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Prepared by
GILLETTE RESEARCH INSTITUTE, INC.
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SUMMARY

Work in this program has been mainly concentrated in two areas: (1) studying the relation of structure strength to the chemical nature of the matrix and the resultant bond strength between asbestos fibers and matrix; (2) achieving orientation of asbestos fibrils in composites and determining the ultimate strengths of macroscopic asbestos fibers (MF) as well as colloidal ultimate asbestos fibrils (UAF).

We have found that structure strength depends greatly on the chemical nature of the polymeric matrix. Matrix materials well suited to asbestos reinforcement include phenolic resins and polymers containing free carboxyl groups. We have also found that ice is greatly reinforced by asbestos. Little or no strengthening by asbestos has been found in the following matrixes: nylon, polypropylene, polyurethanes, and gelatin.

We have prepared phenolic structures, reinforced with oriented MF, which had strengths up to about 100,000 psi. The MF tested singly averaged almost 200,000 psi. Thus, the oriented structures which contained 50 volume percent asbestos demonstrated complete utilization of the MF strength.

We have found UAF to be at least as strong as MF. Partially oriented arrays of UAF were prepared by drawing from colloidal aqueous suspension. The arrays had strengths up to 100,000 psi when impregnated with phenolic, despite the fact that they contained tangled masses of UAF as well as fairly well oriented UAF.

INTRODUCTION

A major purpose of this program has been to study the potential reinforcing capabilities of colloidal asbestos fibrils in polymeric structures. The program represents an extension of work, performed under Contract NASW-1183, which was aimed at determining the feasibility of reinforcing with colloidal asbestos fibrils. Our present study has included work on all of the following seven items specified in the contract:

"1. (a) Chemical incorporation of surfactant-dispersed asbestos fibrils in matrix.
    (b) Controlled flocculation of fibril dispersion.
2. Asbestos fibrils dispersed in polymer-forming organic liquids.
3. Resin impregnation of pre-formed asbestos papers.
4. Investigation of oriented fibril composites.
5. Investigation of other systems for obtaining improved structural forms.
6. Determination of mechanical properties of fibril-matrix composites to assess degree of improvement insofar as practical.
7. Definition of problems remaining for achieving structural potential."

This Final Report summarizes all work done in the one year contract period. Work done in the first nine months has been previously reported in the three Quarterly Progress Reports submitted; work in the last quarter is reported herein for the first time. The principal investigation on this project is Dr. Anthony M. Schwartz.

EXPERIMENTAL AND RESULTS

A. METHODS AND TECHNIQUES

1. Dispersing Asbestos

Many of the experimental methods employed under the previous contract, NASW-1183, were used in the present work. We had had experience with two different types of colloidal, ultimate asbestos fibril (UAF) dispersions. The first type is that obtained when macroscopic size asbestos fibers (MF) are dispersed in a suitable surfactant solution. The art of preparing these surfactant-dispersed suspensions is described in a series of patents to I. J. Novak and co-workers, the principal patent being U.S. 2,626,213. We had improved this process to the point where we could readily produce 100% UAF instead of the UAF-MF mixtures which result from Novak's procedure. The second type of colloidal UAF dispersion is the type obtained when MF is dispersed in the specific organic liquids we found effective. These include certain polyols, polyamines, alkanolamines, carboxylic acids, and others. The suitable dispersion media apparently have a strong molecular attraction for the asbestos and effectively separate asbestos agglomerates into the ultimate fibrils. In the present program we found a new class of surfactants, the phosphate esters, which are effective in dispersing MF to UAF in aqueous solution. These appear to be as effective dispersants as oleate soap and Aerosol OT. Data are given in Section B.1 and Table I for asbestos papers prepared from aqueous dispersions made with the phosphate esters.

We have also, in the present program, found new organic media which effectively disperse asbestos. For example, we have directly dispersed asbestos in a urethane prepolymer of the triol/diisocyanate type. However, as reported in Section B.2e below, asbestos reinforcement did not give a tensile strength increase in the urethane made from this prepolymer.

2. Recovering UAF From Surfactant Dispersions

The colloidal asbestos obtained by dispersing in aqueous surfactant solutions necessarily contains an adherent residue of surfactant when recovered from the water. The amount of surfactant deposited on the fibrils is dependent on the technique of water/asbestos separation as well as on the level of surfactant chosen to accomplish the initial dispersion in water. If the dispersion is formed into a mat by evaporation of the water, all of the surfactant is retained in the mat. If the asbestos is recovered by filtration, a large proportion of surfactant can be removed in the filtrate, leaving relatively little on the fibrils. (This latter technique is used in the manufacture of the commercial Novabestos paper which contains about 5% surfactant on the weight of asbestos). Both the evaporation and filtration techniques were used in our previous program and have been used in the current program. We have, in addition, developed a new technique for recovering UAF in a partially oriented, yarn-like array. Both of the previous techniques produced randomly oriented mats of asbestos. The new technique for producing yarn-like UAF arrays is as follows:

Asbestos (grade 3A) is dispersed in sodium oleate solution by Novak-type, slow stirring. This effects about 10% conversion of the asbestos to UAF. The dispersion is filtered through 80 pore/inch open-cell polyurethane foam to remove the large splints of undispersed asbestos. A few ml of the filtrate (which contains the UAF) is poured into a several hundred-fold excess volume of distilled water. This dilution makes the colloidal dispersion of UAF unstable, but no visible flocculation can be seen. A fine wire or needle is then dipped in the "solution" and slowly withdrawn. The UAF tend to accumulate on the wire and then to cluster together as the wire is withdrawn, so that, if the withdrawal is made slowly and evenly, a filament-like array several inches long and a fraction of a mil in diameter can be lifted out of the water. The array comes up virtually free of excess water. Although the arrays appeared fairly uniform in diameter to the naked eye, examination under the microscope showed the occurrence of bulbous regions and necked-in regions (Figure 1 is a photomicrograph of a section of one of the arrays). Examination under the electron microscope showed that the arrays probably are comprised of tangled masses of UAF, joined together by relatively well-oriented UAF (oriented longitudinally). Figure 2 is a typical electron micrograph of an array, and shows the rather loose fibril packing. Fibril tangling and bent fibrils can be seen in the figure. Despite these flaws, the arrays display high strengths, suggesting that the UAF may indeed be as strong as predicted, i.e., 1 million psi, or more. Strength data for the arrays, both untreated and resin-impregnated, are reported in Section C.

B. ASBESTOS-MATRIX BOND IN COMPOSITES

1. Effect of Residual Surfactant on the Asbestos

When UAF is obtained by dispersing MF in surfactant solutions, we always retain some surfactant on the UAF. As pointed out in Section A.2 above, the amount of surfactant residue depends on the technique of recovering

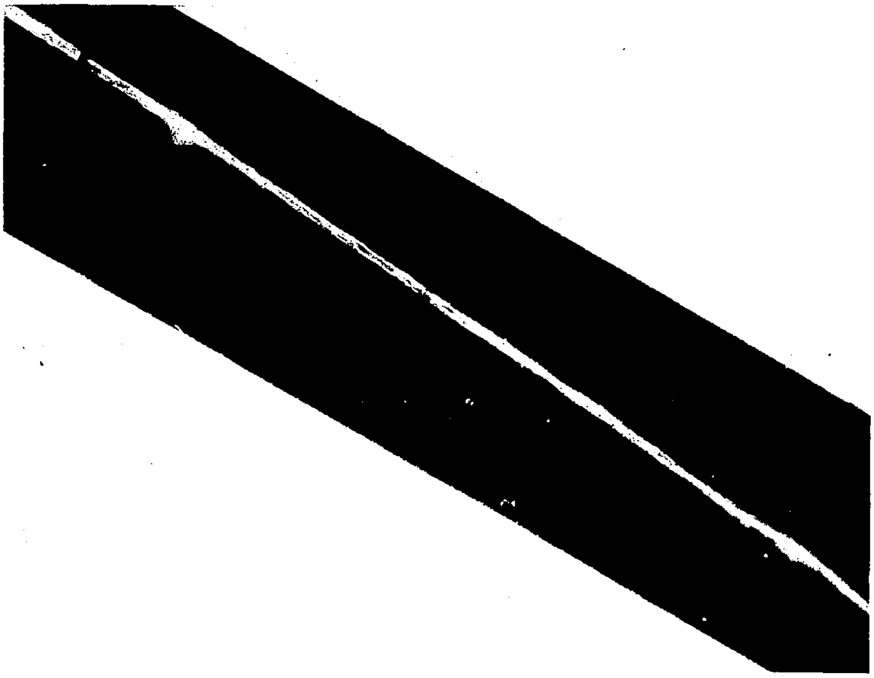

Figure 1.- Photomicrograph of a UAF Array Obtained by Coagulation and Drawing. (Magnification = 200 X.)

Figure 2.- Electron Micrograph of a Section of a UAF Array (Array Essentially the Same as the One Shown in Figure 1). Magnification = 15,000 X.

the UAF. The residue affects the ultimate bonding of asbestos to matrix in our composites. The effects of surfactant residues on the strengths of selected asbestos papers and asbestos/resin composites is shown in Table I. The papers containing high proportions of surfactant were obtained by evaporation of asbestos/surfactant dispersions. As indicated in the table, a few papers containing very little surfactant were made by filtration of the original dispersions. The paper obtained by filtration of an ethylene glycol dispersion of asbestos contained, of course, no surfactant.

In general, it can be seen that high proportions of residual surfactant tend to reduce the strength of asbestos/resin composites. (This was also found to be the case in ice matrix, as shown in Table IV). The fact that the highest strengths are obtained with the Novabestos-reinforced composites is probably due to orientation. Note that the isotropic paper made by disorienting Novabestos produces a phenolic composite which is intermediate in strength between the oriented and cross-orientation directions of the Novabestos/phenolic composite (See Table III). This strongly indicates that orientation, rather than a residual coating of 5.5% oleate soap, is responsible for the higher strengths obtained with the commercial Novabestos paper.

The surfactant/asbestos papers containing 33% or more surfactant are remarkably strong compared to the low surfactant-content papers, before resin impregnation. In these papers, the surfactant may be acting as a lubricant, preventing the asbestos fibers from cutting each other when placed under tension. When these are impregnated with resin, the surfactant apparently interferes with resin/asbestos bonding.

TABLE I

EFFECT OF RESIDUAL SURFACTANT ON STRENGTH PROPERTIES OF ASBESTOS PAPERS AND ASBESTOS/RESIN COMPOSITES

Surfactant Employed in Dispersing Asbestos	Impregnating Resin	Composition of Composite, (Wt. % asbestos/% surfactant/% resin)	Density g/cc	Thickness, mils	Elongation, %	Tensile Strength, psi
Aerosol OT	none	67/33/0	1.1	7.8	2	820
"	phenolic	32/15/53	1.5	9.9	3	4600
"	polyester	36/17/47	1.5	10.0	4	5700
Sodium Oleate	none	67/33/0	.94	2.8	3	4000
"	phenolic	52/25/23	1.4	2.1	2	5600
Phosphate QS-5	none	67/33/0	.85	2.5	4	680
"	phenolic	45/22/33	1.4	2.7	1	5100
"	polyester	39/20/41	1.4	2.8	4	5600
Phosphate QS-10	none	67/33/0	.82	3.3	3	900
"	phenolic	41/20/39	1.3	3.0	2	7900
"	polyester	39/19/42	1.4	2.8	12	2800
Morpholine Linoleate	none	67/33/0	.83	3.1	4	6100
"	phenolic	40/20/40	1.4	2.6	1	5200
Aerosol OT	none	100/0 /0[a]	.59	36.1	3	60
"	phenolic	53/0 /47[a]	1.6	21.1	7	6500
"	polyester	44/0 /56[a]	1.4	30.8	6	4200
none[b]	none	100/0 /0	.65	15.7	6	120
"	phenolic	46/0/54	1.5	12.5	5	10,500
"	polyester	45/0/55	1.4	15.4	6	3500
Oleate Soap[c]	none	95/5 /0	.48	4.0	2	40
"	phenolic	60/ 4/36	1.4	5.2	4	11,500
"	polyester	25/ 2/73	1.2	5.4	5	2800

a - Paper made by filtering surfactant dispersion, surfactant concentration is unknown, but nearly zero.
b - From dispersion in ethylene glycol
c - Isotropic paper made from redispersed Novabestos paper

The new class of dispersing surfactants, the phosphate esters (Rohm and Haas) is also reported in Table I. These are about equal to Aerosol OT in dispersing ability and produce papers which are about as strong as the Aerosol OT papers.

2. Matrixes for Asbestos Reinforcement

During this program a number of matrix materials have been investigated. We have found some of these to be markedly strengthened when asbestos was incorporated in them, while other matrix materials were not improved in strength. The final structure or composite strength depends very greatly on the chemical nature of the matrix and on the resultant bond strength between matrix and asbestos fibers. Our studies of various asbestos/matrix systems are described in the separate sections a. through g., which follow. Table II gives typical strength values for several of the various matrix materials, both unreinforced and reinforced with asbestos. These data are for isotropic structures containing about 50 volume % asbestos; exceptions are noted in the table. The data in Table II show that marked strength improvement was obtained when asbestos was incorporated in the carboxylated resins, in ice, in polyester resin, in polyvinyl alcohol and in phenolic resin. Little or no strength improvement was obtained in nylon, polypropylene, the silicone rubber, or the urethanes.

a. Asbestos reinforcement of phenolic resin

All of our studies have been done with Phenolic Resin 1111 (Ironsides), a commercial product intended for reinforcement with asbestos. Table III lists typical strengths we have obtained in phenolic/asbestos composites. In each case the composites were made by impregnating an

TABLE II

REINFORCEMENT OF VARIOUS MATRIXES BY ASBESTOS

Composites are about 50% asbestos, 50% matrix, except as noted

Matrix Material	Type of Composite	Yield Strength, psi	Initial Modulus, psi	Ultimate Elongation, %	Tensile Strength, psi
Phenolic	Unreinforced phenolic	7,400	253,000	4	8,400
"	Isotropic sheet	11,800	640,000	4	12,300
"	Oriented paper	9,200	960,000	3	17,200
"	Oriented MF whiskers	65,000	22,000,000	0.4	84,000
Polyester	Unreinforced polyester	1,500	90,000	6	4,000
"	Oriented paper	10,000	610,000	3	14,400
Polyvinyl alcohol	Unreinforced	420	44,000	180	2,900
"	Isotropic sheet	4,700	260,000	4	7,700
"	Oriented paper	8,300	476,000	4	15,500
Polyacrylic acid	Unreinforced	440	51,000	180	1,400
"	Isotropic sheet	2,900	800,000	1	6,600
Acrysol P-6-N	Unreinforced	290	1,000	2800	750
"	Isotropic sheet	800	120,000	3	2,600
Elchem 1273	Unreinforced	2,400	190,000	2	2,400
"	Isotropic sheet	3,100	380,000	4	7,400
Gelva C5V10	Unreinforced	1,400	160,000	2	2,000
"	Isotropic sheet	3,300	516,000	3	11,000
Polymerized linoleic acid	Unreinforced	300	23,000	34	1,000
"	Isotropic sheet	1,700	118,000	7	6,000
Polypropylene	Unreinforced melt spun fiber	13,500	250,000	400	24,000
"	Reinforced melt spun fiber[a]	10,000	270,000	200	13,000
Silicone	Unreinforced	1,200	95,000	20	3,100
"	Isotropic sheet	1,300	180,000	5	3,700

Matrix Material	Type of Composite	Yield Strength, psi	Initial Modulus, psi	Ultimate Elongation, %	Tensile Strength, psi
Nylon	Unreinforced film	1,700	31,300	1000	4,900
"	Reinforced film[b]	1,300	15,200	930	3,700
"	Unreinforced fiber	21,000	26,600	130	27,800
"	Reinforced fiber[c]	20,600	29,300	120	25,200
Polyurethane	Unreinforced wet spun fiber	625	4,600	590	7,600
"	Reinforced wet spun fiber[d]	1,400	22,300	520	6,100
Ice	Unreinforced	---	---	---	420
"	Isotropic sheet	1,800	110,000	1	1,800
Gelatin	Unreinforced	8,100	216,000	12	12,700
"	Isotropic sheet	6,300	331,000	8	12,700
"	Oriented paper	11,400	408,000	5	12,400

a - 2% asbestos in composite
b - 4% " " "
c - 1.2% " " "
d - 25% " " "

asbestos paper or mat with a solvent solution of the Resin 1111, followed by heating to evaporate off solvent and bring the resin to a thermoplastic pre-preg stage, and final curing with heat and pressure to give a dense structure.

The advantage of orientation is clearly demonstrated by the commercial Novabestos paper. As shown in Table III, this paper is about three times as strong in its oriented direction as in the direction perpendicular to orientation. The effect is evidenced both before and after resin-impregnation. If the asbestos fibers are disoriented, a considerably weaker structure is formed. We have demonstrated this by redispersing a sheet of the Novabestos in ethylene glycol, using a short period of shearing in the Osterizer. The dispersed fibers were then formed into an isotropic sheet by evaporating off the glycol, thus retaining the small proportion of oleate soap which is contained in Novasbestos. Strength data for this isotropic sheet are also given in Table III, and show the loss in strength in disorientation. The effects of residual surfactant on the strength of phenolic/asbestos composites have already been discussed in Section B.1. The 5.5% soap residue on Novabestos apparently did not interfere with phenolic/asbestos bonding and the isotropic composite reinforced with fibers from Novabestos was equal in strength to the isotropic composite made by phenolic impregnation of the surfactant-free mat obtained by filtering an ethylene glycol dispersion of asbestos. A 25% soap content markedly reduced the strength of a phenolic/asbestos composite.

The excellent bonding of phenolic resin to clean asbestos is demonstrated by the following experiment to see whether macroscopic fibers could act as reinforcing whiskers:

TABLE III

ASBESTOS/PHENOLIC COMPOSITES

Composite made from:	Composition, by weight % asbestos/% soap/% phenolic	Tensile Strength, psi
Novabestos paper (test in oriented direction)	95/5/0	400
	57/4/39	17,200
Novabestos paper (test perpendicular to oriented direction)	95/5/0	120
	57/4/39	7,200
Isotropic mat of fibers from Novabestos paper	95/5/0	40
	60/4/36	11,500
Isotropic mat from asbestos dispersion in ethylene glycol	100/0/0	100
	46/0/54	12,000
Isotropic mat from asbestos dispersion in soap solution	67/33/0	4,000
	52/25/23	5,600

A number of fibers about 10-15 microns in diameter were hand-picked from 3A grade asbestos. These averaged about one-half inch in length. They were laid out in a line in an overlapping pattern and then slightly twisted together to form a rope, several inches long and averaging about 4 fibers in diameter. The rope was impregnated with phenolic resin and heat-cured. Sections of the rope about one-inch or more in length were broken on the Instron Tensile Tester. Thus, there were no fibers running the full specimen length which could be gripped by both Instron jaws. The specimens had tensile strengths as high as 97,000 psi. To our knowledge, this is the highest strength that has been obtained with asbestos reinforcement. Considering that their calculated asbestos/phenolic volume ratios were 50/50, the average asbestos fiber stress in the composites (based on average fiber area) is as high as 194,000 psi. Thus, the asbestos fibers used as whiskers demonstrate 100% utilization of their strength, if we assume that this small fiber sampling averages about the 165,000 psi value we found for 52 individually tested fibers (see Section C). High utilization of fiber strength demonstrates that the phenolic resin is an excellent matrix for asbestos reinforcement.

b. Reinforcement of ice matrix with asbestos

All of the ice-asbestos composites were prepared by impregnating pre-formed dry asbestos papers with water and then freezing. The experimental techniques for preparing composites and testing them for strength with the Instron tensile tester have been fully described in the First Quarterly Report.

Table IV summarizes the strength data for the various ice/asbestos composites prepared and tested. The data point up the following important facts in regard to the presence of residual dispersing surfactant on the asbestos:

(1) The presence of high proportions of surfactant (Aerosol OT or sodium oleate) caused large strength variations in the ice/asbestos composites. The composites range from weaker to stronger than the original dry surfactant/asbestos paper. Since the original papers are uniform in strength, it is evident that in the process of impregnating with water and freezing we produced non-uniformity.

(2) The ice/asbestos composites made from pure asbestos papers (glycol dispersed and cast) were remarkably uniform in strength and showed a significant reinforcing effect of the asbestos.

(3) The ice/asbestos composites containing small proportions of surfactant were also uniform in strength and the strengths were higher than those of the pure asbestos/ice composites.

These findings related closely to our previous observations on the effect of surfactant in asbestos/resin composites (Table I). High proportions of surfactant (about 20 vol %) gave us phenolic/asbestos composites which were weaker than those containing little (about 4 vol %) or no surfactant. With the phenolic matrix the composites containing 0 or 4 vol % surfactant were equally high in strength. In our ice/asbestos composites

TABLE IV

ASBESTOS PAPERS AS REINFORCEMENTS FOR ICE

Asbestos Paper Obtained from:	Composition of Composite, by wt., % Asbestos/% Surfactant/% ice	Void Volume, %	Thickness, mils	Elongation, %	Tensile Strength, psi
Dispersion in glycol	100/0/0	75	7.3	5	110
"	45/0/55 (25/0/75)^{a}	--	7.2	1	1830
"	"	--	7.3	2	1580
"	"	--	7.3	2	1610
Dispersion in sodium oleate solution	67/33/0	49	2.8	3	4000
"	43/21/36 (23/28/49)	--	2.8	2	840
"	"	--	2.8	2	5300
"	"	--	2.8	1	1400
Dispersion in sodium oleate solution, filtered	88/12/0	75	11.8	2	230
"	37/5/58 (19/6/75)	--	11.5	1	3200
"	"	--	12.6	2	3900
Dispersion in Aerosol OT solution	67/33/0	57	10.0	3	690
"	37/19/44 (19/24/57)	--	9.5	-	340
"	"	--	9.7	-	2330
"	"	--	10.0	-	6210
Dispersion in Aerosol OT solution, filtered	93/7/0	67	29.4	5	130
"	49/3/48 (28/5/67)	--	28.9	3	3600
"	"	--	29.4	3	4300
Dispersion in morpholine linoleate, cured	80/20/0	61	5.7	3	2100
"	43/11/46 (23/16/61)	--	5.0	1	7400
"	"	--	5.8	2	10,900
Dispersion in linoleic acid, filtered, cured	67/33/0	45	20.9	7	6000
"	46/23/31 (23/32/45)	--	15.7	1	12,800
"	"	--	16.6	2	6200
-------	0/0/100^{b}	--	----	-	420 ± 120

Volume ratio given in parenthesis.   b. Literature value for tensile strength of ice.

small amounts of surfactant (5-6 vol%) may be acting to lubricate the asbestos fibrils, preventing them from cutting each other when placed under tension. This could explain why these composites are stronger than those made with pure asbestos. High proportions of surfactant could interfere with ice/asbestos bonding or produce non-uniformity (structural flaws) through solution of surfactant in water on impregnation and uneven redistribution on freezing.

Data are also given in Table IV for composites made from linoleic acid-type asbestos papers. These presumably contain no water-soluble surfactant and probably contain little or no monomeric linoleic acid, since they are heat-cured in their preparation. The original dry papers consist of asbestos and polymerized linoleic acid and are slightly brittle. When these were impregnated with water and frozen we obtained composites of widely variable strength, suggesting that we have non-uniform bonding between ice and the coated asbestos, just as we have in the high-surfactant specimens.

c. Asbestos-reinforced polypropylene

UAF was obtained by the following technique: AY grade asbestos was dispersed in sodium oleate solution by slow stirring, filtered to remove visible splints, and the filtrate containing the colloidal UAF was coagulated by adding water. The water was removed by filtration and the mat of UAF was dried. The UAF retain about 6% sodium oleate (by analysis) and are readily dispersible in surfactant solutions (e.g., sodium oleate or Aerosol OT) or appropriate organic liquids (e.g., linoleic acid or ethylene glycol). On redispersion, no fibrils are visible in the light microscope.

UAF obtained by the above technique was melt-blended into polypropylene as follows: 5g polypropylene (Hercules, Inc. Profax 6411 J) pellets was heated to 275°C, melting to a viscous consistency. Into this was stirred 0.1 g of UAF. Fibers were spun from this melt (by dipping in and pulling out the stirring rod). The spinnability was judged to be much poorer than polypropylene alone (also melt spun at 275°C). Very long unreinforced fibers could be spun. Only much shorter reinforced fibers could be spun. The reinforced fibers tended to be non-uniform in diameter along their lengths, exhibiting alternating necked-in and bulbous regions.

Asbestos reinforcement, at the low 2% loading we were able to obtain, did not produce an increase in strength (see Table II). Drawn, reinforced fibers showed a strength increase over the undrawn fibers which appeared to be solely due to polymer orientation, not asbestos fibril orientation. Asbestos loadings higher than 2% were not tested since we were not able to melt spin fibers from the molten dispersions. The added asbestos did, of course, increase modulus and decrease the elongation of polypropylene.

d. Asbestos-reinforced nylon

A low-melting nylon (duPont Zytel 69) was used. Although we were able to blend up to 4%, by weight, of UAF into molten Zytel 69, we were not able to spin fibers out of the melts containing over 1.25% asbestos. Films were made, up to 4% asbestos loading.

There appears to be no reinforcing effect of UAF, up to the 4% maximum loading tested (see Table II). The nylon, like polypropylene, is oriented by drawing and showed the expected higher strength on orientation. Reinforced samples also increased in strength on drawing, but the strength increase can be ascribed solely to nylon polymer orientation. A few films were tested in the direction perpendicular to orientation, after drawing, to determine whether we might be effecting a cross-orientation of asbestos. There was no measurable increase in strength in the cross-oriented direction which could suggest such an orientation of asbestos.

e. Asbestos-reinforced polyurethanes

Because of the difficulty encountered in attempting to incorporate more than a few percent asbestos in a drawable polymer (nylon or polypropylene) by melt-blending, a somewhat different approach was taken. That is, to disperse the asbestos in a monomeric liquid and then copolymerize with a second monomer. The urethane systems were chosen since, by appropriate selection of the polyol and isocyanate components, a wide range of drawable polymers of varying stiffness can be produced. Furthermore, the polyols tend to be excellent dispersing media for asbestos. Experimentally, three different techniques were used to make urethane/asbestos composites: (1) disperse asbestos in a polyol and then react with toluene diisocyanate vapor; (2) disperse asbestos in a polyol and then react with liquid diisocyanate; (3) disperse asbestos in a polyol-diisocyanate prepolymer and then complete polymerization with a diamine or diol chain extender.

Asbestos (AY grade) was dispersed in polybutylene glycol B 500 (Dow) by high speed mixing and shearing in an Osterizer. The dispersion was filtered to produce a wet mat comprising 35% asbestos and 65% of the glycol by weight. The mat was suspended for 60 minutes in a saturated toluene diisocyanate (TDI) atmosphere at 140°C. This treatment produced a final composite which had a tensile strength of 2000 psi. Without asbestos the B-500/TDI copolymer formed as a viscous liquid and would not solidify at room temperature. An unreinforced solid polymer was made by reacting B-500 polybutylene glycol (10 g) with liquid TDI (6.8 g) and then reacting with ethylene glycol, using tripropylamine catalyst. Fibers were melt-spun from this polymer, but were found to be very weak due to the presence of small bubbles.

The occurrence of bubbles was overcome by changing the experimental technique to solution spinning. The B-500/TDI prepolymer, containing tripropyl amine catalyst, (with or without asbestos) was extruded from a syringe needle into an aqueous ethylene diamine solution and drawn to about 150% of extruded length. Ethylene diamine concentrations of 10 to 25% were found satisfactory for the various propolymer/asbestos mixtures which we extruded. Tensile data for various fibers made by solution-spinning are given in Table V. To obtain the highest asbestos loading, 11%, the initial dispersion of asbestos in B-500 was carried out at 3% asbestos, by weight, and then this dispersion was filtered to remove part of the B-500 leaving a 20% asbestos paste. This paste was then mixed with TDI, amine catalyst was added, and then the mix was extruded into the diamine solution.

As shown in Table V. the asbestos showed no reinforcing effect in this type of urethane polymer. The various strengths obtained for the unreinforced polymer are apparently due to slightly different degrees of drawing of the fibers in spinning. We were generally able to draw the fibers about 50% of their length just after extruding into the diamine solution. Drawing more than 50% usually broke the fibers. The exact amount of drawing was not determined for the fibers in Table V. but that they were not drawn exactly the same amount is evidenced by their different final diameters.

Direct dispersion of asbestos in a urethane prepolymer was also accomplished. The prepolymer, Mondur CB75 (Mobay) is a triol/TDI type. No reinforcing effect of asbestos was found, however, in any of the urethanes we made from this prepolymer.

In continued studies, a polyurethane was found which could be loaded with as much as 25% asbestos and which retained some degree of drawability at this loading. This urethane is Estane 5740X071 (B. F. Goodrich), a thermoplastic, unreactive type (i.e., it contains no free isocyanate groups). The technique for preparing the asbestos-Estane composites was as follows:

AY grade asbestos was dispersed in ethylene glycol by high speed shearing in an Osterizer for 90 minutes. The asbestos/glycol ratio was 1/200, thus a rather fluid dispersion was obtained. The dispersion was then allowed to sit for 16 hours so that the small proportion of undispersed splints and non-asbestos debris (e.g., rock) would settle to the bottom.

TABLE V

REINFORCEMENT OF URETHANE POLYMER WITH ASBESTOS

Wt. Ratio, Asbestos/Polymer	Test Filament Diameter, mils	Elongation, %	Tensile Strength, psi
0/100	59	200	1300
.6/99.4	22	260	1500
0/100	14	300	3800
1.6/98.4	13	300	4000
0/100	17	480	2500
11/89	22	500	1200

Essentially all of the asbestos was determined to be in the supernatant glycol. This liquid was decanted off and examined under the light microscope. Only a few asbestos fibers were visible, most were too small to be detected (under .2 micron). The dispersion was then filtered through Sharkskin filter paper. The filtrate contained no particles visible in the light microscope. Water was then added to the filtrate thus causing the submicroscopic fibrils to flocculate. The flocked fibrils were filtered and dried. They were readily dispersible in dimethyl formamide (DMF) solutions of Estane. These DMF dispersions contained no asbestos fibers visible in the light microscope. The dispersions were used to prepare three types of composites: (1) isotropic films, made by casting the dispersion in a Teflon tray and evaporating off the DMF: (2) wet-spun filaments, made by extruding the dispersion through a syringe needle into a DMF-water solution and drawing the filaments about 100% as they formed; (3) dry-spun filaments, made by melt extrusion of chopped films from (1) above. Two asbestos loadings were used in the composites, 2.5% and 25%, by weight. Tensile data for the various composites and for the unloaded Estane are given in Table VI. At the 25% asbestos loading, no satisfactory samples could be made by melt extrusion, however wet-spun filaments were readily made.

The data in Table VI show no strengthening effect of asbestos in this polyurethane. The initial modulus is greatly increased by asbestos loading, as expected. If any orientation of UAF was effected by spinning

TABLE VI

THERMOPLASTIC POLYURETHANE REINFORCED WITH ASBESTOS

Weight Ratio, asbestos/urethane	Test Specimen	Elongation, %	Tensile Strength, psi	Initial Modulus, psi
0/100	Film	590	7,600	4,600
2.5/97.5	"	520	5,700	22,300
25/75	"	10	3,800	192,000
0/100	Wet-spun filament	800	3,600	1,400
2.5/100	"	600	2,500	10,000
25/75	"	20	4,000	48,000
0/100	Melt-extruded filament	1400	6,400	9,000
2.5/97.5	"	40	3,900	58,000

or extruding, it is not evidenced by these tensile data. This extensive investigation of urethanes has not found one which is strengthened by asbestos reinforcement.

f. Asbestos reinforcement of gelatin

Composites were prepared by impregnating various asbestos papers and mats with aqueous gelatin solutions and then evaporating off the water at room temperature. The strengths of typical composites are given in Table II. These show no reinforcing effect of asbestos in gelatin.

g. Asbestos-reinforced carboxylated resins

The following resins were used: Gelva C5 V10 (Monsanto), a vinyl acetate/carboxy acid copolymer; Elchem 1273 (duPont), a similar copolymer; Acrysol A-1 (Rohm and Haas) polyacrylic acid; and Acrysol P-6-N (Rohm and Haas), an acrylic polymer. Composites were prepared by impregnating asbestos papers and mats with solutions of the resins in water or ethanol or with aqueous solutions of the ammonium salts of the resins. Typical strength values are given in Table II, and show that all of the resins are reinforced by asbestos.

Somewhat closely related is the reinforcement of polymerized linoleic acid by asbestos. We found under the previous contract that asbestos could be directly dispersed to UAF in linoleic acid. By filtering the dispersion to remove the excess linoleic acid, a mat was obtained which could be heat-cured to produce a fairly strong composite. We have now prepared additional composites of this type and have also successfully made unreinforced films of the polymerized linoleic acid. As shown in Table II, the strength of the polymerized linoleic acid is greatly increased by asbestos reinforcement.

C. Orientation and Ultimate Strength of MF and UAF

Throughout this program we have assumed that UAF represents the highest strength form of chrysotile asbestos. No direct strength measurement can be made on the 300 Angstrom diameter UAF, but tensile measurements of MF splints (macroscopic bundles of asbestos fibers) show an increase in strength as splint diameter decreases (and presumably the splints are more free of flaws). Fine diameter fibers, in the range of 10-20 microns diameter, have tensile strengths reportedly as high as 824,000 psi (Zukowski and Gaze, Nature 183 (No. 4653, 35-7 (1959)). Indeed, we have in the present studies measured strengths as high as 767,000 psi for 10 micron diameter fibers. The average value for 52 tested fibers was over 165,000 psi. The predicted high strength for UAF is, in fact, based on these fiber values, extrapolating the strength vs. diameter curve. The larger the fiber, the greater is the chance that flaws can exist; only the single UAF should be theoretically flawless. We have found (see Section B.2.a.) that full utilization of MF strength can be achieved by orienting the MF in a phenolic matrix. By using the tiny, yarn-like UAF arrays (described in Section A.2.) we have now also demonstrated that the UAF are at least as strong as MF. A number of the arrays were prepared and tested for tensile strength. Some were tested untreated; others were impregnated with phenolic resin to provide a coherent matrix.

The highest value measured for an untreated array was 35,000 psi and the highest value for a phenolic-treated array was 100,000 psi. Thus, despite the evident flaws (see Figure 2), we get high strength. Since we have not measured their densities, we do not know the void volume in these arrays. It is possible that the actual strengths are much greater than these values, calculated on the basis of diameters measured under the light microscope.

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