Grafting of 3-Chloro-2-Hydroxypropyl Acrylate onto Chrome Tanned Collagen Fibers

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Synopsis

Grafting of 3-chloro-2-hydroxypropyl acrylate onto chrome tanned collagen fibers, initiated by the redox system bisulfite/persulfate, has been investigated. Using the method of statistical planning of experiments regression equations have been obtained, describing the effect of monomer concentration and of initiation system constituents concentrations on monomer conversion, degree of grafting of collagen, and on physical properties of resulting composites. The relationship between the content of poly(3-chloro-2-hydroxypropyl acrylate) in the composite and the swelling ability, water absorption, and tensile strength of the same is discussed. Moreover, results of morphology investigation of composites, prepared by grafting of various acrylic monomers onto collagen fibers, as obtained by electron microscopy, are presented and discussed.

INTRODUCTION

Grafting of acrylates onto insoluble collagenous materials is one of the possibilities of substrate property modification. Such modification is of importance mainly for improving appearance and processing properties of leathers. In recent works[1-17] grafting is initiated mainly by the redox system bisulfite/persulfate; monomers used for grafting were namely methyl methacrylate (MMA),[3-8] ethylacrylate,[1] butylacrylate,[1-3,5,10,11,13-16] butyl methacrylate,[3] 2-ethylhexyl acrylate,[3] styrene,[3] acrylonitrile,[3] various bifunctional acrylates,[3,4] and mixtures of the above monomers. Among the polar monomers the use of acrylic acid,[3,4] methacrylic,[3] maleic,[4] and fumaric[4] acids has been reported. As to polar nonionic monomers, 2-hydroxyethyl methacrylate (HEMA)[18] was used; the reaction was, however, initiated by Ce(IV) ions.

In our previous paper[19] we used for grafting of collagen fibers the mixture of HEMA and MMA; it has been established that, with increasing the polyacrylate contents in the composites prepared, their water absorption ability and tensile strength are equally increased. In the present work we used for grafting onto collagen fibers 3-chloro-2-hydroxypropylacrylate (CHPA), which can be easily prepared by direct reaction of acrylic acid with epichlorohydrine catalyzed by chromium complexes.[20] For complex evaluation of the effect of reaction conditions on the grafting process and on the properties of resulting composites, we used the method of statistical planning of experiments.[21]

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Journal of Applied Polymer Science, Vol. 31, 2021–2033 (1986)
 CCC 0021-8995/86/072021-13$04.00

EXPERIMENTAL

Materials

The fibrous collagen material was obtained by milling of chrome tanned leather shavings and was used in the form of aqueous suspension with average dry substance contents of 6.4%. CHPA was prepared by heating of mixture containing 1 mol of acrylic acid, 1 mol of epichlorohydrine, and 1 g of catalyst (complex chromium salt of isobutyric acid),[20] under continuous mixing, for 3 h at 70°C and 2 h at 100°C. The product was used for grafting without further purification. Commercial MMA was purified before use by shaking with sodium carbonate solution and distillation. The analytical grade chemicals, obtained from various suppliers, were used without additional treatment.

Grafting

Collagen fibers were grafted at room temperature, in the presence of air, in closed rotating 500 mL glass flasks, containing porcelaine spheres (diam 25 mm) for easier homogenization of the mixture. Collagen fibers suspension (100 mL, 6% of dry substance) was introduced in the flask, the pH value adjusted to 7.2 ± 0.2 and the required quantities of potassium persulfate ($K_2S_2O_8$), CHPA and emulsifier (1% of total volume) added. Sodium bisulfite ($NaHSO_3$) was dosed after 15 min and after further 4 h of mixing the reaction mixture was diluted by triple volume of distilled water and filtered off by suction through a sieve (156 mesh cm^{-2}) of phosphorous bronze, diameter 115 mm. The fiber cakes obtained were compressed for 10 min by a pressure of 1.5 MPa and after drying at room temperature test pieces were cut out; these were dried for 48 h at 80°C and for 48 h in a desiccator over 36% sulfuric acid.

Electron Microscopy

The morphology of original and modified collagen fibers was studied by transmission electron microscopy using the apparatus Tesla BS-613 (Czechoslovakia). Diluted fiber suspensions were deposited on microsieves (400 mesh mm^{-2}), excess water was removed by succion, and the samples were dried in a desiccator over phosphorus pentoxide and then platinum-plated *in vacuo*. Observations were performed at an accelerating voltage of 80 kV, and micrographs recorded on glass plates at 1:10 000 magnification.

Analytical and Testing Methods and Definitions

Dependent variable values y_i were determined using the methods described in our previous paper.[19] They are defined by following equations:

CHPA conversion

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

Degree of collagen grafting

$$y_2 = \frac{W_P}{W_C} \times 100\ (\%) \tag{2}$$

Swelling ability

$$y_3 = \frac{V - V_0}{V_0} \times 100\ (\%) \tag{3}$$

Water absorption capacity

$$y_4 = \frac{W - W_0}{W_0} \times 100\ (\%) \tag{4}$$

Tensile strength

$$y_5 = \frac{F}{A}\ (\text{MPa}) \tag{5}$$

where I_0 and I are integrated areas of CHPA elution peaks obtained by gas chromatografpy of the mixture before and after reaction, W_P and W_C are PCHPA and collagen weights in the composites obtained, are V_0 and V are volumes of test piece before and after the determination of swelling ability, W_0 and W are weights of test pieces before and after determination of water absorption capacity, and F is the force (N) required for break of test pieces with cross section A (mm^2).

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

RESULTS AND DISCUSSION

For the description of the influence of grafting conditions on the dependent variables y_i, defined by eqs. (1)–(5), we have used a three-factor planned experiment. Effects of x_i on y_i can be expressed mathematically by second degree polynomials:

$$y_i = b_0 + b_1\tilde{x}_1 + b_2\tilde{x}_2 + b_3\tilde{x}_3 + b_{11}\tilde{x}_1^2 + b_{22}\tilde{x}_2^2 + b_{33}\tilde{x}_3^2 + b_{12}\tilde{x}_1\tilde{x}_2 + b_{13}\tilde{x}_1\tilde{x}_3 + b_{23}\tilde{x}_2\tilde{x}_3 \tag{6}$$

where $\tilde{x}_i$ are coded levels of CHPA (x_1), $K_2S_2O_8$ (x_2), and $NaHSO_3$ (x_3) concentrations in the reaction mixture. Considering our previous results from HEMA[22] and HEMA–MMA[19] grafting onto collagen fibers, concentration ranges of individual x_i factors (Table I) were modified so as to cover the expected optimum ranges of dependent variables y_i values, defined by eqs. (1)–(5). Results are summarized in Table II; computed values of the regression coefficients b_i for type (6) equations are given in Table III.

The CHPA conversion (y_1) is characterized by a maximum (calcd. 101%) at CHPA, $K_2S_2O_8$, and $NaHSO_3$ concentrations of 0.68, 0.48, and 0.36%, respectively. According to the F-criterion value, the mathematical model

TABLE I
Relation between Original and Coded Independent Variables x_i

		$\tilde{X}_i$ level				
Factor	Conc of (%)	−1.682	−1	0	1	1.682
x_1	CHPA	0.3000	0.4419	0.6500	0.8581	1.000
x_2	$K_2S_2O_8$	0.0200	0.1376	0.3100	0.4824	0.6000
x_3	$NaHSO_3$	0.1000	0.1608	0.2500	0.3392	0.4000

TABLE II
Results of CHPA Grafting onto Collagen Fibers

Expt No.	x_1 (%)	x_2 (%)	x_3 (%)	y_1 (%)		y_2 (%)			y_3 (%)		y_4 (%)		y_5 (MPa)	
				Meas.	Calcd	Meas.	Calcd	Calcd[a]	Meas.	Calcd	Meas.	Calcd	Meas.	Calcd
1	0.4419	0.1376	0.1608	31.7	33.7	2.07	2.11	2.33	17.7	17.1	85.9	79.8	3.51	3.40
2	0.8581	0.1376	0.1608	38.0	41.1	4.56	4.62	5.43	15.0	13.6	113.1	109.8	4.51	5.53
3	0.4419	0.4824	0.1608	56.0	53.8	4.85	3.93	4.12	18.1	17.4	102.0	96.3	6.70	6.56
4	0.8581	0.4824	0.1608	63.3	61.8	7.38	7.75	9.05	18.8	17.3	120.8	113.4	8.73	8.55
5	0.4419	0.1376	0.3392	55.4	61.7	5.80	5.76	4.08	12.9	15.4	69.9	79.2	5.66	6.52
6	0.8581	0.1376	0.3392	56.3	63.2	6.42	7.67	8.05	12.6	14.3	79.0	86.5	7.01	7.84
7	0.4419	0.4824	0.3392	95.9	97.5	5.84	6.12	7.06	11.3	13.7	129.0	134.2	7.69	7.36
8	0.8581	0.4824	0.3392	96.7	99.5	9.04	9.33	13.83	14.3	16.0	120.7	128.6	7.74	8.54
9	0.3000	0.3100	0.2500	76.7	74.4	4.23	4.77	3.84	16.5	14.8	112.8	112.1	4.26	4.43
10	1.0000	0.3100	0.2500	86.7	82.3	10.60	9.58	14.45	13.7	13.9	134.6	132.7	8.35	7.21
11	0.6500	0.0200	0.2500	41.1	32.5	4.63	4.01	4.45	16.4	15.6	73.5	69.9	6.90	5.68
12	0.6500	0.6000	0.2500	78.1	80.0	6.78	6.93	8.46	17.9	17.2	118.3	119.2	8.68	8.93
13	0.6500	0.3100	0.1000	31.9	33.3	2.82	3.25	3.46	14.2	17.2	76.8	91.1	6.07	6.05
14	0.6500	0.3100	0.4000	96.7	88.5	8.56	7.66	10.48	19.2	14.7	120.3	103.4	9.62	8.67
15	0.6500	0.3100	0.2500	83.6	83.8	7.90	8.09	9.06	14.2	14.9	102.1	125.3	7.66	7.52
16	0.6500	0.3100	0.2500	82.4	83.8	7.48	8.09	8.93	13.0	14.9	130.9	125.3	6.89	7.52
17	0.6500	0.3100	0.2500	83.5	83.8	9.52	8.09	9.05	12.1	14.9	127.9	125.3	7.58	7.52
18	0.6500	0.3100	0.2500	90.6	83.8	8.02	8.09	9.81	16.6	14.9	118.1	125.3	7.59	7.52
19	0.6500	0.3100	0.2500	82.9	83.8	7.63	8.09	8.98	15.3	14.9	141.1	125.3	7.52	7.52
20	0.6500	0.3100	0.2500	78.5	83.8	7.91	8.09	8.50	17.8	14.9	130.8	125.3	7.71	7.52
	Error of experiment			± 3.93			± 0.73			± 2.14		± 13.47		± 0.30

[a] From monomer conversion.

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

Coeff.	y_1	y_2	y_3	y_4	y_5
b_0	83.8146	8.0926	14.8748	125.2692	7.5209
b_1	(2.3518)	1.4310	(−0.2936)	(6.1114)	0.8280
b_2	14.1120	0.8703	(0.4996)	14.6406	0.9639
b_3	16.4225	1.3100	(−0.7389)	(3.6581)	0.7777
b_{11}	(−1.9371)	(−0.3236)	(−0.1837)	(−1.0210)	−0.6016
b_{22}	−9.7573	−0.9271	(0.5417)	−10.8582	(−0.0762)
b_{33}	−8.0942	−0.9322	(0.3825)	−9.9205	(−0.0568)
b_{12}	(0.1126)	(0.3263)	(0.8382)	(−3.2277)	(−0.0338)
b_{13}	(−1.4887)	(−0.1504)	(0.5880)	(−5.6547)	(−0.2039)
b_{23}	3.9158	(−0.3683)	(−0.5129)	(9.6331)	−0.5817
$I_{x,y}$	0.9801	0.9566	0.5205	0.9000	0.9153
Type of extreme	Maximum	Maximum	Minimax	Minimax	Minimax

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

for y_1 is adequate; increasing concentrations of both constituents of initiation system have a statistically significant positive effect on y_1 (Fig. 1), but effect of the monomer concentration is not significant. The highest conversion was obtained at molar ratio (MR) $NaHSO_3/K_2S_2O_8$ of about 2 (theoretical MR is 0.5). This observation supports our previous assumption,[19] namely that in the presence of atmospheric oxygen the major portion of bisulfite is rapidly oxidized and only a part of bisulfite reacts in the redox reaction with persulfate resulting radicals. Effect of CHPA concentration on y_1 is small in comparison with the effect of initiation system constituents in the given experimental range, because the concentration of radicals from the initiation system is very high (assuming 100% efficiency of initiation approx. 1 radical to 5 CHPA molecules).

In our previous papers[19,22] concerned with grafting of hydrophilic acrylates onto collagen fibers, it has been established that there is a direct relationship between monomer conversion and the grafting degree of collagen fibers, due to almost quantitative bonding of the synthetic polymer with collagen. Composites obtained by CHPA grafting onto collagen, when extracted with methanol, acetone or their mixtures, provided no extracts; it can thus be assumed that the polymer is either strongly bonded to the collagen fibers or crosslinked. Since the mode of the bonding between collagen and PCHPA was not studied in this paper, it is necessary to understand that the term "grafting" presents the creation of bond polymer without differentiation of the nature of bonding. Thus, also the term "degree of grafting" expresses first of all the composition of the reaction product, and we have no evidence for chemical bonding of PCHPA to collagen or its physical deposition after crosslinking. According to the literature[10-16] and results of electron microscopy (see further), the second possibility is likely to be dominant. Comparison of grafting degree values, computed from nitrogen content in the composite (y_2) and from CHPA conversion (Table II), has shown that the unbonded PCHPA portion could be maximum 10% and

is presumably removed with the liquor after filtration of the reaction mixture. The y_2 value is influenced on a statistically significant level by respective concentrations of all the constituents present in the reaction mixture. The mathematical model of the y_2 dependence (Table III) is adequate and in the experimental range a maximum of y_2 function has been observed. As expected, the effect of the initiation system composition on y_2 is similar like its effect on the CHPA conversion (Figs. 1 and 2) which is in agreement with the observation that the unbonded PCHPA portion is of little significance. Unlike the case of the y_2 function, the CHPA concentration has a significant positive effect on the y_2 function (Fig. 3). This result is obvious, because the definitions of both functions implicate that the y_2 function must be essentially more influenced by monomer concentration than the y_1 function.

The regression equation describing the relationship between the swelling ability of the composite (y_3) and the reaction mixture composition is nonadequate ($I_{x,y} = 0.5205$) and the regression coefficients are statistically insignificant (Table III). The swelling ability of grafted samples is higher than the one of unmodified fibrous material; it is, however, not significantly influenced by PCHPA content variation in the composite in the range of about 3–10%.

The water absorption capacity (y_4) is, according to the regression equation derived (Table III), significantly influenced by the concentrations of constituents of the initiation system in the reaction mixture (Fig. 4), the effect of increasing CHPA concentration being low but positive. These observations are in agreement with the effects of the reaction parameters on the monomer conversion as well as on the degree of grafting, and thus the water absorption capacity is positively influenced by increasing proportion of the hydrophilic polymer in the composite. In comparison with samples prepared from ungrafted collagen fibers, the water absorption capacity of PCHPA modified samples is about two times higher.

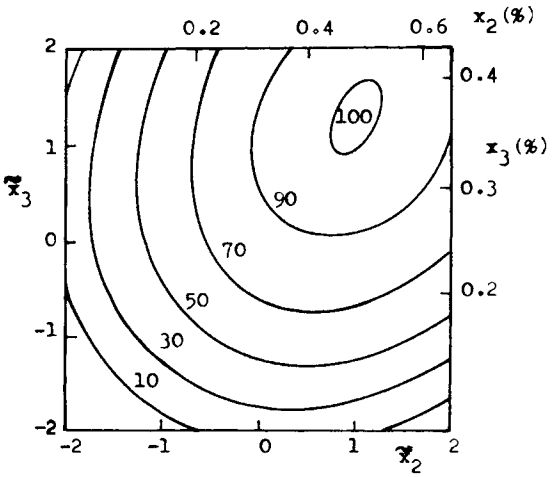

Fig. 1. Contour lines for CHPA conversion (y_1, %) as a function of $K_2S_2O_8$ (x_2) and $NaHSO_3$ (x_3) concentrations, at constant concentration of CHPA (0.65%).

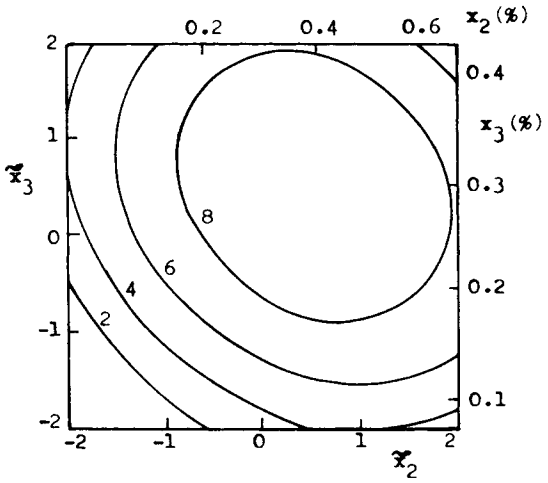

Fig. 2. Contour lines for degree of grafting (y_2, %) as a function of $K_2S_2O_8$ (x_2) and $NaHSO_3$ (x_3) concentrations, at constant concentration of CHPA (0.86%).

The tensile strength of composites (y_5) is equally influenced by the concentrations of all the reaction mixture constituents on a statistically significant level (Table III); it has an increasing trend in the direction of increasing x_i values (Figs. 5 and 6). Like the water absorption capacity, the tensile strength is also positively influenced by increasing PCHPA content in the composite. The highest tensile strength values (about 8 MPa) are by about 40% higher than the ones of samples prepared from ungrafted collagen fibers; they, however, do not reach the respective values of samples modified by the HEMA–MMA mixture (up to 17 MPa)[19] which is due to lower content of synthetic polymer in the composite (lower monomer concentration range).

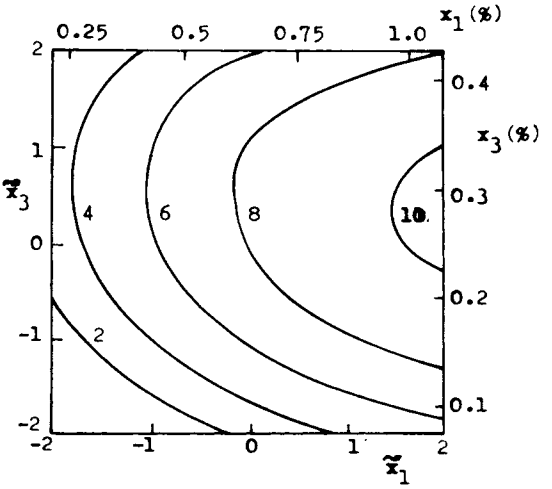

Fig. 3. Contour lines for degree of grafting (y_2, %) as a function of CHPA (x_1) and $NaHSO_3$ (x_3) concentrations, at constant concentration of $K_2S_2O_8$ (0.48%).

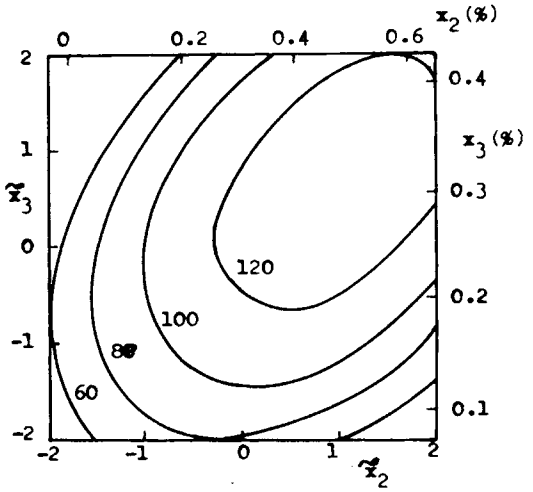

Fig. 4. Contour lines for water absorption capacity (y_4, %) as a function of $K_2S_2O_8$ (x_2) and $NaHSO_3$ (x_3) concentrations, at constant concentration of CHPA (0.47%).

In the papers by Jordan et al.[13,16] morphology of composites prepared by leather modification using acrylic polymers is described. As in our case involving homogenized substrate (collagen fibers), the situation can be different from the one of leather; we have investigated the morphology of several samples prepared by grafting of MMA, HEMA, HEMA–MMA mixture, and CHPA, resp., onto collagen fibers. This electron microscopic study is limited to the morphology of individual fibriles or small bundles of the same (max. 6–9 of individual collagen fibriles).

Ungrafted collagen fibriles (Fig. 7) show a typical structure of transversal periodical bands resulting from tropocollagen molecules overlap. PMMA-grafted fibrous substrate (about 50% PMMA) is characterized by the presence of synthetic polymer aggregates (Fig. 8). These aggregates are granular

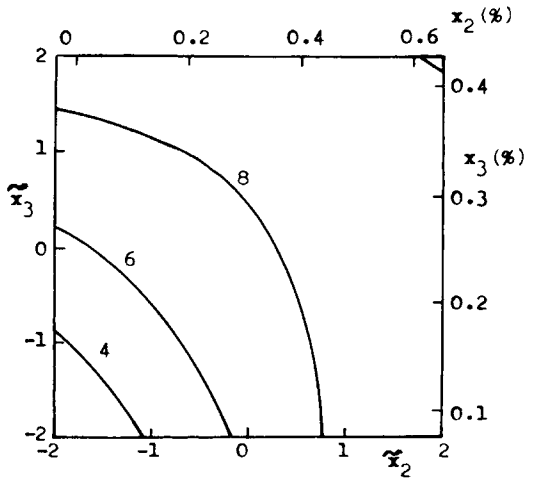

Fig. 5. Contour lines for tensile strength of composites (y_5, %) as a function of $K_2S_2O_8$ (x_2) and $NaHSO_3$ (x_3) concentrations, at constant concentration of CHPA (0.86%).

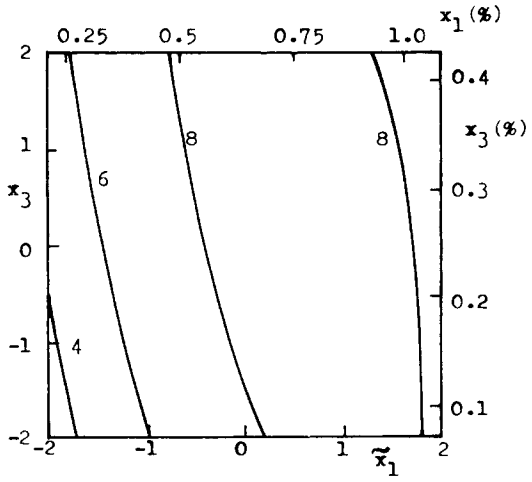

Fig. 6. Contour lines for tensile strength of composites (y_5, %) as a function of CHPA (x_1) and $NaHSO_3$ (x_3) concentrations, at constant concentration of $K_2S_2O_8$ (0.48%).

in structure with the tendency to grow perpendiculary to the fibrile axis, which is in agreement with their hydrophobic character. We were, however, not successful in finding a relationship between the initial bonding point of PMMA aggregates and the details of the periodical band structure of collagen fibriles. In addition to the bonded PMMA, there are free particles and PMMA aggregates present in the system; in the crosspoints or areas of parallel alignment of fibriles, effects of capillary forces on PMMA deposition (larger aggregates) can be observed.

HEMA-modified collagen fibers show on the electron micrographs a quite different behavior (Fig. 9). PHEMA is also randomly distributed on the

Fig. 7. Transmission electron microscopy (TEM) micrograph of unmodified chrome-tanned collagen fibers.

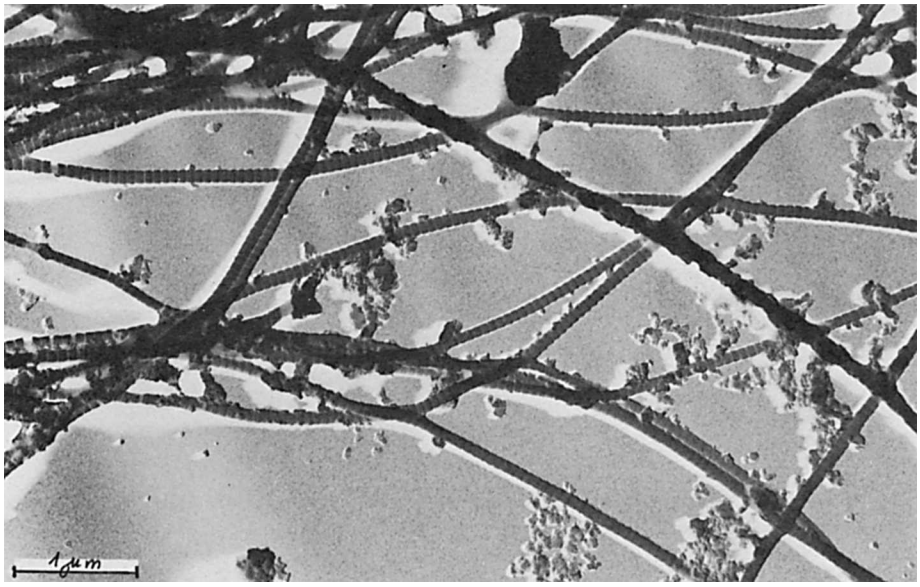

Fig. 8. TEM micrograph of MMA grafted collagen fibers.

fibrile surface and the bonding points are in no relationship to the band periodicity; but, unlike the PMMA-modified samples, there is a tendency of polymer growth rather along the collagen fibriles in layers of thickness, comparable to the one of fibriles suggesting a favorable mutual interaction between the collagenous substrate and the hydrophilic PHEMA. This PHEMA deposition on the fibrile surface is, however, not homogenous, and tendency to continuous coating formation has not been observed. Effects of

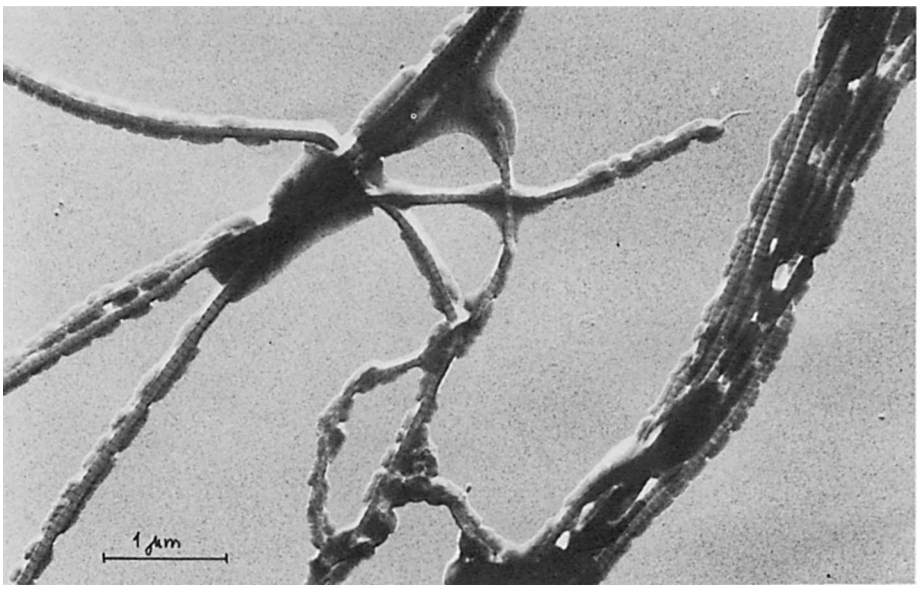

Fig. 9. TEM micrograph of HEMA grafted collagen fibers.

capillary forces leading to the formation of large PHEMA aggregates filling the interfibrilar spaces in crosspoints or between fibriles, aligned in parallel closely to each other, are here more evident than in case of samples prepared by MMA grafting.

Samples modified by HEMA–MMA mixture (Fig. 10) exert the additivity of morphological characteristics of systems prepared by grafting of collagen fibers by individual monomers. Segments of fibriles could be observed on which the synthetic polymer was deposited in the form of an almost continuous layer, bonded granular formations as well as free particles not adhering to fibriles. Because, according to copolymerization parameter values of the HEMA/MMA combination, the homopolymer formation is rather unlikely, the individual morphologies are supposed to be copolymers, containing various proportions of individual monomers. As no extractables were obtained from these samples, the observation of free copolymer, unbounded to fibriles, is somewhat surprising and suggesting the possibility of crosslinking. In comparison with the collagen fibers modified only with PMMA, the positive effect of the presence of hydrophilic PHEMA on the polymeric portion bonding to the collagen fibriles, observed on the micrographs, can be considered to be conclusive.

Micrographs of PCHPA grafted collagen fibers show a quite specific behavior (Fig. 11). The modifying component tends to form a continuous layer on the fibriles, especially in areas subject to the action of capillary forces. A pronounced difference from all the preceeding systems is in that PCHPA tends to fibrillation. A thin fibrillar network of elastomeric PCHPA seems to be formed in sites where the collagen fibriles linked by means of PCHPA layers are deformed or shifted. This phenomenon is typical for the microplastic deformation of several polymers.

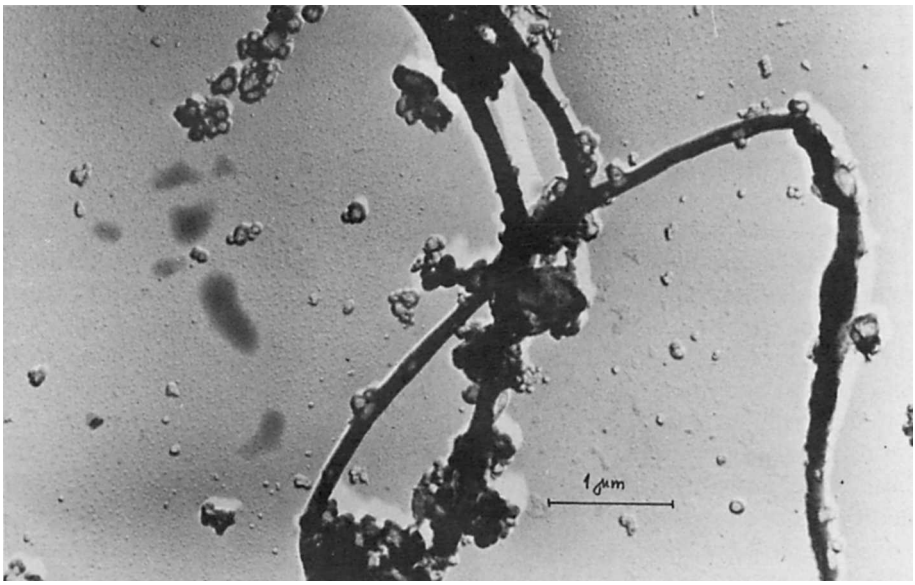

Fig. 10. TEM micrograph of HEMA–MMA mixture grafted collagen fibers.

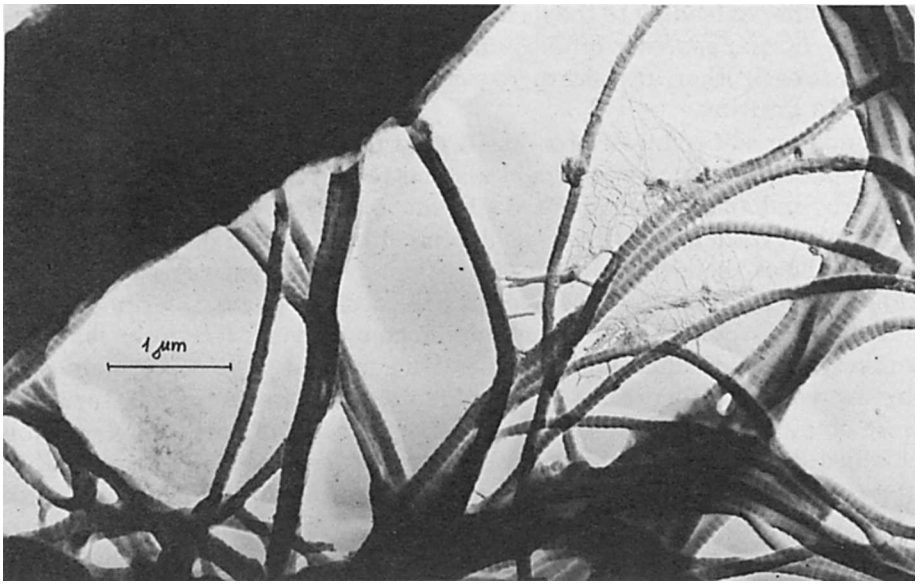

Fig. 11. TEM micrograph of CHPA grafted collagen fibers.

CONCLUSION

Effect of reaction conditions, defined by CHPA, $K_2S_2O_8$, and $NaHSO_3$ concentrations on the grafting process of CHPA onto collagen fibers and on the properties of the composites obtained has been investigated. Results obtained by the method of statistical planning of experiments have shown that the CHPA conversion is influenced mainly by the initiation system composition; to achieve a 100% CHPA conversion under the experimental conditions adopted, a quadruple excess of bisulfite is necessary in its mixture with persulfate (compared with the theoretical MR 0.5). From the composites prepared no PCHPA could be extracted by organic solvents, which suggests that PCHPA is either bonded to collagen fibers or crosslinked. With increasing CHPA conversion the contents of the synthetic polymer in the composite is increased proportionally to the measured grafting degree value; simultaneously the water absorption capacity and tensile strength of composites are equally increased. The results obtained are analogical to the ones of collagen fiber modification by HEMA or HEMA–MMA mixture

Electron microscopic study by composites prepared by collagen fiber modification with PMMA, PHEMA, PHEMA–PMMA blend, and PCHPA, resp., has shown that the bonding sites of the synthetic polymer onto collagen fibriles cannot be specified. The synthetic polymer is bonded randomly, and it is evident that the role of physical effects like the accessibility of individual fibriles or capillary forces in their crosspoints or in places, where the fibriles are arranged in parallel close to each other, is more important than the chemical effects. It can be assumed that the differences in the modification of individual fibriles will become more important with increasing degree of their aggregation. The bonding mode of collagen fibriles with synthetic polymers is in agreement with their hydrophilic or hydrophobic character. The question of the physical or chemical nature of links

between the modifying polymer and the collagen fibers could not be settled by morphological characterization. The PCHPA fibrillation in case of collagen fibers modified by this polymer suggest, however, a high degree of mutual adhesion between the synthetic constituent and the collagenous substrate.

The authors wish to thank Dr. F. Rybnikář from our Institute for the micrograph preparation.

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Received March 27, 1985
Accepted September 18, 1985