

309

EFFECT OF TANNING AGENTS ON THE GRAFTING OF VINYL POLYMERS TO COLLAGEN*

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The influence of tanning agents on the grafting of methyl methacrylate onto collagen has been investigated. The results obtained indicated that zirconium and aluminium tanning lead to increased degree of grafting, whereas chromium, syntan and vegetable tannages lead to a decrease in percentage grafting. Although Ce (IV) has been shown to oxidise the Cr (III) complexes that are involved in tanning, percentage grafting is not reduced very much. More than the competition of tanning agents for grafting sites, the initiator-tanning agent reactions govern mainly the grafting efficiency.

Preliminary investigations on grafting vinyl polymers onto tanned collagen (leathers) carried out by Rao,^{1,2} Nayudamma *et al*,³ reported that in the application of grafting techniques in leather processing, the grain surface becomes rough on grafting unless it is fixed by some suitable tanning agents. Some investigations on grafting of leathers were also carried out using chrome tanned leathers.⁴⁻⁶

The influence of chrome tannage as well as other tannages on grafting has not yet been studied systematically. The object of the present investigation is to study the individual effect of various common tannages practised in the industry and assess their influence on grafting.

Experimental

(a) Materials

*Based on the thesis of K.S.B. approved for the award of the Ph.D. Degree of the Madras University.

Collagen powder, prepared by standard methods was used.¹ Basic chromium sulphate (B & C extract powder) and zirconium sulphate used were of commercial quality. Basic aluminium sulphate was prepared according to standard methods.⁷ Other reagents used were of laboratory grade.

(b) Tanning methods

All the tannages (cross-linking) were carried out as described by Ranganathan⁸ and Rao⁶ and analysed by Official Methods of Analysis.¹⁰

(c) Mode of grafting

The grafting of methylmethacrylate onto various tanned hide powders was carried out using ceric ammonium nitrate ($2.5 \times 10^{-2}M$) initiating technique. The procedure used for graft copolymerisation reaction has been described in the earlier publications.^{1,2,11}

(d) Determination of degree of tannage was carried out using the method of Rao.¹¹

(e) Percentage grafting

The percentage grafting was estimated from total nitrogen content.¹¹ Nitrogen was estimated by micro kjeldahl method. After allowing for tannin content, percentage grafting was calculated.

(f) Spectrophotometric investigations

Spectrophotometric investigations on the interaction of Ce(IV) and tanning (mineral) solutions were carried out on a Beckman DU spectrophotometer. Tanning solutions (containing 1.0 g Cr₂O₃ or 1.2 g of Al₂O₃ or ZrO₂ in 400 ml) were prepared at [HNO₃] = 0.05 M. A solution of ammonium ceric nitrate [5.0 × 10⁻² M in Ce(IV) and 0.05 M in (HNO₃)] was also prepared. After an addition of equal volume of tanning solutions (1.5 ml) and ammonium ceric nitrate (1.5 ml) spectra were recorded at room temperature as a function of time over a period of 3 hours. The absorbance changes were maximum at 350 nm and therefore optical densities at that wavelength alone were monitored.

Results

The percentage grafting of methylmethacrylate onto leathers tanned by various tanning agents using Ce(IV) as the initiator have been tabulated in Table 1. The degree of tannage also has been given alongside of percentage grafting. The treatment of vegetable tanned hide powder with Ce(IV) leads to darkening of colour. Chrome tanning complexes are found to react with Ce(IV) and results of spectrophotometric investigations are presented in Table 2.

Discussion

The percentage grafting under comparable conditions shows a remarkable dependence on the nature of tannage. While the phenol-

based tannages such as vegetable and syntan reduce the percentage grafting appreciably, the mineral tanning agents such as Cr(III), Zr(IV) and Al(III) increase percentage grafting. The differential behaviour of different tanning agents can also be attributed to the levels of hydrophobicity and swelling characteristics of the fibre, reactions of the tanning agents with initiators and monomer and also the reactive sites of collagen. This observation that grafting on Zr(IV) tanned leathers is more efficient than on Cr(III) tanned leather shows that the filling nature of Zr(IV) tannage does not interfere in grafting.

TABLE I

Effect of tanning agents on Ce(IV) initiated grafting of poly (methylmethacrylate) onto collagen

Tanning agents	Grafting %	Degree of tanning %	Fixed mineral oxide †
Normal hide powder	150	—	—
Wattle	36	30.3	—
Myrob	32	17.9	—
Syntan	32	22.2	—
Chromium (III)	99	13.8	6.3
Zirconium (IV)	350	26.9	8.8
Aluminium (III)	299	2.4	7.1

[Ce(IV)] = 2.5 × 10⁻² M, [HNO₃] = 0.025 M
[Methylmethacrylate] = 0.5 M

* Degree of tanning was estimated from the total nitrogen content as in the case of percentage grafting.

† Obtained by the analysis of mineral oxide.

The importance of the initiators and their properties in grafting has already been established. Any possible reaction of the initiator with tanning agent can introduce large differences in the percentage grafting. The vegetable tanning materials and syntans, in general, have phenolic OH groups which are easily oxidisable into quinones by power-

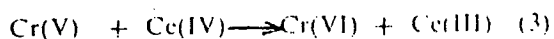
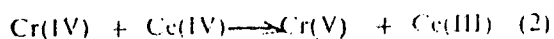
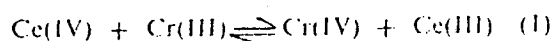
ful oxidants such as Ce(IV). In the case of such reactions, one would expect darkening of tanned hide powder, which is indeed observed. These oxidation reactions will not only reduce the amount of available initiators for the grafting reactions but also will produce radical ions that are capable of quenching polymerisation.

TABLE 2
Spectrophotometric investigations on the reaction of mineral tanning agents with cerium (IV)

Tanning solutions	Optical density at 350 nm						
	0 (min.)	30 (min.)	60 (min.)	90 (min.)	120 (min.)	150 (min.)	180 (min.)
Chromium (III)	0.648	0.620	0.605	0.595	0.579	0.560	0.550
Zirconium (IV)	0.823	0.816	0.813	0.812	0.812	0.806	0.804
Aluminium (III)	0.762	0.762	0.758	0.759	0.759	0.754	0.756

[Ce(IV)] = 2.5×10^{-3} M, [HNO₃] = 0.025M.

Similarly, in the case of Ce(IV) initiated grafting procedure on chrome tanned leather, the following non-complementary reactions are of relevance.¹²



The reactive intermediates Cr(V) and Cr(IV) may participate in redox reactions with organic radicals. It is conceivable that reactions represented in equations (1) to (3) may reduce the amount of Cr(IV) available for grafting. Chain transfer reactions involving higher valent Cr are also possible. No such reactions can be envisaged between Al(III) - Ce(IV) and Zr(IV) - Ce(IV) complexes. Although Al(III) and Zr(IV) complexes involved in tanning are assumed to contain coordinated OH groups, it is unlikely that Ce(IV) may in fact be involved in any complex formation or redox processes. This argument has been substantiated by the following spectrophotometric investigations on tanning solutions.

On mixing Ce(IV) solutions (2.5×10^{-3} M) with tanning solution (0.25 g Cr₂O₃ / 400 ml, 0.3 g Al₂O₃ / 400 ml and 0.3 ZrO₂ / 400 ml) spectrophotometric changes are observed only with Cr₂O₃ solution over a period of 3 hours. The decay of Ce(IV) is monitored at 350 nm. The absence of any reaction of Al(III) and Zr(IV) with Ce(IV) is indicated by the constancy in the absorbance (Table 2).

As for the possible competitive inhibition by tanning agents, the main groups involved with different tanning agents vary. The mechanism proposed for syntan and vegetable tannage involves the participation of terminal NH₂, CONH, CONH₂, and other aromatic OH groups.¹³ Similarly, Zr tannage involves free NH₂ and CONH groups.¹⁴ The side chain carboxyl groups are known to participate in chromium and aluminium tanning. On the other hand, the mechanism proposed by Rao *et al*¹⁵ for grafting of methylmethacrylate using Ce(IV) as initiator involves the participation of CONH, OH and NH₂ groups. Deaminated hide powder has been shown to graft less than normal hide

powder.¹¹ Therefore, if the tanning agents behave as competitive inhibitors, it would be expected that vegetable, syntan and Zr tanning materials will behave as competitive inhibitors for grafting. The chromium and aluminium will not block the reactive sites for grafting. The percentage grafting, however, decreases a great deal with tannage. This observation can be explained in the following manner. Since in grafting only a few reactive sites are involved, the degree of grafting depends mostly upon the ability to grow long chains of graft polymer rather than to grow at many sites. The inhibition due to competition for the reactive sites may be low.

The results presented in Table I, however, show that chromium, inspite of its competitive nature for grafting sites, lowers grafting whereas zirconium, even with its reactivity towards grafting sites, leads to enhancement.

In the light of the above arguments, it can be seen that swelling type of tannage such as zirconium lead to a high percentage grafting. Lack of any possible chemical reaction between Zr(IV) and Ce(IV), is an advantage that zirconium and aluminium tanning have over other tannages. As in any solid phase reaction (in this case solid matrix being collagen) swelling of the fibre will lead to increased surface area and accessibility to the reactive sites, for the reactions to occur. Chrome tanning, by its well known ability to crosslink the protein, may decrease the swelling character of the fibre. It is known that Cr(III) reacts with Ce(IV) producing Cr(V) and Cr(IV) intermediates,¹² which may be involved in the redox processes. The accepted mechanism of chrome tannage¹⁴ does not involve the functional groups that are required for grafting and yet the degree of grafting is lower. Syntan and vegetable tannages (condensed as well as hydrolysable) lead to marked lowering in the percentage of

grafting as compared to the normal hide powder. Although these tannages are of filling nature, the possible reactions of vegetable tanning materials with Ce(IV) involving radical formation and reduction in initiator concentration may be the reason for the decreased grafting efficiency.

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