Dyeing of Chrome Tanned Collagen Modified by In Situ Grafting with 2-EHA and MAC

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Received 13 February 2005; accepted 1 September 2005
DOI 10.1002/app.23160
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this study deals with the modification of the chrome tanned collagen (leather) by in situ grafting with 2-ethyl hexyl acrylate (2-EHA) and methacrylic acid (MAC) to improve its dyeability using Amecid Floxine 2GN (C.I. Acid Red 1) and Remazol Black B (C.I. Reactive Black 5). The optimum condition of in situ grafting has been evaluated. FTIR spectra of the ungrafted and the in situ grafted chrome tanned collagen showed that the corresponding band of the acrylate carbonyl ester occurs at 1730–1735 cm^{-1} when compared with the ungrafted ones. The colorimetric data of the in situ grafted and dyed samples exhibited improvement in color shade, dye bath exhaustion, wash and light fastness relative to the ungrafted and dyed ones. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 174–179, 2006

Key words: chrome tanned collagen; grafting polymerization; 2-ethyl hexyl acrylate; methacrylic acid; acid and reactive dyeing

INTRODUCTION

The modification of the natural and synthetic leather polymers through grafting copolymerization had been previously investigated.[1–5] The application of grafting techniques in leather processing resulted in roughened grain surface, unless suitable tanning agents are employed to minimize this undesirable side-effect.[6,7] The in situ grafting polymerization of leather has been studied for many years to enhance the esthetic and mechanical properties, such as tensile strength and scuff resistance. The grain layer of leather is weaker than the corium, so the application of the polymers to strengthen this layer was examined for many leather applications.[8] For base coats, acrylic emulsion polymers were a preferred class of binders, because of their wide range of combination varieties for different leather products. The new technology of synthetic polymers has provided superior combinations for good dry flex endurance, also, the technology provided improved wet flex endurance and wet intercoat adhesion applications.[9] The treated leather with graft copolymer of methacrylic acid and bentonite in a ratio 1:1, which is used as retanning agent, had good fullness and physical properties.[10] Also, the microemulsion solutions of different copolymers, such as methyl methacrylate, *n*-butylacrylate, and methacrylic acid, were applied as retanning agents in chrome tanned goat skins.[11] El Amma[12] explained the significant differences in the application properties of the tanned leather with different acrylate polymers. The affinity of dyes to natural polymers are generally more when compared with the affinity to synthetic ones, even though their dye uptake may be limited, the fastness properties of the dye treated graft copolymers might show remarkable importance.[13]

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Journal of Applied Polymer Science, Vol. 101, 174–179 (2006)

EXPERIMENTAL

Materials

Commercially available buffalo chrome tanned collagen was obtained from the local tannery at Cairo, Egypt. Methacrylic acid (MAC) and 2-ethyl hexyl acrylate (2-EHA) were obtained form Lab Scan India. Benzoyl peroxide (BP) was obtained from Sigma–Aldrich. Other chemical reagents were used as laboratory grade. The two commercial dyes used were as follows: Amecid Floxine 2GN (anionic dyestuff) C.I. Acid Red 1 (ABI) and Remazol Black B (Vinyl Sulfone Reactive) C.I. Reactive Black 5 (DYS).

Grafting method[14]

A sample tube of 100 mL capacity was charged with a calculated quantity of the chrome tanned leather (3.5–5 g), equal molar ratio of 2-ethyl hexyl acrylate and methacrylic acid (5:5), and benzoyl peroxide (1.5%) as initiator, and 40 mL methanol (99%) was added. The sample tube was tightly closed and kept in

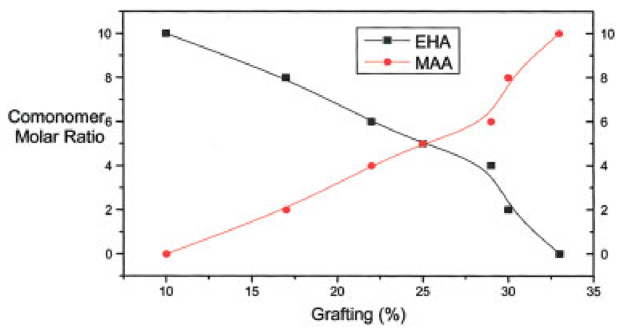

Figure 1 Effect of the comonomer ratios of (2-EHA) and (MAC) on the grafting yield of chrome tanned collagen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

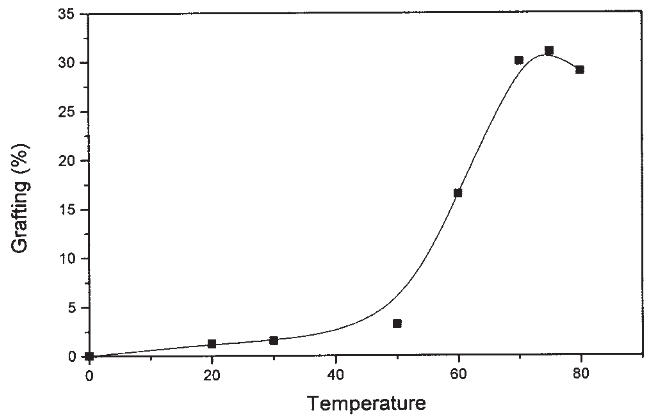

Figure 2 Effect of the in situ grafting temperature on the grafting yield of the chrome tanned collagen.

a thermostatically water bath at 70°C for 3 h. The in situ grafted leather samples were obtained from the reaction vessel, and the homopolymers were extracted using suitable solvent mixture (ethanol:water = 1:1) in Soxhlet for 18 h, then dried at 50°C overnight. The degree of the grafting was calculated as follows:

$$\text{Grafting yield (\%)} = \frac{W - W_o}{W_o} \times 100$$

weigh where W_0 is the weight of the sample before grafting and W is the weight of the sample after grafting.

Standard dyeing method[15]

All percentages are based on shaved leather. Both the ungrafted and grafted leather samples were dyed as follows: 1% dye, 100% liquor for 30 min at 40°C followed by the addition of 1.5% formic acid (30%) for 15 min at 55°C, finally, washing of the dyed samples for 10 min. The dyeing process was taken place using glass bottles housed in thermostatically controlled water bath.

TABLE I
Grafting Yield of Leather Using Different Co-monomor Ratios of (2-EHA) and (MAC)

Grafting yield (%)	2-Ethyl hexyl acrylate (mol)	Methacrylic acid (mol)
10	10	0
17	8	2
22	6	4
25	5	5
29	4	6
33.5	2	8
33	0	10

FTIR spectroscopy

The spectra of the ungrafted and grafted leather samples were carried out using Bomem–Micelson, Fourier Transfer Infrared Spectrophotometer.

Dyeing properties

i. Dye-bath exhaustion using spectrophotometric measurements: calibration curves of Amecid Floxine 2GN and Remzol Black B were drawn by measuring the absorbance of each prepared concentrations (1–10 mg/L). Then the dye uptake of the used dyestuff was calculated by sampling the dye-bath solutions before and after the dyeing processes.
ii. Kubelka–Munks (K/S) and CIE-Lab parameters[16]: the color strength (K/S) and CIE-Lab parameters (L^*, a^*, and b^*) of the grain and flesh sides of the grafted samples were measured using Ultra Scan XE (Hunter lab).
iii. Light and washing fastness
   a. fastness to artificial light: leather specimen of not less than 1×6 cm^2 are exposed to artifi-

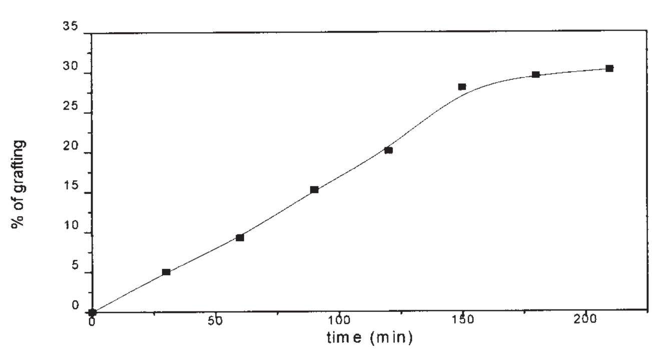

Figure 3 Effect of the in situ grafting time on the grafting yield of the chrome tanned collagen.

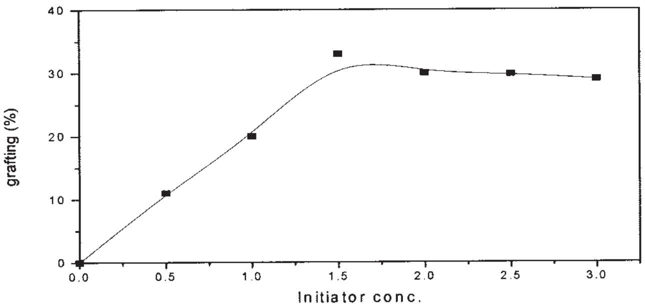

Figure 4 Effect of benzoyl peroxide (initiator) on the grafting yield of the chrome tanned collagen.

cial light under IUF 402 and DIN54004[17] conditions with eight fastness standards that consist of pieces of wool cloth dyed with standard blue dyes of different degrees of fastness.

b. fastness to washing: according to IUF423 and Heidemann et al.[18] this property was tested by washing leather in neutral synthetic detergent (alkali-free) bath and assessing the change in shade and coloring of accompanying textile fabric.

RESULTS AND DISCUSSION

Effect of comonomer ratios

Figure 1 shows the effect of the comonomer of 2-ethyl hexyl acrylate (2-EHA) and methacrylic acid (MAC) on the grafting percentage of the in situ grafted chrome tanned collagen at constant benzoyl peroxide (1.6%), temperature (70°C) and time (3 h). The level of the grafting steadily increased until 25%, at equal comonomer ratio (5:5), this is attributed to the fact that increasing the comonomer concentration might have a high possibility of forming homopolymers (Table I).

Effect of temperature

Figure 2 shows the effect of the in situ grafting temperature on the grafting percentage of chrome tanned collagen, the curve illustrated that, the temperature increased from 0 to 70°C, and the level of the grafting increased until maximum at 70°C was reached, further increase in temperature causes an increase in the free radical levels and consequently, the rate of homopolymer formation was increased relative to the rate of the in situ grafting.

TABLE II
Effect of the Grafting Yield on the Dyeing Measurements of the Grafted and Dyed Leather with Amecid Floxine 2GN

Grafting yield (%)	K/S		% *E*
	Grain	Flesh	
4	6.0	10.0	46
9	6.0	11.0	50
13	6.7	12.0	54
17	7.0	14.0	60
20	11.0	17.0	60
25	8.3	17	60

Effect of time

Figure 3 shows the effect of the in situ grafting time on the grafting percentage of the chrome tanned collagen, the curve illustrated that the grafting percentage was gradually increased with increasing the time from 0 to 180 min until a maximum at 25% was attained, followed by a decrease in the percentage indicating that the rate of grafting was dependent on the reduction of the free active sites of the chrome tanned collagen.

Effect of initiator on grafting yield of the chrome tanned collagen

Figure 4 shows the effect of the concentration of the initiator (benzoyl peroxide) on the grafting yield of the chrome tanned collagen, the curve illustrated that the increasing in the initiator concentration from 0.5 to 1.6% causes an increase in the grafting yield until

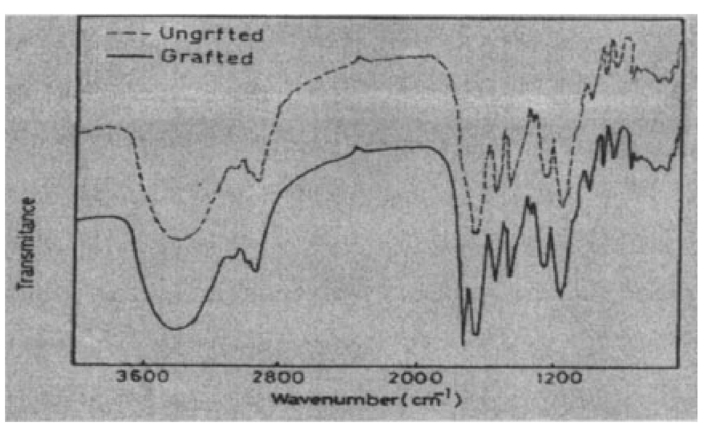

Figure 5 FTIR spectra of the ungrafted and grafted chrome tanned collagen.

TABLE III
Effect of the Grafting Yield on the Dyeing Measurements of the Grafted and Dyed Leather with Remazol Black B

Grafting yield (%)	K/S		% *E*
	Grain	Flesh	
4	10.3	23.0	90
9	10.5	23.0	88
13	10.8	24.0	88
17	10.9	24.0	90
20	11.0	29.0	95
25	11.2	34.0	95

33.5%. Further increasing the initiator concentration leads to leveling-off the rate of the in situ grafting because of the lowering in the free active sites of the chrome tanned collagen, so the rate of the homopolymerization was increased.

Effect of grafting yield on the dyeing measurements of chrome tanned collagen

Tables II and III and Figures 6 and 7 show the color strength (K/S) and the dye bath exhaustion of the in situ grafted chrome tanned collagen, with different grafting yield (4, 9, 13, 17, 20, and 25), at 1% dye concentration. Clearly, the in situ grafting with 2-EHA and MAC improved the color strength of the dyeings and also the dye bath exhaustion. It is evident that, when the grafting level increased to 20%, in case of Amecid Floxine 2GN and to 25% in the case of Remzol Black B, both color strength and dye-bath exhaustion were increased. The shade intensification furnished by the in situ grafting could be attributed to the increasing the density of the free active sites of the chrome tanned collagen that could be reacted with the used dyestuffs.

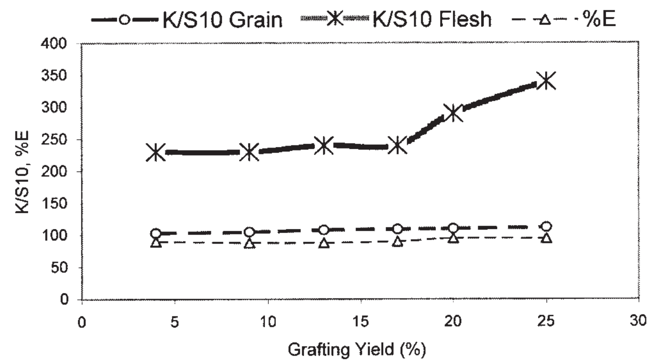

Figure 7 Effect of the grafting yield on the dyeing measurements of the grafted and dyed leather with Remazol Black B.

Effect of the grafting yield on the corresponding colorimetric data of the in situ grafted and dyed chrome tanned collagen

Table IV shows the corresponding colorimetric data of Amecid floxine 2GN obtained by the dyeing of the chrome tanned collagen that is in situ grafted with 2-EHA and MAC at various levels. The results indicated that, the in situ grafting produces lighter (L^*) and redder leather when compared with the ungrafted ones. Table V gives the corresponding colorimetric data, in case of Remazol Black B, it was observed that, the in situ grafting resulted in lower lightness and bluer leather when compared with the ungrafted ones. The results obtained using the two different dyes (anionic and vinyl sulfone reactive) demonstrated that the intensification of the shade furnished by the in situ grafting could be attributed to 2-EHA and MAC, which had been adsorbed to higher extent on the flesh side than that on the grain side owing to the well-known structural differences between the two sides. A less compact fiber structure and larger interfibrillar

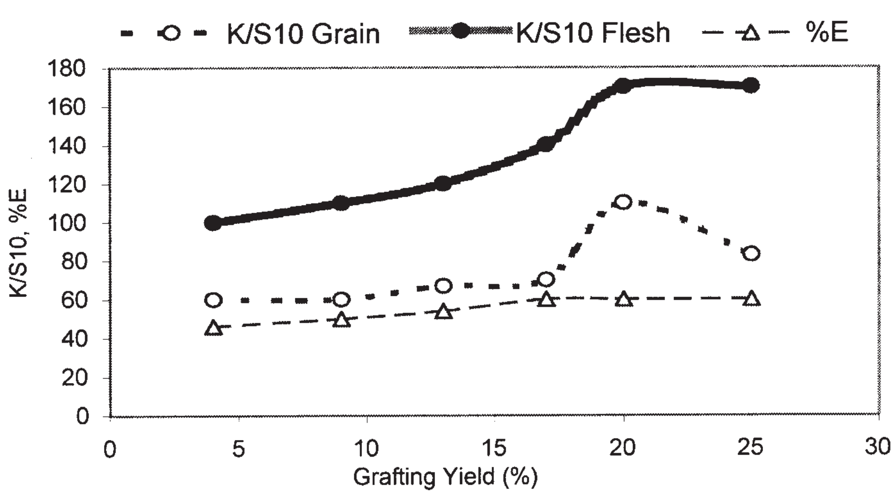

Figure 6 Effect of the grafting yield on the dyeing measurements of the grafted and dyed leather with Amecid Floxine 2GN.

TABLE IV
Effect of the Grafting Yield on the Colorimetric Data of the Grafted and Dyed Leather with Amecid Floxine 2GN

Grafting yield (%)	*L**		*a**		*b**	
	Grain	Flesh	Grain	Flesh	Grain	Flesh
4	45.81	37.39	38.34	35.13	0.38	0.01
9	44.25	27.55	32.56	28.38	−0.45	2.04
13	43.49	39.92	34.95	34.08	1.19	1.15
17	43.30	32.44	35.83	36.75	7.78	5.46
20	36.85	31.76	34.78	29.84	1.75	−1.33
25	40.98	33.48	36.35	38.35	1.89	5.56

space in the flesh side might be caused by the preferential reactivity towards the used comonomer.

Effect of the grafting yield on the wash and light fastness of the in situ grafted and dyed chrome tanned collagen

Table VI shows the effect of the grafting yield on the wash and light fastness of the in situ grafted and dyed chrome tanned collagen, it was observed that, both of wash and light fastness were gradually improved, when the grafting yield was increased to 20 and 25%, in case of Amecid floxine 2GN and Remazol Black B respectively, this may be due to the hydrophobic character of the long chain hydrocarbon of 2-ethyl hexyl acrylate. In case of 1% Amecid Floxine 2GN that reacts physically (by the hydroxyl, sulfonic, and the corresponding cationic groups of the in situ grafted chrome tanned collagen), but in case of 1% Remazol Black B, which might be reacted physically and chemically (using the addition reaction between the vinyl sulfone groups in the dye and the active protons of the in situ grafted chrome tanned collagen). The used dyes were reacted with the grafted leather by the carboxylic anions (methacrylic acid) and the amino groups of the used dyes. The difference in the fastness properties obtained by the two different dyes might be attributed to the above differences in the mode of the reaction.

TABLE V
Effect of the Grafting Yield on the Colorimetric Data of the Grafted and Dyed Leather with Remazol Black B

Grafting yield (%)	*L**		*a**		*b**	
	Grain	Flesh	Grain	Flesh	Grain	Flesh
4	32.60	16.34	−7.60	−1.44	−11.26	−5.91
9	31.07	18.32	−5.73	−1.39	−12.42	−6.53
13	30.66	19.22	−5.31	−1.78	−11.83	−7.38
17	31.90	18.59	−6.20	−1.52	−12.67	−7.19
20	37.42	19.99	−7.94	−3.71	−5.47	−6.70
25	30.18	14.19	−6.82	−0.17	−8.90	−4.41

TABLE VI
Effect of the Grafting Yield on the Fastness Properties of the Dyed Leather

Used dyes	Grafting yield (%)	Fastness with respect to color: Washing, Cotton staining	Washing, Wool staining	Light
Amecid Floxine 2GN	3.9	3	2	5
	9.2	3	2–3	6
	13	3	2–3	6
	17	4	3	6–7
	20	4	4	7
	25	4	3	6
Remazol Black B	3.9	4–5	4	4–5
	9.2	4	3	4–5
	13	4	4	5
	17	4	4	6
	20	5	4	6
	25	5	4	6–7

CONCLUSIONS

The best in situ grafting condition of the chrome tanned collagen with 2-EHA and MAC was obtained at comonomer ratio of 2:8 respectively, benzoyl peroxide (initiator) concentration 1.6%, time 3 h, and temperature 70°C to get grafting yield up to 33.5% while the optimum grafting yield at which the dyeing properties of the in situ grafted chrome tanned collagen (leather) were optimized to 20 and 25%, this was done at the comonomer ratios 6:4 and 5:5, in case of using Amecid Floxine 2GN (anionic dye) and Remazol Black B (vinyl sulfone reactive dye) respectively. Using monomers which have long chain hydrocarbon such as 2-ethyl hexyl acrylate improve the fastness properties, especially wash fastness, due to its hydrophobic character.

NOMENCLATURE

E dye bath exhaustion
K/S color strength
*L** lightness of the color
*a** redness of the color
*b** blueness of the color

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