

Reactions of Metal Salts with Human Hair Containing Synthetic Polymer

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Synopsis—Human HAIR FIBERS containing synthetic POLYMER with functional groups capable of acting as donor groups in coordination complexes were reacted with METAL SALTS (acceptor groups) and examined for changes in the wet load extension properties. Mercury(II), a particularly effective “acceptor group” in this system, was found to produce extremely large increases in the wet load EXTENSION PROPERTIES of hair fibers containing either a tertiary amine polymer, an alcohol polymer, or a nitrile polymer.

INTRODUCTION

Harris and Brown (1) in 1946 showed that the disulfide bonds of wool fibers play an important role in the wet strength properties which increase almost linearly with the cystine content. Evidence for their contribution was obtained by reducing and methylating wool fibers to different extents and determining both the wet and dry load extension properties. This work also showed that the dry strength of wool fiber, through 30% extension, is not appreciably affected through a 60% decrease in the cystine content. In 1951, Alexander *et al.* (2) indicated similar results from the oxidation of wool fiber with peracetic acid. Related results have been obtained in our laboratories for hair fibers that have been bleached with home commercial bleaching products (3).

Since the wet tensile properties of human hair are adversely affected by two frequently used chemical treatments [permanent waving (reduc-

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tion-oxidation) and bleaching (oxidation)], and since the wet tensile properties are altered more by these treatments than the dry properties, the objective selected was to explore means for increasing the wet load extension properties of keratin fibers through mild conditions (room temperature, aqueous media, and short reaction times) of reaction.

Our approach involved polymerizing vinyl monomers within the keratin fibers (4–8) to alter their chemical reactivity (9) and subsequently reacting the polymer-containing fibers with metal salts. It was believed that these reactions might increase the cross-link density and/or decrease the saturation water content of the fibers, methods which have been suggested (10) to be effective for increasing the wet load extension properties of wool fibers containing no synthetic polymer.

EXPERIMENTAL

The keratin fibers used in this investigation were from brown Caucasian human hair.* The monomers were purified in the usual manner followed by distillation. Other chemicals were of reagent grade or of the highest purity available.

For polymerizing in hair, single fibers were immersed in 20 ml of 6% ammonium thioglycolate ($\text{pH} = 9$) for 3 min, washed with deionized water, and then immersed in 20 ml of water-alcohol mixtures of vinyl monomer (10%) and cumene hydroperoxide (4%) for 60 min at room temperature. Enough alcohol was added to the system to completely solubilize the hydroperoxide and/or monomer. The amount of polymer within the fibers was estimated by weight pickup as determined at 55% RH. Treatment with metals involved immersion of fibers in metal salt solutions at times and concentrations indicated in the text.

Unless stated otherwise, the following procedure was used for determining the changes to the stress-strain properties of the fibers. After being mounted 5 cm apart on tabs, the fibers were placed in deionized water at 24°C for at least 1 hour and stretched to 20% of their initial length on an Instron tensile tester,† at a rate of extension of 0.25 cm/min. The fibers were then relaxed in water, overnight, dried at room temperature, and treated and stretched again under the same conditions. In this manner, before and after measurements were made on 3 to 10 fibers per treatment. Changes in the mechanical properties are expressed as the percentage change in the work to 20% extension (W_E), the elastic

* Purchased from De Meo Brothers, New York, N.Y.

† Instron Corporation, 2500 Washington St., Canton, Mass. 02021.

limit (E_L), and the force to 20% extension (F_{20}). The statistical results were calculated using the method of paired differences.

RESULTS AND DISCUSSION

Reactions of Metal Salts with Polymer-Containing Keratin Fibers

In the initial experiments, polycarboxylic acid-containing hair [poly(methacrylic acid), (PMA)] and polyalcohol-containing hair [poly(ethylene glycol monomethacrylate), (PEGM)] were reacted with salts of magnesium and calcium. For the PMA-containing fibers the possibility for salt link formation existed as well as the possibility for coordination. Results from these experiments (Table I) show no encouraging positive changes in the work of elongation (W_E) for these treatments. The failure of these treatments to produce increases in the load extension properties of the fibers is presumably due to a failure to complex, which is probably a result of the poor complexing capabilities of these two metals (11). Therefore, stronger complexing metals were selected for examination.

Table I
Reaction of Grafted Keratin Fibers with Calcium and Magnesium

Salt	Polymer in Fibers	pH	% Change W_E	Significant Beyond $\alpha = 0.05$ Level
CaCl ₂	PMA (19.8%)	10	-5.5	Yes
Ca(NO ₃) ₂	PMA (19.8%)	2	-1.5	Yes
MgCl ₂	PEGM (21%)	10	+1.8	No
CaCl ₂	PEGM (21%)	7	+0.12	No
CaCl ₂	PEGM (21%)	10	+1.4	Yes

Several transition metal salts, including salts of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), mercury(II), and zinc(II) were each reacted with hair fibers containing PMA. The results from these experiments are summarized in Table II. The treatments with nickelous chloride, cupric acetate, and mercuric acetate were all encouraging in producing increases in the work to 20% extension.

Some of these same metals were also examined for their reaction with hair containing [poly(*N,N*-dimethylaminoethyl methacrylate), (PDEM)], Table III. For the tertiary amine-containing hair, these data show a positive increase in the W_E only for the mercuric acetate treatment. This increase is 16%. These results may be interpreted in terms of a

Table II
Reactions of Metal Salts with PMA-Containing Hair

Salt ^a	pH	% Change W_R	Significant Beyond $\alpha = 0.05$ Level
MnSO ₄	2	+1.6	No
FeSO ₄	2	+0.5	No
CoCl ₂	7	-0.6	No
NiCl ₂	7	+4.9	Yes
Cu(OAc) ₂	7	+4.7	Yes
Hg(OAc) ₂	2	+4.1	Yes
Zn(OAc) ₂	3.5	-3.9	Yes

^a Salt concentrations are all 0.1M and treatment times 2-5 hr. The hair fibers contained between 16.2 and 19.8% PMA.

Table III
Reactions of Metal Salts with PDEM-Containing Hair

Metal	Metal Concn(M) ^a	pH ^b	% Change in W_R from Polymerized State ^c
CdSO ₄	0.1	2.0	-5.5
Pb(OAc) ₂	0.1	3.5	-5.7
AgClO ₄	0.1	3.0	-14
Zr(OAc) ₄	0.29	7	-3.4
Cu(OAc) ₂	0.27	7	-1.3
Hg(OAc) ₂	0.1	(0.1N HOAc)	+16 [-1.4] ^d
Zn(OAc) ₂	0.1	3.5	-5.9

^a Fibers in the above experiments contained on an average 14% PDEM and all reaction were carried to 1/2 hr at room temperature.

^b Where pH adjustments were made glacial acetic acid was used.

^c Results are all significant beyond the $\alpha = 0.05$ level.

^d Estimated change from the untreated state assuming a 15% lowering due to reduction and polymerization.

rebuilding (crosslinking) mechanism or in terms of a reduction in the saturation water content of the fibers by the attachment of hydrophobic residues. In either case, the greater effect for the tertiary amine (PDEM)-containing hair as compared to the carboxylic acid-containing hair probably results from a more rapid penetration of the reagent into the fibers under the reaction conditions and a greater propensity for mercury to coordinate with nitrogen than with oxygen (12). As a result of these experiments mercuric acetate was selected for further study.

Effect of Polymer Functionality on Mercuric Acetate Reaction

Four different vinyl monomers—dimethylaminoethyl methacrylate (DEM), acrylonitrile (AN), ethylene glycol monomethacrylate (EGM),

and methacrylic acid (MA)—were separately polymerized in hair fibers by the procedure described in the experimental section of this report. The fibers were calibrated to 20% extension in water, treated with 0.1M mercuric acetate at room temperature for 1/2 hour and re-extended to 20% of their length in water. Data describing the resultant changes in the W_E of the fibers are summarized in Table IV.

Table IV
Effect of Monomer Functionality

Monomer	Av % Polymer in Fibers	% Change in W_E from Polymerized State ^a
DEM	14	+16
AN	12	+48
EGM	21	+23
MA	16	+4

^a Results are all significant beyond the $\alpha = 0.05$ level.

Large increases in the wet load extension properties of the fibers containing PDEM, PAN, and PEGM resulted after treatment with mercuric acetate; however, relatively small effects were produced by the same treatment to the carboxylic acid-containing hair (PMA). Since mercury(II) is an excellent electron acceptor and has been shown to coordinate with various kinds of donor groups (12), reaction of mercuric acetate with polymer-containing keratins possessing donor groups such as polytertiary amine, polynitrile, or polyhydroxy and/or those donor groups normally present in the hair structure, e.g., amino, guanidino, hydroxyl, carboxyl, and mercaptan (free or formed from disulfide), should occur readily. Therefore, coordination reactions are believed to be responsible for the observed changes in the tensile properties of the polymer-containing fibers described in Table IV. The reaction of mercuric acetate with hair fibers containing PDEM has been studied more extensively than the reaction of this same reagent with the other polymer-containing fibers and additional results from these studies are described below.

Effect of the Polymerization Reaction on the Tensile Properties of Hair

Since the reductive-polymerization procedure employed in these studies consists of a two-step process, the first step being reduction and the second step being actual polymerization, the possibility of altering the mechanical properties by reduction as well as alteration due to the

incorporation of polymer within the fibers exists. For estimating degradation resulting from each of these reactions 12-in. fibers were cut into two 6-in. sections, weighed, and mounted on cellulose acetate tabs 4 in. apart. Subsequent to calibration to 20% extension, the fibers were relaxed in water, reduced, and treated with DEM according to the procedure described in the experimental section. These fibers were then cut from the tabs and reweighed to determine the amount of polymer. The range of polymer in the fibers was from 5 to 11%. These same fibers were remounted on cellulose acetate tabs 2 in. apart and restretched to 20% at one-half the previous extension rate. Assuming the fibers to be uniform and unaltered by the treatment, the two sets of load extension curves should be equivalent. A set of control fibers was treated similarly with all reagents except monomer in the reductive-polymerization procedure. The results from this experiment are summarized in Table V.

Table V
Effect of Polymerization on the Tensile Properties

Parameter	Reduced-Unpolymerized Controls (% Change) ^b	Reduced-Polymerized Fibers (% Change) ^b
W_E	-14	-13
W_R^a	-15	-11
E_L	-15	-14
F_{20}	-14	-11

^a Work recovered on 20% extension.

^b Results are all significant beyond the $\alpha = 0.05$ level.

The data indicate that the wet extension properties of hair fibers treated under the conditions of reductive-polymerization, as used in this work, are decreased from 10 to 15%, and that the reduction step is primarily responsible for the observed decreases. In addition, the amount of PDEM incorporated into the fibers, within the limits of these experiments, does not appreciably affect the wet load extension properties.

Effect of Time on the Reaction of Mercuric Acetate with PDEM-Containing Hair Fibers

Hair fibers containing between 9.6 and 10.6% PDEM were treated with 0.1M mercuric acetate in 0.1N acetic acid at different time intervals at room temperature (24°C). Figure 1 illustrates graphically the change in the W_E (reaction of mercuric acetate with the fibers) with time. This reaction is rapid and for all intents and purposes is completed

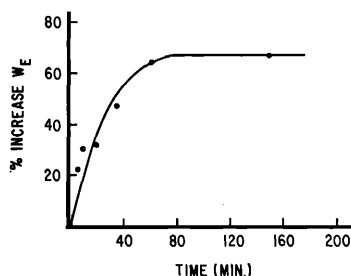


Figure 1. Rate of reaction of mercuric acetate with PDEM-containing hair fibers

after 60 min. As a result of these data, subsequent experiments were carried to 120 min reaction time to ensure equilibration.

Effects of Concentration of Mercuric Acetate on its Reaction with PDEM-Containing Hair Fibers

Figure 2 illustrates graphically the results of experiments made at three different concentrations of mercuric acetate. The reaction time was 2 hours at equilibrium. The data plotted in Fig. 2 show a non-linear relation between the percentage increase in the W_E versus the per cent polymer in the fibers, and the effect of concentration appears to diminish above 0.05M mercuric acetate. Furthermore, the data show increasing tensile effects with increasing amounts of synthetic polymer in the fibers, suggesting that this reaction of mercuric acetate with PDEM-containing hair differs from its reaction with unaltered hair which was examined earlier by Menkart and Speakman (13).

Increases in the work of extension of 50–100% are common after polymerization and reaction with mercuric acetate for hair fibers con-

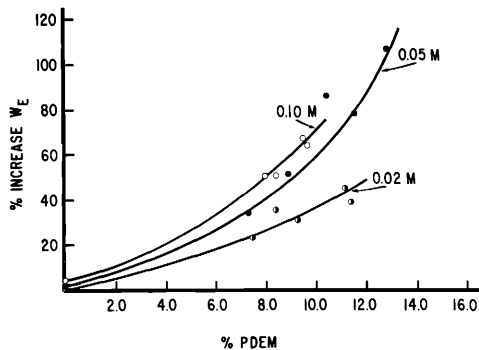


Figure 2. Effect of concentration of mercuric acetate on its reaction with PDEM-containing hair fibers

taining 10–15% PDEM. Interestingly, the elastic limit is affected to a slightly greater extent by this treatment than either the W_E or the F_{20} . In fact, increases in the elastic limit of above 100%, from the polymerized state, were achieved.

SUMMARY AND CONCLUSIONS

Reaction of certain synthetic polymer-containing keratin fibers with mercuric acetate in aqueous media at room temperature for 30–90 min produces large increases in the wet load extension properties. Keratin fibers containing synthetic polymer with tertiary amine groups, alcohol functions, or nitrile groups are particularly effective in this reaction. The increases in the wet load extension properties of polytertiary amine-containing hair appear to be related to the amount of synthetic polymer in the fibers, up to 15% weight gain, and the reaction appears to diminish at a concentration of approximately 0.05M in mercuric acetate. Other metals, i.e., Cu(II) and Ni(II), have been found to produce similar effects.

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