

# Fabrication Methods for Latex-Based Elastomer Composites Reinforced with Long Discontinuous Fibers

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## SYNOPSIS

Rubber- or elastomer-based composites have so far been reinforced with randomly dispersed staple fibers of very short lengths. In this work, methods have been devised to produce composites where the dispersed fibers have considerably greater lengths. This achievement was possible by applying the rubber or elastomer as latex when mixing it with the fibers. As compared with earlier processes, the viscosity is considerably lower, thus permitting easier mixing so that longer staple fibers can readily be used.

## INTRODUCTION

This research work involves preparation methods for elastomer composites with rubber matrix using latex as raw material for the matrix. The composites were reinforced with staple fibers, which were dispersed in the matrix in randomly distributed directions and locations. Staple fibers are here regarded as cut or chopped fibers, which can either be bonded to each other as a nonwoven mat or they can be unbonded, that is, not bonded to each other.

The methods used earlier to reinforce elastomers with textile staple fibers have allowed only short or very short fibers to be used. The maximum lengths have been about 8–12 mm. For the reinforcement of elastomers, especially rubber, most of the regular textile fiber materials have been used: cotton, rayon, nylon, and polyester. Also other fiber types can be used: glass, aramids, steel, and carbon. Shredded textile waste is also used.<sup>1,2</sup>

Mixing difficulties, deriving mainly from the high viscosity of most common elastomer materials during the processing stages, have caused problems in the introduction of short staple fibers for composites with elastomer matrix, especially when traditional elastomer processing methods have been used.<sup>1,3</sup> The reason for this is that the high viscosity of rubber

compounds necessitates the use of very strong forces when mixing the fibers into the matrix. In the process, strong forces act on the fibers resulting in strong breakage, so that the reinforcement potential of the fibers is lost to a considerable extent in many cases.<sup>4</sup> The only way to incorporate longer fibers has been to laminate them in the form of fiber strands, for example, as cords or webs between layers of rubber compounds.

Short staple fibers have gained importance for reinforcement of elastomer composites primarily because of their improvement of processing conditions during elastomer products fabrication and due to improvements in certain mechanical properties of the elastomer products. Short fibers are less effective in reinforcing low modulus materials than materials of higher modulus.<sup>1,4–6</sup> Since it is the continuous phase of the composite, the matrix must act not only as a protective encapsulant or binder of the fibers, but also as the stress transfer medium between the applied forcefields and the discontinuous reinforcing fibers.<sup>4,5,7,8</sup>

One way to overcome the disadvantages of the high viscosity of rubber compounds is to introduce the rubber matrix into the composite in the form of latex. Natural and synthetic latices have a viscosity that is, for practical purposes, somewhat higher than that of water. Latex consists of polymer particles, 0.5–5  $\mu\text{m}$  in diameter dispersed in water; the particles are kept separated from each other by electrical charges. Negatively charged latices typically have pH 10–12 and positively charged types have a pH

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of around 4.5. In the coagulation process, the particles stick together and form larger bodies. The coagulation process can be done either chemically, by changing the pH, or thermally, by elevating the temperature of the latex, or a combination of both.<sup>9</sup>

There is a scarcity in the literature studied of reports of the influence of longer staple fibers on elastomer composites. One major drawback in the fiber reinforcement of rubber-based elastomer composites thus far has been the difficulties experienced in combining fibers of greater aspect ratio, that is, ratio fiber length to fineness, into the matrix.

## EXPERIMENTAL

The methods chosen for this study depended on the raw material used, both for the matrix and for the reinforcement fibers. The latex types were natural or synthetic latices as delivered, in thickened form or in the form of a coagulate-water mixture.

One method used was to mix unbonded staple fibers into latex. Another method was to impregnate preformed, bonded structures of staple fibers with latex, and then to remove the water content from the latex. One way to remove the water was by evaporation or drying. Another way was by first coagulating the latex and thereafter to press out mechanically the water from the fiber-polymer composite material, either by flat plate presses (hydraulic and mechanical) or by roll press. Residual water was then removed.

## Materials

### Latex

The natural latex had an addition of 6½ parts vulcanizer per hundred parts dry rubber. The vulcanizing system consisted of 57% zinc oxide by weight,

24% sulfur, 16% zincmercaptotiazol, and 3% difenylguanidine. Coagulation agents for chemical coagulation citric acid in ethanol solution or CaCl<sub>2</sub> in water solution were used. In the heat coagulation experiments, a functional organopolysiloxane coagulation agent (Coagulant WS) was mixed with the latex. Nonionogenic surfactant (Emulwin W) was added to the latex to improve the wetting of the fibers (Coagulant and Emulwin are products of Bayer Ag).

Synthetic latices Primal HA 16 acrylic latex (Rohm and Haas) and Impranil DNL, or the identical Acramin PUD aliphatic polyester polyurethane dispersion latex (Bayer Ag), were used.

Viscosity is a most important parameter when a latex-based matrix is to be mixed effectively with fibers. The viscosity of a latex can be controlled either by adding a thickening agent, by decreasing the water content (concentration), or by coagulating the latex. In these cases the viscosity is increased. There is no practical way of lowering the viscosity of latices. As chemical coagulation agents citric acid as ethanol solution, CaCl<sub>2</sub> as water solution, or Coagulant WS (Bayer) were used.

### Fiber Material

The unbonded staple fibers were Grilon NV 2, polyester of 1.7 dtex fineness/6 mm length, 1.7 dtex/12 mm, 3.3 dtex/18 mm and 6.7 dtex/26 mm. Bonded staple fiber was used in the form of fiber mats, which were made by carding and crosslapping. Some qualities were bonded mechanically by needling and others were bonded chemically. In all cases, the fiber material used was polyester. The basis weights varied between 85 and 205 g/m<sup>2</sup> and the thickness varied between 5.25 and 9.70 mm. The properties of the fiber mats are presented in Table I.

Because this study concentrated on devising favorable manufacturing technologies for latex-based

**Table I Properties of Reinforcement Fiber Mats**

Mat						Tensile and Elongation								Mat No.	
No.	Fiber Type Fineness/ Length dtex/mm	Finish	Manufg. Method	Basis Weight w g/m <sup>2</sup>	Air Perme- ability l/m <sup>2</sup> s	Bend. Resist		Thick- ness Shirley d mm	MD Force F N	Elong %		CD Force F N	Elong %		
						⊥	=			Break	Tot.		Break		Tot.
4	6.6/64	None	Needling	205	1695	30.0	40.0	5.25	180	145	157	264	119	137	4
8	7.3/53	None	Chem. Bond.	87	3860	165	87	9.65	13.8	29	64	16.8	48	82	8
9	6.7/64 4.4/100	None	Needling	530	307			1.9							9
10	7.2/52	None	Needling	85	3990	160	49	9.70	13.7	26	60	15.3	49	84	10

composites, no particular attention was paid to the fiber/matrix bond. Thus the fibers or mats were used without any previous surface treatment by dipping or bonding agents, that is, the reinforcement fiber materials were used as delivered. No coupling or bonding agent was added to the elastomer.

## TEST METHODS

The mats were tested for basis weight according to standard test method SFS 3192.<sup>10</sup> The air permeability through the reinforcement fiber mats was measured with an air permeability measurement apparatus (type 843a, Karl Frank GmbH, Weinheim-Birkenau, GFR), pressure difference 1 mbar, according to standard test method SFS 4782.<sup>11</sup> The air permeability for multilayer structures was measured with the mats placed on top of one another in the Frank apparatus.

Tensile strength and elongation at break of the mats were tested on an Alwetron type 14-1 tester (Ab Lorenzen & Wettre, Stockholm, Sweden) according to test method EDANA 20.2-73.<sup>12</sup>

Stiffness, as well as resistance to bending of the mats, was measured by the Cantilever method according to the standard test method SFS 4861.<sup>13</sup>

Thickness of the mats was measured with the Shirley Thickness Gauge (Shirley Developments Ltd, Manchester, UK) according to standard test method SFS 3380.<sup>14</sup>

The actual length of the fibers present in the mats was tested by picking fibers out of the mat and laying them straight out on a fabric of black velvet and measuring the length. 10 fibers were picked to form a population representative for each fiber dimension told by the manufacturer to be included in the mat. The picking was done with tweezers and fibers that broke during the picking operation were discarded. The average value of the 10 fibers in each population was taken as the actual length of the fiber as present in the mat.

Inherent viscosity of latex was measured with a Brookfield Model RVT viscosimeter (Brookfield Engineering Laboratories Inc., Stoughton, MA, USA).

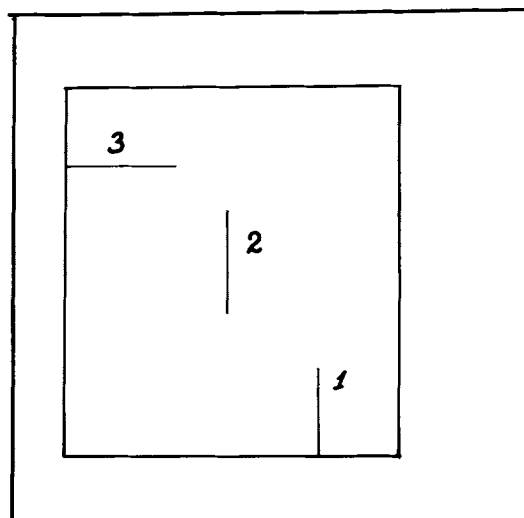
The temperature distribution on the composite sample plates after coagulation was tested using a thermometer with a PT-100 sensor. Temperature was tested on 6 different sites: one in a corner, one in the middle of each of two edges, one half-way from the center to each of two edges, and one in the center.

The evenness of the energy distribution in the microwave oven was tested using a plate of expanded polystyrene. The plate had 144 identical cups evenly distributed on its top surface. The cups were equally filled with water of room temperature (*ca.* 5 mL). The plate was inserted in the oven, heated 1 min, and the temperature of the water in the cups was measured and recorded immediately after the heating.

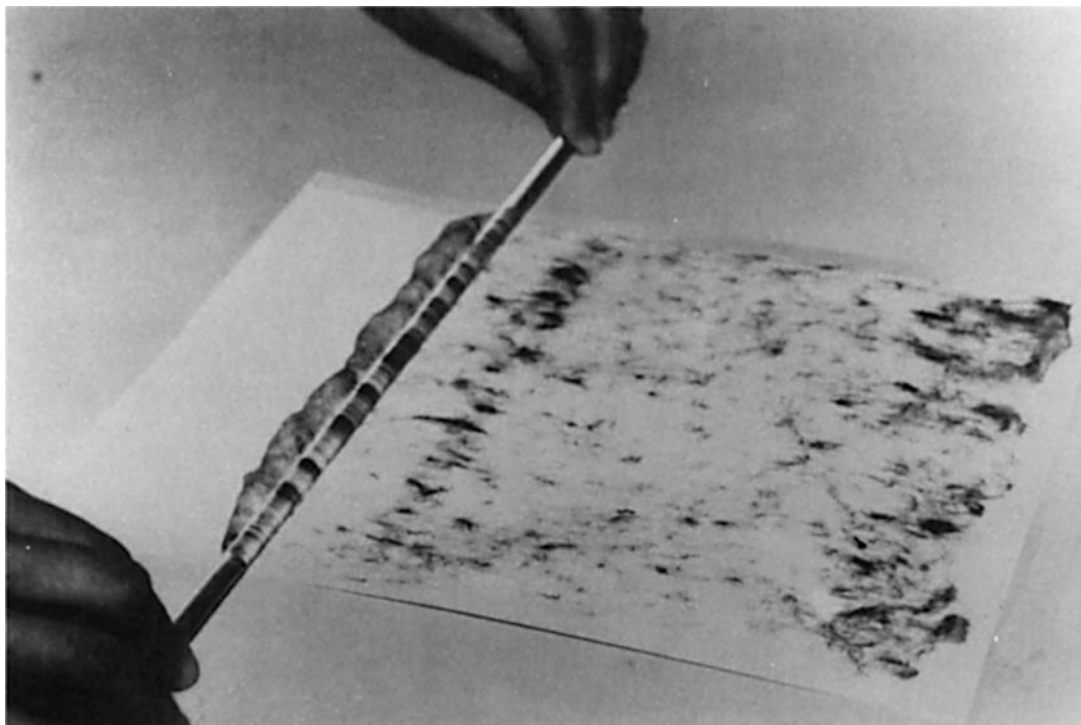
The coagulation temperature for the latex was tested by keeping 50 mL of latex in a water bath, stirring it with a thermometer until coagulation occurred. At that point in time, the coagulation temperature was noted from the thermometer (method suggested by Bayer Ag).<sup>15</sup>

The homogeneity of the composite samples was assessed by cutting the samples according to Figure 1 and viewing the cut. The scale was: 0 = surface of cut completely homogeneous, 1 = fiber mat slightly detectable but no void, 2 = mat partially unsaturated with voids in matrix, 3 = large unsaturated areas of mat and large voids in matrix. The homogeneity value for each sample was listed as the average of the assessment values for three sites.

The evenness in distribution of the fibers in a latex-fiber mixture was tested so that the fiber-latex mixture with fibers dyed dark was spread out over a white board, as shown in Figure 2, and was dried at 105°C. The dark fibers were clearly visible against the white background. The dispersion of fibers was judged by comparing the samples to each other.



**Figure 1** Sites of cuts for homogeneity assessment in composite sample, 1 = machine direction at edge, 2 = machine direction at center, 3 = cross-machine direction at edge.



**Figure 2** Evaluation of fiber distribution.

The length of fibers in the finished composite samples with polyurethane matrix was tested by heating a 300 mm × 300 mm sample in a beaker with 100% purum acetic acid for several hours until the matrix had disintegrated completely. Thereafter, the remaining fiber mat was lifted out of the beaker, washed with water, and dried in an oven. The fiber lengths in the mat were analyzed using the method described above.

## FABRICATION

Pretrials of viscosity adjustment were made using both natural and synthetic latices. To 200 g Primal HA 16 were added 4 g Acrysol ASE 60, whereafter Conc.  $\text{NH}_3$  was added gradually, and the changes in inherent viscosity were measured with a Brookfield viscosimeter, and were recorded as shown in Figure 3.

The series of experiments consisted of:

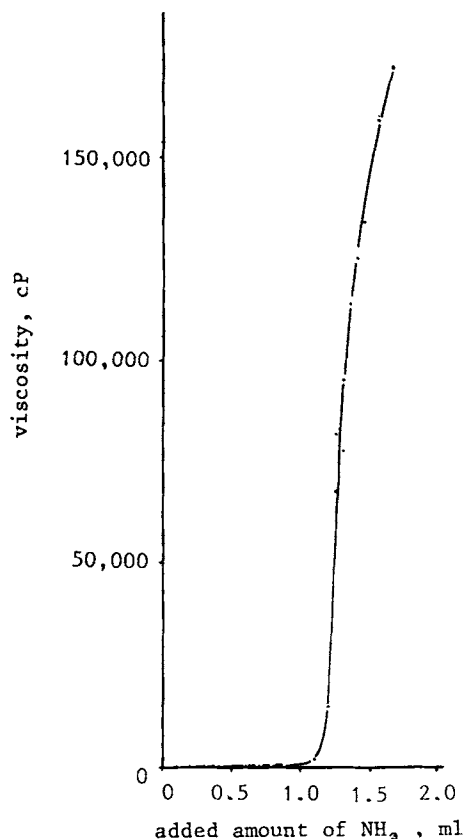
1. Mixing of unbonded discontinuous fibers into a latex of various viscosity,
2. Mixing of loose discontinuous fibers into coagulate of latex,
3. Impregnation of reinforcement structures with coagulated latex,
4. Impregnation of reinforcement fiber structures with latex and subsequent coagulation.

The general dispersibility of unbonded staple textile fibers with latex liquids was tested by dispersing the fibers with a Heidolph propeller agitator.

### Mixing of Unbonded Fibers into Latex

One and one-half g Acrysol ASE 60 was added to 100 g Primal HA 16 acrylic latex and was thickened by adding gradually  $\text{NH}_3$  to correspond to approximately 170,000 mPa s viscosity. To this latex preparation 2.25 g polyester fibers, 1.7 dtex/6 mm were added and mixed with a Heidolph agitator at 1300 rpm. The effect of time on the dispersion was tested for evenness of fiber distribution by the test method described above. The mixing times were 1 min, 2 min, 4 min, 6 min, 8 min, and 10 min. The trial was repeated in two experiments using longer Polyester fibers of the dimensions 1.7 dtex/12 mm or 3.3 dtex/18 mm, respectively. Otherwise the conditions remained the same as in previous experiments with thickened latex.

Entanglement around the propeller shaft was observed after 10 min mixing with fibers of the dimensions 1.7 dtex/12 mm and 3.3 dtex/18 mm, but not with 1.7 dtex/6 mm fibers.



**Figure 3** Viscosity change of synthetic latex (Primal HA 16) during thickening operation (Acrysol thickened with NH<sub>3</sub>).

A thicker composite sample was formed by thickening 100 g Primal HA-16 acrylic latex with Acrysol ASE and NH<sub>3</sub>, as described earlier, and by adding 2.25 g dyed polyester fiber 3.3 dtex/18 mm. The mix

was agitated with the Heidolph propeller mixer at 1300 rpm for 10 min. The mixture was then poured onto a clock glass and dried at 105°C in an oven. A control cake, without fibers, was made in an identical manner.

In a following experiment, unbonded staple fibers (3.3 dtex/18 mm polyester) were processed through a Shirley Analytical Fiber Opener and were mixed with latex as above. The mixture was then formed into a sheet and dried at 105°C for 15 h. The fibers were observed to distribute better into the latex than in a corresponding experiment with unopened fibers. Air removal was tried by vacuuming the fiber-latex mixture in a desiccator at 48 kPa absolute pressure before forming the sample, but air bubbles remained to a great extent in the sample.

**Studies Involving Latex Coagulation**

The latex was coagulated either chemically, thermally, or by a combination of both methods. For chemical coagulation Na<sub>2</sub>O<sub>2</sub>O<sub>5</sub>, CaCl<sub>2</sub>, or citric acid were used. For thermal coagulation either a regular or microwave oven was used. During the coagulation, the inherent viscosity of the latex increased considerably, but was impossible to measure exactly with the available instruments. In the rotating viscosimeter of the Brookfield type, the coagulated latex particles stuck to the spindle.

Coagulated or coagulating latex was used in three ways to form elastomer composites. One way was to mix unbonded staple fibers into coagulated latex. The second way was to first coagulate the latex, followed by impregnation into a structure of bonded staple fibers. The third way was to impregnate non-

**Table II** Studies Involving Latex Coagulation

Mixing Order and Methods for Coagulate/Reinforcement Mixing	Coagulation Processes	Water Removal Process
Unbonded discontinuous fibers into coagulate	Coagulation outside the preformed bonded fiber structure	Pressing Drying
Coagulate into preformed bonded fibers structure	Coagulation inside the preformed bonded fiber structure	
Latex into preformed fiber structure before coagulation	Coagulation combined with mixing latex and unbonded discontinuous fibers	
	Chemical coagulants	
	Combination of heat and chemical coagulation	
	Regular oven	
	Microwave oven	

coagulated latex into a reinforcement structure of bonded discontinuous fibers and after that the latex was coagulated inside the fiber mat. Thereafter the water content was removed from the coagulated latex. The items studied are listed in Table II.

#### **Mixing Unbonded Staple Fibers into the Coagulated Matrix**

Fifty g Impranil DNL polyurethane dispersion latex was coagulated in a glass beaker with 2.5 g  $\text{Na}_2\text{S}_2\text{O}_5$  dissolved in 10 mL  $\text{H}_2\text{O}$ , under agitation by magnetic agitator. One-half g dyed polyester fiber, Grilon 1.7 dtex/12 mm, was added to the coagulated mixture and was mixed by hand with a glass rod. The dispersion of the fibers was judged by viewing the mixture. The fiber-coagulate mixture was collected on a fabric, wrapped, and was dewatered using a mechanical press. The resultant fiber-matrix composite was dried at  $105^\circ\text{C}$  to give a compact cake-like elastic sample. The sample was cut to judge homogeneity and occurrence of voids.

#### **Impregnating Coagulate into Structures of Bonded Staple Fibers**

One hundred g latex (Impranil DLN) and 5 g  $\text{Na}_2\text{S}_2\text{O}_5$  were mixed until coagulation. The mixture was thereafter spread on both surfaces of a chemically bonded  $87\text{ g/m}^2$  fiber mat (No. 8, Table I). The mat was then pressed four times through nip rollers, with the pressure increased between each

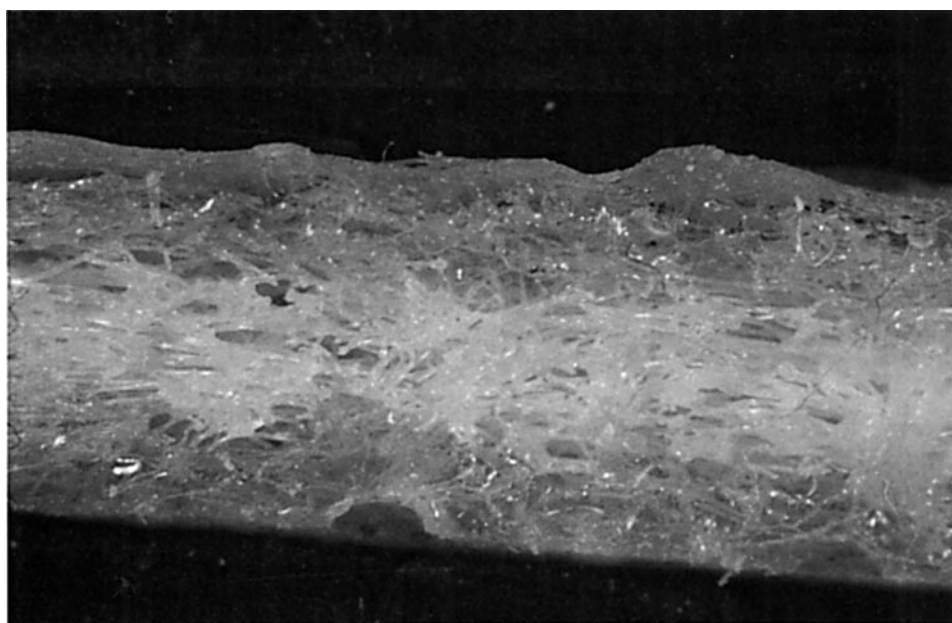
run. The sample was dried and cured at  $105^\circ\text{C}$ . The sample was cut to give a view of the cross section, as shown in Figure 4, for judgement of homogeneity and distribution of matrix and fiber material.

#### **Coagulation Inside the Bonded Mats of Staple Fibers**

*Preliminary Trials.* Coagulation inside the bonded mats of staple fibers was done using chemical coagulation alone or thermal and chemical coagulation in combination. As coagulating chemicals a solution of citric acid in ethanol (ratios 5 : 95 or 15 : 85 by volume), or  $\text{CaCl}_2$  (20% water solution), or Coagulant WS (Bayer AG) were used. For thermal, coagulation both regular and microwave ovens were used.

As reinforcement structures, needlebonded mats of polyester were used (No. 8, Table I). The samples in these experiments were cut to squares having edges with lengths varying between 8 and 30 cm.

*Chemical Coagulation.* The conditions during, as well as the results from, the experiments are listed in Table III. For Trials 11–20, Table III, needled  $205\text{ g/m}^2$  polyester mat (No. 4, Table I) was used. Natural latex with vulcanizer and stabilizer included was used for all experiments. The general procedure for Trials 11–20 was to immerse the mat into the coagulant solution in a beaker. Thereafter the pretreated mat was immersed in a latex bath where it



**Figure 4** Cross section of composite sample, coagulate forced into reinforcement mat.

**Table III Elastomer Composites with Chemical Coagulation. Experimental Conditions**

Trial No.	Mat <sup>a</sup> Dry Weight	Pretreatment Citr. Acid + Ethanol Coagulant		Coagulation Process		Water Removal		Vulcanization Time h	Weight after Vulcaniz. g	Rubber % of Mat Weight	Homog. Assessm. <sup>c</sup>	Comments
		Ratio	Condi- tion	Rubber Type	Physical Treatment	Press Type	Pressure MPa					
11	4.03	15 : 85	Dried	NR Latex 100%	Immersing, Press with PP-Spatula	2× Roll Press	—	—	42.85	963	1.33	
12	3.86	5 : 95	Dried	Same	Same as above	2× Roll Press	—	—	17.78	361	1.0	
13	4.11	15 : 85	Dried	Same	Same as above	2× Roll Press	—	—	33.3	710	0	
14	4.3	5 : 95	Wet	Same	Same as above	2× Roll Press	—	—	20.55	378	1.33	
15	2.01	20 : 80	Wet	Same	Same as above	2× Roll Press	—	1.5	16.17	705	2.3	
16	1.88	20 : 80 <sup>b</sup>	Wet	Same	Same as above	2× Roll Press	—	1.5	17.96	855	2.0	
17	1.93	20 : 80	Dried	Same	Same as above	Hydr. Press	6.1	2	19.45	908	0.67	Distorted in Roll Press
18	1.98	20 : 80	Dried	Same	Same as above	2× Roll Press	—	1.5	20.54	937		Distorted in Roll Press
19	1.87	20 : 80	Pressed	Same	Same as above	2× Roll Press	—	1.5	11.85	534		Distorted in Roll Press
20	1.94	20 : 80	Wet	Same	Same as above	Hydr. Press	6.6	2	10.01	416	2.67	

<sup>a</sup> Mat needed 205 g/m<sup>2</sup> PES (No. 4) for all trials.

<sup>b</sup> 0.2 g Triton X added.

<sup>c</sup> Homogeneity assessment of cut through sample: 0 = completely homogeneous, 1 = Fibers slightly detectable, 2 = Mat incompletely saturated, voids, 3 = Large unsaturated areas. The numbers listed are averages of three cuts.

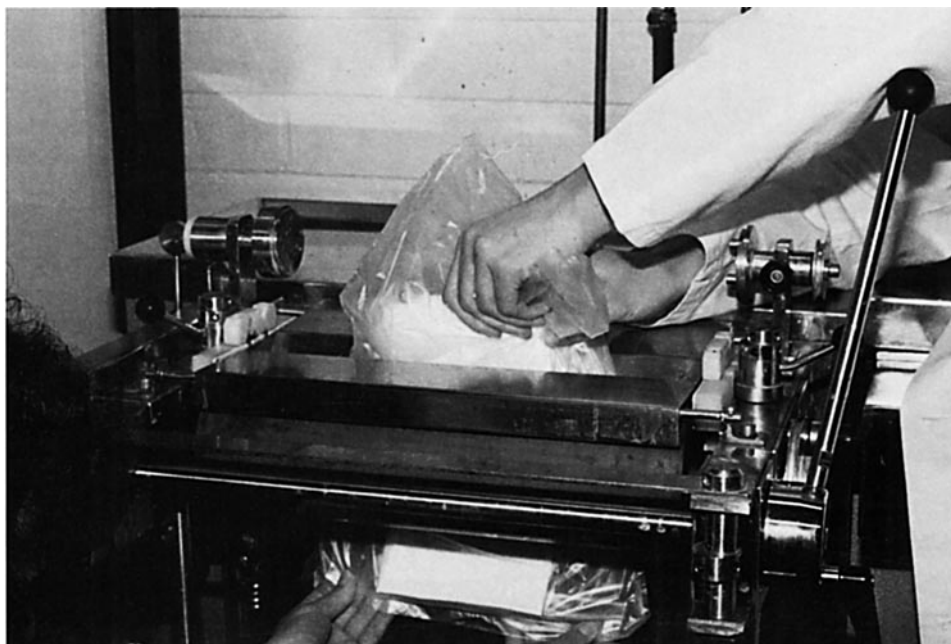


**Figure 5** Latex impregnation into reinforcement mat.

was agitated with a polypropylene spatula to make sure latex was introduced all through the sample, as seen in Figure 5. Thereafter water and excess latex were pressed out as shown in Figure 6. The spatula and the press tools were of well-releasing materials, for example, polypropylene or polyethylene to ensure a tack-free processing. After press-

ing, the sample was vulcanized in an oven at 105°C for 1½–2 h.

Comparative experiments were made by drying the added coagulant in the mats before immersion into latex (Trials 11, 12, and 13, Table III) and by immersing the wet coagulant-treated mat into the latex (wet-in-wet, Trials 14 and 15, Table III).



**Figure 6** Water removal with roll press after coagulation.



Working wet-in-wet simplifies the processing. The effect on the coagulation by surfactant was tested by adding Triton X-100 to the coagulant impregnation bath (Trial 16, Table III).

Coagulation could be seen to begin during impregnation by a change in color shade shortly after the first contact between latex and the fibers covered by coagulating agent.

*Combined Heat and Chemical Coagulation.* Natural latex with added vulcanizer and stabilizer was used in the heat coagulation trials (Trials 21–33, Table IV). In another experiment, polyurethane latex (Acramin PUD) was used. Coagulating agent (Coagulant WS) and surfactant (Emulvin W) were added to the latex prior to impregnation. The measured coagulation temperature for the natural latex was 47–48°C and for the polyurethane latex it was 63°C with the test method mentioned (Bayer method). As reinforcement for the experiments with natural latex needled polyester mat (No. 4, Table I) was used. The mats were impregnated with latex in the same manner as described earlier, but they were not pretreated with any coagulant and no coagulation could be seen during the impregnation.

In the experiment with polyurethane latex, a mat with 6.7 dtex/64 mm and 4.4 dtex/100 mm polyester fiber (No. 9, Table I) was used. Mat pieces, size 30 cm × 30 cm, were immersed into a mixture of 700 g Acramin PUD, 8.05 g Emulvin, and 5.39 g Coagulant WS, using the same method as described earlier.

A trial series was performed to compare the microwave oven and the regular oven for the coagulation and to investigate the differences between these methods of heating for coagulation of natural latex inside a reinforcement fiber structure. The microwave oven was a Philips M 510. As regular ovens a Memmert type UL 40 (Memmert, Schwabach, FRG) or a Heraeus type RT 500 (W. C. Heraeus GmbH, FRG) were used.

The coagulation times for the samples with natural latex matrix varied from  $\frac{1}{2}$  to 8 h in the regular oven (Trials 21–23, 31, and 33, Table IV) and 0.8 to 48.5 min in the microwave oven (Trials 24–30 and 32, Table IV). The coagulation of the sample with polyurethane matrix was made at 70–75°C, 1 h, 20 min, in regular oven.

After coagulation in the microwave oven, the temperature of the elastomer sheets was measured directly after taking them out of the oven according to the temperature measuring system described under tests.

### Water Extraction

After coagulation in the oven, the samples were pressed for water removal. The effect of different pressing methods was tested by comparing roll and flat plate pressing, as shown in Figures 6 and 7. The roll press was a foulard type Matis HFR 30379A (Werner Matis Ag, Zürich, Switzerland), the hydraulic flat press was a type MKH E 60 M (Keski-Suomen Teräsrakenne, Jämsänkoski, Finland), which was capable of 250 kN and the mechanical hand lever press from Vilh. Pedersen, Hoeng, Denmark, with a calculated max capacity of 13 kN. In the roll press, polyethylene films were used as seen in Figure 6; in the flat press, polypropylene sheets were used as shown in Figures 7 and 8. Strong monofilament fabrics between the pressing surfaces and the sample facilitated the removal of water. The samples were pressed at 0.33 MPa in the hand lever press (Trials 32 and 33), 3 MPa (Trials 27 and 28), 5–6 MPa (Trials 21, 22, and 23) and 6–7 MPa (Trials 29 and 30). The trials are reported in Table IV. In the roll press, the samples distorted badly (Trials 18 and 19, Table III, Trials 24 and 25, Table IV). The sample with polyurethane matrix was pressed in a flat press between strong monofilament fabrics at 2 MPa.

After water removal, vulcanization at 105°C for  $1\frac{1}{2}$  h was done for all samples made of natural latex. These conditions are generally used for natural rubber.<sup>2</sup> The vulcanization gave elasticity to the samples. The sample with polyurethane matrix was dried in regular oven at 105°C for 2 h.

The homogeneity of the composite samples was tested according to the method described in the "Test Methods" section. The values in Tables III and IV are the average values of homogeneity for three readings from each sample.

## RESULTS

An example of the increase of the inherent viscosity when a thickening agent is applied to a synthetic latex dispersion, of the type used in the experiments, is shown in Figure 3. Natural latices behave in a similar manner.

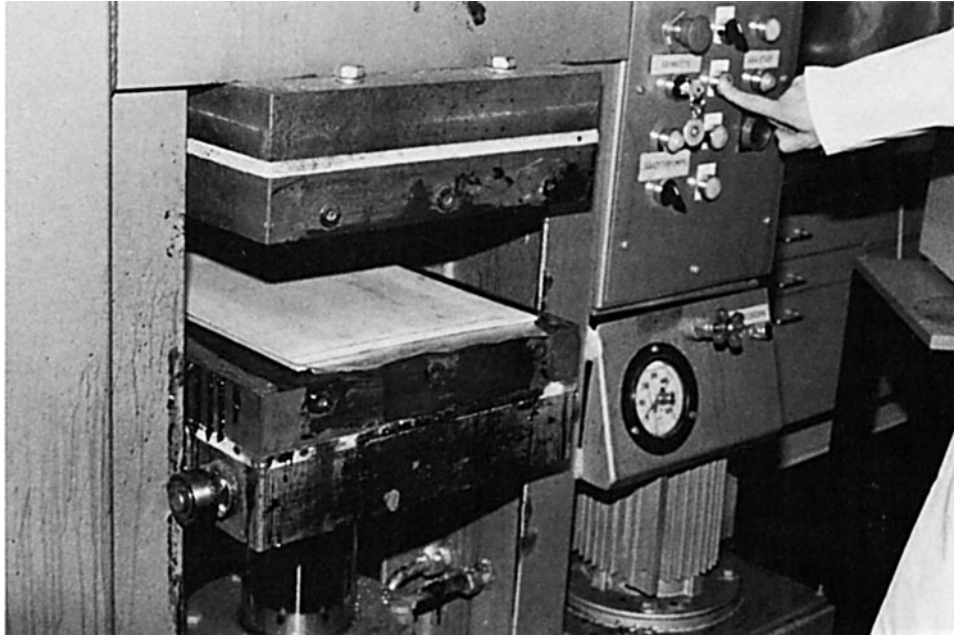
In the experiments of mixing unbonded 1.7 dtex/6 mm polyester staple fibers and acrylic latex with a Heidolph mixer, the best dispersion, when judged by spreading the fibers over a white board, was achieved after 8–10 min mixing. As a control, this experiment was repeated without thickening the la-

**Table IV Elastomer Composites with Heat/Chemical Coagulation. Experimental Conditions**

Trial No.	Mat <sup>a</sup> Dry Weight g	Pretreatment	Coagulation Process			Water Removal			Vulcanization Time h	Weight after Vulcaniz. g	Rubber % of Mat Weight	Homog. Assessm. <sup>b</sup>	Comments
			Rubber Composition	Oven Type	Temp. °C	Time	Press Type	Press. MPa					
21	1.405	None	NR Emulvin WS Water Coagulant WS 0.8%	Regular Oven	45	0.5 h	Hydr. Press PE-films	5.1	2	18.523	1218	0	
22	1.408	None	Same as above	Regular Oven	45	1.5 h	Hydr. Press PE-films	6.1	1.5	24.428	1635	0	
23	1.314	None	Same as above	Regular Oven	45	2 h	Hydr. Press PE-films	6.1	1.5	19.286	1368	0	
24	0.493	None	Same as above	Microwave Oven	45	2 min 1 min	Roll Press	—	1.5	7.09	1338	0	Badly Distorted
25	0.473	None	Same as above	Microwave Oven	55 45	2.4 min 1.5 min	Roll Press	—	1.5	7.53	1492	0	Badly Distorted
26	0.995	None	Same as above	Microwave Oven	41 40	2.5 min 1.5 min	Hydr. Press PES Wires	3.3	1.5	14.27	1334	0	More Coagulation on Edges
27	1.22	None	Same as above	Microwave Oven	40 50	1.0 min 1.5 min	Hydr. Press Ni-Nets	3.2	1.5	16.44	1248	0	More Coagulation on Edges
28	1.16	None	Same as above	Microwave Oven	44 48	0.8 min 0.8 min	Hydr. Press PES Wires	3.1	1.5	17.14	1378	0	More Coagulation on Edges
29	1.23	None	Same as above	Microwave Oven	50 60	1.0 min 1.0 min	Hydr. Press PES Wires + Ni-Nets	7.0	1.5	19.82	1511	0	More Coagulation on Edges
30	8.26	None	Same as above	Microwave Oven	28-39	21 min	Hydr. Press PES Fabric	6.0	1.5	126.40	1430	0	PES Fabric Stuck to Surface, More Coag. on Edges
31	7.92	None	Same as above	Regular Oven	50	5 h	Hydr. Press PES Fabric	7.5	1.5	158.80	1905	1	More Coagulation on Edges
32	9.06	None	Same as above	Microwave Oven	28-49	48.5 min	Mech. Hand Lever Press	0.33	1.5	141.5	1462	0.33	More Coagulation on Edges
33	9.16	None	Same as above	Regular Oven	29-33	8.2 h	Mech. Hand Lever Press	0.33	1.5	126.44	1280	0.33	More Coagulation on Edges

<sup>a</sup> Mat needed 205 g/m<sup>2</sup> PES (No. 4) for all trials.

<sup>b</sup> Homogeneity assessment of cut through sample: 0 = completely homogenous, 1 = fibers slightly detectable, 2 = mat incompletely saturated, voids, 3 = large unsaturated areas. The numbers listed are averages of three cuts.



**Figure 7** Water removal with flat press after coagulation.

tex and with 10 min mixing time. In the control experiment no homogeneous mixture could be obtained after 10 min mixing time; the fibers remained as lumps and could not be spread out evenly over the white board. The experiments show that the viscosity has a crucial influence on the distribution of

unbonded textile fibers in a liquid medium. When 1.7 dtex/12 mm or 3.3 dtex/18 mm fibers were mixed with latex, poor dispersion was achieved because of fiber entanglement into the mixer. Air was observed to be drawn into the fiber-latex mixture in the stage when fibers were added. The latex did



**Figure 8** Removal of sample after pressing.

not wet the fibers quickly enough to drive away all air before the mixer dragged the fibers into the mixture.

The dried composite sample of a mixture of thickened acrylic latex and dyed polyester fiber 3.3 dtex/18 mm formed a cake that was internally hollow. A control sample without fibers, made in the identical way, behaved likewise in drying. Cutting of the samples showed that the outer surface formed a tight film of polymer and that the matrix contained numerous smaller voids.

The experiment in which unbonded staple fibers were processed through a Shirley Analytical Fiber Opener before mixing with latex produced a sheet with air bubbles. The fiber distribution was better than when using unopened fibers. Treating the fiber-latex mixture with vacuum before drying did not remove the air inclusions.

The experiment in which polyurethane dispersion latex was coagulated, and 1.7 dtex/12 mm polyester fiber was added to the coagulated latex and was mixed, indicated that the fibers dispersed to an acceptable level into the coagulate. The experiment also showed that coagulation combined with pressing offers a practical method to remove the water without causing larger voids. An important factor in favor of the mixing and fiber distribution is, apparently, the viscosity. However, numerical measurements of the viscosity of the coagulated latex were unobtainable with a Brookfield Viscosimeter. When latex was mixed till coagulation and spread on both surfaces of a fiber mat, the coagulate stayed on both surfaces. Only minor traces could be detected in the internal parts of the mat, as seen in Figure 4; no thorough impregnation of the bonded fiber structure was achieved.

Releasing-surfaced press plate surfaces of polyethylene or polypropylene proved necessary to prevent tacking of the matrix elastomer to the press parts. This was noted when pressing out the water after coagulating latex inside the bonded fiber structure. Tools with poor releasing property were observed to tear lumps of coagulated material out from the samples when tool and sample were separated.

The fiber mats, pretreated with more diluted coagulant solution (Trials 12 and 14, Table III), produced less deposition in the mats than those pretreated with stronger solution (Trials 11, 13, 15, and 16, Table III). No significant difference in the amount of coagulated rubber could be noted between the coagulant treated mats that were dried before immersion into latex and the wet coagulant-treated

mats that were immersed into the latex (wet in wet) (Trials 11–16, Table III).

Even latex distribution throughout the mat during the coagulation process required mechanical working of the mat, for example, with a spatula during the impregnation stage (Fig. 7). Otherwise the coagulation concentrated on the surfaces, leaving the interior of the mat virtually void of latex.

The combined heat and chemical coagulation at 45°C for between  $\frac{1}{2}$  and 2 h (Trials 21–23, Table IV) clearly produced more coagulate precipitation from the latex than the chemical coagulation with citric acid (Trials 11–20, Table III).

In coagulation with microwave oven temperature, differences of up to 26°C could be noted between different sites of measurement, directly after taking the coagulated elastomer sheets out of the oven. Similar temperature differences were noted in testing the evenness of energy distribution of the microwave oven with the water-cup method described in the "Test Methods" section. The center of the oven especially tended to remain colder, leaving the corresponding part of the sample only partly coagulated.

Neither the temperature nor the time had any significant influence on the amount of polymer coagulated (Trials 25–33, Table IV). Compared to coagulation in a regular oven, the microwave gave a faster reaction, but level and evenness of temperature were more difficult to control. The combined heat and chemical coagulation method was found to significantly improve the homogeneity of the products compared with the purely chemical coagulation, judging from the homogeneity assessments as shown in Tables III and IV. Combined chemical and heat coagulation gave better homogeneity than chemical coagulation, as shown in Table IV. Chemical coagulation resulted in voids occurring mostly in the interior of the sample sheets, leaving the fiber structure uncovered by rubber.

Uncontrolled water removal from the sample surface destroyed the surface of the composite sample. Placing strong monofilament fabrics between the pressing surfaces and the sample made the removal of water more even.

The homogeneity, when tested according to the method described in the "Test Methods" section, was found to depend on the method of pressing after the coagulation step. The roll press gave uneven homogeneity (Trials 11–17, Table III). The hydraulic press gave practically completely homogeneous samples at pressures between 3.1 and 7.5 MPa (Trials 21–29, Table IV). The mechanical hand le-

ver press (approx. 0.33 MPa) gave somewhat less homogeneous samples (Trials 32 and 33, Table IV).

The length of the fibers in the composite sample with polyurethane was tested with the test method described earlier. The average length of fibers picked from the processed composite sample was 62.1 mm, and the average length of the fibers picked from the fiber mat was also 62.1 mm.

## DISCUSSION

### Mixing Unbonded Staple Fibers into Latex

Mixing unbonded staple fibers into latex resembles dispersion of fibers into water, which is done in wet-laid nonwovens production. The dimensions of the fibers used in the experiments were identical to those used in wet-laid nonwovens, as were the mixing methods. An increase in the viscosity of the latex before mixing improved the evenness of the fiber distribution and the distribution evenness also improved with the mixing time. The distribution evenness decreased with increased fiber length. All the effects mentioned above occur also when mixing fibers with water in the manufacture of wet-laid nonwovens.

Mixing of loose staple fibers with latex caused air bubbles to distribute into the mixture. The bubbles originate from air entrapped when the staple fibers are introduced into the liquid. Similar air bubbles also occur in the initial mixing stages in wet-laid nonwoven manufacture. In the later stages of wet-laid nonwoven manufacture, however, the water and the air bubbles are removed.

Preopening of the fibers with a fiber opener or card improves the distribution evenness because it opens mechanical fiber entanglements before the fibers are mixed into the latex. Also, in wet-laid nonwoven production, badly opened fiber bundles cause uneven fiber distribution.

The large voids in the dried noncoagulated latex-based composites occurred because the outer surface had formed a gas-tight skin, which was later blown up by the vapor pressure from the inside.

### Coagulation

The use of coagulation in combination with fiber-latex mixing indicated that water can be removed from the fiber-rubber mixture by pressing. The reason for this is apparently that the rubber particles after the coagulation, because of their tackiness are attached to each other and to the fibers. Thus the

water that emerges in the pressing cannot transport rubber particles. The coagulated particles also were too large to pass between the fibers in a bonded fiber mat, which was demonstrated in the trial to impregnate coagulate into a fiber structure. In addition, the pressing closed voids that remained closed through the subsequent fabrication steps apparently due to the tackiness of the rubber during the pressing stage.

### Coagulation Inside the Structure of a Bonded Fiber Mat

The idea with coagulation inside the structure of a bonded fiber mat was to bring latex of low viscosity into the fiber structure in intimate contact with the fibers, then to coagulate the latex to form larger particles, and finally to remove the water and the voids by pressing.

The chemical coagulant was added to the fiber mat before latex addition. This procedure was chosen in order to keep the rubber particles uncoagulated and small until the latex reached the coagulant-coated fibers in the interior of the fiber mat. However, the coagulants initiated the coagulation at the surface of the fiber mat before the latex had reached the interior. The coagulated particles at the surfaces of the fiber mat hindered additional latex from penetrating to the interior of the mat, thus causing voids. The voids discovered in the homogeneity test indicated that latex did not penetrate to the void places, since no traces of rubber could be seen on the fibers.

When mats not treated with coagulating agents were impregnated into latex (for combined heat and chemical coagulation) voids were less frequent and no coagulation was seen in the impregnation stage. Thus it is obvious that coagulation at the mat surface during impregnation causes voids when using mats pretreated with coagulants (for chemical coagulation). Comparison between combined heat and chemical and purely chemical coagulation indicates that heat facilitates the coagulation reaction.

In the thermal coagulation trials the microwave oven gave quicker coagulation, apparently because the heat was generated simultaneously throughout the composite sample. The uneven energy distribution caused uneven coagulation.

### Water Extraction

In the roll press, the sample becomes loaded with shearing forces due to slippage between the rolls and

the release films or sheets that had to be used for release.

In the roll press, the water and excess latex exit along a line in the roll nip and along the surface of the sample. This may contribute to excessive collection of coagulate on the sample surfaces. Subsequently, parts of the interior sample are left void of matrix since the emerging liquids may bring latex particles to the surfaces. The hydraulic flat press yields even and plane samples with less voids, apparently because the water and excess latex can exit more slowly over the entire surface of the sample.

The drying time for noncoagulated samples was considerably longer (e.g., 15 h) than that for coagulated samples ( $1\frac{1}{2}$ –2 h, including vulcanization).

### Fiber Length Retainment

The fact that no difference could be found between the length of fibers measured from the reinforcement fiber mats before and after composite making indicates that elastomer composites can be made without breaking relatively long staple fibers.

## CONCLUSIONS

A unique property of the latices is the coagulation, during which process the viscosity changes as well. From such a coagulated latex mixture, the water can be removed to a large extent by mechanical pressure.

Coagulated latex can be prepared to have acceptable viscosity for mixing and distribution of reinforcement fibers into an elastomer latex matrix. The water can, to a large extent, be removed by pressing. Here the choice of proper pressing method and pressing surfaces is critical for a good result. Flat press was found to be better for most applications than roll press.

Coagulation of latex also offers a method to introduce the elastomer matrix into an existing reinforcement fiber structure. The latex is brought into the structure before coagulation and is then coagulated within the fiber structure, either chemically using a coagulant agent or, in some cases, combined with elevated temperature. The produced porous structure is compressed by pressure in connection with the water removal.

The removal of water by pressure also saves energy compared with removal by drying since the drying time is shorter. Thus, coagulation before water removal from latex gives an advantage over water removal by drying alone. The comparative experi-

ments between water removal by pressing from coagulated latex and drying of uncoagulated latex show that this advantage is available also when producing latex-based composites with the help of coagulation.

The results indicated that low viscosity elastomers could be obtained by using elastomer latex. The application of lower viscosity elastomer prepolymers would make it possible to use gentler mixing methods than those used in regular rubber mixing. By using rubber in latex form and coagulation process, it is possible to make an elastomer composite with fibers dispersed throughout the composite without breaking the fibers during the manufacturing process. This can be done even if the fibers are considerably longer than reported earlier.

Mixing of unbonded staple fibers into untreated latex proved difficult due to entanglement in the mixer propeller and because of inclusions of large numbers of air bubbles. A method was developed to judge the quality of dispersion of fibers mixed into a latex matrix by spreading out the fiber matrix mixture over a board. Impregnation of coagulated latex into a preformed fiber structure did not give penetration of elastomer matrix into the interior of the structure.

From the experiments, it is concluded that no solid fiber matrix composite of more than a few mm thickness could be made by drying an object formed out of a thickened, noncoagulated latex-fiber mixture, because water removal from such a latex piece was disturbed by the occurrence of large voids.

A major problem in the process was the release of the samples from the pressing surfaces and the water removal from the sample surface. The tack was overcome by selecting pressing surfaces of polyethylene or polypropylene.

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