

Wool-Polymer Systems: Effect of Vinyl Polymers on Water Absorption

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Synopsis

Acrylamide, acrylic acid, and acrylonitrile have been polymerized *in situ* within wool fibers and the water-absorption properties of the resultant wool-polymer systems compared with those of wool and the polymers measured separately. At high humidities, polyacrylamide and, to a lesser extent, poly(acrylic acid) caused increased water uptakes when expressed as a function of the original weight of wool, due to the hydrophilic nature of these polymers. This increase was less than that expected from the water contents of the wool and polymers measured as separate entities. Chain entanglements in the polymer-keratin network may be responsible for some reduction of water content. The presence of polyacrylonitrile in wool reduced the water content at high humidities to less than that of wool alone, indicating that "volume exclusion" of water by the polymers is also a contributing factor. At low humidities, the water content of the wool-polyacrylamide system is equivalent to the sum of the water contents of wool and polymer taken separately; in the case of poly(acrylic acid) the water content is less than that of wool and polymer considered separately, and this is attributed to ionic bonding. For wool containing polyacrylonitrile there is a reduction in water content at low humidities, indicating interaction between the polymer and polar sorption sites in the wool.

INTRODUCTION

Considerable research has been directed towards improvement of technological properties of wool by internal deposition of polymers. Thus, rate of felting shrinkage may decrease¹⁻⁵ or increase,⁶ depending on the particular polymer used; abrasion resistance,^{2,4,5} elastic properties,^{2,3,7} and uptake of dye^{2,4} may also be affected by the presence of polymers.

Water sorption by wool might also be expected to change with introduction of polymers, and the extent of this change may vary according to the hydrophilic character of the polymer. It is possible to deposit large amounts of polyacrylonitrile in wool,^{8,9} but, because of the nonpolar nature of this polymer, only small changes are observed in water uptake of the treated wool when expressed as a function of the wool content of the product.^{7,8,10} Similarly, Williams et al.¹¹ reported small reductions in water content following graft polymerization of styrene in wool. The only re-

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port on sorption properties of wool containing hydrophilic polymers appears to be that of Korshak et al.,¹² where mention is made of increased wicking properties following graft copolymerization of poly(methacrylic acid).

This paper presents water sorption data for wool containing varying amounts of two water-soluble polymers—poly(acrylic acid) and polyacrylamide—and an insoluble polymer—polyacrylonitrile. Sorption data for the polymers in the free state and for a control wool sample were also obtained. Changes in water content are considered relative to the wool-polymer product and also to the wool content of the copolymer. The experimental results are discussed in terms of the known effects which physical and chemical modifications have on various regions of the wool-water isotherm.^{8,10}

EXPERIMENTAL

Wool

The wool fabric used was a light-weight plain weave worsted fabric made from Merino 64-70's wool, the only finishing treatments applied being a light scour with non-ionic detergent, followed by drying and steaming.

Monomers

Research-grade acrylonitrile and acrylic acid were purified immediately before use by vacuum distillation, while acrylamide was recrystallized from ethyl acetate.

Polymerization in Wool

The ferrous ion-peroxide initiator system was used.² Fabric circles (7 cm. diameter, to lie flat in a 250-ml. Erlenmeyer flask) were wet out in 96% ethanol, thoroughly rinsed in water, soaked in a 0.1% aqueous ferrous ammonium sulfate solution for 2 hr. at 50:1 liquor ratio, squeezed, and allowed to air-dry. After rewetting in alcohol and rinsing as above, polymerization was carried out in 0.1% hydrogen peroxide solution containing the appropriate concentration of monomer, a 50:1 liquor ratio at 85°C. for 1 hr. being used. Air above the solutions was displaced with nitrogen. The monomer concentration was varied to give the desired uptake of polymer by the wool. The treated fabrics were washed for 7 days in daily changes of distilled water. Polymer uptakes were determined gravimetrically, the samples being dried at 10^{-4} mm. Hg and 100°C. for 1 hr. before and after the treatment. The weight uptakes of polymer are expressed as the percentage weight change of the untreated dry wool.

Formation of Pure Polymers

Each monomer was polymerized from 10% solution in 0.02% aqueous ammonium persulfate containing 2% isopropanol, at 85°C. for 2 hr.¹³

The poly(acrylic acid) was isolated by drying to constant weight *in vacuo* at 20°C.; polyacrylamide was precipitated from solution by addition of methanol, filtered, and vacuum-dried to constant weight. Films of these two polymers were prepared for sorption measurements by casting from aqueous solution. The water-insoluble polyacrylonitrile was washed, dried to constant weight under vacuum, and cast into a film from dimethylformamide solution.

Water Sorption

Water absorption isotherms were obtained by measuring the equilibrium water content at various humidities. The samples were suspended from a calibrated quartz spiral spring balance mounted in an evacuable glass sorption chamber, and the water vapor pressure read from a wide-bore differential mercury manometer. The apparatus was enclosed in an efficient air thermostat maintained at $35 \pm 0.01^\circ\text{C}$. Absorption isotherms

TABLE I
Uptake of Water Vapor by Polyacrylamide and Wool-Polyacrylamide Copolymers (Based on Weight of Wool)

Relative humidity, %	Equilibrium water content, %					
	Wool	Wool + polymer (percentage polymer)				Free polymer
		22.1%	45.1%	63.1%	82.3%	
5	2.5	3.1	3.8	4.1	4.5	2.1
10	3.8	4.9	5.5	6.1	6.8	3.7
20	6.0	8.2	8.8	10.0	11.0	6.7
50	11.3	15.8	18.9	21.0	24.2	15.1
80	18.8	24.8	30.8	36.4	41.8	32.5
90	23.7	32.5	42.0	50.0	59.0	53.0
95	29.0	45.6	54.8	73.8	85.3	—
100	37.4	59.6	80.5	102.0	124.2	—

TABLE II
Uptake of Water Vapor by Poly(acrylic Acid) and Wool-Poly(acrylic Acid) Copolymers (Based on Weight of Wool)

Relative humidity, %	Equilibrium water content, %					
	Wool	Wool + polymer (percentage polymer)				Free polymer
		21.6%	46.5%	61.2%	77.8%	
5	2.5	2.6	2.7	2.7	2.7	1.0
10	3.8	4.0	4.2	4.2	4.3	1.8
20	6.0	6.2	6.4	6.7	7.3	2.9
50	11.3	11.7	12.6	13.4	14.4	8.0
80	18.8	18.9	21.2	23.1	25.4	26.2
90	23.7	23.1	29.0	31.8	35.6	46.5
95	29.0	27.8	36.0	41.5	46.4	—
100	37.4	40.4	43.5	54.6	64.0	—

TABLE III
Uptake of Water Vapor by Polyacrylonitrile and Wool-
Polyacrylonitrile Copolymers (Based on Weight of Wool)

Relative humidity, %	Equilibrium water content, %					
	Wool	Wool + polymer (percentage polymer)				Free polymer
		22.0%	56.6%	105.3%	126.1%	
5	2.5	2.5	2.4	2.35	2.25	0.16
10	3.8	3.8	3.6	3.6	3.6	0.30
20	6.0	6.0	5.7	5.9	6.1	0.58
50	11.3	12.0	12.2	12.7	12.9	1.52
80	18.8	19.5	20.1	20.7	20.8	3.0
90	23.7	24.8	25.7	25.5	25.6	4.4
95	29.0	30.2	29.8	28.8	28.6	5.5
100	37.4	36.5	35.8	33.3	32.9	7.0

were taken by initially evacuating the sorption chamber, then increasing the humidity stepwise in the manner previously described.⁸ The equilibrium water content was read at each humidity and expressed as weight per cent of the vacuum dry sample. In the case of the wool-polymer samples listed in Tables I-III the equilibrium water content was converted to weight per cent of the original wool content.

RESULTS AND DISCUSSION

Isotherms were measured on wool samples at four levels of polymer content for each of the three polymers, on a control wool sample, and also on the pure polymer samples. The range of concentrations of monomer in the treatment solutions were such that the samples contained approximately 20, 40, 60, and 80% polymer on the weight of wool for the hydrophilic polymers. Tables I, II, and III, contain sorption data for wool-polyacrylamide, wool-poly(acrylic acid) and wool-polyacrylonitrile, respectively. Data for the appropriate free polymer and the control wool sample are also included.

The samples containing no polymer were subjected to control treatments in the absence of monomer. There was a tendency for the control isotherm to be higher than that for completely untreated wool at the highest humidities, presumably due to slight degradation of the wool during treatment.^{8,10} It was not possible to obtain reliable equilibrium water content values at greater than 90% R.H. for the two water-soluble polymers because the rapid increase in water uptake with increasing humidity in this range caused the polymers to go into solution and drop from the spiral spring before equilibrium was attained.

The equilibrium water contents listed in Tables I-III are expressed as a percentage of the original weight of wool rather than of wool + polymer. On this basis the large increases in water content indicate that incorporation of hydrophilic additives can greatly enhance the water-sorption ca-

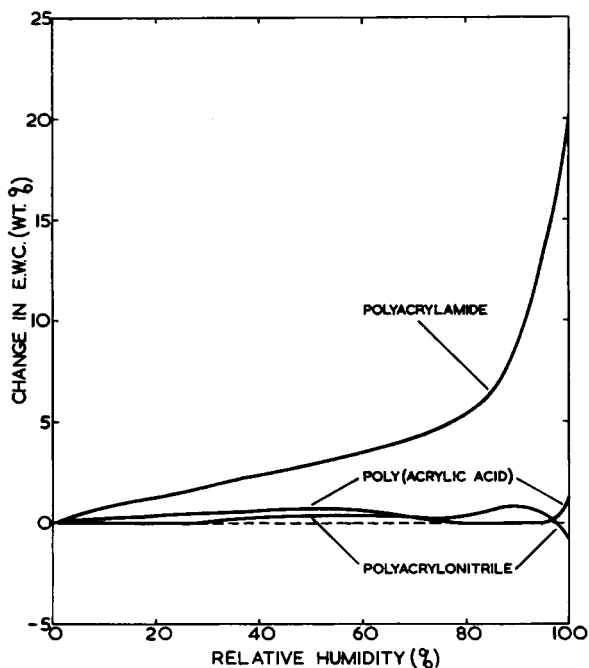


Fig. 1. Change of equilibrium water content of wool following application of 20% of polymer.

capacity of wool. The presence of the nonpolar polyacrylonitrile results in only slight changes in water content at low and intermediate humidities, while at high humidities large amounts of polymer cause a reduction in water uptake. However, the reduction in uptake at low humidities, when considered in terms of the increase expected due to sorption by the pure polymer, indicates interaction with polar groups in the wool. This view is supported by observations¹⁴ that acrylonitrile reacts with amino groups of wool; thus this reduction in equilibrium water content would be similar to that obtained following partial modification of amino groups by acetylation⁸ or deamination.¹⁵

In order to compare the water sorption properties of wool containing equal amounts of the different polymers, plots of polymer content versus equilibrium water content of the wool at the various humidities listed in Tables I-III were drawn, in the manner described for partially deaminated wools.¹⁵ Values for equilibrium water content of wool containing 20% and 80% by weight of each polymer were obtained from these graphs. The water content of the control wool was subtracted from these values and the results plotted in Figures 1 and 2 to give the difference isotherms, i.e., the plot of relative humidity versus the change of apparent water content of the wool resulting from addition of polymer.

The increased water uptake by wool containing polyacrylamide and to a lesser extent, poly(acrylic acid), may be expected from consideration of the

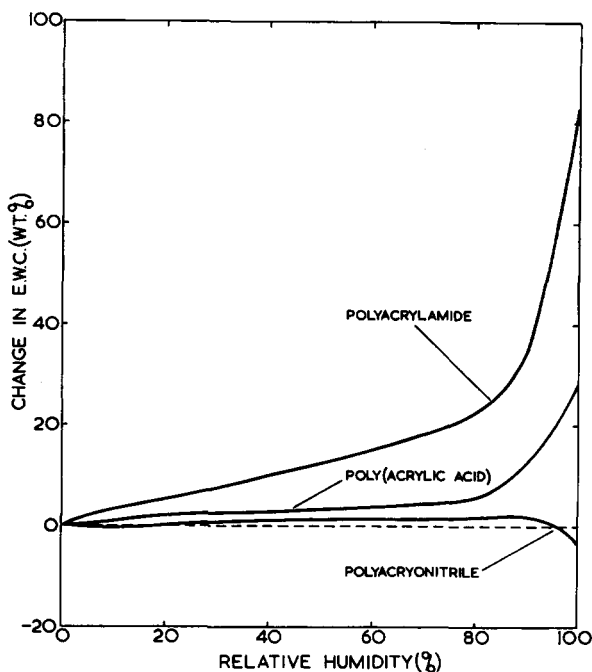


Fig. 2. Change of equilibrium water content of wool following application of 80% of polymer.

free polymer isotherms. However, although the free polymers go into solution at humidities above 90% R.H., finite equilibrium water uptake by the wool-polymer systems indicates that the presence of wool is restricting water uptake by the polymers at high humidities.

The water contents presented so far have been based on the original wool content of the system (i.e., water content expressed on weight of wool), as is usual for chemically modified wools.^{8,10,15-17} However, in the present case large polymer:wool ratios are used, and there is obviously considerable scope for interaction between polymer and wool. The effect which these interactions have on water uptake of the wool-polymer systems can be more readily assessed by plotting, as a function of relative humidity, the difference between water content of the wool-polymer system (S) (expressed on weight of wool + polymer) and that expected from sorption by free polymer (P) and wool (W), i.e., the plot of $S - (P + W)$ versus relative humidity. These plots are shown for the three polymers in Figures 3 and 4, where the wool-polymer ratios are the same as those used in Figures 1 and 2.

The dotted line forming the abscissa in Figures 3 and 4 is the plot which would be obtained if the contributions of the wool and the polymer were exactly additive, i.e., if the wool had no effect on water sorption by polymer and polymer had no effect on water sorption by wool.

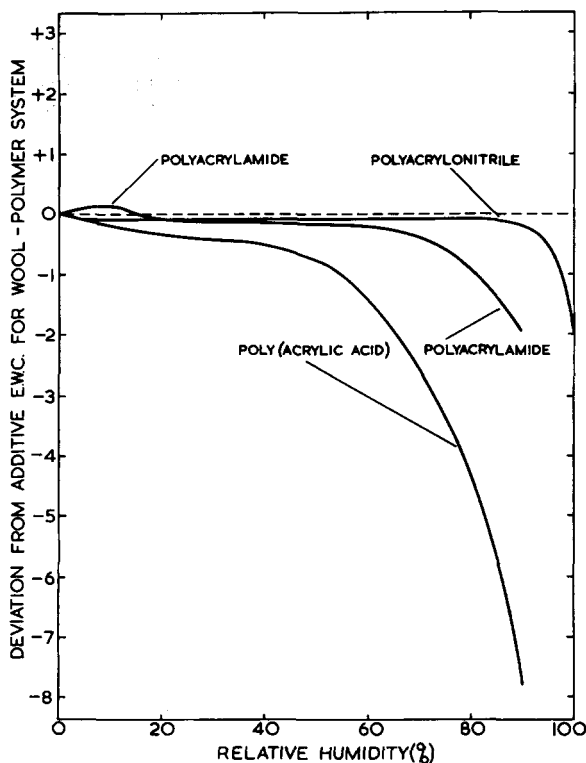


Fig. 3. Deviation from additivity of equilibrium water content of wool-polymer system (20% polymer on weight of wool).

Sorption by the polyacrylamide-wool system is approximately additive up to about 60% R.H., after which sorption by the copolymer is reduced, whereas, for the poly(acrylic acid)-wool system, deviation from additivity commences almost from zero humidity. A possible explanation for the behavior observed for poly(acrylic acid) in wool may be ionic interaction between —COO^- groups of the polymer and —NH_3^+ groups of the wool, which could not occur with polyacrylamide. Both groups are normally strongly hydrophilic, but in the wool-polymer system, where the polymer is formed *in situ*, they may be physically close enough to prevent water binding by either group. With polyacrylamide, the strongest interaction would be hydrogen bonding with polar groups in the wool. These hydrogen bonds would be readily broken by water, even at low water contents, thus enabling the polar groups in the wool-polyacrylamide system to participate in water sorption to a greater extent than in the wool-poly(acrylic acid) system.

The isotherm for normal wool in the region above 80% R.H. shows a rapid increase of water content as a function of humidity, because of condensation of loosely bound or "liquid" water inside the wool structure.^{8,10}

Furthermore, disruption of covalent bonds results in an increased water uptake in this region.⁸ Therefore, the total amount of water taken up by wool at saturation is determined, not only by the number of polar sorption sites, but also by the number and strength of the cohesive forces in wool which resist swelling. Thus the saturation water content is affected by the equilibrium between these cohesive forces and the swelling pressure of the water absorbed by the wool.

The less-than-additive water uptake exhibited by each polymer-wool system at higher humidities involves the equilibrium between ability of the

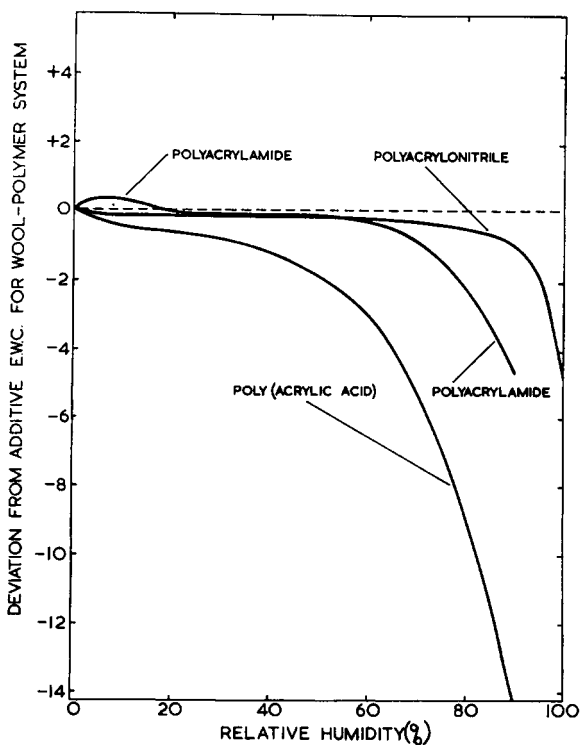


Fig. 4. Deviation from additivity of equilibrium water content of wool-polymer system (80% polymer on weight of wool).

system to swell and the swelling pressure of the water vapor. It is apparent that wool-polymer interactions radically alter this equilibrium for all the polymers considered. In particular, the interaction with wool appears to prevent the hydrophilic polymers swelling sufficiently to go into solution.

This restriction to swelling may occur by the following mechanisms.

Chain Entanglement. There is a high probability of chain entanglement between the polypeptide chains of the wool keratin and the growing polymer chains. The existence of chain entanglements, which prevent molec-

ular chains from moving freely, may be similar in effect to the introduction of covalent crosslinks. If chain entanglement does occur, then the polymer deposited in the wool will have a higher degree of crosslinking than the free polymer, and these additional constraints will tend to restrict swelling of the polymer. However, for the two water-soluble polymers, considerable swelling does occur before equilibrium is established with the retractive forces in the wool-polymer network.

Volume Exclusion. It has been demonstrated recently that the presence of bulky molecules in wool fibers affects the water content even without chemical reaction or permanent modification of the wool keratin.^{8,10,17} This is manifested as a reduction in water content, which is most marked at high humidities, and has been termed volume exclusion of water molecules.⁸ This mechanism does not necessarily imply that there is direct replacement of water with an equal volume of additive, e.g., it has been shown that for the wool-ninhydrin system a specific amount of ninhydrin excludes variable amounts of water, depending upon the cohesive forces present in the system. Thus, ninhydrin treatment of wool degraded by acid hydrolysis gives a greater reduction in equilibrium water content than ninhydrin treatment of undamaged wool.⁸ This feature is most clearly exhibited by the wool-polyacrylonitrile system, where the water content at 100% R.H., expressed as a percentage of the weight of wool, is even less than that for unmodified wool. This obviously cannot be entirely due to polymer-wool interactions acting as pseudocrosslinks, since the polymer was formed while the wool was in the water-swollen state, so this type of constraint should not be operative at levels of swelling less than this original water-swollen state.

CONCLUSIONS

The presence of polyacrylamide, and to a lesser extent of poly(acrylic acid) appears to increase the water content of wool (based on weight of wool).

At high humidities, water sorption by all three wool-polymer systems is appreciably lower than the additive water uptake of normal wool and free polymer—probably due to a combination of chain entanglement and volume exclusion of water from the wool by the presence of polymer.

At low humidities the water content is additive for the wool-polyacrylamide system. For the wool-poly(acrylic acid) system, the water content is less than additive, probably as a result of ionic bonding between wool and poly(acrylic acid). Polyacrylonitrile in wool causes a slight reduction of water content of the wool in this humidity region, indicating blocking of some polar sorption sites.

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Résumé

L'acrylamide, l'acide acrylique et l'acrylonitrile ont été polymérisés *in situ* au sein de fibres de laine et les propriétés d'absorption des systèmes laine-polymère résultants ont été comparées avec celles de la laine et des polymères mesurés séparément. A humidité élevée le polyacrylamide et, pour une moindre mesure l'acide polyacrylique, causaient une absorption d'eau plus élevée lorsqu'on l'exprime en fonction du poids original de la laine par suite de la nature hydrophile de ces deux polymères. Cet accroissement était inférieur à celui attendu au départ de la teneur en eau de la laine et des polymères mesurés comme entités séparées. L'enlacement de chaînes dans le réseau polymère-kératine peut être responsable pour une certaine réduction de la teneur en eau, pour la présence de polyacrylonitrile dans la laine réduit la teneur en eau aux des degrés humidité élevée, à une valeur plus faible que celle de la laine ce qui indique que "l'exclusion de volume" de l'eau par les polymères est également un facteur qui contribue au phénomène. Aux basses humidités, la teneur en eau du système polyacrylamide-laine est équivalent à la somme des teneurs en eau de la laine et du polymère pris séparément; dans le cas de l'acide polyacrylique la teneur en eau est inférieure à celle de la laine et du polymère considéré séparément et ceci est attribué à la liaison ionique entre les polymères. Pour la laine contenant du polyacrylonitrile, il y a une réduction de la teneur en eau aux basses humidités, ce qui indique une interaction entre le polymère et les sites de sorption polaire dans la laine.

Zusammenfassung

Acrylamid, Acrylsäure und Acrylnitril wurden *in situ* in Wollfasern polymerisiert und die Wasserabsorption der gebildeten Wolle-Polymer-Systeme mit der an Wolle und Polymeren getrennt gemessenen verglichen. Bei hoher Feuchtigkeit erhöhten Polyacrylamid und in geringerem Ausmass Polyacrylsäure wegen der hydrophilen Natur dieser Polymeren die als Funktion des ursprünglichen Gewichts der Wolle ausgedrückte Wasseraufnahme. Diese Erhöhung war geringer als nach dem an Wolle und Polymeren separat gemessenen Wassergehalt zu erwarten war. Kettenverschlingungen im Poly-

mer-Keratinnetzwerk können für eine gewisse Herabsetzung des Wassergehaltes verantwortlich sein. Die Gegenwart von Polyacrylnitril in Wolle setzte bei hoher Feuchtigkeit den Wassergehalt auf einen geringeren Wert als den von Wolle allein herab, was zeigt, dass "Volumsausschluss" des Wassers durch die Polymeren ebenfalls einen Beitrag liefert. Bei niedriger Feuchtigkeit ist der Wassergehalt des Wolle-Polyacrylamidsystems der Summe der Wassergehalte der Wolle und des Polymeren für sich äquivalent im Falle der Polyacrylsäure ist der Wassergehalt geringer als der von Wolle und Polymerem für sich, was auf ionische Bindung zurückgeführt wird. Bei polyacrylnitrilhältiger Wolle tritt bei niedriger Feuchtigkeit eine Reduktion des Wassergehaltes ein; das spricht für eine Wechselwirkung zwischen dem Polymeren und polaren Sorptionsstellen in der Wolle.

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