

**POLYMER-LEATHER COMPOSITES.
VI. MECHANISM OF DEPOSITION OF SELECTED
ACRYLATE MONOMERS BY POLYMERIZATION
INTO 5-OUNCE CHROME-TANNED CATTLEHIDE**

E. F. JORDAN, JR., B. ARTYMYSHYN, AND S. H. FEAIRHELLER

Eastern Regional Research Center
Philadelphia, Pennsylvania 19118*

Abstract

Three acrylate monomers, methyl methacrylate, n-butyl acrylate, and a comonomer mixture of fixed n-butyl acrylate (59 percent) and methyl methacrylate, were polymerized into 5-oz cattlehide by two processes. In one, the monomers were polymerized into the fibrous matrix by the standard emulsion process developed at this Center using a potassium persulfate-sodium bisulfite redox initiating system at room temperature. In the other, the same three monomers were introduced by bulk or solution polymerization into acetone-dried panels in a closed system at 60°C. The rate of change of density with composition was completely different for the two types of composites. The widest range of composition was studied, far exceeding the practical range, to provide basic information on the mechanism of deposition and bound polymer formation for the emulsion process. It was observed that both the efficiency of producing chemically bound polymer and the number of polymer branches on the collagen declined as monomer content was incrementally increased. Because branch frequency thus decreased compared with the theoretical maximum, a controlling grafting mechanism was precluded. Characteristic kinetic constants that reflected the influence of changes in reaction variables indicated that deposition was controlled by emulsion polymer instability rather than being influenced by grafting. A mechanism was suggested involving aggregation of polymer in leather by coalescence of emulsion particles to form macrodimensional layers near the surfaces of cattlehide, fed by monomer diffusing to rapidly accumulating occluded radicals. Polymer-polymer crosslinking and strong adsorption of polymer coils to fiber surfaces accompanied by some surface grafting produced the bound polymer in this scheme.

*Agricultural Research Service, U.S. Department of Agriculture.

Introduction

This paper provides the results of a detailed study of preparation conditions, kinetics, and molecular weights based on an established practical method of depositing acrylate and other vinyl monomers by polymerization into 5-oz chrome-tanned cattlehide. The paper is essentially a review of earlier work published in polymer journals (1,2). The completed series (1-5) is not to be confused with the well-known series of Korn and Harris *et al.* (6-12) which provided practical methods for graft polymerizing Nigerian sheepskins and other leathers by emulsion polymerization using potassium persulfate and sodium bisulfite as redox initiators. In fact, the work described herein was intended to complement the work of Korn and Harris (6-12) by providing greater insight into the mechanism of deposition and bound polymer formation in the modification of leather over the widest feasible range of composite composition, well beyond the accepted practical range.

A primary objective was to ascertain the extent to which graft polymer constituted the bound (unextractable) polymer for all possible compositions. For this purpose, studies of deposition and bound polymer efficiency with changes in the amount and type of monomer introduced in the float were emphasized. Thus the number of grafted branches on collagen compared with that expected of a controlling graft mechanism could be ascertained. In addition, extensive kinetic studies of the relative rates of formation of polymer in the float and in the matrix (deposited) and the fraction of this that was bound to the matrix were obtained to further delineate the dominant mechanism by matching experimental data to significant theoretical constants that permit such a choice to be made.

Thus, this paper presents a more comprehensive reinterpretation of accumulated knowledge on these very complex systems. The paper that immediately follows (13) is more practical in presenting micrographs that depict the polymer in its characteristic morphology in the leather and in comparing the mechanical properties of the composites themselves with their untreated leather controls.

It is well established today that composite materials based on synthetic polymers are only lightly (few percent) grafted (14a,b). Grafts appear at phase boundaries only. This leaves the modifying bulk polymer as an incompatible dispersed phase that is ungrafted but isolated and thus unavailable for polymer extraction (14a). Although the same reasoning probably applies to fiber composites (15, 16), an extensive literature on cotton (17, 18) and wool (15) composites suggests that chemical grafting reactions produced the bound polymer. Neglecting the mechanistic specificity required in using ceric ion on cotton (19-21), most of the other proposed mechanisms operate through a primary radical attack on the fiber molecule to provide graftable reaction sites (15, 22, 23). Several workers, however, suggest that much of the bound polymer is merely absorbed or entrapped around fibril or protofibril surfaces in cotton and wool (15) and other natural fibers (16). A dominant grafting mechanism has been proposed to account for all

bound polymer formed in leather (24), whether made by ceric ion redox initiation (25-30) or other means (6-12, 31-33).

In this work, three acrylate monomers, methyl methacrylate (MMA), n-butyl acrylate (BA), and a fixed mixture of n-butyl acrylate (59 percent) and methyl methacrylate (BA + MMA) were polymerized to 100 percent conversion into 5-oz chrome-tanned blue cattlehide by two methods. In one, the monomers were polymerized into hydrated panels by the standard emulsion process developed at this Center. In the other, acetone-dried panels were saturated with the same monomers in bulk or benzene solution and were polymerized at 60°C in sealed systems using bis-azoisobutyronitrile (AIBN) as the initiator. Thus, two different types of composite material were developed for comparison. In the emulsion process the total polymer and the polymer that formed in the float and that which deposited in the matrix as homopolymer and bound polymer were separately ascertained. In the rate studies, where variable reactant concentrations were utilized, the same isolation techniques were employed. For all systems studied, the widest feasible range of composition was investigated. Apparent densities were obtained on all composites and their untreated controls, but the number-average molecular weights were determined on the bound, deposited, and float polymer of only selected composites. Finally an attempt was made to cast the specialized information obtained in forms more readily comprehensible to readers not before involved in the polymer field.

Experimental

Although the procedures for preparing the composite materials of this work by both processes studied, and for determining their physical properties, have been reported extensively elsewhere (1-4), a brief outline is given below for the convenience of the reader.

POLYMERIZATION PROCEDURE

Panels (8.9 x 15.2 x 0.235 cm) of 5-oz chrome-tanned blue-stock grain-split cattlehide were cut consecutively from all possible locations from hides from different tanneries. Untreated control panels were included with each treated panel. In the emulsion method, the panels to be treated were tumbled at ambient temperature under emulsion conditions with the appropriate monomer for 24 hr, after first conditioning them for 30 min with the potassium persulfate-sodium bisulfite redox initiating system. Composite composition was obtained gravimetrically from methanol or air-dried panels; bound polymer composition was obtained from panels extracted with hot benzene to remove homopolymer. Standard conditions were: water 5:1 based on dry leather; $K_2S_2O_8$, 4 mole percent based on monomer; $NaHSO_3/K_2S_2O_8$, 0.5; Triton X100 (1.03 percent) 2 cc/g based on wet leather. For kinetic studies, the conditioning period was omitted and smaller

panels ($\sim 0.2X$) were used (2). Variable changes were made using the standard conditions as points of departure, and reaction time was varied incrementally. In the bulk or solution process, panels saturated with pure monomers, or monomers diluted with benzene, were polymerized using bis-azoisobutyronitrile (AIBN) as initiator in sealed systems at 60°C.

PHYSICAL PROPERTIES

Real densities were determined by use of a helium air pycnometer and apparent densities by measurement of panel volumes (1). Neat polymer densities were, in g/cc: MMA, 1.146; BA + MMA, 1.103; BA, 1.072, respectively. Light microscopy on stained sections was used to determine the thickness of the polymer layers (see text) of deposited polymer at grain and corium surfaces (1). Bound polymer was isolated by preferential removal of collagenous material by means of 6 N hot hydrochloric acid for extended times (1, 3). Molecular weights were obtained with a Mercolab 501† membrane osmometer.

Results and Discussion

A. POLYMERIZATION PRINCIPLES AND COMPOSITE FORMATION CONCEPTS

Before proceeding with the results of this investigation, a brief presentation is given below of the principles governing the initiation and growth of polymer chains in ordinary homogeneous polymerization (such as polymerization of pure monomer) and the special type of isolated (heterogeneous) chain growth that characterizes emulsion polymerization. Contrast is also provided between the latter type and the growth process that defines an exclusive or dominant graft polymerization reaction pathway which proceeds through a chain transfer mechanism (22, 23).

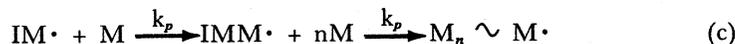
Homogeneous chain-growth polymerization is characterized by three simultaneously occurring reactions. Starting with a spontaneous decomposition of an initiator to slowly release free radicals, $I\cdot$, homolytically



Initiation of monomer, M , follows its fast reaction with $I\cdot$



Growth of polymer chains (propagation) then follows the initiation step

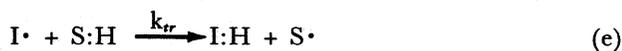


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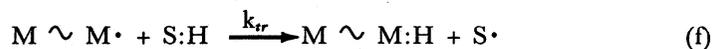
and chains are terminated when two growing chains meet



Thus, as the initiator slowly releases its radicals in step (a), polymer radicals are continuously formed in step (b), grow in step (c), and stop growing in step (d). The lifetime of a growing chain is less than 1 sec. Each step has a characteristic rate, R , governed by a rate constant, k , whose subscripts describe its function as in equations a to d. A basic assumption is that the rate of step (b), R_i , exactly equals the rate of step (d), R_t , so that the initial radical concentration stays constant and is much less than the monomer concentration as polymerization proceeds. Thus polymer macromolecular radicals rapidly grow and reach chains of monomer units (degree of polymerization, \overline{DP}_n) of 1,000 to 10,000 typically by the time growth terminates. Molecular weight is largely governed by the inverse rate of initiation; the higher this rate the lower the molecular weight, because the rate of termination is now higher. If other organic molecules (S:H) are present containing a plurality of protons, two additional reactions (called chain transfer) can occur. Primary radicals can transfer



and macroradicals can transfer



The solvent radicals, $S \cdot$, can also add monomer and continue the chain growth as in equation c. However, transfer constants, k_{tr} , are usually much smaller than initiation constants, k_i , (reaction b) so that steps e and f occur infrequently. Nevertheless step e, with collagen, L:H, substituted for S:H, is the usual mechanism written for grafting reactions (22-24) even though the leather is out of phase with the polymerization locus, while radicals are being generated directly in the same phase with abundant monomer.

An even more stringent exclusion of leather occurs when emulsion polymerization is employed. In emulsion polymerization reactions (a) through (f), excluding (e), are operative but with certain critical differences. Radicals, $I \cdot$ (now $SO_4^{\cdot -}$ if persulfate is used (34)) generated in the aqueous phase add quickly ($\sim 1 \times 10^{-5}$ sec) (35-36) to monomer present in colloidal micelles existing in the aqueous phase, to form a strictly limited number of polymer particles in the early (0-7 percent conversion) stages of the polymerization. Monomer quickly diffuses at a steady rate from relatively large monomer droplets ($\sim 1 \mu\text{m}$ in diameter) to the tiny particles, through the aqueous phase, to continue the polymerization. The individual particles increase in size at a steady rate, usually reaching 500 to 1,000 Å (0.05 to 0.10 μm) at the end of the polymerization. The rate of an emulsion polymerization becomes dependent (7 to 60 percent conversion) on only the

number of particles generated and the equilibrium concentration of monomer in the particles. Thus initiation and chain growth proceed in isolation (heterogeneously) in remote particles and, because of rapid capture in particles, nascent radicals are even less available to produce grafts by chain transfer (reaction e). If, however, the emulsion system should become unstable through loss of surfactant, the particles will coagulate into large masses and free-radicals will accumulate (occlude). The polymerization mechanism then proceeds along the homogeneous pathway by reactions a through f.

In this work, where polymerization was usually continued to 100 percent conversion (except for the kinetic data) the total polymer formed was located partially in the float while the leather contained the rest of the polymer. Of the latter polymer, here referred to as deposited polymer, roughly half was benzene-extractable homopolymer and the rest was unextractable bound polymer. This distribution varied with the monomer used and with the time before polymerization was complete. By ascertaining the amount and type of polymer formed and its distribution, important information became available concerning fractional deposition, weight fraction, efficiency of deposition and bound polymer formation, and their influence on molecular weight and apparent extent of grafting. These important parameters will be discussed by reference to the equations below.

Consider a 50/50 mixture as a typical composite of leather and polymer. If the components are considered to have unit density, one-half is leather, one-fourth is bound, and one-fourth is homopolymer. The last two together constitute the deposited polymer fraction. Thus the fraction deposited, W_d , and the fraction bound, W_{2b} , is in accordance with the equation

$$W_d = W_2/W_1; W_{2b} = W_b/W_1 \quad (1)$$

where W is weight and subscript 1 is leather, 2 is polymer and b is bound polymer. Limits here are between 0 and ∞ as composition changes from untreated leather to pure polymer. In contrast weight fraction deposited, w_d or w_a , and bound, w_b follow the relations

$$w_d = w_2 = W_2/(W_2 + W_1) \quad (2)$$

$$w_b = W_b/(W_b + W_1) \quad (2a)$$

These models have limits between 0 and 1.0 as composition changes from pure leather to pure polymer. The efficiency of deposition, ϵ_d , is given by

$$\epsilon_d = W_2/W_T = \frac{\text{weight of polymer in the leather}}{\text{total weight of polymer formed in the float and leather combined}} \quad (3)$$

while the corresponding efficiency of bound (grafted) polymer, ϵ_b , is

$$\epsilon_b = W_b/W_T \quad (4)$$

Efficiency of bound or grafted polymer, ϵ_b , must remain high (≥ 50 percent) as monomer concentration (containing a fixed mole fraction of initiator), W_2 feed, is increased to large amounts while leather amount, W_1 , is kept constant in order to provide significant support to the grafting mechanism outlined above. This can best be seen by reference to Figure 1, which pictures four conditions of the bound or grafted frequency fraction, F_b .

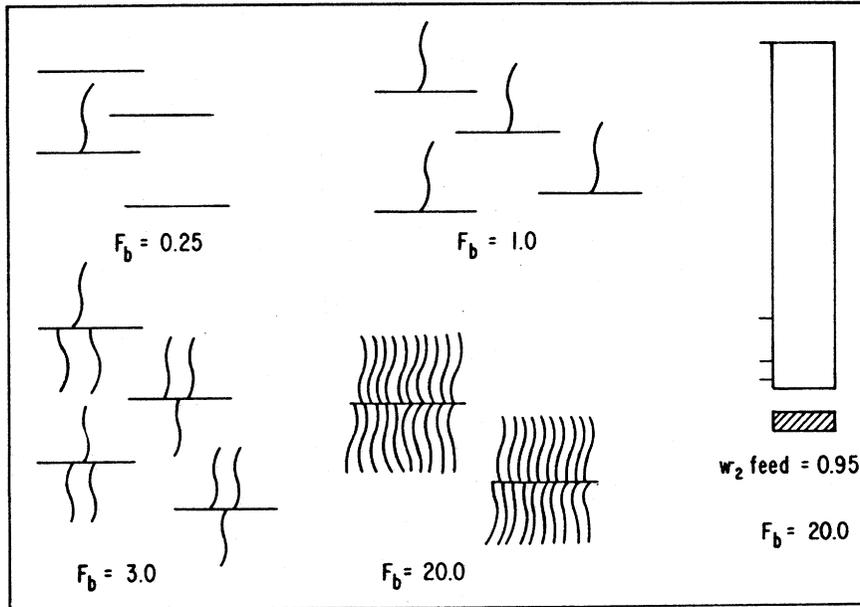


FIGURE 1. — Schematic diagram illustrating concepts involving grafting frequency, F_b , for polymer-leather composites. Four different bound (grafted) polymer frequency fractions, F_b , are illustrated. Solid lines are tropocollagen molecules and wavy lines, synthetic polymer branches, each of molecular weight 300,000. Clear rectangle at right represents monomer concentration required to produce illustrated F_b branches relative to leather amount (shaded rectangle). Pips correspond to each F_b .

This parameter is defined

$$F_b = \frac{\text{weight fraction of bound polymer} \times \text{molecular weight of collagen}}{\text{weight fraction of leather} \times \text{molecular weight of the polymer}} \quad (5)$$

The branch molecular weight (curved line) is assumed to be the same in using equation 5 in Figure 1 as that of collagen (straight line) namely 300,000, although it could have been any value. If a grafting mechanism controlled the formation of

bound polymer, as pictured, bound polymer efficiency would have to remain high as more monomer was introduced to achieve a high F_b , of 20 as an example of a value arbitrarily selected and pictured. This is because a dominant grafting mechanism requires that radical reactivity be transferred efficiently (fast rates) from the primary radicals to collagen. Thus many branches can develop on the collagen molecule. However, the monomer feed composition w_2 feed must be dramatically increased (right hand figure) to produce a high F_b . The hatched block is leather. A dominant grafting mechanism would steadily produce many branches on collagen as more feed was introduced as pictured (position of pips at left correspond to each F_b). Any competing reactions would produce polymer preferentially in the float. Dominance of a competing mechanism therefore would reduce ϵ_b steadily as feed increased with a corresponding increase in float polymer. Thus, F_b would also stay small. It will be seen that this actually happened. The foregoing theory, while seemingly complex, represents the main principle operating in any process for treating leather with polymerizing monomers coupled with the complication of grafting.

B. RESULTS, GENERAL FEATURES

In Table I are listed some of the weight fraction compositions of polymer, w_2 , for the various polymer-leather composites prepared and their apparent densities. In the emulsion prepared composites, densities of the deposited composites generally increased with increase in w_2 while bound composite densities remained low and more resembled untreated leathers. In contrast, bulk-solution deposition produced composites of much greater density that increased to a constant value near that of pure polymer (experimental) and collagen (1.434 g cc^{-1}) (1). The reason for this behavior and the significance of the density relations will be presented in sections below.

Table II presents number-average molecular weights for the various composites of Table I for polymer initially bound to the leather, that merely deposited (homopolymer), and that found in the float. On the assumption that all of the bound polymer was grafted, the polymer branching frequency fraction, F_b , discussed in connection with Figure 1, is also presented. In general, the order of size of molecular weight was $\bar{M}_n \text{ bound} \geq \bar{M}_n \text{ homopolymer} > \bar{M}_n \text{ float}$. The \bar{M}_n for the polymer formed in the absence of leather ($w_2 \text{ feed} = 1.0$) is relatively small. The seeming exception (BA) was masked by a long low molecular weight tail in the molecular weight distribution (1). The relatively high molecular weights found for polymer forming in the confined space of leather is clear evidence for the suppression of termination rate (reaction d) and is called a gel effect. This effect has been almost universally observed for polymer forming in natural fibers (15, 37-40) or in leather systems (1, 10-12). The low value of F_b , representing only an occasional branch on tropocollagen (Figure 1B), even at high mono-

TABLE I
COMPOSITE COMPOSITIONS AND APPARENT DENSITIES

MMA composites ^a				BA + MMA composites ^a				BA composites ^a			
Composition		Apparent density ^b g cc ⁻¹		Composition		Apparent density ^b g cc ⁻¹		Composition		Apparent density ^b g cc ⁻¹	
w ₂	Bound	ρ_a	Bound	w ₂	Bound	ρ_a	Bound	w ₂	Bound	ρ_a	Bound
0.0777	0.0223	0.549	0.536	0.0742	0.0338	0.602	0.618	0.0416	0.0114	0.612	0.605
0.180	0.894	0.660	0.563	0.182	0.140	0.665	0.609	0.123	0.0629	0.646	0.619
0.249	0.203	0.700	0.599	0.294	0.260	0.610	0.572	0.141	0.0853	0.597	0.599
0.396	0.335	0.743	0.643	0.327	0.279	0.614	0.573	0.223	0.173	0.621	0.575
0.443	0.447	0.805	0.769	0.372	0.306	0.712	0.616	0.340	0.259	0.680	0.587
0.598	0.160	0.598	0.419								
0.748	0.212	0.748	0.397	0.528	0.353	0.812	0.605	0.333	0.0616	0.703	0.562
				Bulk or solution polymerization prepared composites							
0.0962		0.775		0.084		0.683					
0.155		0.780						0.143		0.747	
0.189		0.793		0.195		0.807					
0.234		0.874		0.263		0.845		0.223		0.877	
0.292		0.948		0.310		0.962		0.250		0.904	
0.397		1.036		0.442		1.011		0.281		0.936	
0.423		1.081		0.467		0.975		0.346		0.951	
0.645		1.173		0.543		1.134					
0.701		1.154		0.667		1.107					
1.0		1.146		1.0		1.103		1.0		1.072	

^a For the emulsion systems, the corresponding feed (starting) weight fractions, w₂ feed were: 0.103, 0.200, 0.301, 0.401, 0.500, 0.667, 0.750, respectively.

^b Average untreated control apparent densities, ρ_a , were: emulsion 0.5556 g cc⁻¹; bulk-solution, 0.6241 g cc⁻¹.

TABLE II

NUMBER-AVERAGE MOLECULAR WEIGHTS WITH RESPECT TO POLYMERIZATION LOCUS
AND FRACTIONAL NUMBER OF BRANCHES PER COLLAGEN CHAIN

w ₂ feed	MMA composites				BA + MMA composites				BA composites			
	Molecular weights x 10 ^{-5*}		Molecular weights x 10 ^{-5*}		Molecular weights x 10 ^{-5*}		Molecular weights x 10 ^{-5*}		Molecular weights x 10 ^{-5*}		Molecular weights x 10 ^{-5*}	
	\bar{M}_n Bound	\bar{M}_n Homopol.	\bar{M}_n Float	F _b ^b	\bar{M}_n Bound	\bar{M}_n Homopol.	\bar{M}_n Float	F _b ^b	\bar{M}_n Bound	\bar{M}_n Homopol.	\bar{M}_n Float	F _b ^b
0.103			1.95									
0.200	3.48	3.61		0.084	4.92		0.084	4.84			2.95	0.0416
0.301	3.09	5.32		0.247	6.05		0.174	1.82			2.40	0.154
0.401	5.22	5.41		0.289	5.93	8.91	0.195	3.00			2.57	0.210
0.500	5.41	10.05		0.448				2.64			4.04	0.398
0.667	1.96	1		0.294	12.63	9.18	0.105					
0.750	1.92			0.421	11.62	3.65	0.141					
1.00			1.68				7.99					2.77

* To obtain numerical values for the number-average molecular weights, \bar{M}_n , multiply by 100,000.

^b F_b = (w₂ x \bar{M}_n collagen) / (w₁ x \bar{M}_n bound) where \bar{M}_n collagen = 300,000.

mer feed (0.67 to 0.75), indicates low grafting efficiency. The efficiency aspect will now be discussed.

C. SYSTEMS AND DEPOSITION EFFICIENCIES

The relative efficiency of each polymerizing system for depositing polymer in leather (Figure 2), expressed as the slopes of the lines and designated D_e , de-

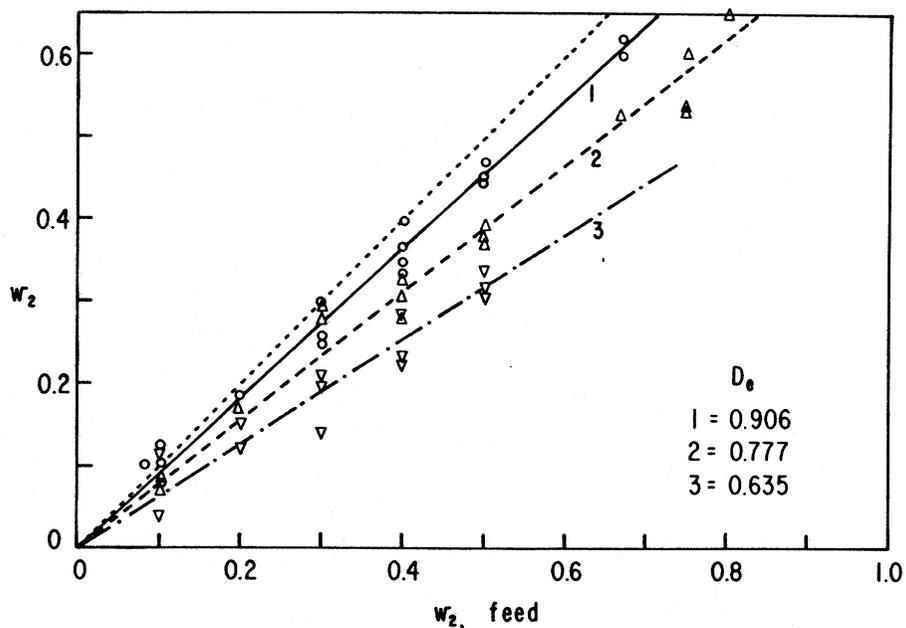


FIGURE 2. — The weight fraction of polymer deposited, w_2 , versus the weight fraction of monomer in the feed, w_2 feed. Designations are: curve 1, MMA; curve 2, BA + MMA; curve 3, BA; dotted line maximum deposition efficiency $D_e = 1.0$. Individual values of D_e (slopes) are listed.

creased in the order MMA, curve 1 > BA + MMA, curve 2 > BA curve 3 for a wide range of feed composition. The maximum efficiency is the dotted line, where D_e is 1.0. A similar order (Figure 3, insert A), was found for the percent polymer deposited (W_d , equation 1 x 100) as a function of time. However percent conversion-time curves for MMA (insert B), BA + MMA (insert C), and BA (insert D), using a feed composition of 0.5, show marked differences in behavior. For MMA, most of the polymer deposited in the leather and little formed in the float. Rates in the absence of leather were relatively small compared to deposited

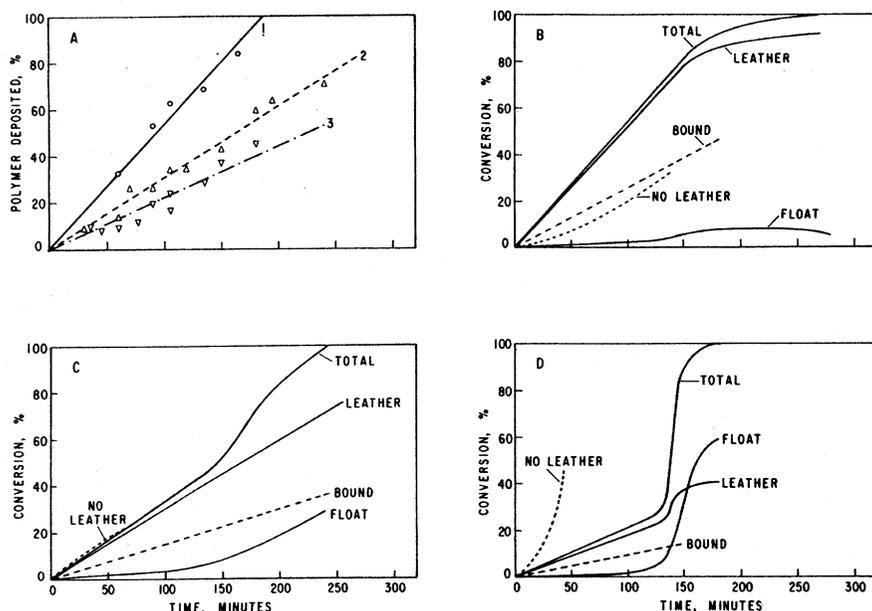


FIGURE 3. — Rate curves for total polymerization including composite formation using w_2 feed = 0.5. Insert A, percent polymer deposited in leather versus time; curve 1, MMA; curve 2, BA + MMA; curve 3, BA. Inserts B, C, D, percent conversion-time curves for MMA, BA + MMA, and BA, respectively.

rates. For BA + MMA and BA, initially most polymer formed in leather, but at a time period before polymerization was complete, the polymerization locus was transferred to the float, accompanied by rate enhancement. For BA + MMA the rate with and without leather was the same but for BA, the presence of leather seemed to retard the polymerization rate. The rate of bound polymer formation was about one-half that of deposited polymer formation for all three systems. These data explain the order of D_e in Figure 2 by indicating that a critical saturation level exists for each monomer type introduced by polymerization into leather. When this level is reached, polymerization activity is transferred to the float. The differences in rates of deposition have kinetic origins, however; this aspect will be treated below.

The efficiency of deposition (ϵ_d , equation 3) is expressed as the solid line for each of the monomers in Figure 4 as a function of monomer in the feed, w_2 feed. The order is the same as for D_e , namely MMA, curve 1 > BA + MMA, curve 2 > BA, curve 3. The dashed curve is ϵ_b , (equation 4) for BA + MMA. All four curves show that as the monomer amount in the initial feed was increased, the efficiency of deposition steadily decreased to low values compared to ϵ_{max} (top of

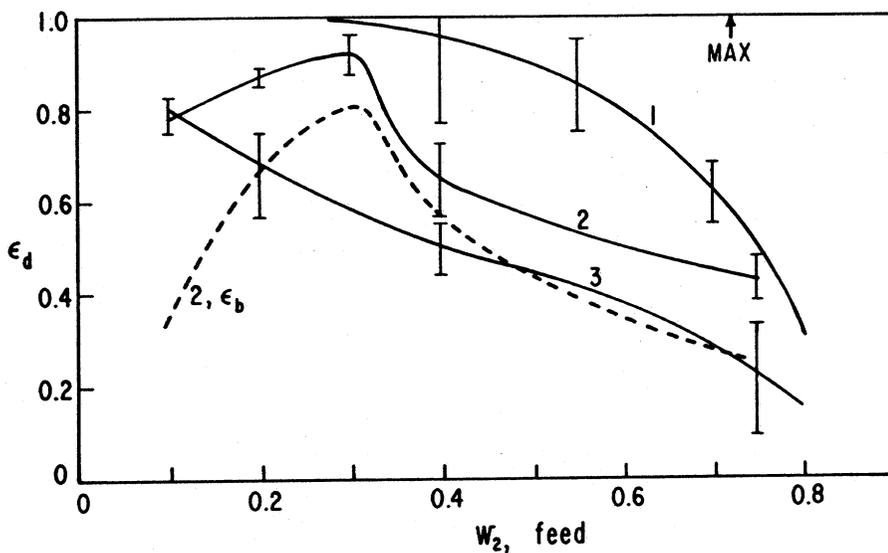


FIGURE 4. — Specific deposition efficiency, ϵ_d , solid lines, and bound polymer efficiency, ϵ_b , dashed line, versus w_2 feed. Curve 1, MMA; curve 2, BA + MMA; curve 3, BA; ϵ_b (dashed line) is for BA + MMA composites. Bars represent the extremes of experimental scatter.

figure). These declining efficiencies as more monomer was introduced account for the small values of the grafting frequency factor, F_b , reported in Table II, especially when monomer feed compositions were large (0.66, 0.75). Actual F_b data for BA + MMA from Table II are plotted (solid circles) in Figure 5 on a curve drawn for an average branch length of $823,180 \bar{M}_n$ for this system, as a function of the weight fraction of bound (grafted) polymer, w_b . The observed values (lower two downward arrows) for w_2 feed of 0.66 and 0.75, respectively, are considerably lower than the F_b required by dominant grafting at high efficiency (marked by higher two downward arrows). The circles are averaged values used to check the curve accuracy. Similar observations would apply to the other system in Table II. As discussed in section A, these trends provide strong evidence negating a controlling grafting mechanism. The effect of the type of deposition process used on composite densities will be considered next.

D. DENSITY AND PLUMPING OF THE COMPOSITES

Figure 6 is a schematic diagram representing all features characteristic of the composite materials of this work. Insert a represents an acetone-dried untreated

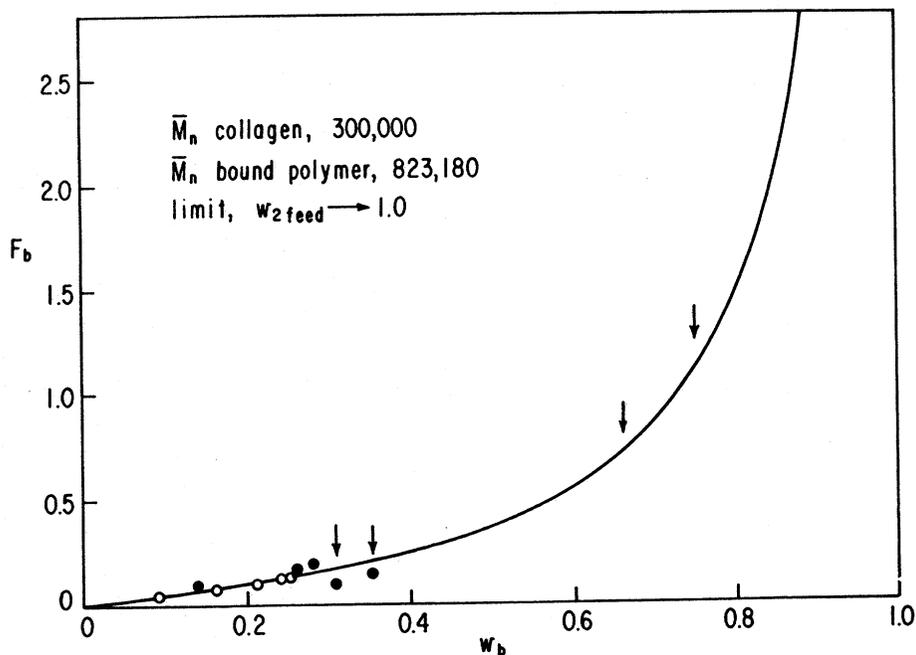


FIGURE 5. — Plot of the bound polymer frequency fraction, F_b , versus the weight fraction of bound polymer, w_b , for average branch molecular weights of BA + MMA composites: actual data from Table II are plotted as solid circles; the open circles are averaged values used to check the curve accuracy. The observed values for w_2 feed of 0.66 and 0.75 (two lower downward arrows), respectively, are considerably lower than the F_b required by corresponding theoretical values (two higher downward arrows).

leather panel showing two idealized fiber bundles, where h_0 is the initial thickness of the panel and A_0 the initial area. After treatment by emulsion polymerization, insert b, the panel thickness increases to h as polymer fills the space around fibers in fiber bundles (3). Density increased monotonically as polymer content increased, Table I. After extraction with benzene to remove homopolymer from the deposited polymer, the panel retains its expanded thickness, insert c, but becomes more porous as polymer is removed; consequently density decreased to values near that of the control, Table I. In contrast (insert d), when polymer is introduced into acetone-dried panels by bulk or solution polymerization, only the free space is available for filling. Thus density increases much more rapidly (Table I) for any given w_2 compared to emulsion deposition. A characteristic feature of the systems in this work using cattlehide as the substrate for modification is that polymer was shown by light microscope examination of stained cross-sections (1, 3) to

reside in the outer grain and split corium regions, leaving a center region almost entirely free of polymer, insert e (1). This was not observed in thinner looser hides, such as goatskins (29) and sheepskins (6-12). Transport of colloidal polymer particles to the inner portions of the matrix was obviously retarded so that polymer concentrated near surfaces in a fashion similar to that displayed by impregnants (41). This phenomenon will be discussed below in connection with the deposition mechanism. Finally an idealized drawing representing the preferential packing of coarse polymer deposited around individual fibers in a fiber bundle is presented in insert f. This morphology will be confirmed in the next paper (13).

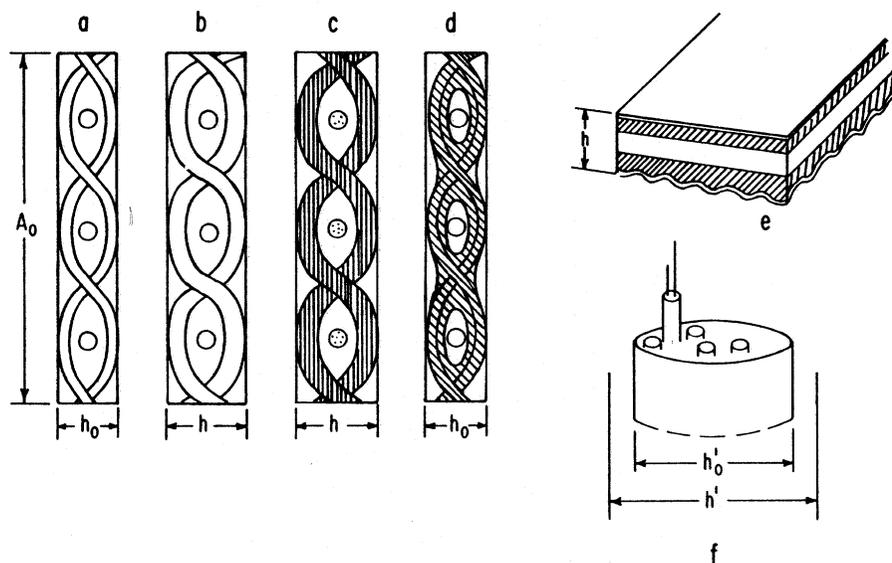


FIGURE 6. — Idealized models of the composites discussed in this work. Insert a, untreated 5-oz cattlehide, acetone-dried, showing two fiber bundles; insert b, polymer deposited from emulsion; insert c, insert b, but after benzene-extraction; insert d, location of bulk or solution polymerized monomers; insert e, cattlehide panel showing polymer preferentially deposited in layers at grain (top) and split corium regions (bottom) but with an apparent clear zone at the surfaces; insert f, schematic of fiber bundles with polymer deposited around fibers. Fibrils are indicated in one protruding fiber; these were only occasionally surrounded.

A theory relating density to composition based on the models in Figure 6 was presented in Part I (1) and will not be repeated here. This theory was based on the simple principle that the apparent density of any composite, ρ_a , g cc^{-1} , was the ratio of 1 g of the composite to the sum of volumes of the components, as

$$\rho_a = 1 \text{ g} / [\text{vol. hide substance} + \text{vol. polymer} + \text{vol. free space}] \quad (6)$$

where the volume of hide substance (essentially collagen) was obtained from its density, $\rho_r = 1.434 \text{ g cc}^{-1}$, obtained using a helium-air pycnometer (1). From the density, the effect of polymer composition on the extent of plumping (8) of the composite (increase in thickness, h in cm, Figure 6) can readily be predicted for any type of composite. For this prediction, the equation is

$$h = V/A = (1/W_1) / \rho_a \quad (7)$$

where V is the composite volume and A its area, which retains its initial state, A_0 , in Figure 6. However, the exact form of equation 6 will vary with the process used for deposition (1), based on the models in Figure 6.

A test of this theory is given in Figure 7 for composite materials made with BA + MMA. In insert A densities (curve fitted by computer, dashed line) are com-

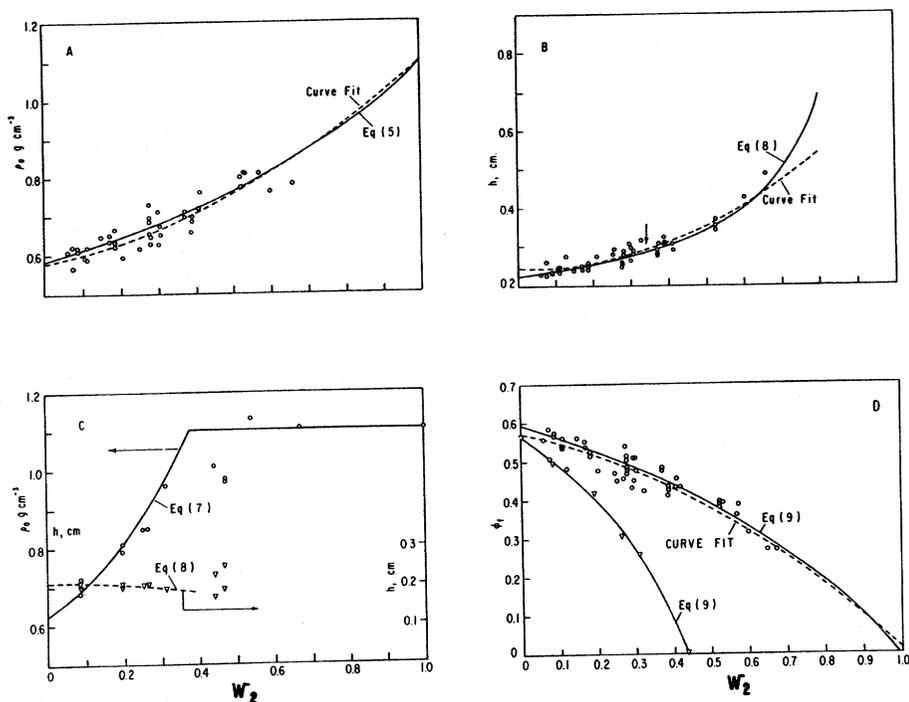


FIGURE 7. — Plot of apparent density, ρ_a (insert A) and specimen thickness, h , in cm (insert B) versus the weight fraction of polymer in the composite, w_2 for deposition of BA + MMA from emulsion. Plot of ρ_a and h versus w_2 (insert C) for BA + MMA composites formed by bulk or solution polymerization. Volume fraction of free space, ϕ_f , versus w_2 (insert D) for BA + MMA composites prepared by both methods.

$$R_i = K[V]^a \quad (10)$$

$$\text{so that } \ln R_i = \ln K + a \ln [V] \quad (10a)$$

where R_i is the rate produced by changes in each variable. Typical rate data obtained are shown in Figure 8 for changes in persulfate ion concentration (initiator

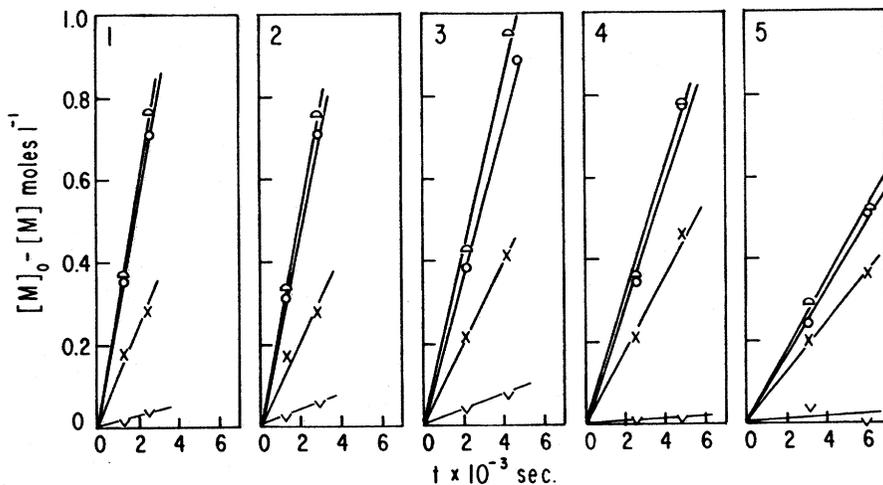


FIGURE 8. — Initial rate of monomer consumption versus time for the MMA composite system at various initiator concentrations. The order of the rate curves in each insert, top to bottom, is: R_x , R_a , R_b , R_c . Initiator concentrations, $[I]$ moles l^{-1} were: 1, 0.195; 2, 0.155; 3, 0.0750; 4, 0.0582; 5, 0.0402.

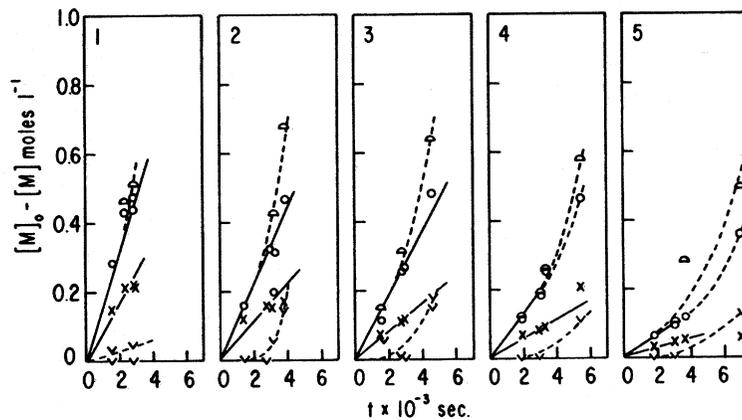


FIGURE 9. — Initial rate of monomer consumption versus time for the MMA composites at varied leather amounts. The order of the rate curves in each insert, top to bottom, is: R_x dashed; R_a , solid; R_b , solid; R_c , dashed. Leather concentrations, $[LH]$, moles l^{-1} , were: 1, 1.96; 2, 1.37; 3, 1.3; 4, 0.690; 5, 0.319.

concentration, $[I]$) and for leather amount in Figure 9. Total polymerization rate R_T is the curve of greater slope in each insert, the rate of deposition, R_d , the next curve, bound polymer rate of formation, R_b , third curve, and the rate of polymerization in the float R_f , the bottom curve in both figures. A plot of the rate as a function of the initiator concentration in accordance with equation 10a is shown in Figure 10. The slope of the lines is the exponential quantity a for the two polymerization loci, R_d and R_b in equation 10. It is called the exponential intensity factor for the variables shown in Table III. By matching experimental values of the exponential intensity factor a , rates of deposition, R_d , and rates of bound polymer formation, R_b , with corresponding values for emulsion theory, column 2, and graft theory, column 3, a choice may be made between operating mechanisms.

The overall results in Table III reveal that the controlling mechanism for the rate of deposition, R_d , for all three systems (MMA, BA + MMA, BA) is closer

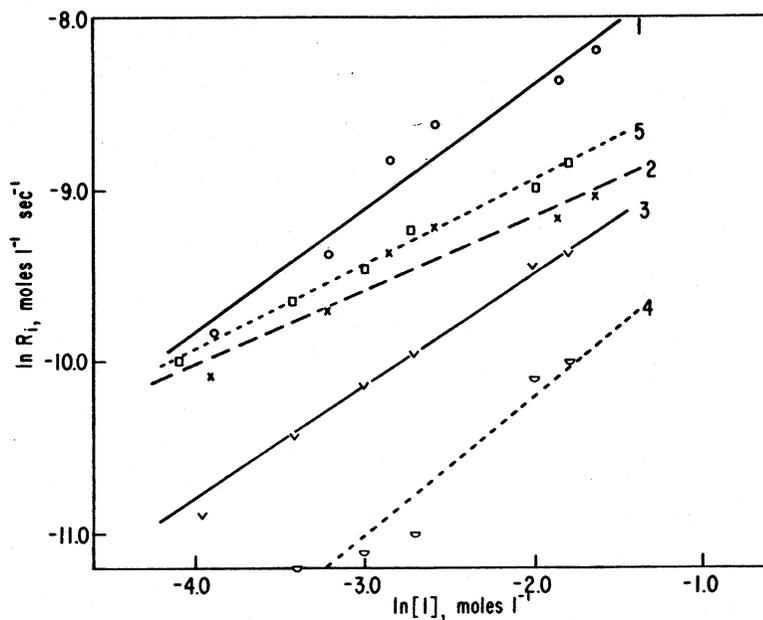


FIGURE 10. — Rate of polymerization, R_i , versus the initiator concentration, $[I]$, plotted in accordance with equation 10a for the following systems: curve 1, R_d , MMA; curve 2, R_b , MMA; curve 3, R_d , BA + MMA; curve 4, R_b , BA + MMA; curve 5, no leather, BA + MMA. The slope is the exponential intensity constant a for the variable, $[I]$ in equation 10 and for the data in Table III.

TABLE III

KINETIC EXPONENTIAL INTENSITY CONSTANT, a , OF EQUATION (10)
FOR ALL COMPOSITE SYSTEMS

Reaction Variable ^b	Emulsion theory equation 9	Graft theory equation 8	Intensity Constant, a							
			MMA ^c			BA + MMA ^c			BA ^c	
			R_d	R_b	R_d	R_b	R_d	R_b	R_d	R_b
[I]	0.4	0.5	0.723	0.444	0.657	0.841	—	—	—	
[M]	0	1.5	0	0	0	0	0	0	0	
[L]	0	0.5	0.885	1.05	0.636 \rightarrow 0 ^c	0.745 \rightarrow 0 ^c	0.667 \rightarrow 0 ^c	0.702 \rightarrow 0 ^c	—	
[S]	0.6	0	0.509	0.294	0.494	0.480	—	—	—	
[I] no leather					0.500					
[M] no leather					0					
[S] no leather					0.793					

^a Rates, R , in moles 1 sec⁻¹.^b Quantities in brackets are concentration terms. They are: initiator, [I]; monomer, [M]; leather, [L]; surfactant, [S].^c The dependence of the total polymerization rate, R_p , moles 1 sec⁻¹, decays to $a = 0$ in 1 hr of reaction at an average conversion of 17%. Initial $R_d = R_r$.

to that of the emulsion mechanism than that of the grafting mechanism. However the dependence (expressed by the intensity constant, a) on initiator concentration, $[I]$, was greater than either 0.4 or 0.5 specified for both mechanisms. This is clear evidence for a gel effect (section B) that would occur if monomer polymerized from accumulating buried radicals present in aggregating polymer masses in a confined space. In the absence of leather the dependence on $[I]$ was reduced to 0.5. Most significantly, the dependence on monomer $[M]$ was zero and was finite on surfactant $[S]$, providing strong evidence for a polymerization proceeding in emulsion. The effect on leather amount is deceiving. R_d and R_b both appear to be affected by leather amount initially, but experiments were presented (2) to show that the magnitude of the constant a rapidly decayed to nearly zero at around 20 percent conversion. The erratic behavior of the constant a for bound polymer rate, R_b , suggests that bound polymer is a secondary consequence of the rate of deposition and thus is not in control of the deposition process. In fact, unextractable polymer did not have to be grafted to be bound. It was demonstrated repeatedly in Part II (2) that when preformed BA + MMA polymer was used to impregnate cattlehide leather under conditions similar to *in situ* polymerization, the same weight percentage of bound polymer was found (50 percent) as was formed by emulsion polymerization. It may be concluded that the kinetic behavior suggests an emulsion polymerization that becomes unstable and deposits polymer within the leather matrix. Consequently high graft densities, except at fiber surfaces, appear unlikely. An alternate mechanism having greater statistical probability is presented below.

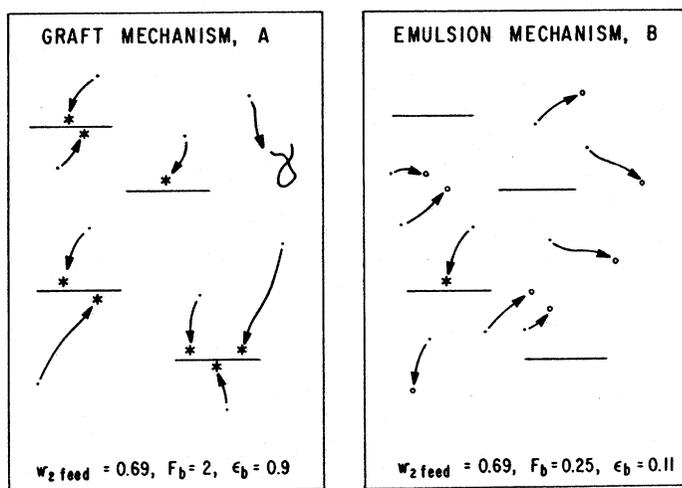


FIGURE 11. Schematic illustrating dominant grafting mechanism for the quantities indicated at the bottom (insert A) and dominant emulsion mechanism (insert B) for the same feed composition.

F. MECHANISM OF DEPOSITION AND BOUND POLYMER FORMATION

Figure 11, insert A, pictures, schematically, the consequences of a dominant grafting mechanism in view of the discussion in section A and section E. Nascent primary radicals formed slowly in the aqueous phase (reaction a, section A) preferentially attack collagen molecules and transfer their activity (stars) (reaction e, section A). If each of these grew chains of 300,000 molecular weight, the grafting frequency constant, F_b , would be two at the end of reaction when the monomer feed was 69 percent; graft efficiency would thereby be high. In contrast, insert B, if an emulsion process prevailed, radicals formed in the float would preferentially initiate and continue polymerization in isolated emulsion particles. Only occasionally would one attack a collagen molecule as pictured. If the feed was also 69 percent in monomer and branch length the same, F_b would be much more in line (F_b 0.25) with what was actually found experimentally, Table II, because efficiency, ϵ_b , was low. Consequently, it appears, Figure 12, as though emulsion particles are nucleated and grow conventionally (insert A) in the

DEPOSITION MECHANISM

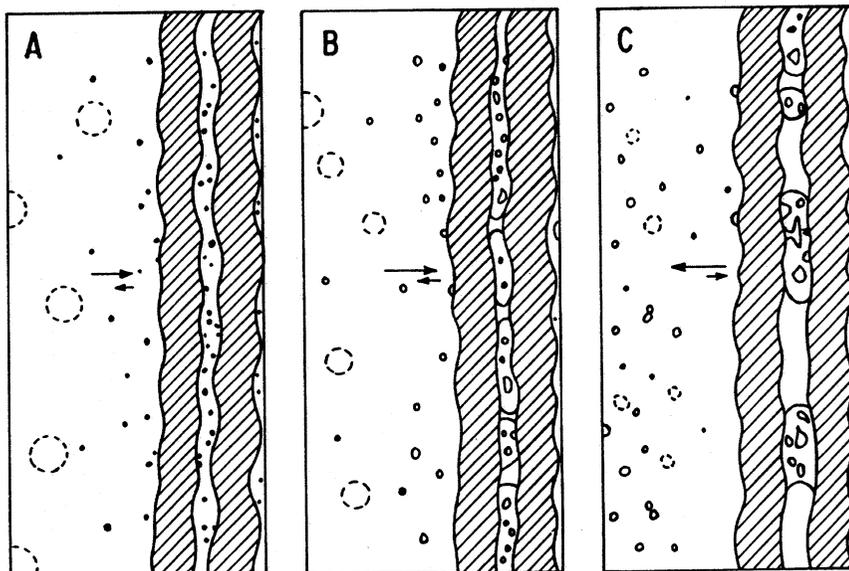


FIGURE 12. Schematic illustrating an emulsion polymerization just initiating (insert A) and continuing (insert B) in the vicinity of leather fibers (shaded) having diameters of $2 \mu\text{m}$, and situated at the edge of a fiber bundle. Aggregated polymer development is shown starting in insert B and causing fiber bundle expansion in insert C. Tiny circles are polymer particles and dashed circles are monomer droplets. Particles are drawn slightly larger than to scale to enhance visibility.

float but also preferentially in the matrix within fiber bundles, near individual fibers (shaded) which, as pictured, have diameters of approximately 20,000 Å. The overall scale here is only approximately correct (3, 45). Preferential initial growth in the matrix is required because it is known (2, 9) that persulfate ions migrate rapidly to positions within the matrix. Particles then grow, insert B, being fed by diffusion from micron size droplets (dashed circles) of monomer which decrease in size as polymerization continues. Particles in the leather become unstable and coagulate, forming adhering islands between the individual fibers. At saturation, insert C, fiber bundles have increased in size because of massive packing of polymer between fibers as shown. Polymerization now takes place rapidly in the float. Monomer droplets by this time are small and finally vanish at the end of polymerization. The development of layers (Figure 6, insert e) and the formation and migration of occluded radicals can best be seen in Figure 13. Insert 1 shows (braces) sections consisting of an assembly of fiber bundles situated near the edge of a panel. Polymer aggregates start to form in the bundle around fibers, and increase in size (inserts 2 and 3). Buried (occluded) radicals (dots) also

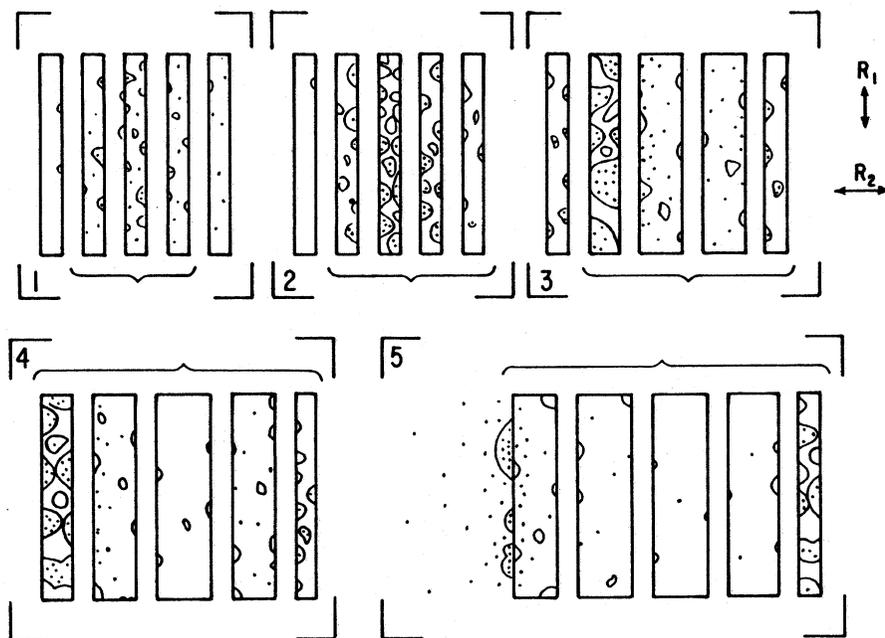


FIGURE 13. Schematic diagrams representing the deposition of polymer in leather as a function of time (time increasing, 1 to 5). Diagram represents individual fiber bundles selected at different positions in the layered region (the region in braces). R_1 is the rate of fiber fitting; R_2 is the rate of fiber expansion. R_1 exceeds R_2 in inserts 1, 2, 3, but is exceeded by R_2 in 4 and 5.

accumulate. Monomer diffuses through the polymer layer to the occluded radicals and polymerizes (insert 3), thus expanding the bundles (inserts 3 and 4). In this fashion the polymer layer (brackets) grows in size while the occluded radical population is swept toward the panel edge because of greater resistance of monomer diffusing toward the interior. Finally (insert 5), polymerization actively is transferred to the float where polymerization continues at a fast rate because of the large number of active centers and layer growth ceases. This morphology will be confirmed in the next paper (13). Bound polymer in this scheme would result from polymer-to-polymer chain transfer to yield insoluble cross-linked polymer (observed, 20 to 50 percent of bound (1)) and by strong adsorption and entanglement at the large fiber surface. It is also at this interphase that most of the truly grafted polymer would form. Immobilization of relatively thick polymer layers (5,000 Å) near surfaces that then can resist removal by solvation, have been reported (14c).

Summary

From data on composite materials made by polymerizing three acrylate monomers (MMA, BA + MMA, BA) into cattlehide by two processes, it was concluded that grafting played a minor role in forming the considerable amount of bound polymer observed. In the emulsion process developed at this Center, declining bound polymer efficiency and branching frequency as monomer amount was incrementally increased to very large amounts provided strong evidence that graft polymerization did not control the mechanism. Support for this was obtained from kinetic constants for change in reaction variables which favored an emulsion process that became unstable. As an alternative, a deposition mechanism for the aqueous process was suggested, involving the aggregation of growing polymer particles from emulsion to form macrodimensional layers near the surface of fibers, fed by diffusing monomer to occluded radicals to continue deposition and expand the leather. The relation of this mechanism to that of simple impregnation of preformed polymer was demonstrated. Bound polymer present in leather apparently resulted from polymer-polymer crosslinking in confined spaces and from strong immobilization of multilayer adsorption and minor grafting to fiber surfaces. The bulk-solution process also studied in this work was designed to produce composite materials having different densities and mechanical properties.

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