium acetate), and crosslinking (formaldehyde).
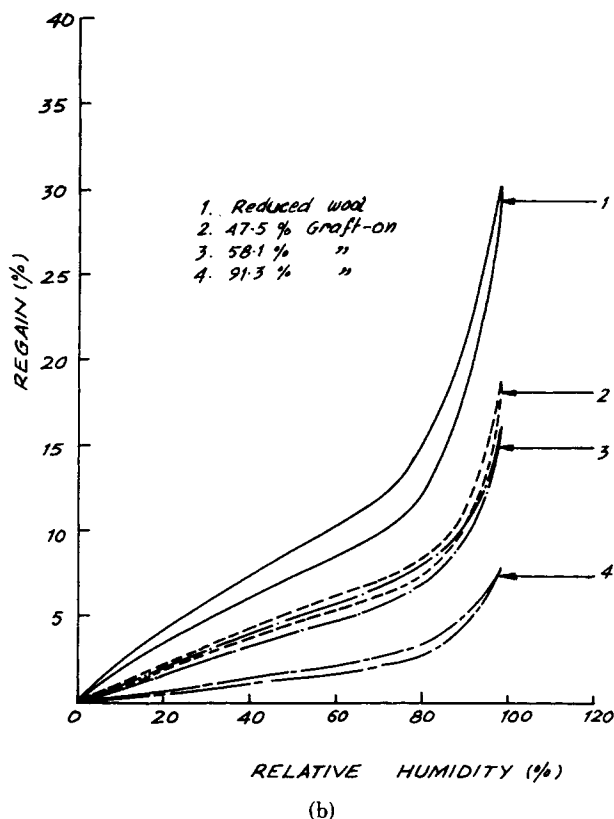
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Graft-copolymerization of methyl methacrylate (MMA) and natural and chemically modified wool was carried in dimethylformamide using mutual irradiation techniques. The details of the treatments and grafting are given in detail elsewhere.[15]

Various methods have been used for conducting the sorption measurements.[16,17] We have carried the experiments in a dessicator kept at a temperature of 25°C. The relative humidity was maintained by using different salt solutions.

RESULTS AND DISCUSSIONS

The sorption-desorption curves were obtained at 25°C for natural, oxidized, reduced, methylated and cross-linked wools and their graft copolymers with methyl methacrylate. Figures 1(a) and 1(b) show a typical curve obtained for natural and reduced wool. Comparison of the equilibrium water content attained over the whole range of humidities may be made by the curves. There is a marginal decrease in the moisture uptake at lower humidities for reduced, methylated, and crosslinked wools. Above 80% relative humidity the reduced sample show a more rapid change of percentage regain and at higher humidities

1. Natural wool
2. 17·6 % Graft-on with MMA
3. 41·1 % „   „   „
4. 63·3 % „   „   „

(a)

Fig. 1. Absorption and desorption curves for the graft copolymers of natural wool and chemically modified wool with methyl methacrylate: (a) natural wool; (b) reduced wool.

Fig. 1 (*Continued from previous page.*)

it contains more water than the unmodified sample. The percentage regain in case of methylated wool is somewhat reduced at higher humidities as compared to the unmodified wool, possibly due to introduction of hydrophobic alkyl groups in the wool. The adsorption isotherm of oxidised and crosslinked wool is similar to natural wool.

As the wool fibers are swollen by absorption of water the swelling is opposed by retractive forces in the fiber. At equilibrium the forces causing swelling and those opposing swelling are in a state of balance. Thus it should be expected that in the cystine reduced fibers the forces opposing swelling should be weaker than in unmodified wool. It has earlier been reported[6] that, a sample which had been reduced to remove 90% of the disulfide bonds when exposed to a saturation vapor pressure adsorbed 1% more water than the unmodified wool. We have also observed an increase of 0.7% in adsorbed water in reduced wool. Since the increase is very small, therefore, the role of sulfhydryl groups in sorption does not seem to be of great importance.

Below 80% relative humidity, the incoming water is either attached to specific hydrophilic sites or is associated with the keratin structure or other water molecules with reasonably high energy of binding. The extent of absorption is dependent on the existence of polar sites rather than the absence of network constraints. There is an increase of swelling of the reduced wool above 80% relative

VARMA AND SADHIR

TABLE I
Sorption, Desorption, and Percentage Hysteresis Values of Graft Copolymers of Natural and
Modified Wool

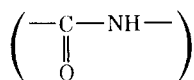| Wool	% Graft-on	Soption at 65% relative humidity (Regain %)	Desorption at 65% relative humidity (Regain %)	Hysteresis %
Natural wool	0	9.3	11.0	1.7
	17.6	8.0	9.3	1.3
	41.1	6.9	7.9	1.0
	63.3	5.9	6.4	0.6
Oxidised wool	0	9.4	10.5	1.0
	35.8	7.5	8.5	1.0
	53.4	7.0	7.9	0.9
	87.1	5.0	5.5	0.5
Reduced Wool	0	9.2	11.2	2.0
	47.5	5.7	6.6	1.0
	58.1	5.4	6.2	0.9
	91.3	2.0	2.5	0.5
Methylated wool	0	9.2	11.0	1.8
	74.3	4.9	5.6	0.7
	94.7	4.9	5.5	0.6
	129.7	3.6	4.1	0.5
Crosslinked wool	0	9.5	10.9	1.4
	21.9	9.0	10.1	1.1
	42.8	6.2	7.2	1.0
	53.1	5.0	5.8	0.8

humidity. It seems, therefore, that above 80% relative humidity, the absorption is controlled by the ease of swelling of the network. This may be interpreted as the disulfide crosslinks in unmodified wool forming stable links and the peptide chains between these links being forced apart by the incoming water at high humidities. If these links are disrupted, then it becomes easier to force the chains further apart. These results support the solution theory of absorption given by Kotz[18] for absorption at high humidities.

Crosslinking with formaldehyde can occur between amino and guanidino groups. There should have been a lower absorption of water because of the blocking of amino groups and crosslink formation. However, only a little change in the absorption isotherms of the crosslinked and oxidised wool is observed.

The absorption and desorption curves for the graft copolymers of methyl methacrylate and natural wool and chemically modified wool are also given in Figures 1(a) and 1(b). It is obvious from these figures that grafting of wool with MMA reduces the absorption of water. This decrease depends upon the percentage graft-on as well as on the chemical treatment of wool.

It has been reported[19] that thiol groups are the main sites for grafting in reduced wool. Blocking of these hydrophilic sites by grafting of a hydrophobic monomer may be responsible for the decrease in absorption of water.
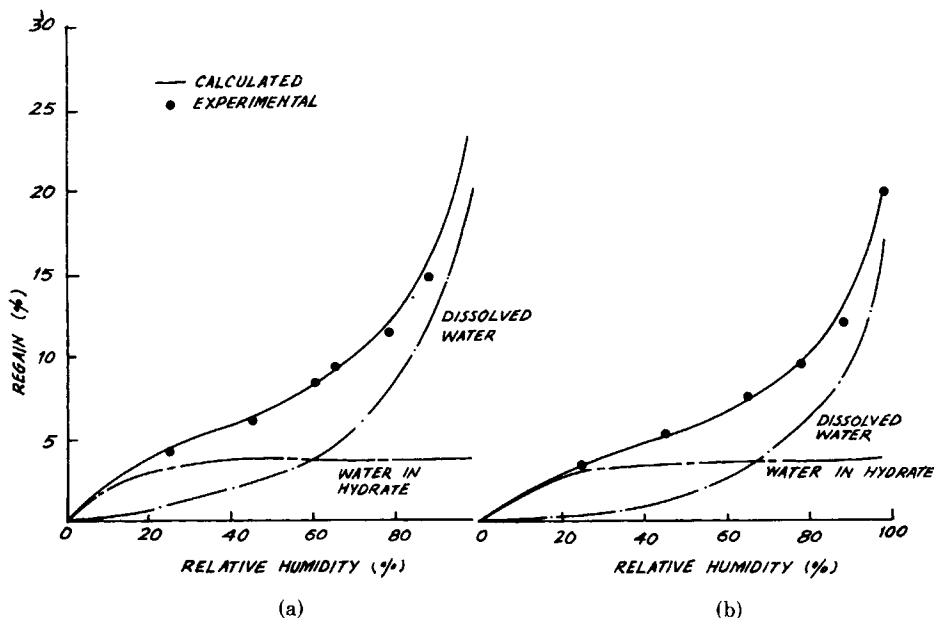
Wool contains amide groups

$$\left(\begin{array}{c} -C-NH- \\ \parallel \\ O \end{array} \right)$$

TABLE II
Molecular Weight of the Unit Capable of Combining with One Mole of Water (M) and Fraction
Accessible to Water (R/M) Molecules for MMA Grafts of Natural and Modified wool

Wool	% graft-on	M	Fraction accessible (R/M)
Natural wool	0	540	0.23
	17.6	608	0.20
	41.1	736	0.17
	63.3	888	0.14
Oxidised wool	0	416	0.29
	35.8	554	0.22
	53.4	648	0.19
	87.1	849	0.14
Reduced wool	0	428	0.29
	47.5	643	0.19
	58.1	804	0.15
	91.3	1523	0.08
Methylated wool	0	417	0.29
	74.3	564	0.22
	94.7	835	0.15
	129.7	908	0.13
Crosslinked wool	0	444	0.27
	21.9	589	0.21
	42.8	619	0.20
	53.1	899	0.14

in the main chain, to which water can be hydrogen bonded, and other water attracting groups such as OH, —NH$_3$$^+$, —COO$^-$, —CONH$_2$ in the side chains. The methylation of the polypeptide chain may also partly take place with the enolic form thus reducing the sites for hydrogen bonding.

Grafting at the enolic sites may also take place. All these factors are thus responsible for the reduction in equilibrium water content of the grafted wool sample. Table I gives the percentage regain values for sorption and desorption at 65% relative humidity and percentage hysteresis values of different grafted wools. It is evident from the table that as the percentage graft-on increases the hysteresis percent decreases. The water sorption isotherms of the copolymers of wool with polyacrylonitrile, polyacrylamide, polyacrylic acid,[13] and resorcinol-formaldehye resin have earlier been studied. It has been observed that

Fig. 2. Comparison of Hailwood and Horrobin's equation with experimental results for oxidized and grafted wools; (a) oxidized wool; (b) oxidized wool, g-MMA (38.5%); (c) oxidized wool, g-MMA (53.4%); (d) oxidized wool, g-MMA (87.1%).

the copolymers of wool and polyacrylic acid show an enhanced water sorption throughout the range of the humidity; though the isotherm so obtained is less than the added isotherm of wool and polyacrylic acid. The higher absorption of water in the copolymer of wool and polyacrylic acid has been attributed to the hydrophilic nature of the polyacrylic acid. Similarly the copolymer of wool with polyacrylamide shows an increased equilibrium water content than unmodified wool. The addition of resorcinol-formaldehyde resin to wool reduces the percentage equilibrium water content.[10] Sorption of water is also reduced by addition of propiolactone to wool.[20]

The percentage regains are decreased to a large extent in case of highest grafted reduced wool and methylated wool. If the regain is calculated on the weight of wool only then the percentage regain is reduced from 30.4% in case of ungrafted reduced wool to 15.3% in case of 91.3% reduced wool. This large reduction in percentage regain is perhaps due to reduced swelling brought about by the bulking action of the grafted polymer which is obvious at higher graft-on percentage. Williams et al.[14] have reported considerable overall water sorption reduction in grafted wools after calculating the moisture regain on the wool content only.

Reduced water absorption in case of the copolymers of wool and. methyl methacrylate may be due to the hydrophobic nature of the poly(methyl methacrylate). Another reason for the lesser water absorption can be the chain entanglement involving the polypeptide chain and the polymer molecules. Further polymer is capable of introducing cross-links to provide additional constraints to the swelling of the keratin network.

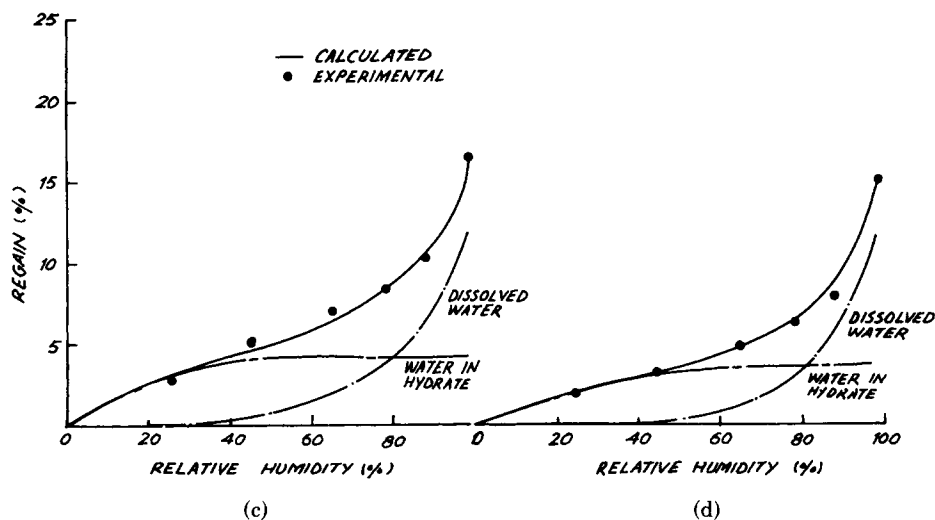Investigations have been made to examine the validity of the Hailwood and

Fig. 2 (*Continued from previous page.*)

Horrobin[21] analysis of adsorption isotherms for the copolymers of wools. On the assumption that part of the adsorbed water forms hydrates and part is in simple solution in the fiber, they derived the following expression for the adsorption isotherm:

$$Mr/1800 = Kh/(1 - Kh) + KK_1h/(1 + KK_1h) \qquad (1)$$

where r is the regain, h is the relative humidity, K and K_1 are the constants, and M is the molecular weight of the unit which combines with one molecule of water to form a monohydrate. The value of M derived from the isotherm was greater than the average residue weight R, presumably because of the inaccessibility of the crystalline regions to water molecules and the value of R/M has been taken as a measure of the fraction which is accessible. Equation (1) can, therefore, be used to calculate values of M, the molecular weight of the unit capable of combining with one mole of water. The detailed procedure used for such calculations was similar to what has been reported by Speakman et al.[11] The values of M obtained in this way are given in Table II which includes values of R/M, the fraction accessible to water molecules, the average residue weight R being taken as 122.

The value of M increases and the fraction accessible decreases with increase in percentage graft-on in natural and all the modified wools. A systematic reduction in the value of fraction accessible suggests that the polymer is getting deposited in the amorphous region.

The experimental results for absorption isotherms are compared with the results calculated by Hailwood and Horrobin analysis. These values are in agreement for natural wool, chemically treated wool and grafted wools. A few typical comparisons of the experimental and calculated values have been shown in Figures 2(a)–2(d). Considering an ideal solid solution formation between the hydrate and water, the proportion of water adsorbed as hydrate and the water as solid solution have been calculated. The same has been shown in Figures 2(a)–2(d) for oxidized, 35.8% grafted, 53.3% grafted, and 87.1% methyl methac-

rylate grafted oxidized wools. It is observed that, in general, there is a slight change in the percentage of water in hydrate form as the percentage graft-on increases. But water in the form of solid solution decreases with an increase in percentage graft-on.

References

1. J. B. Speakman, *J. Soc. Chem. Ind.*, **49**, 2097 (1930).
2. A. C. Goodings, *Am. Dystuff Rep.*, **24**, 109 (1935).
3. J. B. Speakman and C. A. Cooper, *J. Text. Inst.*, **27**, T183 (1936).
4. J. B. Speakman and E. Scott, *J. Text. Inst.*, **27**, T186 (1936).
5. J. B. Speakman and C. A. Cooper, *J. Text. Inst.*, **27**, T191 (1936).
6. I. C. Watt, *Text. Res. J.*, **33**, 631 (1963).
7. E. F. Mellon, A. H. Korn, and S. R. Hoover, *J. Am. Chem. Soc.*, **71**, 2761 (1949).
8. I. C. Watt, *Text. Res. J.*, **30**, 443 (1960); **30**, 644 (1960).
9. I. C. Watt and J. E. Algie, *Text. Res. J.*, **31**, 793 (1961).
10. I. C. Watt, *Text. Res. J.*, **32**, 1035 (1962).
11. C. H. Nicholls and J. B. Speakman, *J. Text. Inst.*, **46**, T264 (1955).
12. C. H. Nicholls and J. B. Speakman, *J. Text. Inst.*, **46**, T424 (1955).
13. I. C. Watt and R. L. D'Arcy, *J. Macromol. Sci.*, **A6**, 705 (1972).
14. J. Williams, V. Stannett, and A. A. Armstrong, *J. Appl. Polym. Sci.*, **10**, 1229 (1966).
15. D. S. Varma and R. K. Sadhir, *J. Appl. Polym. Sci.*, **22**, 883 (1978).
16. M. Wahba and S. Nashed, *J. Text. Inst.*, **48**, T1 (1957).
17. M. Wahba, *J. Phys. Colloid Chem.*, **54**, 1148 (1950).
18. J. A. Katz, *Trans Faraday Soc.*, **29**, 279 (1933).
19. K. Arai, M. Negishi, and T. Okabe *J. Appl. Polym. Sci.*, **12**, 2585 (1968).
20. H. Walter Jones and H. P. Lundgren, *Text. Res. J.*, **21**, 620 (1951).
21. A. J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42B**, 84 (1946).