Modification of Leather Properties by Grafting. I. Effect of Monomer Chain on the Physico-mechanical Properties of Grafted Leather

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ABSTRACT: Although leather has a number of desirable properties such as thermal stability and fire retardancey, in addition to high toughness, it has a few drawbacks such as weight, high water absorption, poor soil and rot resistance, and nonuniformity. If these defects are overcome, leather's usefulness would be further enhanced and its competitive position with respect to synthetics would increase. This study reports the physical and mechanical properties of buffalo leather after chemical graft copolymerization with ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate using benzoyl peroxide as an initiator. The optimum conditions for grafting (e.g., monomer and initiator concentra-
tions, temperature and time of grafting, and solvent leather ratio) were extensively investigated. The study achieved outstanding properties for buffalo leather in reduction of water uptake after grafting, especially on using 2-ethyl hexyl acrylate and butyl acrylate monomers. FT-IR and solid ^{13}C-NMR for leather before and after grafting confirmed the grafting process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1478–1483, 2003

Key words: Modification of leather; graft copolymers; physicomechanical properties; vinyl monomers; water uptake

INTRODUCTION

Chemical modification of natural[1–4] and synthetic[5–9] polymers with the aim of imparting specific, desirable properties through graft copolymerization has been the subject of investigation in recent years. However the literature concerning grafting of acrylate monomers onto milk protein, casein,[6,10] is scanty. The application of acrylates is motivated by their easy polymerizability, commercial availability, and relative low price.[11] Monomers used for grafting were, for instance, methyl methacrylate (MMA), methyl acrylate, ethyl acrylate (EA), butyl acrylate (BuA), butyl methacrylate (BuMA), styrene (St), and their mixtures.[12–16] Best results were obtained by using BuA or its mixture with MMA.[14] Mechanical properties of grafted leathers,[14,17] optimum composition of the initiation system,[18] kinetics of polymerization,[16] and other phenomena were studied. Vinyl monomers of the type $CH_2{=}CHCl$, $CH_2{=}CHOR$, $CH_2{=}CHCOOR$, and so forth react with the leather through formation of free radicals produced by abstraction of hydrogen atoms from the function groups, mostly NH, OH groups of leather. The free-radical center then shifts from the leather molecule to the monomer molecule, and accordingly a polymer chain rapidly grows. If, on the other hand, a monomer molecule is excited because of a reaction with an initiator free radical in its vicinity, homopolymerization occurs. Hayyashi et al.[19] showed that grafting of MMA onto synthetic leather in organic solvents was found to be effective and useful for the bonding of various adherents. The grafting of 3-chloro-2-hydroxy propyl acrylate onto chrome tanned collagen fibers initiated by the redox system bisulfite/persulfate was investigated by Klasek et al.[20] In another publication Klasek et al.[21] reported the grafting of 2-hydroxy-ethyl methacrylate and MMA onto collagen. Jordan et al.[22] reported the emulsion polymerization of MMA, acrylic acid (AA), and BuA or their mixture onto fibrous matrix of chrome-tanned leather.

The present work aims to achieve a chemical modification of natural leather by grafting of some acrylate monomers, studying the optimum conditions for grafting to impart the best desirable properties.

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EXPERIMENTAL

Materials

Commercially chrome-tanned buffalo leather was obtained from Hafiz Abbasi Tanning Company, Cairo,

TABLE I
Effect of Initiator Concentration on the Degree of Grafting of Monomers onto Leather[a]

Initiator concentration (%)	Degree of grafting (%)		
	EA	BuA	EHA
1.25	8.9	5.4	2.54
1.46	15.28	9.75	14.6
1.73	35.66	19.45	39.3
1.98	34.2	15.10	29.5
2.10	28.10	11.5	13.6

[a] Monomer concentration, 25%.

TABLE II
Effect of Temperature on the Degree of Grafting of Monomers onto Leather[a]

Temperature (°C)	Degree of grafting (%)		
	EA	BuA	EHA
0	0.0	0.0	0.0
65	4.50	3.02	9.40
70	35.60	19.45	39.30
75	30.60	17.10	36.20
80	28.60	16.20	35.20

[a] Monomer concentration, 25%.

Egypt. Chemicals used were as follows. Monomers: EA and BuA were chemically pure grades obtained from Merck (Dermstadt, Germany) and used as received. 2-Ethyl hexyl acrylate obtained from BDH (Poole, UK), was also of the purest chemical grade and used as received. Solvents: Methanol, isopropyl alcohol, and ethyl acetate were pure chemical grades. They were obtained from ADWIC (El Nasr Pharmaceutical Chemicals Company, Cairo, Egypt) and used as received. Benzene was a pure chemical grade, obtained from BDH. Benzoyl peroxide and hydroquinone (inhibitor for acrylate monomers polymerization) were obtained from BDH and used as received.

Grafting methods

In a typical graft polymerization reaction a 100-ml capacity sample tube was charged with calculated quantities of leather, monomers, and initiator. A requisite amount of solvent was added to make up suitable ratio (10–40 mL/1 g of leather). Methanol was used as the solvent and benzoyl peroxide as an initiator. The sample tube was sealed and kept in a thermostat at a certain temperature for a certain fixed time. Grafted leather samples were obtained from the
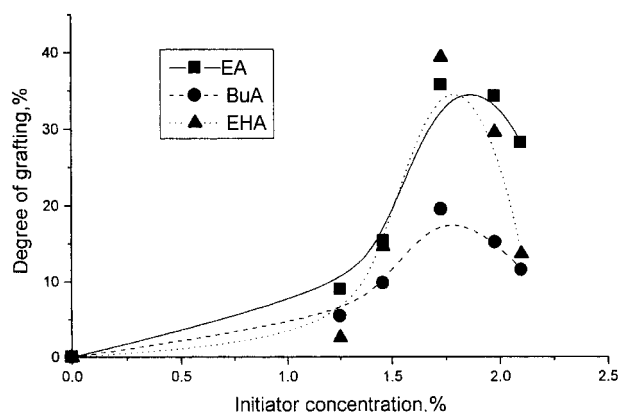
reaction vessel and washed. Homopolymers was released using the suitable solvent (isopropyl alcohol, benzene, and ethanol) by Soxhlet extraction and the leather samples (strips) were dried at 40–55°C. The grafting process was applied for the aforementioned monomers onto leather.

Physicomechanical tests

Degree of grafting

It was determined according to previously mentioned publications.[23]

Water absorption[24]

The test for determination of water absorption capacity was based on the immersion of the test specimens (disks) into water for different interval times (2, 24, 48 h) at different temperatures (30 and 60°C). The water absorption capacity $\acute{\omega}$ was determined from the relationship

$$\acute{\omega}\ (\%) = \frac{w - w_0}{w_0} \times 100$$

Figure 1 Effect of BP initiator concentration on the degree of grafting onto leather. Conditions of reaction: monomers concentration, 25%; reaction time, 3 h; reaction temperature, 70°C.
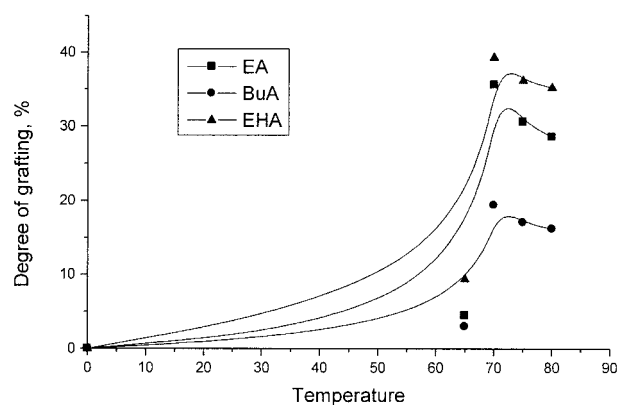

Figure 2 Effect of temperature on the degree of grafting onto leather. Conditions of reaction: monomers concentration, 25%; reaction time, 3 h; BP concentration, 1.73%.

TABLE III
Effect of Time on the Degree of Grafting of Monomers onto Leather[a]

Time (min)	Degree of grafting (%)		
	EA	BuA	EHA
0	0.0	0.0	0.0
60	3.5	2.3	4.2
120	20.6	8.1	12.6
180	35.66	19.45	39.3
240	32.3	18.9	36.1
300	30.1	18.8	35.2

[a] Monomer concentration, 25%.

where w and w_0 represent the grafted and ungrafted leather samples, respectively.

Mechanical properties[25]

Dumbbell-shape specimens (50 mm long and 4 mm neck) were used for the measurement of the ultimate tensile strength and elongation at break. These tests were carried out using an Instron Machine (Model 1195) according to standard methods, The crosshead speed was 50 mm/min.

Instrumental analysis

Spectrophotometric analyses were carried out by (1) FTIR by use of a Bomen-Michielson (USA) FTIR apparatus over the range 200–4000 cm^{-1} and using a KBr disk; and (2) ^{13}C solid NMR measurements on an NTCFT-1180 400-MHz, NMR spectrophotometer apparatus at the University of Texas (Austin).

RESULTS AND DISCUSSION

Grafting of vinyl monomers onto leather samples using benzoyl peroxide (BP) initiator was performed by

TABLE IV
Effect of Monomers Concentration on the Degree of Grafting onto Leather[a]

Monomers concentrations (%)	Degree of grafting (%)		
	EA	BuA	EHA
0	0.0	0.0	0.0
15	10.42	5.40	9.8
20	15.3	7.23	12.52
25	35.66	19.45	39.3
30	25.6	15.2	35.3

[a] Reaction conditions: time, 3 h; BP initiator concentration, 1.73%; temperature, 70°C.

a free-radical graft polymerization process. The various parameters affecting the grafting process are now discussed as follows:

Effect of initiator concentration

The role of BP initiator concentration on the degree of grafting of monomers onto leather is illustrated in Table I. One can see that an increase in BP initiator concentration up to 1.72% is accompanied by a significant increase in the degree of grafting. A further increase of initiator concentration caused a slight decrease in the degree of grafting, as shown in Figure 1. It is expected that the higher the BP initiator concentration, the greater the free-radical formation and consequently an increase of homopolymer formation, and accordingly the degree of grafting is reduced.

Effect of temperature

The influence of temperature on the degree of grafting of the studied monomers onto leather was also investigated and is presented in Table II. It is clearly seen that increasing temperature from 65 to 70°C leads to
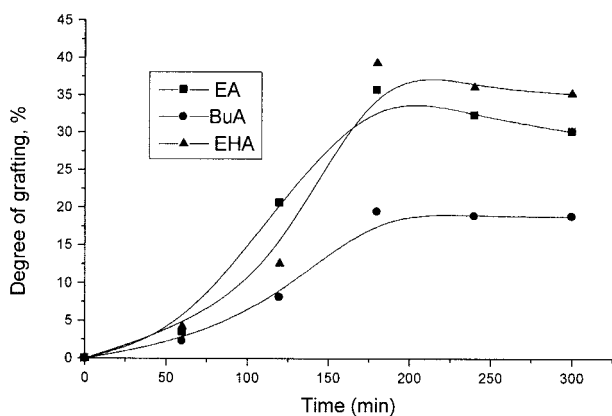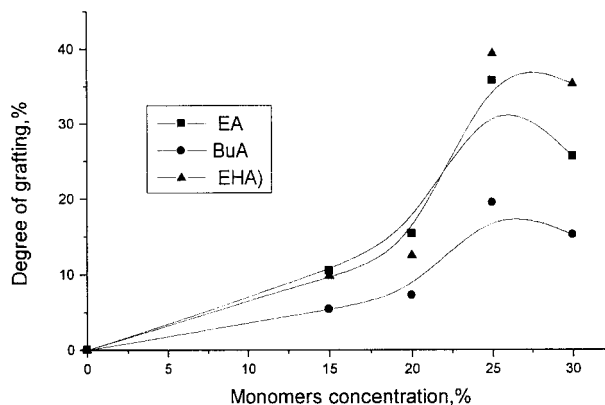

Figure 3 Effect of time on the degree of grafting onto leather. Conditions of reaction: monomers concentration, 25%; reaction temperature, 70°C; BP Concentration, 1.73%.

Figure 4 Effect of monomers concentration on the degree of grafting onto leather. Conditions of reaction: reaction time, 3 h; reaction temperature, 70°C; BP concentration, 1.73%.

TABLE V
Effect of Degree of Grafting of EA onto Leather on the Water Absorption

Degree of grafting (%)	Water absorption (%)		
	3 h/60°C	20 h/30°C	48 h/30°C
Ungrafted leather	122.9	125.9	126.6
3.4	121.9	123.3	124.2
4.5	119.1	120.0	121.0
6.2	116.3	118.2	120.2
7.4	100.0	101.0	103.0
10.4	85.0	89.0	90.0
15.3	80.2	85.0	85.0
25.6	72.5	76.0	80.0
35.2	70.0	71.1	71.0

TABLE VII
Effect of Degree of Grafting of EHA onto Leather on the Water Absorption

Degree of grafting (%)	Water absorption (%)		
	3 h/60°C	20 h/30°C	48 h/30°C
Ungrafted leather	122.9	125.9	126.6
3.69	80.0	81.0	83.57
6.70	69.76	76.7	79.06
10.26	56.6	57.65	62.30
11.20	52.5	54.5	57.10
26.60	50.4	52.0	55.00
35.71	40.3	40.1	43.00

an abrupt increase in the degree of grafting for the monomers. A further increase of temperature results in a slight decrease in the degree of grafting, as illustrated in Figure 2. These results can be attributed to the increase in free radicals by increasing temperature, leading to a mutual termination between leather radicals and the remaining free radicals, which favor homopolymerization rather than grafting polymerization.

Effect of time

Table III and Figure 3 clarify the effect of time on the degree of grafting for the investigated monomers. From the data given, it is clearly seen that the longer the time of grafting up to 3 h the greater the degree of grafting (%); however, extra time does not affect the degree of grafting and the curve tends to level off.

Effect of monomer concentration on the degree of grafting

Table IV shows the degree of grafting as a function of monomer concentration in the grafting of EA, BuA, and EHA onto leather. It can be seen that the degree of grafting increases with increasing monomer concen-

tration up to 25%, attributed to the increase of monomer diffusion onto leather, after which the degree of grafting slightly decreases and which may be the result of reduction of the rate of monomer diffusion onto leather and consequently an increase in the homopolymer formation, as shown in Figure 4.

From all the previous results, it can be seen that the optimum conditions for grafting are as follows: time, 3 h-; [BP] initiator concentration, 1.73% with respect to the monomer concentration, 25%; and temperature of reaction, 70°C.

Water absorption

Promising results have been achieved in improving leather properties, especially in water absorption on grafting using EA, BuA, and EHA. As we can see from Tables V–VII, the ability of grafted leather to absorb water was reduced for those samples grafted with EA, BuA, and EHA to be 71, 60, and 40%, respectively, compared with 122–126% for ungrafted leather.

Mechanical properties of grafted leather

This part of study was carried out to investigate the effect of grafting of some vinyl monomers onto leather on the mechanical properties of the studied samples.

TABLE VI
Effect of Degree of Grafting of BuA onto Leather on the Water Absorption

Degree of grafting (%)	Water absorption (%)		
	3 h/60°C	20 h/30°C	48 h/30°C
Ungrafted leather	122.9	125.9	126.6
2.23	110.0	111.0	115.0
4.72	100.0	103.0	106.0
7.23	80.2	82.3	87.5
9.75	75.1	78.0	80.0
11.5	70.1	68.3	73.2
15.2	63.0	66.1	66.0
19.4	60.0	60.1	62.1

TABLE VIII
Relation Between Degree of Grafting of EHA onto Leather and Mechanical Properties

Sample	Degree of grafting (%)	Tensile strength (N/m^3)	Elongation at break (%)
Ungrafted	0.00	14.16	95.00
1	6.72	19.96	107.00
2	9.30	19.96	111.84
3	16.5	20.82	111.90
4	17.7	22.70	111.95
5	18.40	22.75	115.56
6	29.2	22.80	150.56
7	39.30	22.82	158.00

TABLE IX
Relation Between Degree of Grafting of BuA onto
Leather and Mechanical Properties
(Tensile Strength, Elongation)

Sample	Degree of grafting (%)	Tensile strength (N/m³)	Elongation at break (%)
Ungrafted	0.00	14.16	95.00
1	6.68	14.27	96.48
2	7.91	14.97	97.60
3	12.35	14.97	99.90
4	15.00	14.98	110.20

The tensile strength and elongation at break of both the grafted samples and the untreated samples are given in Tables VIII and IX.

As shown from Table VIII a characteristic improvement in the tensile strength of the grafted leather samples was achieved compared with that of ungrafted leather, which indicated that the grafted leather samples by EHA or BuA can act as a lubricant between the leather fibers and hence enhance the elasticity of the leather fibers.

Spectroscopic analysis

IR spectroscopy

IR analysis was made for the ungrafted and grafted leather to confirm the formation of grafted copolymers and to get some knowledge about the structure (Figs. 5, 6, and 7). The characteristic band in the range of 1730–1736 cm^{-1} indicates the presence of the C=O ester of acrylate, and the decrease in the intensity of the band at 1660–1670 cm^{-1} corresponds to the C=O amide of leather in the peptide band. Another proof for grafting of acrylate monomers onto leather is illustrated in the bands at the region of 2980–2880 cm^{-1}, corresponding to hydrogen of CH, CH$_2$, and CH$_3$
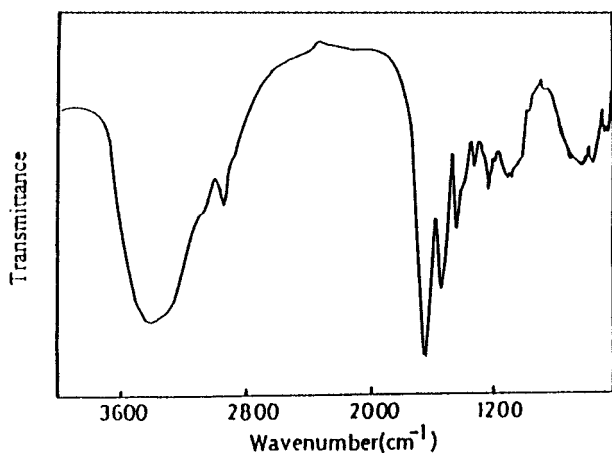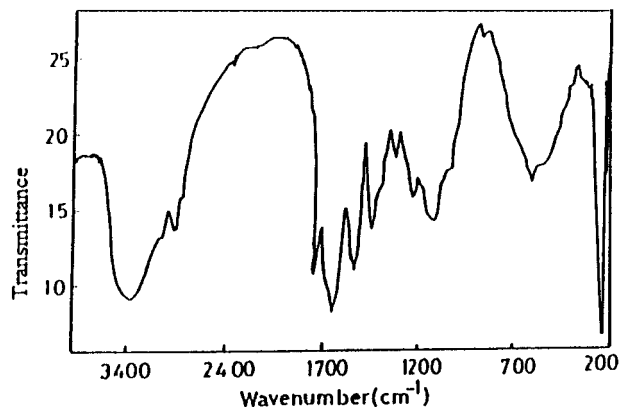
Figure 6 IR spectra of leather-*g*-BuA having 19.45% degree of grafting.

aliphatic. The intensity of the band was increased because of graft polymerization onto leather by acrylate esters (ethyl, butyl, and ethyl hexyl).

^{13}C solid NMR of ungrafted and grafted leather

The ^{13}C solid NMR spectrum in Figure 8 shows carbonyls in the range of 171–177 ppm characteristic for amide and acrylate carbonyl groups of grafted and ungrafted leather. The comparison of ungrafted and grafted leather in the range of 23–70 and 75–125 ppm showed an increase in the number of aliphatic side-chain carbons, and a decrease in the intensity of peaks in the range 130–133 ppm for C=N peptide bonds.

CONCLUSIONS

Grafting of the vinyl monomers onto leather samples enhanced the mechanical properties of the treated samples. The improvement increased with increasing monomer chain length from EA to BuA to EHA. Water
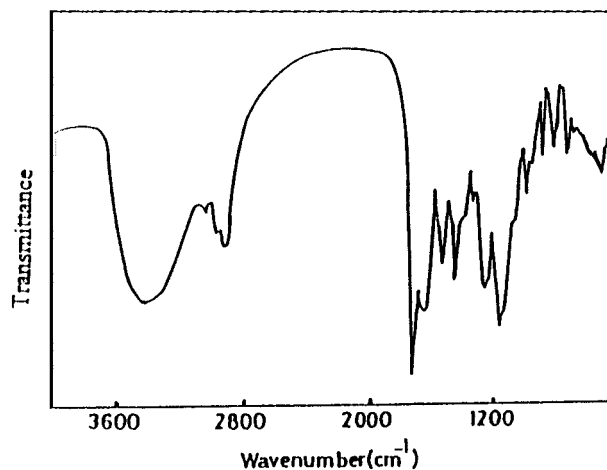
Figure 5 IR spectra of ungrafted leather.

Figure 7 IR spectra of leath-*g*-EHA having 39.3% degree of grafting.
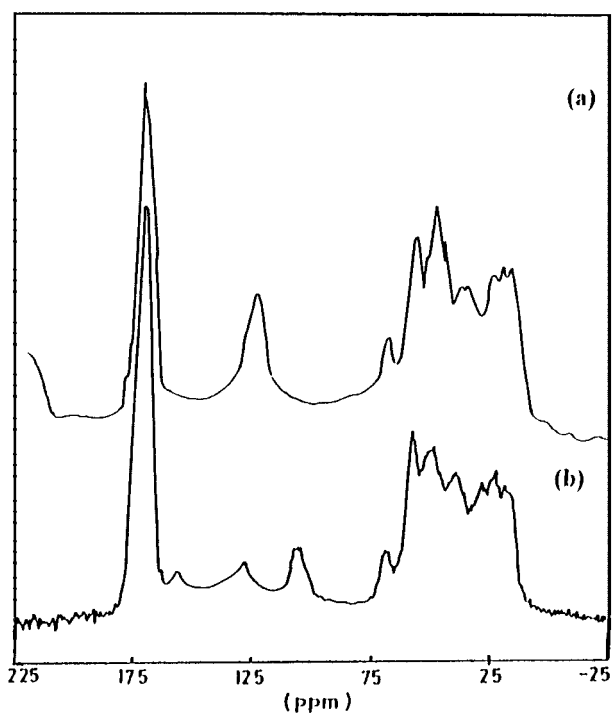
Figure 8 Solid ^{13}C-NMR spectra of (a) ungrafted leather sample, (b) grafted leather sample.

absorption of the grafted leather samples was reduced with increasing chain length from EA to BuA to EHA.

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