

## GRAFT POLYMERIZATION. VII. NOVEL SOURCE OF REDUCTANT FOR GRAFT POLYMERIZATION OF LEATHER

E. H. HARRIS, H. A. GRUBER, AND M. M. TAYLOR

### Abstract

Glutaraldehyde retannage has been found to provide an *in situ* source of reductant in the redox couple for the free radical initiated graft polymerization of methyl methacrylate onto chrome tanned sheepskin. Persulfate ion was the oxidant used. Monomer to polymer conversion was essentially quantitative. The graft efficiency was independent of monomer and oxidant levels, as well as of the graft molecular weight, which averaged 79 percent. The best graft efficiencies previously found with completely external redox couples were on the order of 60 percent. Acid hydrolysis was used to isolate the grafted chains for viscosity molecular weight determination. Molecular weights of the isolated grafts increased with increasing levels of monomer at a given level of oxidant. However, increasing amounts of oxidant at a given level of monomer did not bring about the expected reduction in the graft molecular weight. These results suggest that there are a limited number of reductant sites available on which the increasing levels of oxidant and monomer had no additional effect. Physical test data from these leathers showed changes from the control leathers similar to those found in previous studies.

### Introduction

A number of investigators (1-4) have studied graft polymerization as a means of achieving permanent modification of the properties of leather. High energy radiation as well as redox systems have been employed to initiate graft sites on the collagen. For use in the tannery, the redox systems are probably the more practical choice of the two methods. Ceric ion [Ce(IV)] would appear to be the oxidant of choice, since the hydroxyl side chains of amino acids in collagen can act as the reductant in this redox couple. These amino acids are listed in Table I. These hydroxyl bearing amino acids could then supply a large number of known potential graft sites, since collagen has about 510 equivalents of hydroxyl groups per mole of collagen (5). In addition, the mechanism for the production of radicals by the Ce(IV) redox couple would be expected to produce little, if any, homopolymer. From a practical viewpoint, these advantages are out-

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TABLE I

## HYDROXYAMINO ACIDS IN COLLAGEN

Amino acid	Moles/Mole of Collagen
Hydroxyproline	321
Serine	96
Threonine	57
Hydroxylysine	20
Tyrosine	16
Total 510	

weighed by the yellow color imparted to the substrate and by the introduction of heavy metal ions into the tannery effluent. Also, Ce (IV) is soluble only below a pH of about 3 and gives optimum grafting on collagen in the pH range of 2.0 to 2.5 (3). We have found the persulfate ion-bisulfite ion redox couple to be the most useful of the redox pairs studied (6), since it does not suffer the problems attendant to the use of Ce (IV) initiation.

During our investigation (6) of the variables involved in the use of this redox couple to initiate grafting, we found that the oxidant could be absorbed and bound by the blue stock. Then, at a later time, the absorbed ion could take part in the redox initiation when supplied with a reductant. Although not published at that time, we also had observed that at least two reductants, glutaraldehyde and tetrakis hydroxymethyl phosphonium chloride, behaved in a similar manner. Thus, by binding either redox component to the collagen and then at a later time adding the complementary member, grafting could be initiated. This novel two-step technique permits the ionic free radicals to be formed entirely within the physical structure of the blue stock, and would be expected to prevent, or at least minimize, any homopolymer formation in the float. Also, it would be expected to increase the efficiency of grafting by shortening the free radicals' diffusion path. This would follow from the completion of the redox couple *in situ* rather than in the external float. Also, the cationic nature of the substrate should minimize diffusion of any ionic free radicals into the external float.

This potential for enhancement of efficiency in grafting warranted further investigation. The authors initially investigated the use of glutaraldehyde retanned blue stock as the substrate. Graft polymerization was accomplished with four levels of potassium persulfate and three levels of methyl methacrylate. The molecular weight of the isolated graft chains was determined by viscometry. The tensile strength test was used to compare control and grafted leathers.

## Experimental

### MATERIALS AND PROCEDURES

Commercially chrome-tanned Abyssinian sheepskins were retanned with glutaraldehyde according to this recipe:

Glutaraldehyde 12 percent blue weight  
(Commercial 25 percent solution)

Water 100 percent blue weight

Drum 7½ hr, final pH 4.5.

Wash overnight and drain.

T<sub>s</sub> 96°C and dry substance 19.1 percent

The skins were horsed up to drain and then cut into 1¼-in. wide strips (Figure 1). They were numbered as shown to identify the left and right sides for physical testing and chemical analysis. Odd numbered strips were used for controls and even numbered strips were graft polymerized with low inhibitor grade methyl methacrylate (MMA)\*, as received, according to the recipe, in which all percentages are based on the average dry substance of the blue stock:

Water 1000 percent  
K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1, 2, 3, or 4 percent  
Emulphogene BC-840† 2.75 percent  
Purge with CO<sub>2</sub> and tumble 30 min  
Methyl methacrylate (MMA) 25, 55 or 100 percent  
Purge with CO<sub>2</sub> and tumble 24 hr and wash overnight.

### PREPARATION FOR PHYSICAL TESTING AND CHEMICAL ANALYSIS

The control and grafted leathers were dehydrated with absolute methyl alcohol as previously reported (4) and conditioned at 50 percent RH and 23°C before testing.

The tensile strength test was made according to the accepted procedure (7).

The amounts of total and bound polymer were determined by methods described in an earlier publication (8).

### ISOLATION AND VISCOMETRY OF THE GRAFTED POLYMER

The air dried samples were ground in a semimicro Wiley Mill and then

\*Appropriate care must be taken with methyl methacrylate because of its reactive nature and flammability.

†Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

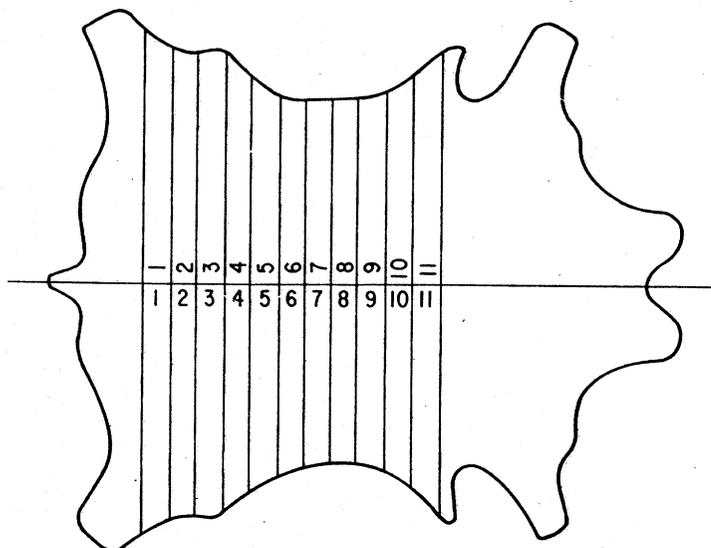


FIGURE 1.—Pattern for physical testing. Odd numbers for control strips, even numbers for treated strips. Left and right sides are coded by orientation of numbers.

exhaustively extracted with ethyl acetate in a Soxhlet apparatus for 72 hr. The solvent was allowed to evaporate from the samples and the residues were hydrolyzed with 6 *N* HCl for two hr. The isolated graft polymer was then collected on a coarse sintered glass funnel and washed with water, 0.2 *N* NaOH, water, 0.2 *N* HCl and water. All water washes were continued until a neutral pH was obtained before proceeding with the next eluent. The graft polymer was then air dried, weighed, taken up in 2-butanone and filtered through a sintered glass funnel before being made up to the appropriate concentration. Dilutions were made and the viscosities were determined at 30°C with a Cannon-Manning semimicro viscometer. The intrinsic viscosities were then computed with an IBM 1130 computer. These values were used in the equation  $[\eta = KM^a]$  to determine the molecular weights. Appropriate literature values for *K* and *a* were used (9).

The total polymer content and the extractable polymer content were obtained as previously described (8). From these analytical values, the bound polymer content was obtained by difference.

### Results and Discussion

One drawback of our previously reported graft polymerization procedure is that both redox components are simultaneously added to the float. Thus they can immediately react to form ionic free radicals before the individual components diffuse into the blue stock. While these free radicals can also diffuse into

the blue stock and initiate grafting sites, undoubtedly there are losses due to side reactions during this diffusion process. Any such losses would lower the efficiency of initiation of graft sites. One potential loss could be the formation of homopolymer as a latex in the float. This would then be absorbed into leather as a polymeric impregnant. Permitting the redox couple to react only within the physical confines of the blue stock should effectively minimize this loss of free radicals and thereby increase the probability of initiation of graft sites.

The only possibility of preventing the redox reaction from occurring in the float while allowing it to proceed in the blue stock is to bind either the oxidant or the reductant to the blue stock. The complementary member could then be added to the float. We have already reported (6) on one workable approach to this technique. It involved the initial combination of persulfate ion with chrome stock and the later completion of the redox couple by introduction of bisulfite ion. This technique was effective in initiating graft polymerization. Although our work was not published at that time, we were able to treat blue stock with glutaraldehyde or with tetrakis hydroxymethyl phosphonium chloride and later complete the redox couple with persulfate ion to carry out a graft polymerization reaction.

While we believed that both of these techniques were worth investigating further, we initially chose to use glutaraldehyde retanned blue stock as the substrate based on current industry use of glutaraldehyde as a retanning agent.

While we knew that glutaraldehyde retanned stock could act as the reductant for a redox couple, we did not know to what limit its reductant capability could be utilized, nor were we aware of its effect on the chemical and physical properties of the graft copolymer. We chose four levels of oxidant. Assuming sufficient reductant capacity, this would give four levels of ionic free radicals. Each free radical cannot be expected to initiate a graft site, but if the free radical population is increased by known increments, there should be some proportionality in increase of graft sites. We chose three levels of methyl methacrylate. Thus for any given level of persulfate ion we expected to find essentially the same number of graft sites and thereby have the potential for increasing the graft efficiency as well as the graft molecular weight. By varying the monomer levels from 25 percent up to 100 percent, a fourfold range of graft molecular weights was expected. This would require a complete monomer-to-polymer conversion, which our system essentially provides. Then, with a fourfold increase of the persulfate ion level, we should achieve an overall 16-fold range of graft molecular weights. This in turn gave the potential for determining their effect on the physical test properties of the leather.

By the use of gas chromatography during each experiment we were able to demonstrate an essentially complete conversion of monomer to polymer. This is confirmed by the analytical data shown in Table II. The deviations of the total polymer found compared to the theoretical amount can be explained by variations in the amount of hide substance in any given piece of wet stock. The

graft efficiency data are noteworthy, particularly when compared with those from our earliest attempts, which yielded only about 30 percent (11). In later studies (6), we were able to raise this to about 60 percent. In both studies, the complete redox pair was present in the float. Now, by using the glutaraldehyde retained blue stock as the reductant source, we have raised the graft efficiency further. Even including the low value of 63 percent, the average value is 79 percent.

These values even exceed some of those reported for Ce(IV) initiated grafts, where the primary free radical should be formed directly on the collagen. Exact comparisons are difficult to make, since not all investigators reported their results in suitable form. Additionally, the substrate and monomer must also be taken into account. Prentiss *et al.* (3) reported "high" graft efficiency for MMA on hide powder, but when using (2-aminoethoxy) ethanol as the model compound obtained only 46 percent graft efficiency. In our laboratory we have observed graft efficiencies of 59 percent and 64 percent in replicate runs with this initiator.

TABLE II  
EFFECT OF TREATMENT LEVELS ON POLYMER PROPERTIES

Offered, % <sup>a</sup>		Polymer, % <sup>b</sup>		Graft <sup>c</sup>	
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	MMA	Total	Bound	Efficiency, %	Mol. Wt.
1	25	20.0	16.1	80	850,000
1	55	35.0	26.4	76	971,000
1	100	51.3	39.0	76	2,641,000
2	25	21.4	17.6	82	849,000
2	55	36.6	29.3	80	1,230,000
2	100	51.7	41.6	80	1,678,000
3	25	22.2	13.5	63	764,000
3	55	36.3	29.5	81	1,226,000
3	100	49.2	37.6	76	1,461,000
4	25	19.4	16.0	84	1,046,000
4	55	37.2	30.8	82	1,393,000
4	100	52.0	44.0	85	1,821,000

<sup>a</sup> Percentages are based on the average dry substance of substrate.

<sup>b</sup> These data are averages obtained from left and right sides. The percentages are based on the product weight. The theoretical values for total polymer are 20, 35.5 and 50 percent for the respective monomer levels used.

<sup>c</sup> Graft efficiency is the percent of the total polymer that is bound. The molecular weights were obtained by viscometry.

The viscosity molecular weight data are both interesting and disappointing. The disappointment lies in the lack of the expected range of control of graft molecular weight, as previously outlined. The only apparent control of graft molecular weight with this substrate is through the amount of monomer offered. For any given monomer offering, an increase of the persulfate ion level from one up to four percent gave little or no change in the graft molecular weight. However, when the monomer level for any persulfate ion level is increased, a real and distinct relationship is seen. In Figure 2 we show this relationship as a graph.

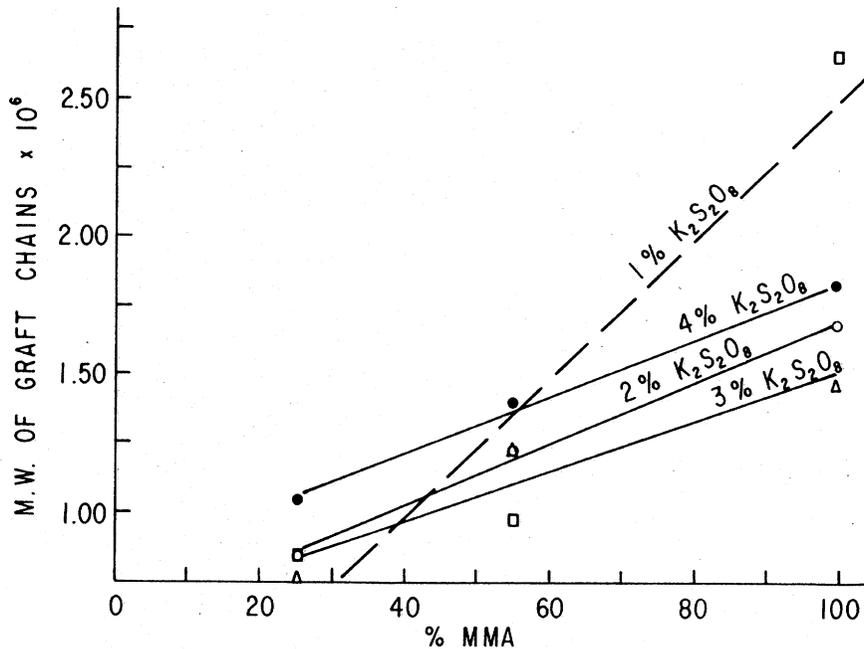


FIGURE 2. — Effect of monomer levels on the graft molecular weight at each level of oxidant.

While we have plotted all the data points, we consider the value of one molecular weight to be anomalous, *i.e.*, 2.6 million. We have drawn a dashed line to emphasize the distortion this value causes in the family of curves presented by the remaining data points. The other levels did give a good line fit by the least squares method.

By the nature of the polymerization process, exact multiples of molecular weight changes cannot be expected as the appropriate factors are altered. In addition, our molecular weights are determined by viscometry and are polydisperse (10). They can be used only as approximations. Even so, they are useful. With the molecular weight data, in combination with analytical data of Table II, we calculated the average number of grafts per mole of collagen, shown in terms of

the graft molecular weight in Figure 3. By the method of least squares, we drew the best fitting line. We deleted the one high molecular weight value of 2.6 million as a probable outlier in these calculations. One point lies outside the majority of values, for reasons that are not known at present. Little change occurred in the molecular weight of the graft for a given monomer level as the persulfate level was raised from one up to four percent of the substrate dry substance (Table II). Yet, if sufficient reductant were available, a large decrease should have been found because of the greater number of free radicals formed. This finding suggests that the reductant capacity of the glutaraldehyde retanned chrome leather — at least as prepared in this study — is limited. In fact, the one percent persulfate level seems able to utilize fully all available reductant present.

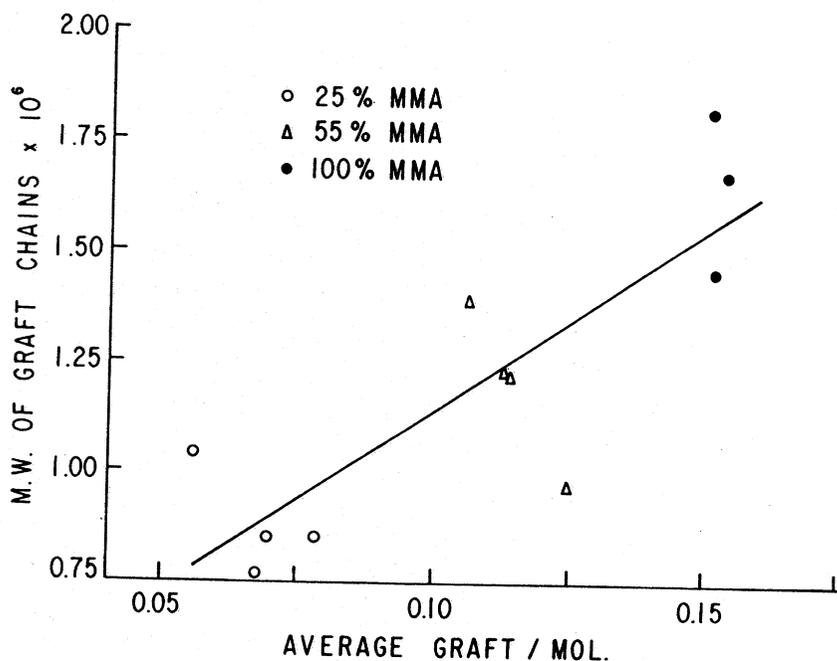


FIGURE 3. — Average grafts per mole of collagen.

While the average number of grafts per mole of collagen seems to be related to the monomer levels used, we do not know why. At this point in the investigation, we believe that the polydispersity of the graft molecular weights precludes answering that question.

Although we have been able to achieve improvements in the grafting technique, the results have not shown improvement in the previously obtained physical test values. The physical test data obtained in the current investigations

(Table III) show a pattern similar to that found in earlier work (4). As the total polymer content is increased, the leather thickness is increased. The percent change in elongation at tensile break does not give a consistent pattern related to either the polymer content or the molecular weight of the grafted polymer. Only four out of the twelve values were positive, and these were very modest gains. The percent change in load at tensile break was, with one exception, always increased. These increases were less than the increases in thickness, thus all tensile strength values were lower than the controls.

We could not demonstrate a useful relationship between the graft molecular weight and the physical test properties of these leather. The total polymer content is directly related to the increase in thickness. The molecular weight of the graft polymer does not seem to be related to any tensile strength property. Taylor (12) reported similar results from a study of the effect that a chain transfer agent had on the grafting of MMA onto chrome-tanned sheepskin.

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1	25	40	4	18	-16
1	55	62	11	18	-28
1	100	98	-32	-4	-52
2	25	46	0	13	-24
2	55	52	13	21	-19
2	100	91	-8	18	-44
3	25	46	-10	22	-16
3	55	66	13	30	-22
3	100	84	-6	14	-38
4	25	40	-14	12	-13
4	55	50	-13	13	-24
4	100	83	-46	8	-42

<sup>a</sup> Percentages based on average dry substance of substrate.

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### Summary

By the novel method of binding one of the redox pairs to the collagen and then, at a later time completing the couple, we have successfully initiated graft

polymerization of chrome stock at ambient temperatures. Glutaraldehyde re-tanned chrome stock was successfully grafted with methyl methacrylate. The apparently limited capacity of this leather as a reductant did not permit the expected control over the graft molecular weight. The control that was achieved suggests that the physical test values of the leather are affected by the amount of polymer formed in the leather and the nature of the polymer itself. The results also show that the graft efficiency is independent of the graft molecular weight; therefore the argument that the unextractability of polymer is due to its high molecular weight, chain entanglement, and/or chain branching, rather than grafting, is not borne out.

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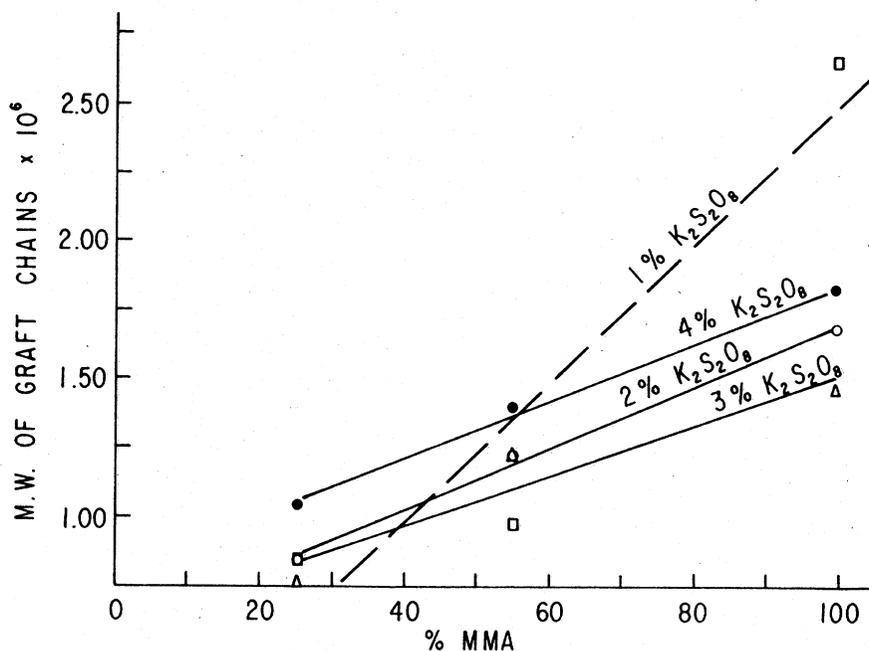


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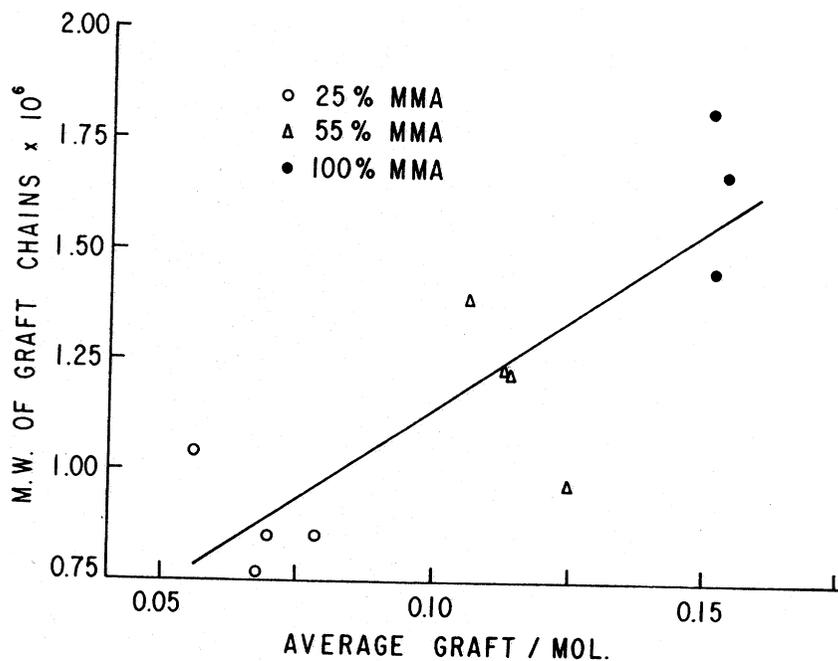


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