

Stress-Strain Properties in the Decrimping Region of Chemically Modified Crimped Keratin Fibers, with Special Reference to the Stability of Crimp Structure

E. BALASUBRAMANIAM, *Department of Physics, Papua and New Guinea University of Technology, Lae, Papua, New Guinea*

Synopsis

The effect of disulfide rupture, reoxidation, and crosslinking with formaldehyde on decrimping parameters of wool keratin is studied in an attempt to establish the comparative role of cystine-type of bonding in the decrimping region. Large changes in crimp shape accompanied by changes in decrimping forces and energy suggest that the stability of crimp shape is obviously dependent on cystine linkages.

INTRODUCTION

By considering the crimped wool fiber as a thin, uniform elastic rod in the form of a uniplanar sinusoidal wave the plane of which rotates or oscillates about the axis, Walls¹ derived an equation which approximates to a form which can be written as

$$QT\sqrt{1 + 1/p} + \sqrt{1 + 1/p} = \sqrt{s/s - l}$$

where the crimped length at stress T is given by l and s refers to the straight length of the fiber.

Further support for this suggestion was given by Balasubramaniam and Whiteley.² In this paper, it was found convenient to see Wall's model to analyze the stress-strain curve for this region, because the sample used gave an excellent straight-line relationship between the plot of $\sqrt{s/s - l}$ and T and, secondly, this model is particularly useful in that the value of P calculated from the intercept depends only on the crimp shape of the fiber and is independent of fiber diameter or elastic modulus, thus enabling the study of changes in crimp shape after subjecting the fiber to various chemical treatments, such as disulfide rupture, reoxidation, and crosslinking with formaldehyde.

EXPERIMENTAL

Stress-strain measurement in the decrimping region and the measurement of the force to decrimp F_c , the decrimping energy E_c , the crimp shape factor P , and the factor Q , which depends on shape and elastic modulus, were car-

ried out as previously described³ on 20 wool fibers before and after chemical modification.

The fibers were divided into two groups for chemical modifications. The first group of ten fibers was used for crosslinking experiments with formaldehyde⁴ and the second group for disulfide rupture with thioglycolic acid. The thiol groups produced were either blocked by methylation⁵ or without blocking were relinked by reoxidation.⁶ After chemical modification, all fibers were soaked in distilled water at 20°C for 20 hr before decrimping.

RESULTS AND DISCUSSION

Crosslinking

The effect of formaldehyde on E_c and F_c is shown in Table I. The decrimping energy E_c has increased by a factor of 1.4, and only a slight increase in F_c (a factor of 1.08) is observed. This is rather unexpected if it is assumed that crosslinking has occurred, however, in the studies of stress-strain properties of wool fibers in the Hookean, yield, and postyield regions, Watt and Morris⁴ (Fig. 1) do not indicate marked changes in modulus at low extensions.

An additional unexpected effect is that there are substantial changes (by a factor of 1.3) in P (Table I), indicating extensive alterations to crimp structure.

There is no general agreement as to where the crosslinking may take place in the matrix/microfibrillar structure of wool fiber. Watt and Morris⁴ deduced from load-extension curves in water (Fig. 1) and the sorption behavior of modified wools that, in the case of formaldehyde, Figure 1 indicates that extensive crosslinking takes place in the microfibrillar regions.

However, treatment with formaldehyde causes increases in torsional rigidity and reduced swelling in formic acid.⁷ These effects are generally considered to arise principally from modifications of the matrix.

It should be emphasized, however, that the increases in torsional rigidity observed by Watt⁷ are rather smaller than might be expected, a torsional properties.

In conclusion, the formaldehyde treatment appears to affect crimp shape. Whether the change involves bending or torsional modulus cannot be ascertained because of the existing state of knowledge relating to torsional properties of wool fiber.

The Reduction of Cystine with Thioglycolic Acid

Blocking

Table II illustrates the effect on the decrimping parameters of reduction with thioglycolic acid followed by blocking the thiol groups to prevent relinkage. These results show that the above treatment has caused drastic modifications to the fiber.

F_c and E_c were reduced by factors of 2 and 5, respectively. These results are in line with the studies on the effect of disulfide breakage on mechanical properties of wool fibers in the Hookean, yield, and postyield regions of the

TABLE I
Effect of Formaldehyde on Decrimping Parameters

Fiber no.	Before treatment			After treatment			Treatment:water ratio		
	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c	E_c
1	0.172	0.310	0.41	0.221	0.295	0.46	1.29	0.95	1.12
2	0.143	0.320	0.43	0.222	0.345	0.71	1.55	1.07	1.66
3	0.212	0.305	0.52	0.259	0.310	0.65	1.22	1.02	1.26
4	0.112	0.315	0.25	0.146	0.370	0.40	1.30	1.18	1.60
5	0.123	0.315	0.29	0.162	0.365	0.44	1.31	1.16	1.52
						Mean	1.33	1.08	1.43
						S.D.	0.126	0.096	0.232

TABLE II
Effect of Reduction and Blocking on Decrimping Parameters

Fiber no.	Before treatment			After treatment			Treatment:water ratio		
	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c	E_c
1	0.396	0.290	0.77	0.91	0.18	0.11	0.23	0.621	0.142
2	0.484	0.250	0.41	0.121	0.19	0.09	0.25	0.760	0.219
3	0.258	0.31	1.01	0.061	0.18	0.21	0.24	0.581	0.211
4	0.101	0.32	0.30	0.036	0.16	0.04	0.36	0.484	0.134
5	0.114	0.33	0.32	0.043	0.15	0.07	0.38	0.468	0.146
						Mean	0.292	0.583	0.170
						S.D.	.072	.118	.041

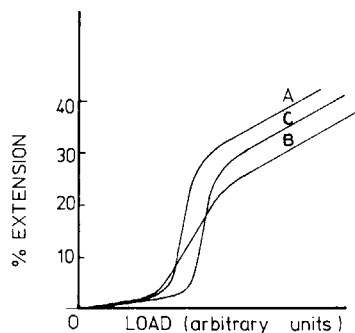


Fig. 1. Load-extension curves for wool fibers in water at 20°C: curve A, unmodified wool fiber; curve B, formaldehyde-treated wool fiber combined formaldehyde 2.5%w/w curve C, benzoquinone-treated wool fiber.

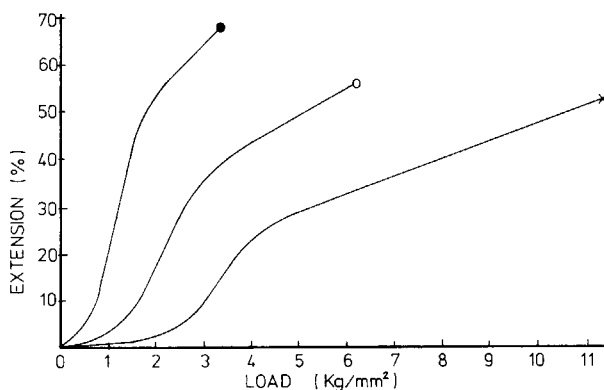


Fig. 2. Load-extension curves of reduced +CH₃I (●), reduced +C₂H₄Br₂ (O), and untreated fibers (x) in distilled H₂O at 20°C.

load-extension curve, Figure 2.^{5,8} The results of these studies show a massive reduction in yield and particularly⁸ the postyield region stress values. These more reactive disulfide bonds⁸ reduced by this treatment are of particular interest in that their effect on mechanical properties indicates that they actively inhibit the unfolding of the alpha-helices in the low-cystine microfibrils. Presumably, therefore, they are located in close proximity to the microfibrile.

Due to drastic modifications caused by the above treatment, the crimp shape factor P is reduced by a factor of 3 (Table II). Since the modulus has also decreased as indicated by the changes in F_c , it is difficult to attach any significance to the observed variations in Q , and therefore the values are not shown in Table II. However, observed changes in F_c , P , and E_c suggest that crimp stability is heavily dependent on disulfide crosslinkages.

Relinkage

Although Geiger, Kobayashi, and Harris⁹ obtained virtually perfect relinkage of reduced disulfides by reoxidation (only a 3% reduction in work done to

TABLE III
Effect of Reduction and Relinking on Decrimping Parameters

Fiber no.	Before treatment			After treatment			Treatment:water ratio		
	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c , kg/sq mm	$E_c \times 10^5$, Joule/m ³	P	F_c	E_c
1	0.118	0.29	0.29	0.095	0.26	0.20	.81	0.90	0.68
2	0.108	0.31	0.31	0.090	0.26	0.19	.83	0.84	0.61
3	0.098	0.29	0.27	0.070	0.26	0.14	.71	0.90	0.51
4	0.122	0.28	0.26	0.100	0.24	0.17	.81	0.87	0.65
5	0.119	0.28	0.29	0.096	0.23	0.19	.80	0.83	0.67
							Mean .792		.624
							S.D. .047		.033

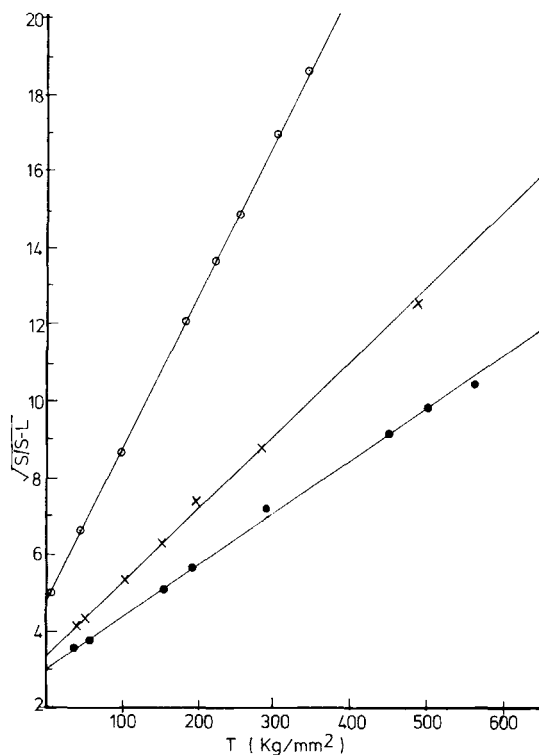


Fig. 3. (O) After reduction and blocking; (x) after reduction and relinking; (●) before reduction and relinking.

extend to 30% extension) or relinkage with methylene iodide, later workers^{5,8} were unable to obtain this degree of relinkage. They considered that the more reactive disulfides could well be under stress in the unstrained fiber so that, on rupture, the cystine residues so formed might move apart. Lindley,⁸ for example, demonstrated that by using an alkyl dihalide with two carbon atoms (ethylene dibromide), he achieved better results than with a single carbon atom (methylene iodide).

In the present study, there appears to be about an 85% recovery in F_c that agrees with Whiteley's⁵ and Lindley's⁸ observations in the yield and postyield regions.

Analysis of the results in Table III indicates that on relinking some of the thiol groups, at least 80% of the decrimping force F_c and 60% of the decrimping energy E_c have been recovered.

The plot of $\sqrt{s/s-l}$ against the tension T for each treatment is given in Figure 3. The slope of these straight lines and the y intercept indicate that both the P and Q parameters have partially recovered after relinking.

Analysis of results shows that approximately 80% of the crimp shape factor P has been recovered. The shape changes in P are probably caused by mechanical treatments after the reduction, because if crimp simply disappeared during reduction, then relinkage would not be likely to restore it.

CONCLUSIONS

The results of the preceding experiments reveal that the changes in decrimping properties resulting from various chemical treatments parallel stress-strain results of the Hookean, yield, and postyield regions, but there are additional complications due to shape change.

Due to drastic modifications caused by reduction, the energy to decrimp (E_c) and the force to decrimp (F_c) are reduced remarkably. Large changes in P suggest that the stability of crimp shape is obviously dependent on cystine linkages.

It is clear that disulfide bonding plays the major role in the stability of crimping; the rupture of such linkages on the incorporation of new crosslinkages produces effects which are broadly similar to those observed at higher extensions.

It is also interesting to note from Figure 3 that the decrimping model fits the data even after reduction. This suggests that no crimp form changes have taken place, in agreement with Khan's¹⁰ observations that reduction causes decrease in crimp amplitude without affecting the crimp form.

The author is indebted to the School of Wool and Pastoral Science, University of New South Wales, Kensington, Sydney, Australia, and also for the financial assistance from the Australian Wool Research Committee.

References

1. G. W. Walls, *Proc. Int. Wool Text. Res. Conf., Aust.*, **D**, 118 (1955).
2. E. Balasubramaniam and K. J. Whiteley, *Aust. J. Appl. Sci.*, **15**, 41 (1964).
3. E. Balasubramaniam and K. J. Whiteley, *J. Appl. Polym. Sci.*, **18**, 3475 (1974).
4. I. C. Watt and R. Morris, *J. Text. Inst.*, **57**, T425 (1966).
5. K. J. Whiteley, *J. Text. Inst.*, **53**, T553 (1962).
6. J. B. Caldwell, S. J. Leach, A. Meschers, and B. Milligan, *Text. Res. J.*, **34**, 627 (1964).
7. I. C. Watt, *3rd Int. Wool Text. Res. Conf., Paris (Cirtel)*, **Part II**, 259 (1965).
8. H. Lindley, *Text. Res. J.*, **27**, 690 (1957).
9. W. B. Geiger, F. F. Kobayashi, and M. Harris, *Ind. Eng. Chem.*, **34**, 1938 (1942).
10. M. A. Khan, M.Sc. Thesis, The University of New South Wales, 1966.

Received December 2, 1974

Revised February 5, 1975