

CROSSLINKING OF COLLAGEN WITH ACRYLAMIDE DERIVATIVES III: IMPROVED CHROME TANNAGE BY COLLAGEN MODIFICATION

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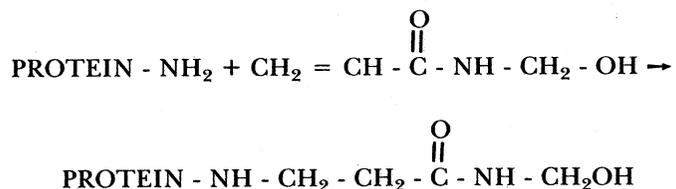
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Abstract

The Michael Reaction has been used with an acrylic-acid derivative to provide additional carboxyl binding sites on collagen during processing of hides into leather. The crosslinked product had a higher shrinkage temperature and a considerably lower lysine and hydroxylysine content than conventionally processed hides. Subsequent tanning led to a higher chrome uptake than that found in the untreated control. The results indicated that both direct crosslinking and improved chrome tanning are possible with this derivative but that these are accompanied by some loss of tensile strength.

Introduction

Modification of collagen by reaction of its side-chain amino groups with acrylic compounds has been the subject of recent research at our laboratory. As a result of this investigation, Fearheller and coworkers have shown that the Michael Reaction can be used for addition of β -carboxyethyl acrylate⁽¹⁾ or acrylamide derivatives including N-hydroxymethylacrylamide⁽²⁾ to collagen. Koenig and Friedman have discussed the application of this reaction to modification of proteins⁽³⁾. Thus, the reaction of N-hydroxymethylacrylamide with amino side chains of lysine and hydroxylysine residues in collagen would proceed as follows:



Presumably, further reactions can occur with the newly-formed derivative and additional acrylic groups. The use of bifunctional acrylic compounds, also offers the opportunity to crosslink hide collagen and should lead to an increase in shrinkage temperature and increased resistance to putrefaction. Thus, bifunctional acrylic compounds are potential novel tanning agents. This has been confirmed in the research previously cited^(1,3). With β -carboxyethyl acrylate, the Michael Reaction leads to a collagen derivative with additional carboxyl groups and with subsequent improvement in chrome tanning⁽²⁾.

Results and Discussion

Amino-acid analysis of hide samples after treatment with DAAA showed that lysine and hydroxylysine content were reduced considerably from corresponding values of untreated samples. These results were in accord with those obtained previously with acrylamide and N-hydroxymethylacrylamide⁽²⁾. The chromatogram of a hydrolysate of the treated sample showed that the apparent methionine peak increased about fourfold, indicating that a new component was eluting at the same time as methionine. In addition, the appearance of two new very small peaks was noted. Table I compares the lysine, hydroxylysine, and methionine content of treated and untreated samples. The results clearly show that the lysyl residues of the hide reacted irreversibly with DAAA.

TABLE I

Amino Acid Analysis (mole percent) of Modified Collagen

Component	Control	Hide Treated with 5% DAAA
LYSINE	3.12	0.17
HYDROXYLYSINE	0.73	0.11
METHIONINE	0.76	2.97

Shrinkage temperatures of hide samples treated with 3%, 5%, and 10% DAAA (percentages based on hide weight) were raised to approximately 75°C, an increase of 20°C. These values, however, dropped to their original levels upon subsequent acidification prior to chrome tanning. Although the amino-acid analyses indicated the stability of the reaction of collagen with DAAA, it appears that acidification causes a change in the treated hide. This effect will be the subject of future investigation.

After chrome tanning, the Cr₂O₃ content of the treated hides was determined and compared with that of chrome-tanned hides that had not been treated with DAAA. For each DAAA level (Table II), the Cr₂O₃ content was at least 30 percent higher in hides reacted with DAAA, showing the efficacy of the presence of additional carboxyl groups.

TABLE II

Cr₂O₃ Analysis After DAAA Reaction

	3% DAAA	5% DAAA	10% DAAA
Treated	4.54%	4.50%	3.76%
Control	3.48%	3.37%	2.88%
Increase	1.06%	1.13%	0.88%
% Change from Control	+30.5	+33.5	+30.6

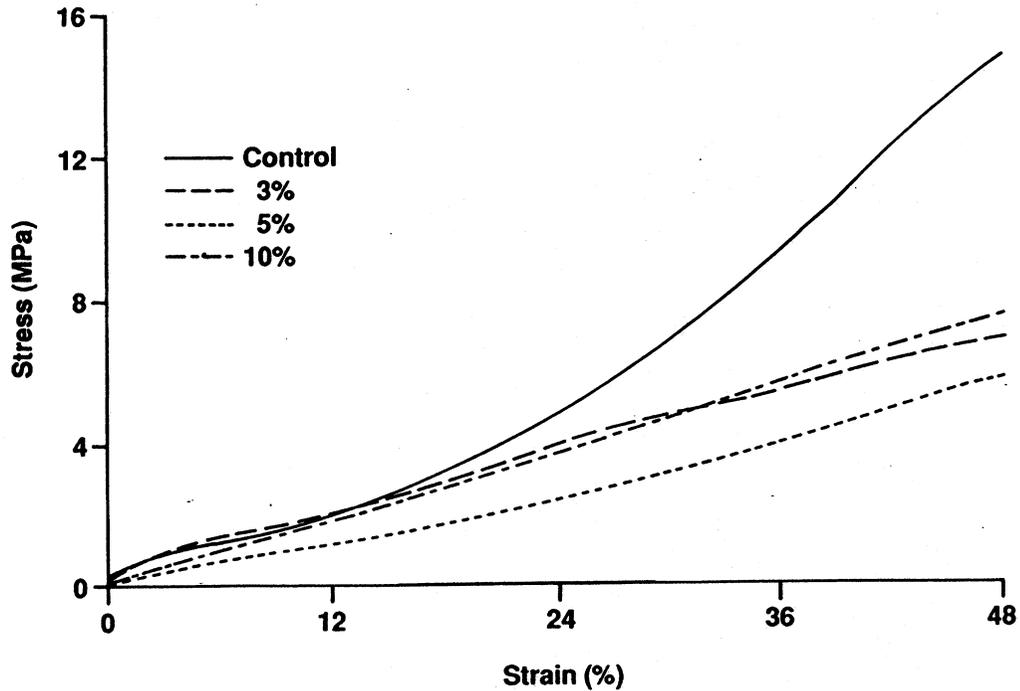
Shrinkage temperatures of the finished hides were consistently higher if they had been treated with DAAA (110°C vs 105°C for the control), but stress-strain properties revealed that the DAAA reaction had led to appreciable decreases in initial modulus, tensile strength,

and work to break. The percent elongation, however, remained essentially unchanged. See Table III and Figure 1. The decreases in strength might be caused by the necessity for effecting the Michael Reaction under strongly alkaline conditions for an extended period of time, although all the materials had been previously limed. Also, considerable swelling occurred in spite of the addition of sodium sulfate.

TABLE III
Variation of Stress-Strain
Properties with DAAA Treatment

% DAAA	Initial Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Work to Break (MPa %)
0	21.9 ± 4.9	16.7 ± 1.8	45.4 ± 4.5	334.0 ± 41.7
3	12.2 ± 1.3	4.9 ± 0.8	37.6 ± 5.1	102.4 ± 25.6
5	8.6 ± 3.0	5.0 ± 0.8	48.2 ± 10.7	112.5 ± 31.4
10	12.3 ± 2.5	7.3 ± 5.8	46.7 ± 14.5	126.6 ± 42.2

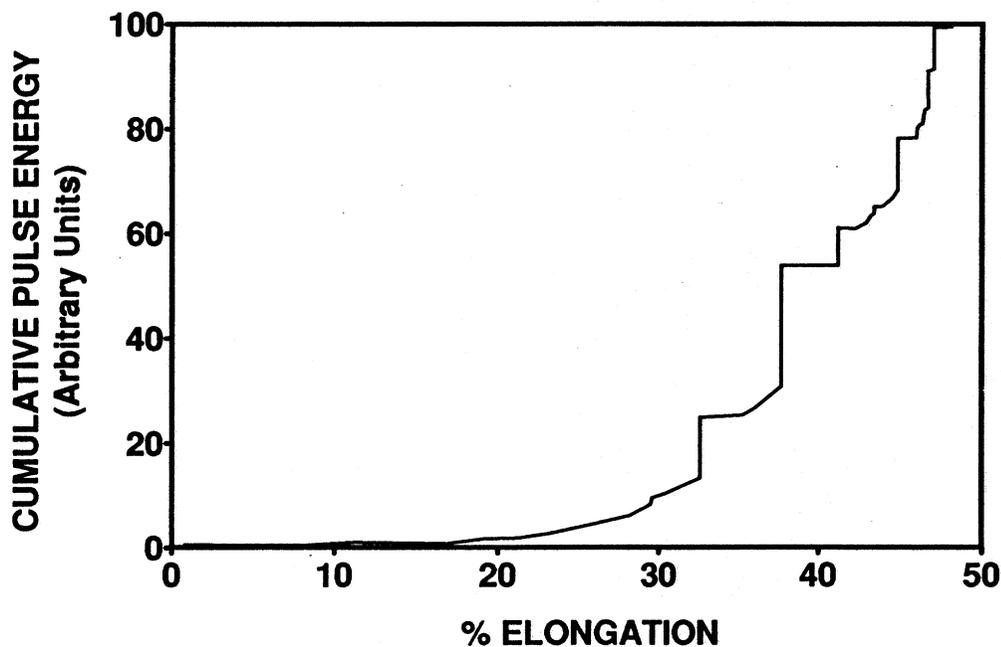
FIG. 1. — Stress vs Strain After DAAA Treatment.



The shapes of the stress-strain curves of the treated materials as shown in Figure 1 are different from those of the untreated. The latter display a region with increased slope that begins at about half the final elongation. This is taken to mean that there is a second

deformation process at high deformations in the untreated material that is lost in the treated. The acoustic-emission data, however, show that the steeply rising part of the stress-strain curves of the control leathers is an interval of high-energy acoustic pulses (Figure 2). We have shown previously⁽⁶⁾ that such pulses are characteristic of breaking fibers. These fiber-breakage emissions also appear on the second half of the stress-strain curves of the treated leathers as well as the control. Although the average number (over the respective samples) of acoustically detected fiber breakages was greater in the treated samples than in the controls, 36 ± 17 vs 29 ± 15 (in arbitrary units), the difference is not statistically significant. The difference in shapes of the stress-strain curves, therefore, would seem to have no fundamental significance beyond that indicated by the reported mechanical parameters.

FIG. 2. — Energy of Acoustic Pulses Emitted During Stress - Strain Test (10% DAAA).



Conclusions

Diacrylamidoacetic acid can be used under Michael reaction conditions to effect the addition of acrylic groups to amino side-chains of collagen. The resulting crosslinked leather shows increases in shrinkage temperature and chrome uptake but these attributes are accompanied by some loss of physical strength, which limits the practicality of the method. The use of more than 3% of DAAA (based on hide weight) appears to be unnecessary.

Acknowledgment

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