On a Correlation Between the Surface Chemistry and the Felting Behavior of Wool[1]

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ABSTRACT

The felting behavior of wool fibers is found to be correlated with their flocculation properties. The interaction between the fibers is suggested as the common factor responsible for this correlation. It is observed that in a felting medium there is attraction between natural wool fibers. Such attraction is observed to be greatly diminished, or absent, after the wool has been shrinkproffed by any one of several chemical modification treatments. Hydrophobic attraction and electrostatic repulsion are proposed as significant components of the interaction between fibers in aqueous media. These components are linked to the surface chemistry of natural and chemically modified wool. It is proposed that the hydrophobic nature of the fiber surface promotes the felting shrinkage of natural wool fabrics, that shrink-resist chemical treatments of wool top make the fiber surface more hydrophilic and may increase the electrostatic repulsion between fibers, and that the influence of surfactants on felting depends on the adsorption energy of the surfactant at the fiber surface. These ideas are presented as a guide for the development of further shrink-resist chemical modifications of wool.

INTRODUCTION

It is well known that a collection of wool fibers moved vigorously in water is subject to felting. This process allows one to shape loose wool into dense felt material which has desirable applications. On the other hand, in the laundering of wool fabrics the same felting process may cause fabric shrinkage which is undesirable. Chemical modification of wool fibers may change their felting characteristics. Research in this area has been quite effective and several chemical shrinkproofing treatments are now available. Some treatments, at high levels of application, even produce wool fabrics which expand, instead of shrink, during washing.

Wool felting has been studied for a long time. Many details and references are given in several review articles (1). Most discussions of the cause and mechanism of wool felting focus on physical fiber properties such as the presence of surface scales, the differential friction effect, crimp and fiber flexibility. This emphasis is natural because of the mechanical nature of the felting process. In this paper we investigate the possibility that felting correlates significantly with the chemistry of wool and, in particular, with the chemistry of the fiber surface. The present availability of chemically modified wool facilitates the search for such a correlation.

The felting of wool and the felting shrinkage of wool fabrics are complicated processes with a great number of mechanical and dynamical variables and the role of fiber chemistry is not obvious. For this reason we will consider the flocculation of a suspension of short sections of wool fibers. This is a much simpler physical process than felting and it may still involve some of the same chemical variables. In the following we first show that in a number of cases a correlation exists between the flocculation and the felting behavior of wool. As a significant factor common to both processes the static interaction between the fibers is suggested. Such interaction is discussed in terms of the surface chemistry of the fibers. Finally, the effect of various chemical modifications on the felting properties of wool is linked to the surface chemistry of the modified fibers.

EXPERIMENTAL PROCEDURES

Fabric

A 6.40 oz/yd^2 scoured and neutralized, undyed woolen flannel containing 32 ends and 29 picks/in. was used.

Shrinkage Tests

The Accelerotor (2) was run at 1780 rpm at 22 C with 200 ml aqueous .01 M buffer solution. Acetic acid-sodium acetate and ammonia-ammonium nitrate buffers were used. Fabric swatches, 5 X 5 in., were marked at 10 cm intervals. Test runs of 2 min were preceded by a 30 sec conditioning run of the fabric in order to equilibrate the fiber surface with the test solution and to eliminate relaxation shrinkage.

Flocculation Experiments

Wool top, domestic fine wool, grade 64's, was cut into 0.5 mm sections with a microtome. After transfer to a filter the cut wool was washed thoroughly with hexane, with ethanol and with distilled water. The air-dried samples were conditioned at 21 C and 65% relative humidity prior to weighing. Suspensions were made by dispersing 0.1 g of cut wool in 5 ml aqueous buffer solution pH 4.8, 0.02 M acetic acid-sodium acetate.

Sedimentation Volume

The 5 ml suspensions were prepared in 10 ml graduated centrifuge tubes (Kolmar). Sedimentation took place in several minutes on standing and occasional gentle shaking until a constant sedimentation volume was read on the tube.

RESULTS AND DISCUSSION

Flocculation of Wool Suspensions

Various samples of cut wool were prepared starting from natural wool top and also from the same wool top after it had been treated chemically for the production of shrink-resist fabric. In dispersing the samples in buffer solution there was a great difference in behavior between natural wool and shrink-resist treated wool. In the case of natural wool the dispersion in water was difficult and the pieces stuck together in flocs. On the other hand shrink-resist treated wool dispersed readily and in single sections with no tendency to flocculate.

Figures 1 and 2 represent typical examples of the distribution of fiber sections in a flocculated suspension and in a nonflocculated suspension. In order to prepare for photography the original suspensions were diluted 50 times with buffer solution and poured into a flat Petri dish. In this operation some flocs broke up and some pieces of

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FIG. 1. Suspension of 0.5 mm long sections of natural wool fibers in aqueous buffer solution, pH 4.8, 0.01 M acetic acid + 0.01 M sodium acetate. Flocculated suspension.

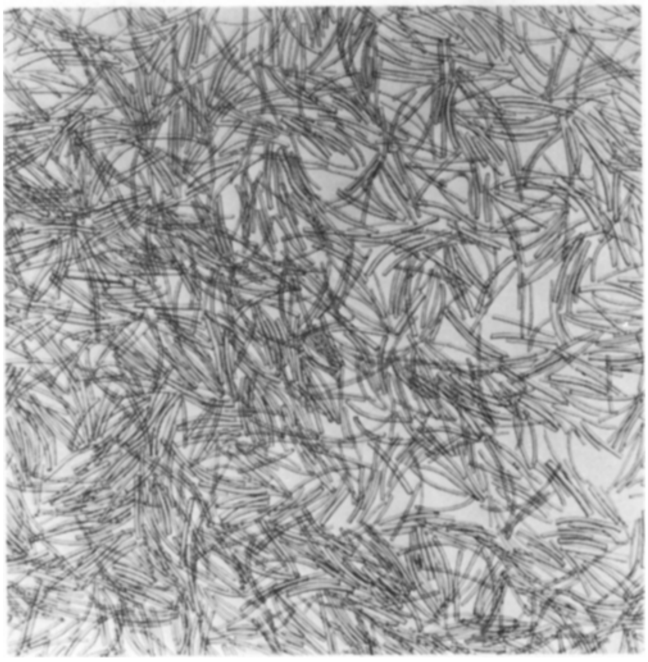

FIG. 2. Suspension of 0.5 mm long sections of chemically treated, nonfelting wool fibers in aqueous buffer solution, pH 4.8, 0.01 M acetic acid + 0.01 M sodium acetate. Stable suspension.

natural wool separated as seen in Figure 1. Nevertheless, the difference between natural and shrinkproofed wool in Figures 1 and 2 is revealing.

The visual inspection of the suspensions was supplemented by the measurement of the sedimentation volume. In aqueous suspensions the wool fiber sections sediment rapidly to the bottom of the vessel. Wool flocs form a bulkier sediment than the single fiber sections in a stable suspension. In the latter case the fibers tend more toward a closest packing. Table I gives the sedimentation volume V_s for samples of natural wool and of shrink-resist treated wool. The V_s values for shrink-resist treated wool are two to three times lower than for natural wool. This means that in all cases examined a treatment which stabilizes wool fabric against felting shrinkage also stabilizes an aqueous wool suspension against flocculation. A detailed quantitative correlation between the values of V_s and the degree of resistance to felting shrinkage may be difficult to establish. Nevertheless, the data suggest strongly that flocculation and felting shrinkage have a factor in common.

Interaction Between Wool Fibers as Factor in Felting

In this section we attempt to rationalize the experimental correlation between flocculation and felting in order to derive a suitable working hypothesis that may be tested against further experiments.

We first consider the flocculation process in colloidal solutions (3). The basic notion is that in flocculating systems the particles tend to stick together upon making contact. Stated otherwise, the attraction between colloidal particles is the driving force of the flocculation process. The degree of flocculation may be expressed, say, in terms of the number of contacts between the particles.

We now turn to the felting (1,4) of loose wool. It is clear that the number of fiber to fiber contacts increases during felting. This analogy with flocculation suggests the simple hypothesis that the driving force in wool felting is attraction between the fibers. The actual kinetics of flocculation and wool felting are, of course, very different. Flocculation has been treated in terms of diffusion of colloidal particles as biased by their mutual interaction. Felting, on the other hand, does not proceed spontaneously by diffusion but requires mechanical agitation of the wool in the felting bath. A second difference is the manner in which contacts are increased. In flocculation there is usually not more than a single contact between any two particles and the particles retain their shape; compare Figure 1. This is quite different in felting where changes in fiber geometry are essential when individual fibers become more and more twisted around and entangled with neighboring fibers. So felting involves sliding contacts between fibers and the rate of felting depends on factors like the fiber flexibility and interfiber friction as discussed in the literature on felting (4,1).

The analogy with colloid chemistry is now extended to fabric shrinkage. In a woven fabric there are a number of fiber to fiber contacts. Attraction between the wool fibers during laundering tends to increase this number of interfiber contacts, giving rise to felting shrinkage of the fabric. The difference with the felting of loose wool is in the

TABLE I

Sedimentation Volume, V_s, of Natural and of Shrink-Resist Treated Wool, Fiber Length 0.5 mm, in Aqueous Buffer Solution pH 4.8

Chemical treatment	V_s ml/g
None	8.8; 8.9
None	9.3; 8.7
None	9.3; 9.4
Wurlan[a]	4.7; 4.5
Harrisett[b]	2.5; 3.1
Kroy[c]	2.9; 3.2
DCAA[d]	3.7
C.S.I.R.O. Hercosett[e]	5.2; 5.8
Corona[f]	4.1; 4.0

[a] Polyamide film on fiber surface by interfacial polymerization (17).

[b] Alkaline chlorination (13).

[c] Acid chlorination (14).

[d] Chlorination with dichlorocyanuric acid (11).

[e] Acid chlorination and resin deposition on surface (12).

[f] Wool moved through corona discharge in chlorine atmosphere (15).

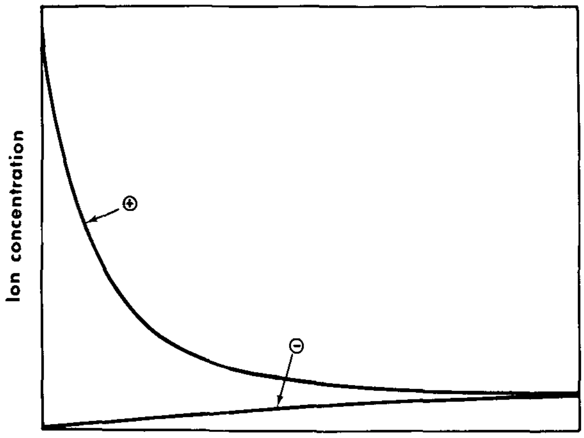

FIG. 3. Shrinkage of wool oxidized with permanganate. Squares: 3.5% permanganate-salt. Circles: 5% permanganate-salt. Data by McPhee and Feldtman (19).

special restraints of the fibers in the fabric dictated by the alignment of the fibers in the particular fabric structure. If the wool fibers have no significant attraction for each other under laundering conditions the fabric will show no felting shrinkage during washing.

Our hypothesis extends logically to the case of repulsive interaction. For some colloidal systems flocculation is a reversible process. After flocculation of the colloid one may change the ionic composition of the aqueous medium such that the colloid is easily redispersed and forms a stable colloid solution. Such deflocculation or repeptization is linked to a change from attraction to repulsive interaction between the colloid particles (3). Similarly, in laundering wool fabric a significant repulsion between the fibers may tend to decrease the number of fiber to fiber contacts, the fibers tend to disentangle and untwist and the fabric expands during laundering. Starting with a sufficiently loose fabric construction, such behavior may lead to the disintegration of the fabric into single fibers.

In summary we suggest that the felting behavior of wool has kinetic and static aspects. The kinetic aspects deal with the relative mobility of the individual fibers when the mass of fibers is agitated. The importance of fiber mobility is generally recognized. In the present paper we explore the static interaction between wool fibers as the possible driving force for the felting of loose wool and for the dimensional changes of wool fabrics under agitation in aqueous solutions. In the next section we relate the pair wise interaction between wool fibers in water to their surface chemistry.

Interaction and Felting of Natural and of Chemically Modified Wool

In a qualitative way the interaction between wool fibers in water is easily connected with their surface chemistry. It is well established that the surface of natural wool fibers is quite hydrophobic (6-8). This means that in an aqueous suspension fiber to fiber contacts are favored for much the same reasons as oil droplets in an oil in water emulsion tend to coalesce. This tendency may be reduced or even reversed by the introduction of polar groups at the fiber surface by chemical modification of wool. Another factor is the surface charge of the fibers. In natural wool the concentration of acidic and basic groups at the fiber surface is very low (9). However, the concentration of, e.g., acidic surface groups may be increased by chemical modification. When such fibers are suspended in an aqueous salt solution electrostatic repulsion may become a significant component of their interaction, depending on the net surface charge of the fibers and on the concentration and valence type of the electrolyte in solution (10). We proceed to discuss some actual modifications of wool in relation to the interaction between the fibers and the felting behavior in water.

There are several oxidative treatments of wool such as chlorination (11-14), corona discharge (15) and permanganate oxidation (16). It is probable that these treatments create acid groups inside the wool fiber and at the fiber surface. The presence of ionized acid groups at the fiber surface decreases the hydrophobic attraction between the fibers and increases their electrostatic repulsion which may become of the same order as the attraction or even larger. So the change of interaction between the fibers explains the shrink-resist effect of oxidative treatments of wool. It also explains the experimental observation that overtreatment by oxidative methods may give a fabric that expands instead of shrinks during washing.

A further test of the interaction hypothesis is the effect of pH on fabric shrinkage. The interaction between oxidized wool fibers in water depends on the degree of ionization of the acid groups at the fiber surface. Hence, for oxidized wool one would expect the fabric shrinkage to decrease with increasing pH of the shrink test solution. This is well demonstrated by the data in Figure 3.

The pH dependence of the felting of natural wool is also of interest. We have measured the felting shrinkage of samples of a natural wool fabric as a function of pH for 2 min in accelerated washing test. Results were: for pH 2.5, 32.4% area shrinkage; pH 4.95, 31.1%; pH 6.85, 32.8%; pH 7.3, 32.3%; pH 8.9, 31.7%; pH 9.6, 30.5%. The shrinkage does not depend significantly on pH even in the range pH = 2 to 6 where the surface charge changes drastically (9). This observation correlates well with the very low charge density at the surface of natural wool fibers where the average distance between ionizable groups is about 70 A (9).

We now apply the concept of fiber interaction to some polymer treatments developed in this laboratory. In the WURLAN treatment (17) a polyamide film is formed at the fiber surface by interfacial polymerization. The treated wool is more hydrophilic than natural wool while the surface concentration of ionizable groups remains low (9). So the shrinkproofing effect of the WURLAN treatment is explained by the decrease of the attraction between the in water suspended fibers while their repulsion remains insignificant. The experience is that overtreatment does not give expanding fabrics. The reason must be that the interaction between the fibers remains constant after they have been fully covered with polymer. It should be noted that the critical surface tension of the polyamide formed at the fiber surface is not very much different from the critical surface tension of natural wool fibers (7). So the reasons for the remarkable increase in hydrophilic character of the fiber surface in the WURLAN treatment are not entirely clear. The entrapment of nonionic wetting agents in the polymer film and the orientation of the polymer in the film surface have been suggested as possible explanations (18).

In another modification wool fibers have been covered with a fluorocarbon film (A.G. Pittman, private communication). The resulting wool is stain resistant but not shrink resistant. This is in line with the fact that a fluorocarbon surface is even more hydrophobic than natural wool. The only exception in this type of treatment turns out to be the modification of wool with a fluorocarbon compound containing acidic groups (18). In this case partial shrinkproofing is obtained and this is believed to be the result of electrostatic repulsion between the charged fibers.

Finally, wool may be combined with polyacrylic acid by the polymerization of acrylic acid in the presence of wool (A.E. Pavlath, private communication). The shrinkage properties of the treated fabrics are correlated with the electrostatic interaction between the fibers. At low pH, when the acrylic acid groups are not ionized, one finds fabric shrinkage. After neutralization of the fabric with, e.g., sodium hydroxide the fabric may expand during washing. On the other hand, the fabric may still shrink if the sodium ions are replaced by bivalent ions such as Zn^{++} or Ni^{++}, after the neutralization reaction, although the shrinkage is less than for the original, untreated fabric. This is in line with the theoretical prediction that the electrostatic repulsion is smaller in the presence of bivalent counterions that it is with monovalent counterions (10).

Felting of Wool in Surfactant Solutions

We have discussed felting shrinkage of wool fabrics agitated in aqueous salt solutions. In practical laundering operations detergent is present as an additional component which may adsorb at the fiber surface and thus change the interaction between the fibers. For instance, a suspension of cut wool in a detergent solution is always stable; compare Figure 2. In analogy, one might expect shrink resistance of fabric laundered in detergent solutions. However, to what extent detergent adsorption modifies fabric shrinkage depends on how effective such adsorption is under laundering conditions.

It appears that in many systems fabric shrinkage is not much changed by the presence of detergent (19). A simple explanation is that any adsorbed detergent layers are wiped off the fiber surfaces where the fibers make shearing or sliding contacts during agitation of the fabric. Such mechanical removal of detergent would allow the original fiber surfaces to interact and felting shrinkage to proceed without influence of the detergent.

The foregoing mechanism is suggested for weakly adsorbed detergent, such as adsorption by hydrophobic interaction. On the other hand, strongly adsorbed detergent should be regarded as part of the wool fiber. For example, ionic detergents might form electrostatic bonds with oppositely charged groups at the fiber surface. Such strong adsorption by salt bonds changes hydrophilic sites at the fiber surface into hydrophobic sites and, hence, should promote fabric shrinkage. A good example of this kind of behavior is probably found in work reported by Thorsen and Kodani (15) on wool shrinkproofed by their corona discharge method. It was observed that the application of cationic softeners, long chain alkyl aryl quaternary amine salts, among others, eliminated shrink resistance, while removal of the cationic compounds restored the shrink resistance.

The proposed model of detergent action compares the adsorption energy of the detergent with the energy dissipated due to washing action. In this approach one expects the detergent effect on fabric shrinkage and wool felting to depend on the severity and nature of the agitation. This should be born in mind when experimental felting data from different sources are compared.

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REFERENCES

1. Wool Sci, Rev. 3:3 (1949); 17:16 (1957); 24:34 (1964).
2. Stiegler, H.W., H.E. Glidden, G.R. Mandikos and G.R. Thompson, Amer. Dyest. Rep. 45:685 (1956).
3. Kruyt, H.R., Editor, "Colloid Science," Vol. 1, Elsevier Publications, New York, 1952.
4. Makinson, K.R., Text. Res. J. 29:431, 439 (1959); 30:598 (1960); 32:364 (1962); 38:831 (1968).
5. Silfhout, A. van, Proc. Kon. Ned. Akad. Wetensch. Ser. B 69:501 (1966).
6. Chaimberlain, N.H., and J.B. Speakman, Trans. Faraday Soc. 29:358 (1933).
7. Mutchler, J.P., J. Menkart and A.M. Schwartz, Advan. Chem. Ser., in press; J. Colloid Interface Sci. 29:439 (1969).
8. Lofts, P.F., and E.V. Truter, J. Text. Inst. 60:46 (1969).
9. Stigter, D., J. Colloid Sci. 19:268 (1964).
10. Derjaguin, B., Trans. Faraday Soc. 36:203 (1940); Verwey, E.J.W. and J.T.G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publications, New York, 1948.
11. Wool Sci. Rev. 32:1 (1968).
12. Feldtman, H.D., J.R. McPhee and W.V. Margaw, Text. Mfr. 92:122 (1967).
13. Frishman, D., and M. Harris, US Patent 2,466,695 (1949).
14. McLauchlan, J.H., U.S. Patent 2,671,006 (1954).
15. Thorsen, W.J., and R.Y. Kodani, Text. Res. J. 36:651 (1966); Thorsen, W.J., Ibid. 31:770 (1961).
16. McPhee, J.R., Ibid. 31:770 (1961).
17. Whitfield, R.E., L.A. Miller and W.L. Wasley, Ibid. 31:704 (1961); Fong, W., L.A. Miller, J.F. Ash, W.W. Ingenthron and H.P. Lundgren, Third International Wool Textile Research Conference, Paris, Sec. 3,417 (1956).
18. Pittman, A.G., Text. Res. J. 33:817 (1963).
19. McPhee, J.R., and H.D. Feldtman, Ibid. 31:1037 (1961).

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