Grafting of 2-Hydroxyethyl Methacrylate and Methyl Methacrylate onto Chrome Tanned Collagen Fibers

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Synopsis

Grafting of 2-hydroxyethyl methacrylate and methyl methacrylate onto chrome tanned collagen fibers, initiated by the bisulfite/pesulfate redox system, has been investigated. Using the method of statistical planning of experiments, regression equations have been obtained describing the effects of the monomers concentration and the composition of the initiating system on the monomers conversion, degree of grafting and on physical properties of grafted collagen. The relationship between the polyacrylate content in the composites prepared and their swelling ability, water absorption capacity, and the tensile strength is discussed.

INTRODUCTION

In about the last 15 years considerable attention has been paid to the grafting of acrylates onto collagenous materials. This modification is focused mainly on leather and hide powder,[1-28] but also on soluble collagenous substrates.[1,29,30] Grafting is initiated mainly by Ce(IV) ions[1-11,29] or by bisulfite/persulfate redox system.[12-28,30] The application of acrylates is motivated[13] by their easy polymerizability, commercial availability, and relative low price. Monomers used for grafting were, e.g., methyl methacrylate (MMA),[1-9,11,12,14-19] methyl acrylate,[6-8,11] ethyl acrylate,[12] butyl methacrylate,[14] butylacrylate,[6,8,11-14,16,21,22,24-27] acrylic acid,[2,7,14,15] methacrylic acid,[14] acrylonitrile,[1,2,6,8,14] 2-ethylhexyl acrylate,[14] styrene,[14] maleic and fumaric acids,[15] various bifunctional acrylatles,[14,15] and their mixtures. Best results have been onbtained by using butyl acrylate or its mixtures with MMA.[12,14] Mechanical properties of grafted leathers,[14,25,27] average mass of grafted branches,[16,18,19] optimum composition of the initiation system,[17,18] kinetics of polymerization,[22,26] morphology of the acrylate–collagen composites,[21,27] character of the polyacrylate—collagen bond,[21-27] and other phenomena were studied.

Recently,[10] the use of 2-hydroxyethyl methacrylate (HEMA) was reported for hide powder grafting initiated by Ce(IV) salts. Polymeric hydrogel prepared from HEMA exhibits good tissue tolerance and high water absorption capacity. Therefore, the improving of hygienic properties of composites containing PHEMA may be expected. In our recent paper,[31] grafting of collagen

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fibers by HEMA using the bisulfite/persulfate initiation system was described. Our results showed that, at optimum experimental conditions, monomer conversion up to 90% can be achieved. Increasing the PHEMA content in the collagen composites has a positive effect on water absorption capacity as well as on its tensile strength. Both these properties are of importance for potential application of grafted collagen as a natural leather substitute.

In this paper, grafting of HEMA and MMA mixtures onto collagen fibers using bisulfite/persulfate initiation system is reported. Using this mixture was motivated by the finding[10] that grafting of HEMA is positively affected by the presence of MMA. The method of statistical planning of experiments[32] was used for evaluation of the reaction conditions effect on the course of grafting and on the properties of prepared composites.

EXPERIMENTAL

Materials

The fibrous material was obtained by milling shavings from chrome-tanned cattlehides and it was used in the form of 6.4% aqueous suspension. Before use, commercial MMA was purified by shaking with sodium carbonate solution and further by its distillation. HEMA was obtained from the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, Prague, and before use it was distilled *in vacuo*. Other analytical grade chemicals, obtained from various suppliers, were used without further treatment.

Grafting

Reactions have been performed at laboratory temperature in closed rotating 500 mL glass flasks, containing china spheres (diam 25 mm) to improve the homogenization of the reaction mixture. Inert atmosphere was not used. The collagen fibers suspension (150 mL) was introduced into the flask, pH adjusted to 7.2 $\pm$ 0.2 and required quantities (Table II) of potassium persulfate ($K_2S_2O_8$), HEMA, MMA, and emulsifier (1% of total volume) were added. After 15 min of homogenization, a sample was withdrawn for the determination of initial monomers concentration, and sodium bisulfite ($NaHSO_3$) was added. After 4 h rotation of the reaction flask residual concentration of both monomers was determined. The reaction mixture was then diluted with triple volume of distilled water and filtered-off by suction through a phosphorous bronze sieve (156 mesh cm^{-2}, diam 115 mm). The fiber cakes obtained were compressed for 10 min (applied pressure 1.5 MPa), and, after drying at room temperature, test pieces were cut out for physical tests. These test pieces were then dried for 48 h at 80°C and for 48 h in a dessicator over 36% sulfuric acid.

Analytical and Testing Methods and Definitions

Monomers concentrations were determined by gas chromatography using a glass column packed with diatomaceous earth containing 4% of poly-

ethylenglycol adipate. Conversions of monomers y_1 (HEMA) or y_2 (MMA) were calculated from the equation:

$$y_1 \text{ (or } y_2) = \frac{I_0 - I}{I_0} \times 100 \qquad (\%) \tag{1}$$

where I_0 and I are integrated areas under monomers elution peaks before and after reaction, respectively.

The degree of grafting (y_3), determined from total nitrogen content using the Kjeldahl method, is defined as follows:

$$y_3 = \frac{W_P}{W_C} \times 100 \qquad (\%) \tag{2}$$

where W_P is the weight of polyacrylates and W_C the weight of collagen in the composites. Therefore, in this paper, the term "degree of grafting" expresses the composition of the grafting product, without differentiation between chemical or physical bonding of nonextractable polyacrylates to collagen.

The test for determination of swelling ability (y_4) and water absorption capacity (y_5) was based on the immersion of the test pieces (disks, diam 20 mm) into water for 24 h at 20°C and their consecutive compression between glass plates (upper plate loading 10 g cm^{-2}). The swelling ability (y_4) was calculated from the relationship

$$y_4 = \frac{V - V_0}{V_0} \times 100 \qquad (\%) \tag{3}$$

where V_0 and V are the test piece volumes before and after the test, respectively.

The water absorption capacity (y_5) was determined from the relationship

$$y_5 = \frac{W - W_0}{W_0} \times 100 \qquad (\%) \tag{4}$$

where W_0 and W are the weights of test pieces before and after the test.

The tensile strength (y_6) of the composites was determined using cut-off bands (20 × 50 mm) on the Instron 1122 apparatus. The distance between the clamps of the tensile machine was 30 mm; the separation velocity was 0.167 mm s^{-1}. The tensile strength (y_6) was calculated from the relationship

$$y_6 = \text{F/A (MPa)} \tag{5}$$

where F is the breaking force (N) and A the cross section of the piece (mm^2).

All these tests were performed four times and the average values of results were used for statistical data processing using Hewlett-Packard 2100 A computer. All concentration data are given in percentage (w/v).

TABLE I
Relation between Original and Coded Independent Variables x_i

Factor	Concn of (%)	$\tilde{X}_i$ level				
		−2	−1	0	1	2
x_1	HEMA	0.0667	0.2667	0.4667	0.6667	0.8667
x_2	MMA	0.0667	0.2667	0.4667	0.6667	0.8667
x_3	$K_2S_2O_8$	0.1733	0.3423	0.5113	0.6803	0.8493
x_4	$NaHSO_3$	0.0133	0.0917	0.1700	0.2483	0.3267

RESULTS AND DISCUSSION

Because the copolymerization parameters of HEMA and MMA are very similar and close to 1 (MMA $r_1 = 0.854$, HEMA $r_2 = 1.125$)[33] the homopolymer formation is highly improbable. In addition to the HEMA—

TABLE II
Results of HEMA and MMA Mixture Grafting onto Collagen Fibers

Expt No.	x_1 (%)	x_2 (%)	x_3 (%)	x_4 (%)	y_1 (%)		y_2 (%)	
					Meas.	Calcd	Meas.	Calcd
1	0.2667	0.2667	0.3423	0.0917	7.50	13.94	21.14	23.11
2	0.6667	0.2667	0.3423	0.0917	15.91	21.27	21.14	29.41
3	0.2667	0.6667	0.3423	0.0917	27.80	29.35	29.44	33.59
4	0.6667	0.6667	0.3423	0.0917	24.44	30.03	24.95	33.00
5	0.2667	0.2667	0.6803	0.0917	18.74	18.83	23.41	28.59
6	0.6667	0.2667	0.6803	0.0917	26.12	28.54	56.26	48.82
7	0.2667	0.6667	0.6803	0.0917	23.88	31.92	39.58	45.08
8	0.6667	0.6667	0.68-3	0.0917	27.97	34.98	54.87	58.41
9	0.2667	0.2667	0.3423	0.2483	72.83	65.88	81.90	82.41
10	0.6667	0.2667	0.3423	0.2483	76.48	77.12	84.91	82.50
11	0.2667	0.6667	0.3423	0.2483	72.43	78.68	87.43	97.95
12	0.6667	0.6667	0.3423	0.2483	83.35	83.27	92.27	91.14
13	0.2667	0.2667	0.6803	0.2483	57.43	60.51	71.24	66.27
14	0.6667	0.2667	0.6803	0.2483	75.65	74.12	80.40	80.29
15	0.2667	0.6667	0.6803	0.2483	76.33	70.99	92.02	87.81
16	0.6667	0.6667	0.6803	0.2483	75.71	77.95	93.81	94.93
17	0.0667	0.4667	0.5113	0.1700	35.87	33.65	66.28	60.51
18	0.8667	0.4667	0.5113	0.1700	54.44	47.95	75.32	73.94
19	0.4667	0.0667	0.5113	0.1700	46.33	45.91	45.25	48.30
20	0.4667	0.8667	0.5113	0.1700	73.45	65.16	83.62	73.42
21	0.4667	0.4667	0.1733	0.1700	59.71	54.68	76.03	64.63
22	0.4667	0.4667	0.8493	0.1700	57.92	54.24	69.65	70.90
23	0.4667	0.4667	0.5113	0.0133	15.00	1.09	11.62	0.57
24	0.4667	0.4667	0.5113	0.3267	90.79	96.00	94.49	96.39
25	0.4667	0.4667	0.5113	0.1700	59.12	54.72	81.77	74.62
26	0.4667	0.4667	0.5113	0.1700	58.40	54.72	76.43	74.62
27	0.4667	0.4667	0.5113	0.1700	60.86	54.72	77.00	74.62
28	0.4667	0.4667	0.5113	0.1700	54.86	54.72	77.14	74.62
29	0.4667	0.4667	0.5113	0.1700	55.86	54.72	77.14	74.62
30	0.4667	0.4667	0.5113	0.1700	38.95	54.72	68.60	74.62
31	0.4667	0.4667	0.5113	0.1700	54.97	54.72	67.40	74.62
Error of experiment					± 7.31		± 5.09	

TABLE II (*Continued from the previous page.*)

Expt No.	y_3 (%)			y_4 (%)		y_5 (%)		y_6 (MPa)	
	Meas.	Calcd	Calcd[a]	Meas.	Calcd	Meas.	Calcd	Meas.	Calcd
1	1.77	2.83	1.91	17.88	18.82	103.19	110.02	6.60	7.37
2	4.09	5.56	4.06	20.12	18.36	100.93	102.28	7.46	8.67
3	6.57	6.90	6.76	18.01	18.10	138.36	123.78	8.54	9.56
4	8.14	10.14	8.23	15.97	15.46	141.92	134.14	8.21	9.66
5	2.51	3.78	2.81	17.38	18.20	122.30	122.26	7.37	7.10
6	7.99	7.45	12.15	19.34	18.78	141.30	124.84	9.11	9.59
7	8.17	9.51	8.19	19.80	20.37	139.74	129.92	8.66	9.14
8	12.23	13.70	13.80	16.85	18.76	138.61	150.59	11.06	10.44
9	12.53	11.24	10.31	16.55	16.20	167.51	144.60	10.83	10.73
10	16.49	16.83	18.41	21.08	20.08	119.50	131.64	12.28	13.20
11	19.48	21.70	19.40	16.56	16.70	127.04	145.82	14.46	15.37
12	28.90	27.81	29.29	17.67	18.40	161.85	150.95	17.10	16.64
13	8.86	8.54	8.58	13.53	13.62	118.41	128.51	10.86	10.81
14	15.24	15.08	17.96	17.07	18.53	122.23	125.86	16.21	14.47
15	21.96	20.66	20.43	13.70	17.01	135.92	123.62	17.24	15.30
16	27.12	27.72	28.26	21.10	19.74	143.57	139.06	17.14	17.76
17	9.84	9.11	8.33	16.45	14.22	107.21	114.86	11.89	11.81
18	20.01	18.90	20.58	15.39	16.49	121.62	122.57	16.17	15.58
19	5.89	5.90	6.15	16.18	16.92	127.43	125.78	8.99	8.70
20	24.47	22.61	26.69	19.28	17.41	142.51	152.75	14.57	14.18
21	14.31	12.72	15.84	17.35	18.78	134.73	138.94	15.01	12.48
22	13.83	13.58	14.90	22.07	19.51	134.91	139.30	11.48	13.34
23	3.00	−0.27	3.11	21.12	20.94	103.41	113.35	4.99	3.06
24	20.74	22.16	21.62	20.24	19.29	137.75	136.41	12.49	13.75
25	14.59	14.45	16.44	18.98	19.33	141.25	146.03	14.27	14.97
26	12.13	14.45	16.89	16.17	19.33	145.78	146.03	17.61	14.97
27	15.24	14.45	16.08	20.81	19.33	144.34	146.03	14.77	14.97
28	14.96	14.45	15.53	20.25	19.33	138.21	146.03	15.12	14.97
29	16.03	14.45	15.53	20.22	19.33	158.21	146.03	11.25	14.97
30	14.38	14.45	12.54	19.92	19.33	145.17	146.03	15.63	14.97
31	13.83	14.45	14.28	18.64	19.33	148.46	146.03	16.15	14.97
Error of experiment	± 1.23			± 1.60		± 6.19		± 1.97	

[a] From monomers conversions.

MMA—collagen copolymer, the only reaction product which is likely to be formed, is HEMA–MMA copolymer, soluble in some organic solvent mixtures, but insoluble in nonpolar solvents.

For the determination of the effect of reaction mixture composition on monomer conversions, nonextractable polyacrylate content in the grafting product, and on some physical properties of the composites, we have used a four-factor planned experiment[32]; its mathematical model is a second degree polynomial in the form

$$y_i = b_0 + b_1\tilde{x}_1 + b_2\tilde{x}_2 + b_3\tilde{x}_3 + b_4\tilde{x}_4 + b_{11}\tilde{x}_1^2 + b_{22}\tilde{x}_2^2 + b_{33}\tilde{x}_3^2 + b_{44}\tilde{x}_4^2 + b_{12}\tilde{x}_1\tilde{x}_2 + b_{13}\tilde{x}_1\tilde{x}_3 + b_{14}\tilde{x}_1\tilde{x}_4 \quad (6)$$

$$+b_{23}\tilde{x}_2\tilde{x}_3 + b_{24}\tilde{x}_2\tilde{x}_4 + b_{34}\tilde{x}_3\tilde{x}_4$$

where $\tilde{x}_i$ are coded concentrations of HEMA (x_1), MMA (x_2), $K_2S_2O_8$ (x_3), and $NaHSO_3$ (x_4) in the reaction mixture. The dependent variables y_i are defined by eqs. (1)–(5). The conversion of x_i values to coded x_i values is given in Table I. The choice of x_i values range is based on our previous results[31] and preliminary experiments. Experimental results and calculated values of y_i are summarized in Table II. The survey of regression coefficients b_{ij} of type (6) equations is given in Table III.

According to the T-criteria values, the conversion of HEMA (y_1) is significantly influenced by the concentration of both monomers and bisulfite (Table III). The conversion of HEMA is higher with increasing its concentration up to a value of 0.6%. The increasing MMA concentration induces an increase in HEMA conversion in the entire experimental range (Fig. 1), which is in agreement with the reported results.[10] The HEMA conversion values (y_1) increase largely with the increase of bisulfite concentration, i.e., with the increase in molar ratio (MR) $NaHSO_3/K_2S_2O_8$ (at constant level of the insignificant factor x_3, describing the persulfate concentration). According to

$$H_2O + HSO_3^- + 2S_2O_8^{2-} \rightarrow 3HSO_4^- + 2SO_4^-$$

the concentration of primary radicals from the initiation system increases only to MR value of 0.5. The observed (Fig. 2) growth of HEMA conversion

TABLE III
Coefficients of Regression Equations Type (6)[a]

Coeff.	y_1	y_2	y_3	y_4	y_5	y_6
b_0	54.7178	74.6151	14.4522	19.3265	146.0316	14.9700
b_1	(3.5746)	3.3554	2.4456	(0.5688)	(1.9275)	(0.9405)
b_2	4.8107	6.2801	4.1766	(0.1214)	6.7417	1.3696
b_3	(−0.1062)	(2.3191)	(0.2146)	(0.1819)	(0.0892)	(0.2132)
b_4	23.7288	23.9559	5.6073	(−0.4104)	5.7650	2.6714
b_{11}	−3.4791	(−1.8475)	(−0.1118)	−0.9930	−6.8298	(−0.3187)
b_{22}	(0.2044)	−3.4397	(−0.0487)	(−0.5401)	(−1.6910)	(−0.8819)
b_{33}	(−0.0630)	(−1.3381)	(−0.3261)	(−0.4583)	(−1.7285)	(−0.5152)
b_{44}	(−1.5435)	−6.5339	−0.8764	(0.1969)	−5.2885	−1.6409
b_{12}	(−1.6619)	(−1.7245)	(0.1288)	(−0.5455)	−4.5220	(−0.2987
b_{13}	(0.5935)	3.4832	(0.2379)	(0.2574)	(2.5779)	(−0.2982)
b_{14}	(0.9753)	(−1.5534)	(0.7172)	1.0846	(−1.3065)	(0.2923)
b_{23}	(−0.5808)	(1.4992)	(0.4164)	(0.7227)	(−1.5277)	(−0.0374)
b_{24}	(−0.6518)	(1.2620)	1.5988	(0.3060)	(−3.1367)	(0.6133)
b_{34}	(−2.5682)	−5.4060	−0.9111	(−0.4899)	−7.0836	(0.0868)
$I_{x,y}$	0.9629	0.9577	0.9626	0.7450	0.7346	0.9208
Type of extreme	Minimax	Minimax	Minimax	Minimax	Minimax	Maximum

[a] Values in parentheses are, according to the absolute value of the T criterion, statistically insignificant.

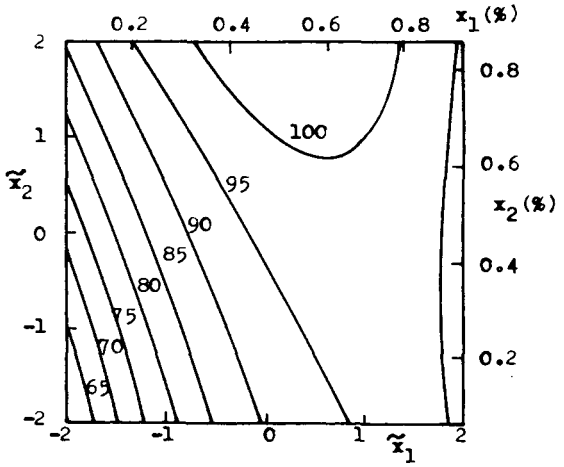

Fig. 1. Contour lines for HEMA conversion (y_1,%) as a function of HEMA (x_1) and MMA (x_2) concentrations, at constant concentrations of $K_2S_2O_8$ (0.51%) and $NaHSO_3$ (0.33%); MR 1.66.

(dependent on the primary radicals concentration) with increasing bisulfite concentration in the entire experimental range, i.e., also at MR > 0.5, suggests that a part of the bisulfite in the system is successively oxidized by air oxygen. Accordingly, only substoichiometric quantities of bisulfite are available for the reaction with persulfate. The optimum composition of the initiation system[17,18] for grafting can be, therefore, defined only when the bisulfite oxidation is prevented. The relatively narrow region of 100% HEMA conversion can be defined by following concentrations of individual constituents: HEMA 0.5–0.7%, MMA > 0.65%, $K_2S_2O_8$ < 0.4%, and $NaHSO_3$ > 0.3%.

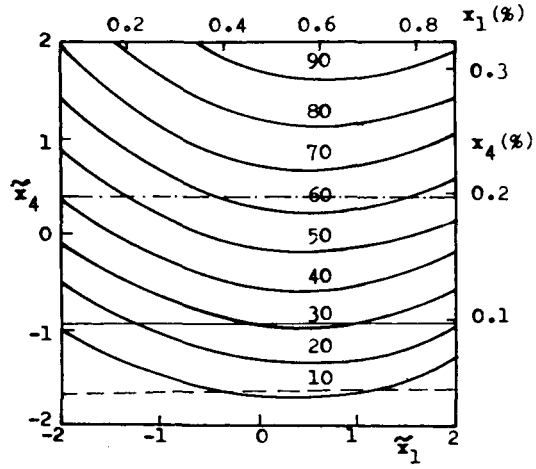

Fig. 2. Contour lines for HEMA conversion (y_1,%) as a function of HEMA (x_1) and $NaHSO_3$ (x_4) concentrations, at constant concentrations of MMA (0.47%) and $K_2S_2O_8$ (0.51%): (—) MR 0.2; (—) MR 0.5; (-.-) MR 1.0.

The MMA conversion (y_2) is significantly influenced by concentrations of all reaction mixture constituents (Table III). As expected, the MMA conversion increases with its concentration in the mixture (Fig. 3). The effect of HEMA concentration is positive in the major part of the experimental area. The increased bisulfite concentration has a positive effect on y_2 for the same reason as in case of y_1 (Fig. 4). The region of highest MMA conversions can be defined by following concentrations ranges of the constituents: HEMA 0.5–0.7%, MMA 0.5–0.8%, $K_2S_2O_8$ < 0.5%, and $NaHSO_3$ > 0.3%. Both regions of highest HEMA and MMA conversions are very similar, and, at given experimental conditions, the resulting copolymer should contain about 32–47 mol % of HEMA.

It is reported[10] that PHEMA can be extracted with methanol, PMMA with chloroform, and the HEMA–MMA copolymer with methanol–acetone mixture. In our case, after extraction of grafted composites with mentioned solvents, no distillation residues were obtained. Therefore, the synthetic polymer is either chemically bonded onto collagen or crosslinked. The quantitative bonding of polyacrylates onto collagen only by strong physical bond is considered to be very unlikely. From a practical point of view (resistance of composites to organic solvents), the chemical bonding of polyacrylates on collagen fibers or their crosslinking would be manifested in the same manner.

The comparison of the measured values of the degree of collagen grafting (y_3) with the respective values calculated from the monomers conversion, assuming 100% bonding of polyacrylates onto collagen fibers, was carried out. This comparison shows (Table II) that only a small portion of polyacrylates is not bonded onto collagen and is removed in the course of filtration. All independent variables x_i exert a statistically significant influence on y_3 (Table III); intensities of these effects are, however, very differentiated. The concentration effect of both monomers and bisulfite are

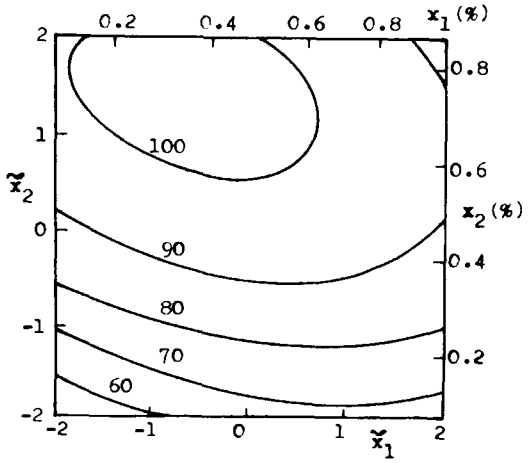

Fig. 3. Contour lines for MMA conversion (y_2,%) as a function of HEMA (x_1) and MMA (x_2) concentrations, at constant concentrations of $K_2S_2O_8$ (0.51%) and $NaHSO_3$ (0.33%); MR 1.66.

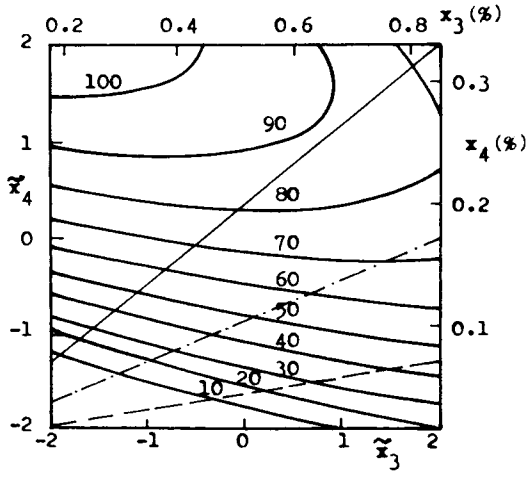

Fig. 4. Contour lines for MMA conversion (y_2,%) as a function of $K_2S_2O_8$ (x_3) and $NaHSO_3$ (x_4) concentrations, at constant concentrations of HEMA (0.47%) and MMA (0.47%); (- - -) MR 0.2; (-.-) MR 0.5; (—) MR 1.0.

positive (Figs. 5 and 6), the effect of persulfate concentration being almost negligible. The conditions required to reach maximum y_3 value are defined by following concentration ranges: HEMA > 0.6%, MMA > 0.5%, $K_2S_2O_8$ 0.2–0.8%, and $NaHSO_3$ > 0.25%. These conditions are almost coincident with these for maximum monomers conversion. Reduced HEMA portion in its mixture with MMA (at the constant weight of HEMA and MMA mixture) induces an increased value of collagen grafting degree y_3 (Fig. 7) and it thus also increases the polyacrylate content C in composites:

$$C = \frac{y_3}{100 + y_3} \times 100 \quad (\%) \tag{8}$$

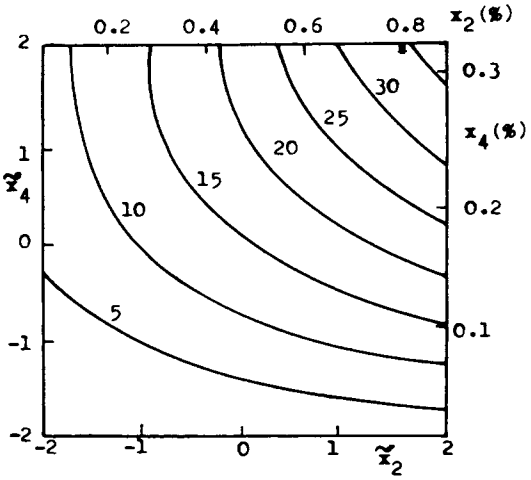

Fig. 5. Contour lines for degree of grafting (y_3,%) as a function of MMA (x_2) and $NaHSO_3$ (x_4) concentrations, at constant concentrations of HEMA (0.47%) and $K_2S_2O_8$ (0.51%).

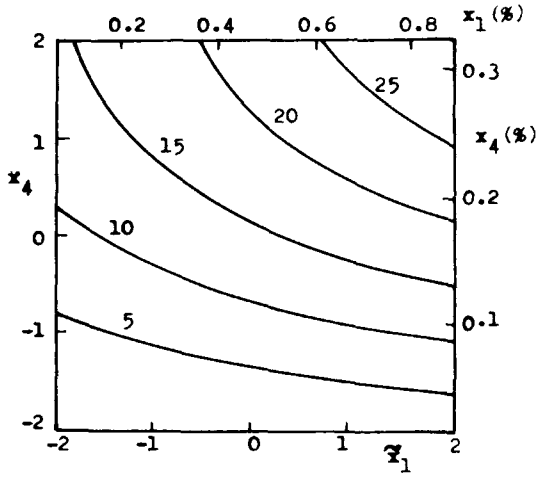

Fig. 6. Contour lines for degree of grafting (y_3,%) as a function of HEMA (x_1) and $NaHSO_3$ (x_4) concentrations, at constant concentrations of MMA (0.47%) and $K_2S_2O_8$ (0.51%).

In our opinion, the beneficial effect of higher MMA portion in its mixture with HEMA on the increasing polyacrylate content in composites could be due to the growing extent of the emulsion polymerization in the system containing water-soluble HEMA.

Swelling ability values of grafted composites (y_4) are influenced by experimental conditions only slightly (Table II); the y_4 value of sample prepared from ungrafted collagen fibers was 15%. An important value, affecting the hygienical properties of fabrics from collagen fibers, is the

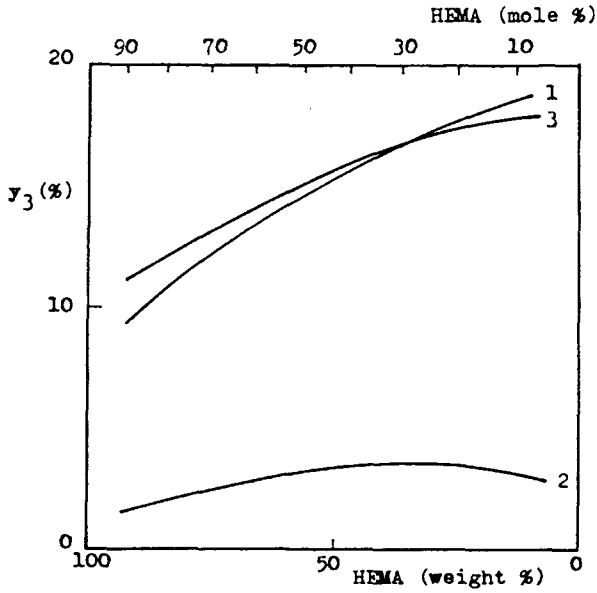

Fig. 7. Degree of grafting (y_3) vs. concentration of HEMA in the mixture of monomers, at constant weight percentage (0.93%) of monomers in the reaction mixture; concentrations of $K_2S_2O_8$ and $NaHSO_3$: (1) 0.2% and 0.2%; (2) 0.2% and 0.08%; (3) 0.8% and 0.2%.

water absorption capacity (y_5). Optimum HEMA concentration for maximum y_5 is about 0.5%; positive effects on y_5 have increasing MMA and $NaHSO_3$ concentrations. These effects of independent variables on y_5 values are similar to their effects on y_1 and y_3 values. Therefore, the proposed negative effect of increasing PMMA content in the composites on their y_5 values is more than compensated by the positive effect of the strongly hydrophilic PHEMA content increase. In comparison with ungrafted collagen fibers the water absorption capacity of modified composites is almost doubled.

The tensile strength of composites (y_6) is positively influenced by increasing of MMA and bisulfite concentrations (Fig. 9). The HEMA concentration effect being equally positive, however, it is on the limit of the statistical significance (Table III). The comparison of the above effects with those of reaction conditions on monomers conversions and on the degree of grafting shows that the tensile strength is, as expected, favorably influenced by the increasing content of polyacrylates in the composite. The highest tensile strength value (18.1 MPa) was obtained at following composition of the reaction mixture: HEMA 0.87%, MMA 0.61%, $K_2S_2O_8$ 0.66%, and $NaHSO_3$ 0.26%. The tensile strength value of sample prepared from unmodified collagen fibers was only 5.3 MPa.

CONCLUSION

Effects of reaction conditions, defined by HEMA, MMA, $K_2S_2O_8$, and $NaHSO_3$ concentrations, on the grafting of the above monomer mixture onto collagen fibers and on the properties of the obtained composites has been investigated. Using the method of statistical planning of experiments, it has been established that the conversions of both monomers are influenced mainly by their concentrations and by concentration of the bisulfite. The effect of persulfate concentration is relatively of minor importance.

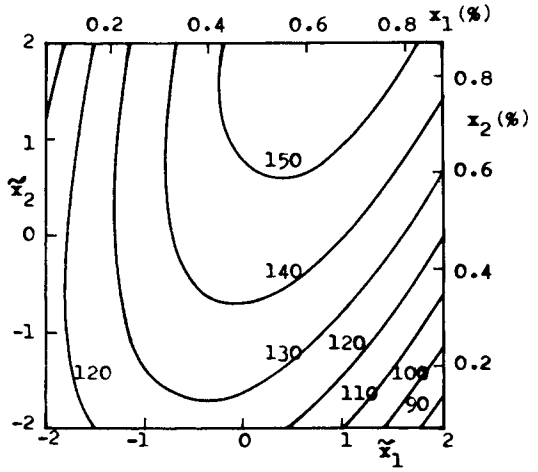

Fig. 8. Contour lines for water absorption capacity (y_5,%) as a function of HEMA (x_1) and MMA (x_2) concentrations, at constant concentrations of $K_2S_2O_8$ (0.51%) and $NaHSO_3$ (0.17%).

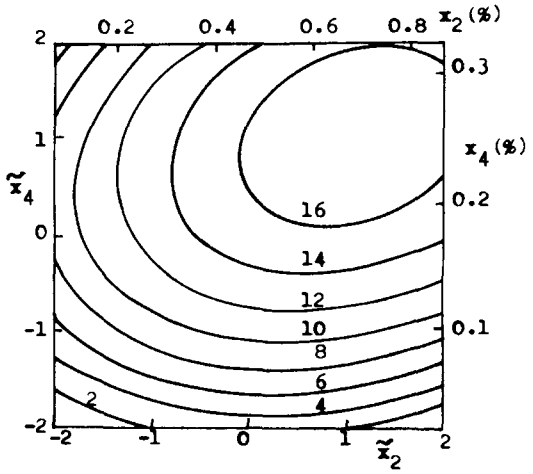

Fig. 9. Contour lines for tensile strength of composites (y_6,%) as a function of MMA (x_2) and $NaHSO_3$ (x_4) concentrations, at constant concentrations of HEMA (0.47%) and $K_2S_2O_8$ (0.51%).

Due to presence of air in the reaction system, a higher amount of bisulfite than theoretical is necessary. Optimum conditions found for the maximum conversions of both monomers are in mutual relation and simultaneously in accordance with the optimum conditions for maximum grafting degree values. The degree of the collagen substrate grafting is improved by increasing MMA/HEMA ratio in the grafting mixture.

Among physical properties of the obtained composites, the swelling ability, water absorption capacity, and tensile strength have been measured. While the swelling ability is only slightly influenced by the reaction conditions, both water absorption capacity and tensile strength are improved with increasing polyacrylate content in composites. In comparison with ungrafted samples, the water absorption capacity is increased about two times and the tensile strength about three times. This tensile strength improvement is perspective for development of materials based on modified collagen fibers. Composites, used till now for some applications as natural leather substitutes, contain up to 20% of hydrophobic binders, unfavorably affecting the hygienic properties of these materials.

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