Copolymers of Wool Keratin: Sorption Properties

I. C. Watt[a]; R. L. D'arcy[a]

[a] Division of Textile Physics, CSIRO Ryde, NSW, Australia

PLEASE SCROLL DOWN FOR ARTICLE

Copolymers of Wool Keratin: Sorption Properties

I. C. WATT and R. L. D'ARCY

Division of Textile Physics
CSIRO
Ryde, NSW, 2112
Australia

ABSTRACT

The internal deposition of polymers in wool fibers forms
copolymers with modified sorption properties. Water
vapor sorption isotherms of some copolymers are presented
to illustrate the influence of the properties of the added
polymer and the effects of interactions between the polymer
and the wool substrate. Changes in water content are not
proportional over the whole isotherm and it is shown that
polymerization causes changes in the state of the water in
wool. The kinetics of water sorption show little change at
low humidities but absorption into copolymers is markedly
slower at intermediate and higher humidities. The mode
of initiation of polymerization has little effect on the
sorption properties of the copolymer. Grafting, compared
to internal deposition without covalent bonding, does not
influence sorption behavior unless cross-links are formed
and these cause a marked reduction in formic acid swelling.
The influence of sorption properties on the observed
physical properties of wool copolymers is discussed.

Small polar molecules, such as water, are readily sorbed by keratin even when the substrate is completely dry. Larger molecules are sorbed more slowly and it becomes necessary to preswell the substrate with water or other small molecules in order that sorption of large molecules may occur. Sorption properties of wool fibers are of interest because wool is usually processed and used with an appreciable water content; also its physical properties are frequently determined in liquid water or a water vapor atmosphere. Measured values of mechanical properties, in particular, are highly dependent on the water content or the presence of other sorbates in the fibers. Any changes in the properties of wool copolymers must therefore be related to the sorption properties.

Copolymers of wool keratin can be formed by the incorporation of a polymer within the keratin structure. This is a restricted case of copolymerization since the natural macromolecule is fully formed prior to the addition of a second polymer. Such a combination of macromolecules might be expected to give a copolymer with some of the properties of each component. The formation of copolymers with natural macromolecules is readily achieved because the techniques of the polymer chemist are usually applicable. Added polymer may be formed in situ by polymerization of one or more monomers utilizing standard methods of initiation or by condensation of reactants. Deposition of a preformed polymer forms a block copolymer in which the added polymer is restricted to the surface or near-surface regions of the wool fibers.

Internal polymerization is frequently initiated by free radicals generated in the wool fibers. These may be formed by chemical means but are usually not part of the keratin structure, and grafting of the polymer to the substrate via a covalent bond can only occur by a chain transfer mechanism. Irradiation of the wool substrate either by preirradiation, in which the wool is exposed to a radiation source before being brought into contact with monomer, or mutual irradiation, in which the substrate is irradiated in the presence of monomer, is another means of forming free radicals. Polymerization initiated by such free radicals yields copolymers with many of the new polymer chains grafted to the wool substrate. In general, mutual irradiation techniques give greater yields of grafted polymer and cause less modification of the keratin structure.

The sorption characteristics of a wool copolymer may depend upon the nature and amount of added polymer, the method of initiation, and the conditions of polymerization. In this paper the sorption characteristics of wool polymers obtained by different techniques are examined and the possible influence of an added polymer on the observed physical properties of copolymers are discussed.

EXPERIMENTAL

Wool fibers with the tips removed were washed in several changes of cold petroleum ether and then rinsed in distilled water until the pH of a small amount of rinse water was unchanged by contact with the wool. The average dry diameter of the fibers was determined microscopically.

Water vapor sorption isotherms were determined gravimetrically by suspending wool samples from a calibrated quartz spiral spring mounted in an evacuable glass chamber which had provision for admitting controlled amounts of deaerated vapor. The vapor pressure was read with a wide-bore differential mercury manometer and the apparatus enclosed in an efficient air thermostat controlled to $\pm 0.01°C$. Changes in the sample weights were calculated from the spring extension and the equilibrium water content (ewc) was expressed as the wt% of the original wool content. Formic acid vapor uptakes were determined in a similar manner.

Polymers were deposited within wool fibers from aqueous solution using a ferrous ion-hydrogen peroxide initiator [1], mutual irradiation in monomer vapor using γ-rays from a ^{60}Co source to generate free radicals in the substrate [2], and condensation of resorcinol and formaldehyde to form a resorcinol-formaldehyde resin [3]. The copolymer samples were thoroughly rinsed with a solvent for the added polymer and then rinsed with distilled water as for the initial cleaning. The amount of added polymer was calculated from the increased weight of the dried sample and expressed as a percentage of the original weight of the dry wool sample.

RESULTS

Water Vapor Isotherms

Water vapor isotherms of three different wool keratin copolymers, which are representative of the changes in isotherm behavior frequently observed, are shown in Fig. 1. A Fe^{2+}/H_2O_2 initiating system was employed for the deposition of polyacrylamide and polyacrylonitrile from aqueous solution, and the resorcinol-formaldehyde resin was formed by condensation of the reactants. The water content values of the copolymers are expressed as a percentage of the original weight of wool, and the dashed curve represents the water vapor isotherm of unmodified wool for comparison. It is apparent in all three cases that the changes in the isotherm are not proportional over the entire humidity range. In fact, for the wool-polyacrylonitrile
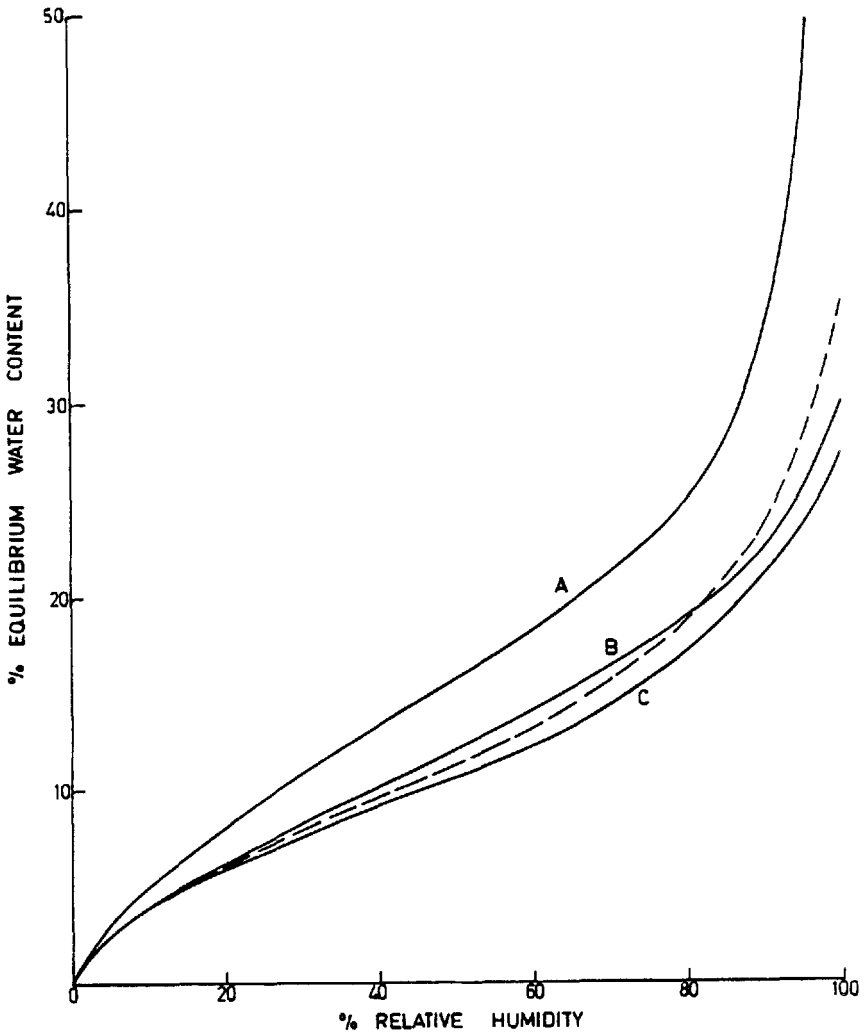
FIG. 1. Water vapor absorption isotherms at 35°C of wool copolymers containing (A) 22.1% polyacrylamide, (B) 54% polyacrylonitrile, and (C) 12% resorcinol-formaldehyde resin. (- -) Unmodified wool. The weight of polymer and equilibrium water content are based on the weight of wool.

copolymer an increased water content at intermediate humidities and
a decreased water content at high humidities are observed. The added
polyacrylonitrile and resorcinol-formaldehyde resin have low intrinsic
water sorption capacities and would be expected to contribute little to
the water sorption of the copolymers. There is however a marked
ewc reduction at high humidities for both copolymers. Polyacrylamide
is strongly hydrophilic and is soluble in liquid water. In this case
increased water sorption of the copolymer, particularly at high
humidities, occurs but there is a limit to the amount of water taken
up at 100% r.h. and the polymer is not leached out in liquid water. In
each case the polymer exhibits sorption properties different from
either of the components, and the water content at high humidities is
less than expected from the added water contents of the components.
Williams, Stannett, and Armstrong [4] have reported that wool-
polystyrene copolymers formed by mutual irradiation initiation give
water vapor isotherms similar to Curve C of Fig. 1 although requiring
greater amounts of added polymers to give the same reduction of ewc
at saturation.

A more detailed analysis of the modifications in water content of a
polymer is shown in Fig. 2 for a wool poly(acrylic acid) copolymer.
The water vapor isotherm of unmodified wool, poly(acrylic acid), and
a wool-poly(acrylic acid) copolymer are shown as Curves A, B, and C,
respectively. The dashed curve represents a theoretical isotherm
calculated on the assumption that the water contents of the copolymer
components are additive. An increase in ewc of the copolymer relative
to unmodified wool is apparent because the deposition of a hydrophilic
polymer enhances the water sorption capacity of wool fibers. However,
comparison with the isotherm calculated on the basis of additivity of
the water contents of the copolymer components shows that the co-
polymer has a reduced sorption capacity. This reduction is apparent
over the whole humidity range of the isotherm but is proportionally
greater at high humidities.

A recent analysis [5] considers the water vapor isotherm of
keratin as being comprised of three component isotherms and can be
expressed by an equation of three terms. The first term of the
equation is associated, in the model, with the formation of a monolayer
of water molecules at specific sites with relatively high affinity for
water; the second term represents the association of water molecules,
in a monolayer, with sites of weaker affinity for water and can be ap-
proximated by a linear relationship; the third term describes the
simultaneous formation of a multilayer on the primarily absorbed
monolayers. The three component isotherms of unmodified wool at
35°C are shown as Curves A, B, and C, respectively, in Fig. 3. A
similar analysis of the wool-poly(acrylic acid) copolymer gives the
three component isotherms shown as Curves A', B', and C' in
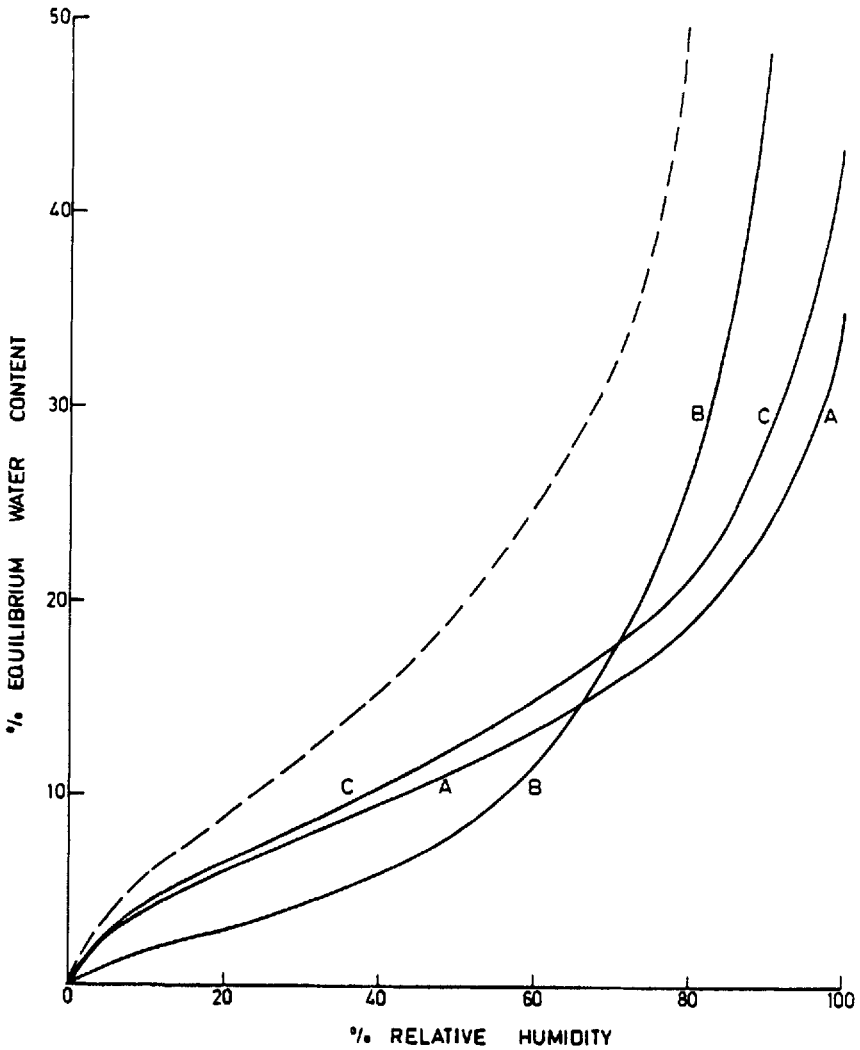Fig. 3. There appears to be a small increase in the number of

FIG. 2. Water vapor absorption isotherms at 35°C. (A)
Unmodified wool. (B) Poly(acrylic acid). (C) Wool containing
46.5% poly(acrylic acid) based on weight of wool. (- -) Theoret-
ical isotherm of wool + 46.5% poly(acrylic acid) assuming ad-
ditivity of water contents.
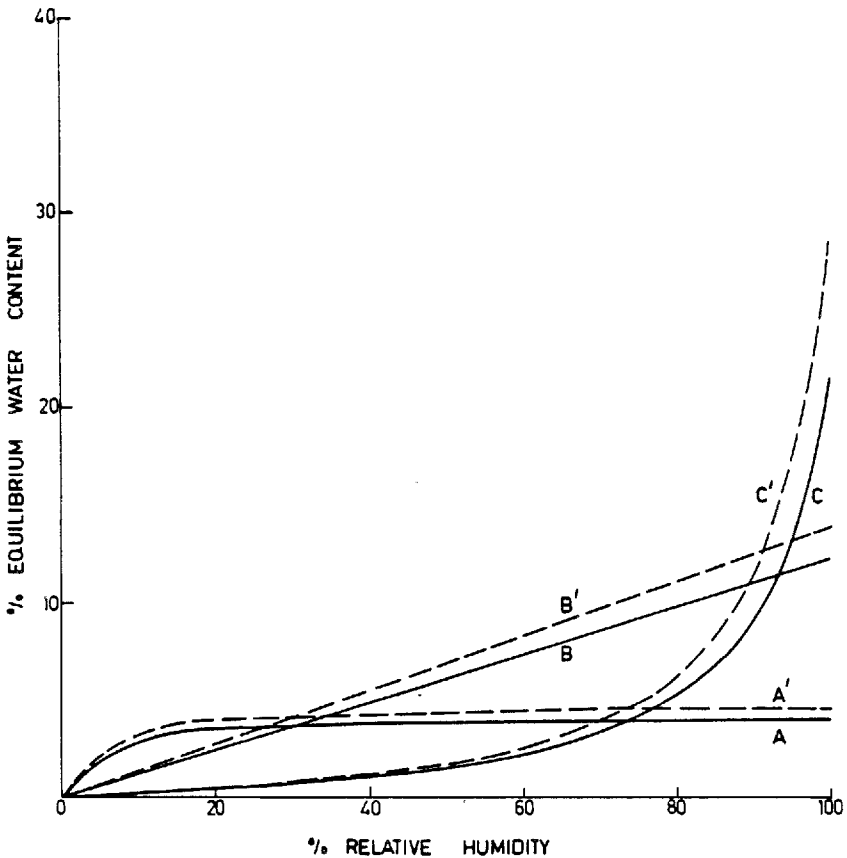
FIG. 3. Component curves of water vapor isotherms at 35°C.
Curves A, B, and C refer to unmodified wool, and Curves A', B',
and C' refer to a wool-poly(acrylic acid) copolymer.

hydrophilic sites with high affinity for water and in the amount of
water associated with weakly binding sites. It is apparent that most
of the change in water content of the wool-poly(acrylic acid)
copolymer is an increase in the amount of water forming a multilayer.

Kinetics of Water Sorption

Changes in the kinetics of water vapor sorption by copolymers
from those observed for unmodified wool may occur for several

reasons. First, the swelling of wool fibers to accommodate polymer means a greater distance for sorbate to penetrate and a longer time to reach equilibrium if the same mechanism of sorption is operative. However, it will be shown that following a change in the relative humidity of the environment the sorption kinetics exhibited by copolymers are different from those of wool after taking into account the changed dimensions of the fibers. The rate of sorption of water
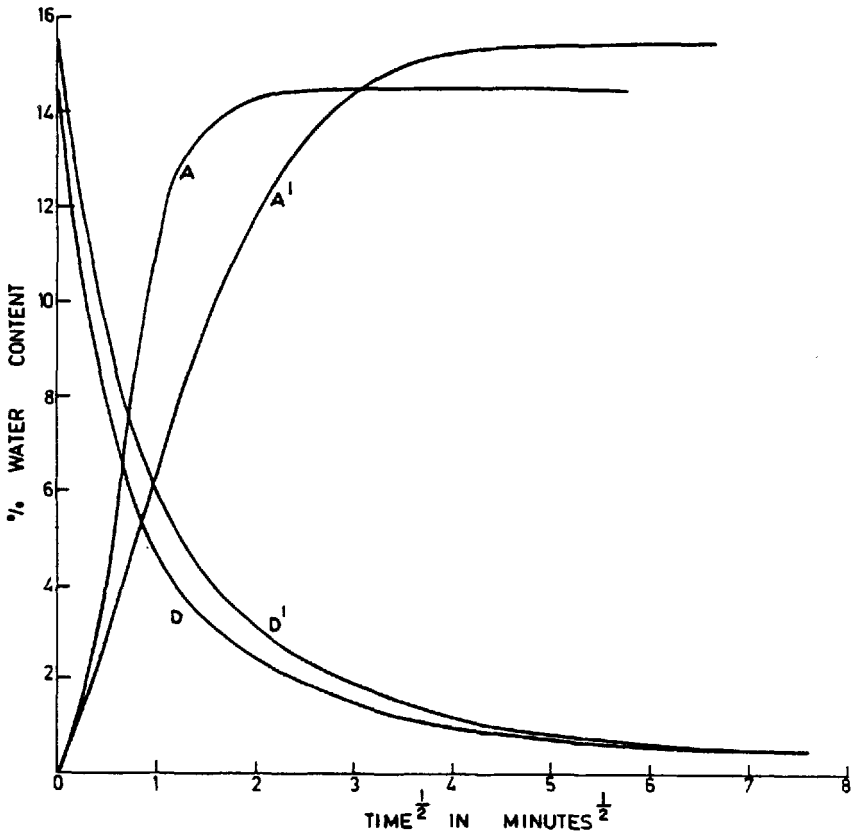

FIG. 4. Absorption and desorption curves between the humidity limits of 0 and 65% relative humidity. (A) and (D) Unmodified wool. (A') and (D') Wool containing 54% polyacrylonitrile based on weight of wool.

by wool is entirely diffusion controlled only at low water contents
[6]. At intermediate and high water contents the wool-water system
exhibits anomalous sorption behavior, and shapes of the sorption
curves are influenced by the size of the humidity change to which the
fibers are subjected and the initial water content of the water.

In Fig. 4 the absorption and desorption curves of water vapor by
wool and a wool-polyacrylonitrile copolymer are compared for
humidity changes over the range of 0-65% r.h. Comparison of the
sorption kinetics of this copolymer with those of wool is particularly
meaningful since the small increase of ewc at 65% r.h. of the co-
polymer is approximately the amount of water sorbed by polyacrylon-
itrile at this humidity [7]. A pronounced difference between the rates
of absorption and a smaller difference in the rates of desorption is
evident. The slower rate of desorption from the copolymer is of the
magnitude expected for the 25% increase in diameter of the copolymer
fibers but the decrease in the rate of absorption is greater than ex-
pected from this diameter change.

Anomalous sorption by keratin occurs by a coupled diffusion re-
laxation mechanism [8]. When the increase in humidity for a
sorption step is made sufficiently small at intermediate humidities,
the resulting water uptake occurs in two stages. The first stage is
diffusion controlled and can be described by Fick's law of diffusion;
at low humidities the entire absorption occurs by this mechanism.
The second stage is additional water uptake to maintain thermo-
dynamic equilibrium during stress relaxation of the fibers. At high
humidities no clear separation of the two stages of absorption is
apparent and the uptake which is typical of anomalous sorption can
not be adequately described by a generalized form of Fick's diffusion
equation.

For unmodified wool fibers, coefficients for the diffusion-controlled
uptake can be calculated with allowances made for variations in the
fiber diameter. Diffusion coefficients for the uptake of water vapor
as a function of humidity up to 80% r.h. are tabulated in Table 1 for
wool and the wool-polyacrylonitrile copolymer. Two-stage uptake is
no longer evident above 80% r.h. for absorption into wool but may be
obtained up to 90% r.h. with the copolymer.

Formic Acid Vapor Absorption

Formic acid, being a larger molecule than water, diffuses into
wool at a slower rate than water at low relative pressures [9]. At
high relative pressures, where sorption is no longer diffusion con-
trolled, formic acid is absorbed rapidly because of its ability to rup-
ture the hydrogen bond network of wool and is capable of swelling the
fibers up to a limit which is imposed by the covalent links of the

TABLE 1. Diffusion of Water Vapor into Wool and a Wool-Polyacrylonitrile Copolymer

| Humidity range (% r.h.) | Diffusion coefficients (cms^2 sec^{-1}) | |
	Wool	Copolymer
0-3	1.6×10^{-10}	1.7×10^{-10}
15-19	1.3×10^{-9}	0.7×10^{-9}
30-34	3.0×10^{-9}	1.3×10^{-9}
50-54	4.8×10^{-9}	2.0×10^{-9}
65-69	5.6×10^{-9}	2.4×10^{-9}
76-80	5.9×10^{-9}	3.0×10^{-9}

keratin network. The amount of formic acid vapor absorbed at saturation is a convenient measure of the constraints, other than hydrogen bonds, which effectively control the degree to which wool fibers can swell; an increase in the saturation formic acid uptake is indicative of the rupture of covalent bonds [10]. Conversely, the introduction of additional constraints to swelling reduces the formic acid uptake [11]. The weight of formic acid absorbed at saturation by a number of copolymers of wool are tabulated in Table 2 together with the corresponding saturation water contents of the copolymers. All values are expressed as a percentage of the weight of wool in the copolymer.

TABLE 2. Saturation Formic Acid and Water Contents of Copolymers

| Copolymer of wool + | Weight increase at saturation for | |
	Formic acid	Water
-	180	35.2
12% Polyacrylonitrile	178	32.5
54% Polyacrylonitrile	185	29.5
27% Polystyrene	183	29.5
27% Poly(divinyl benzene)	135	31.0
12% Resorcinol-formaldehyde	105	27.6

DISCUSSION

The properties exhibited by a wool copolymer will be influenced by many factors. For a copolymer of fixed composition the distribution of added polymer is important. In this paper we are considering only copolymers in which the added polymer is distributed throughout the wool fiber and may modify its bulk properties. Copolymers with the added polymer restricted to the surface regions of the fiber may exhibit markedly different kinetic behavior in sorption with little change in equilibrium water contents. Polymerization may be induced in wool fibers by free radicals not attached to the substrate, but the growing polymer chains probably become entwined with the polypeptide chains of the keratin substrate. Because of the size and configuration of the new macromolecule it is difficult to determine the extent of any covalent bonding which may have occurred. Extraction of a wool copolymer with a solvent for the added homopolymer may remove polymer from the surface of the fibers but not from the interior.

Despite differences in the mode of preparation and the polymers added, all copolymers show a similarity in the features of their water sorption isotherms. The most notable are a reduction in the water content near saturation brought about by hydrophobic polymers, and a reduction below the combined water contents of wool and polymer for hydrophilic polymers. The exclusion of water in this way suggests interaction between the keratin and polymer. A reduction in the uptake of formic acid vapor only occurs when the added polymer is capable of introducing cross-links to provide additional constraints to the swelling of the keratin network. Therefore, it does not appear that the reduction of water content results solely from chain entanglements involving the polypeptide chains and the polymer molecules. The changes in water content of the wool produced by the added polymer are not proportional over the whole humidity range so the product does not behave as a mixture of components. Also there is little evidence of differences between copolymers produced by radiation-initiated polymerization, which presumably involves grafting to the fibers, and chemical initiation by free radicals not attached to the keratin substrate. It is reasonable therefore to term the product a copolymer of wool keratin even in the absence of covalent bonding between the keratin and the polymer.

The nature of the interaction between the keratin and polymer can be examined more closely using the D'Arcy-Watt isotherm [5]. For the wool-poly(acrylic acid) copolymer analyzed here there is a greater amount of water associated with strongly hydrophilic sites than for unmodified wool, reflecting the introduction of such sites by the added polymer. This leads to an increased water content of

the copolymer at low humidities. However, the isotherm of the co-
polymer is less than the added isotherms of wool and poly(acrylic
acid) in this region (cf. Fig. 2). It is apparent that some of the
hydrophilic groups of the copolymer are blocked, probably by
interaction between the side-chain amino groups of keratin and the
carboxyl groups of the polyacrylic acid. The analysis also shows a
small increase in the amount of water associated with weakly bind-
ing sites; in keratin these are predominantly the peptide bonds of
the polypeptide chains and the increase possibly reflects a greater
ease for water molecules to reach these sites or an increase in the
number of such sites in the copolymer.

Absorption of water at high humidities involves condensation of
water onto water molecules which are already associated with
hydrophilic groups, to build a multilayer. The limiting factor in
the amount sorbed by this mechanism is the balance between the
constraints to swelling imposed by the structural network of the
copolymer and the swelling forces induced by the sorbate. The
swelling of wool fibers by polymer does not appear to affect the
subsequent swelling of the copolymer in water or formic acid as
the saturation formic acid content is only reduced by the presence
of polymers which can form covalent cross-links and the saturation
water content does not vary greatly for quite different amounts of
added polymers. Cross-links could contribute to the substantial
reduction in saturation water content achieved by only 12% resorcinol-
formaldehyde resin because the cross-linked resin was formed with
the wool at an intermediate humidity and the cross-links would
oppose any swelling to a higher level. Less water than expected on
the basis of additivity could be absorbed at high humidities since
interactions at lower humidities may have reduced the amount of
water associated with hydrophilic sites. It also appears that water
is displaced from the multilayer because each of the components
may occupy part of the space normally taken up by water in associ-
ation with the other component.

The sorption kinetics exhibited by a copolymer further emphasize
that the copolymer can not be considered as a simple mixture of
components. The unchanged diffusion coefficients at low humidities
are determined largely by the polar character of the material and
show that the mechanism of sorption in this region remains essenti-
ally unaltered despite any conformational differences of the copolymer.
The slower rate of diffusion into the copolymer, which is clearly
evident with increasing humidity, points to the smaller dependence on
concentration as being responsible for the lower diffusion coefficients
of water vapor into copolymer compared to unmodified wool. These
results are in agreement with those reported for the wool-polystyrene
copolymer [4] and suggest that the molecular chains of the copolymer
lack mobility and are unable to move as quickly under the influence

of the incoming water. This concept is supported by the evidence obtained with large humidity changes where relaxation of the fibers also influences the rate of water vapor uptake so that the copolymer absorbs more slowly than wool. However, after making allowance for diameter differences, wool and copolymer desorb at the same rate since relaxation is not an important factor in the desorption process.

The changes in sorption behavior must be considered in the interpretation of copolymer physical properties determined in the presence of a sorbate. Because the molecular architecture of the wool fiber is substantially preserved during polymerization, the physical properties of the copolymer are predominantly those of the wool fiber unless some particular structural feature of the keratin has been modified. For example, the introduction of additional covalent cross-links reduces swelling in formic acid, increases the torsional modulus, and increases the resistance to deformation of a copolymer fiber. In the absence of obvious modifications to the wool structure it is the changes in sorption behavior which appear to have the greatest influence on observed physical properties measured in the presence of a sorbate. Frequently the physical properties of a copolymer in equilibrium with liquid water or water vapor are similar to those of a wool fiber equilibrated with a lower humidity of water vapor.

It is most significant that variations in ewc are not proportional over the whole isotherm since the nature of the association of water with the substrate influences its effect on the properties of the fiber [12]. Water intimately associated with hydrophilic side chains has little effect on the stress-strain relationship of fibers but water directly associated with the polypeptide backbone and water absorbed as a multilayer have a strong influence on the tensile properties. The modified sorption kinetics also indicate that changes in properties will be most evident at high humidities.

REFERENCES

[1] M. Lipson and J. B. Speakman, J. Soc. Dyers Colour., 65, 390 (1949).
[2] A. A. Armstrong and H. A. Rutherford, Text. Res. J., 33, 264 (1963).
[3] J. D. Leeder and A. M. Wemyss, J. Appl. Polym. Sci., 15, 507 (1971).
[4] J. L. Williams, V. Stannett, and A. A. Armstrong, J. Appl. Polym. Sci., 10, 1229 (1966).
[5] R. L. D'Arcy and I. C. Watt, Trans. Faraday Soc., 66, 1236 (1970).
[6] I. C. Watt, Text. Res. J., 30, 443 (1960).

[7] J. D. Leeder, A. J. Pratt, and I. C. Watt, J. Appl. Polym. Sci.,
     11, 1649 (1967).
[8] I. C. Watt, Text. Res. J., 30, 644 (1960).
[9] I. C. Watt, J. Appl. Polym. Sci., 8, 1737 (1964).
[10] I. C. Watt, Text. Res. J., 33, 631 (1963).
[11] I. C. Watt, Nature, 201, 923 (1964).
[12] I. C. Watt, Appl. Polym. Symp. 18, 905 (1971).