UV-0001 #19

STATUS REPORT

PLAINTIFF'S EXHIBIT

UC-4759

NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

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SUMMARY The addition of acrylic acid to asbestos was studied to determine the feasibility of producing an acrylate modified asbestos surface reactive in vinyl polymerization reactions. Under aqueous conditions reasonable organic loadings could only be achieved after long reaction time. Under anhydrous conditions organic loading was chiefly due to precipitation of polyacrylic acid.

The modified asbestos rapidly lost organic material in water due to facile hydrolysis. Samples of treated asbestos were tested for cross-linking ability in a vinyl cured polyester. An average of 37,000 psi in flexural strength was noted for polyester specimens filled with treated asbestos vs. an average of 11,000 psi for polyester controls filled with raw asbestos. Flexural modulus, compressive modulus, and modulus of elasticity were all significantly higher for polyesters filled with treated asbestos, indicating that vinyl cross-linking did take place.

Anion exchange was considered as an alternate means of introducing carboxylate ions to asbestos but was found ineffective for acetate ion and the idea was abandoned.

Asbestos adsorption of magnesium ε-hydroxycaproate was found to be quite weak and unsuitable as a means of placing organic hydroxyl groups on the asbestos surface.

No further work on organic modification of chrysotile is planned.

INTRODUCTION The reaction of carboxylic acids with asbestos results in a combination of magnesium extraction and carboxylate ion replacement of hydroxide ions on the asbestos surface.(1) This reaction has been investigated as a means of attaching reactive organic functional groups, especially vinyl and hydroxyl groups, to asbestos.

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Other potentially useful methods of placing a carboxylate ion surface on asbestos are ion exchange and asbestos adsorption of magnesium carboxylate salts.

Ethylene-acrylic acid copolymers have been reported to cross-link with chrysotile.[3] The modification of the asbestos surface with a reactive monomer theoretically could convert asbestos to a reactive polymer which might be cross-linked if it could be chemically combined in an organic polymerization system. Such chemical incorporation of asbestos as a reactive filler should result in improved strength properties over conventional filled resins due to an effective increase in molecular size.

DISCUSSION Asbestos was allowed to react with acrylic acid in water and in toluene (Table I). Under aqueous conditions both addition and magnesium extraction took place with magnesium extraction predominating at low acid concentration and addition more prominent at higher acid concentration. This is just the opposite of the results found with acetic acid by Smith and Shriver,[1] and is due in part to polymerization of acrylic acid at higher concentration and precipitation of some of the polymer on asbestos. This is evident from unsaturation determinations carried out on the modified asbestos and partial extraction of polyacrylic acid in dimethyl formamide.

When the reaction was run under non-aqueous conditions magnesium extraction was practically nil. At higher concentrations the organic uptake was much faster than that reported for asbestos and acetic acid by Smith and Shriver,[1] and was predominantly polyacrylic acid which is insoluble in the solvent employed, toluene. Organic loadings at low acid concentration were too low and the reaction rate too slow for practical application.

Two types of addition occurred. An infrared spectrum of the reaction product dried at 105° for 3 days showed the presence of both carboxyl groups and carboxylate ions. Immediate washing of the reaction product with heptane resulted in the extraction of only small amounts of acrylic acid approximating the concentration of acrylic acid in the residual reaction solution wetting the product. On drying at 105°, the product showed a rapid weight loss due to solvent for about one day and then a slow but continuous loss of weight over a period of two weeks. Unsaturation values did not decrease with drying time. A mixture of acrylic and polyacrylic acids could be extracted with boiling dimethylformamide. The residual acids on asbestos then contained a higher proportion of

vinyl groups than before extraction. Therefore, addition of carboxylic acids to asbestos occurs by both chemical reaction and physical adsorption; physical adsorption is more effective in the addition of polyacrylic acid than for acrylic acid due to relative solubility and acidity. Physical adsorption of polyacrylic acid is much less noticeable in the aqueous reaction due to the solubility of polyacrylic acid.

The products of acrylic acid reaction with asbestos were white powders resembling asbestos, but of greatly reduced bulk and increased cohesion. The products were hydrolytically unstable; on standing overnight in water, samples lost all organic material.

As a determination of the cross-linking ability of acrylate-modified asbestos, two product samples and a pure chrysotile control were milled with varying amounts of MFG 3482 polyester resin and compression molded. The strength properties of the moldings are summarized in Table II.

There are no significant differences in tensile strength between cured polyester samples filled with raw chrysotile and those filled with acrylate modified chrysotile but elasticity decreases and modulus of elasticity increases with acrylate loading on asbestos.

The polyester specimens filled with treated asbestos show a definite increase in compressive strength over those filled with raw asbestos and compressive modulus is markedly increased.

In flexural properties, the increase in strength with acrylate loading on asbestos is striking. With low acrylate loading, 0.29 equivalents of acrylate ion per formula weight of asbestos (3GWR120), little change over polyester filled with untreated asbestos is noted, but with higher acrylate ion loading, 1.72 equivalents of acrylate ion per formula weight of asbestos (3GWR106-1), flexural strength of filled polyester is almost four times that of samples containing untreated asbestos and flexural modulus is increased by as much as a factor of ten.

This evidence strongly indicates that cross-linking has occurred by vinyl copolymerization of the polyester components with adsorbed acrylate ion.

Acrylate-modified asbestos should be patentable as a composition of matter and a memorandum is being prepared to cover the modification of asbestos with unsaturated carboxylic acids as well as vinyl polymers derived from such systems. The products may be useful in applications demanding very rigid plastic materials.

As an alternate method of attaching carboxylate ions to asbestos, exchange of acetate ions for hydroxide ions was attempted. Downward flow of a sodium acetate solution through a column of chrysotile was impossible due to packing so a slurry of 30 g. of chrysotile in 500 ml. of 6 N sodium acetate was stirred at 108° for a period of 100 hours. Immediate potentiometric titration of the supernatant solution indicated only acetate ions and no measurable hydroxide ion concentration.

The asbestos carboxylate surface could be merely due to adsorbed magnesium carboxylate. To test this hypothesis asbestos was stirred with a hot solution of magnesium ϵ-hydroxycaproate. When the product was merely filtered and dried the ashing weight loss was 56%. When the product was washed with cold water and dried the ashing weight loss was 15%, indicating no remaining organic material. The unwashed product was a plastic adhesive mass which lathered much like "Lava" soap.

CONCLUSIONS The reaction of carboxylic acids with asbestos results in an asbestos surface modified by both carboxylate ions and physically adsorbed carboxylic acid.

The reaction products are very unstable to hydrolysis.

While direct reaction of aqueous carboxylic acids could be used to attach substituted carboxylic acids to asbestos, the reaction is probably too slow for practical purposes.

Under anhydrous conditions, carboxylic acids are also slow to add to asbestos unless polymerization is possible, allowing precipitation of a polycarboxylic acid. High loadings of acrylic acid on asbestos occur chiefly by precipitation as polyacrylic acid.

Precipitation of magnesium carboxylate salts on asbestos does not result in a stable product.

Unfavorable equilibrium rules out anion exchange as a means of introducing carboxylate ions to asbestos.

Cross-linking of vinyl polymerized polyester with acrylated modified asbestos appears to occur as evidenced by a fourfold icrease in flexural strength in a polyester filled with treated asbestos over an asbestos filled control.

EXPERIMENTAL

Reaction of Acrylic Acid With Asbestos

Solvent, acrylic acid, and inhibitor were placed in a round bottom flash equipped with stirrer, thermometer, and reflux condensor. The asbestos was added in small portions with stirring to achieve maximum dispersion and the reaction was heated to the desired temperature. Heating and stirring were continued and samples were pulled at the desired intervals. Unless noted, all samples were immediately filtered and dried at 105°C. See Table I for details.

Determination of Organic Content of the Treated Asbestos

The weight loss on ashing of the dried samples was determined as reported previously.(2)

Determination of Unsaturation

The general procedure followed is that outlined in the Union Carbide Chemicals Division Laboratory Manual, General Methods of Analysis 31-10A1-9.

(1) Weighed samples were placed in three tared 250 ml. glass-stoppered Erlenmeyer flasks. Sample size was determined by the formula:

$$\text{Sample Wt.} = \frac{0.072 \times 0.126 \times 100}{\%\ \text{organic material}}$$

(3) 50 ml. of 0.2 N bromine-sodium bromide reagent was pipetted into each flask and allowed to stand 1.5 hours.

(3) 100 ml. of methanol and 10 ml. of saturated potassium iodide solution was added.

(4) The slurry was then titrated with standard 0.1 N sodium thiosulfate to a starch end point.

$$\%\ \text{Theor. Unsat.} = \frac{5(B-A)N \times 72.07}{\%\ \text{organic} \times \text{sample wt. (in g.)}}$$

A = ml. of N normal sodium thiosulfate for sample
B = ml. of N normal sodium thiosulfate for blank

Results were internally consistent ± 3%.

Ref: 3GWR116

July 10, 1964

Attempted Exchange of Acetate Ions For Hydroxide Ions on Asbestos

A slurry of 30.0 g. of Coalinga Chrysotile in 500 ml. of distilled water containing 246 g. of sodium acetate (6M) was heated to 108°C. and stirred at that temperature for 100 hours. The slurry was filtered rapidly while hot and a 50 ml. sample of the filtrate was titrated potentiometrically with 3 N hydrochloric acid. The titration plot described a smooth curve with a break at the acetate end point.

Reference: 4GWR18 August 18, 1964

Addition of Magnesium ε-Hydroxycaproate to Asbestos

To a warm solution of 343 g. of sodium hydroxide in one liter of distilled water was added dropwise 1103 g. of ε-caprolactone. After the exotherm had subsided, a solution of 847 g. of magnesium chloride in 667 ml. of distilled water was added with stirring. The solution was heated to 100° and 100 g. of CMS grade chrysotile was added in 10 g. portions. Heating and stirring were continued for 10 hours, and the solution was filtered hot. Approximately half of the filter cake was immediately placed in a drying oven at 105° and dried for 3 days. On ashing at 900°C. the weight loss was 56%.

The remaining half of the filter cake was washed with three 100 ml. portions of cold water and then dried as above. The weight loss on ashing was 14.5%.

Reference: 4GWR12 August 12, 1964

Molding of MFG Polyester 3482 With Treated Asbestos

The filler material and polyester were weighed in the proportions indicated in Table II to obtain a total weight of 50.0 g. One per cent of benzoyl peroxide initiator was added to the polyester which was then milled cold with the filler material on a 3 x 8 inch roll mill for five minutes. The charge was transferred to a 5-1/4 inch compression mold, taken to 30 tons pressure, and heated to 120°. All specimens were treated in the same way except samples 3GWR130-10 and 3GWR130-11 which were molded at a total pressure of 15 tons.

Filler Materials

3GWR120

11.1% organic material, 30.4% unsaturated
0.29 equivalents acrylic acid/F. W. Asbestos (554.2 g.)

3GWR106-1

18.3% organic material, 100% unsaturated
1.72 equivalents acrylic acid/F. W. Asbestos (554.2 g.)

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CMS Coalinga Chrysotile

Dried at 105° for 48 hours
Less than 1% organic material

Reference: 3GWR130 July 27, 1964

REFERENCES

(1) C. W. McGary, P. L. Smith, and L. C. Shriver, "New Enterprises: Asbestos Reinforced Resins", Status Report, October 7, 1963, File No. 1342.

(2) C. W. McGary and G. W. Rausch, "New Enterprises, Chemical Reactions of Asbestos", Status Report, July 16, 1964, File No. 2819.

(3) Hendricks, Imhof, Merriam, and Stenstrom, Memorandum Report; New Resins Evaluation, October 31, 1963, Research and Development Department, Union Carbide Plastics Division.

ATTACHMENTS: 2 Tables

Gerald Rausch

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Union Carbide trial exhibit UC-4759: C. W. McGary and G. W. Rausch, New Enterprises Status Report on Chemical...
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TABLE I

Sample Number	Wt. Asbestos	Wt. Acid	Solvent	Volume Solvent	Temp.	Time	Inhibitor	% Inhibitor	Drying Time (Days)	% Organic	Unsaturation % Theory	Comments
3GWR90-1	30.0	24.6	H_2O	700	99	4.5	hydroquinone	1.0	4	3.4		Product extracted w. heptane
3GWR90-2	30.0					8			4	3.7		Product extracted w. heptane
3GWR90-3	30.0					12			4	6.0	100	Product extracted w. heptane
3GWR96-1						1			1	17.6		
									15	15.9		
									18	14.9		
3GWR96-2						2			25	14.1		
									1	20.5		
									15	16.4		
3GWR96-3						3			18	15.5		
									25	14.6		
									1	20.6		
									7	18.0		
									11	16.3		
									15	16.2		
3GWR96-4						6			18	15.1		
									25	13.7		
									3	22.2		
									14	20.0		
3GWR96-5						10			17	18.2		
									24	17.0		
									3	22.8		
									10	20.1		
3GWR96-6						16			14	19.0		
									17	19.0		
									1	28.3		
									2	27.5		
									6	24.6		
									10	23.8		
3GWR96-7						24			13	24.0		
									21	21.4		
									1	29.2		
									2	28.3		
									6	25.8		
									10	24.9		
									13	24.9		
									21	24.0	50	
3GWR104-1	107	288.5	H_2O	2550	100°	3	hydroquinone	1.0	8	1.3		Workup after 24 hr. standing
3GWR104-2	24	60.2	H_2O	500	100°	3	hydroquinone	1.0	10	15.6	98%	Immediate workup
3GWR106-1	120	602	H_2O	2550	100°	3	hydroquinone	1.0	14	16.2	100	Workup after 24 hr. standing
3GWR106-2	24	120	H_2O	500	100°	3	hydroquinone	1.0	10	14.3	100	Immediate workup
3GWR108-1	150	126	Toluene	3375	110°	0	MMHQ (.012 ppm)	--	1	2.2		
3GWR108-2						3			1	3.7		
3GWR108-3									13	2.1		
						6			4	4.6		
									12	3.2		
3GWR108-4						9			4	5.3		
									12	4.2		
3GWR108-5						13			1	7.1		
									2	6.3		
									8	4.5		
3GWR108-6						16			1	9.2		
									2	8.7		
									8	6.9	90	
3GWR112-2	150	1260	Toluene	2240	115°	3			1	15.9		
									13	7.8		
									15	7.7		
3GWR112-3						6			4	20.9		
									11	11.6		
									15	12.8		
3GWR112-4						9			4	20.9		
									11	16.9		
									15	16.6		
3GWR112-5						13			1	38.7		
									2	32.6		
									7	19.8		
									11	19.0		
3GWR112-6						18			1	31.7		
									2	29.1		
									7	26.5	9.0	
									11	25.3		
3GWR120	150	1260	Toluene	2240	110	10	hydroquinone	1.0	3	11.2	30	
3GWR123	150	1260	Toluene	2240	110	10	hydroquinone	0.25	3	10.8	28	
3GWR125	150	1260	Toluene	2240	110	10	hydroquinone	0.05	3	9.5	21	
3GWR127	150	1260	Toluene	2240	110	10	hydroquinone	2.0	3	12.7	25	
3GWR132	150	1260	Toluene	2240	110	14	2,5-diphenyl-p-benzoquinone	0.1	3	8.9	24	Stirrer stopped - Hot spots?
3GWR135	150	1260	Toluene	2240	110	14	2,5-diphenyl-p-benzoquinone	0.1	3	13.5	29	
4GWR1	150	126	Toluene	3375	110	20	2,5-diphenyl-p-benzoquinone	0.1	3	4.0	100	
4GWR4	150	630	Toluene	2870	110	18	2,5-diphenyl-p-benzoquinone	0.1	3	9.0	28	
4GWR8	150	1260	Toluene	2240	110	18	2,5-diphenyl-p-benzoquinone	0.1	3	22.2	17	

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TABLE II

Reference	Resin/Filler		Filler	Tensile Properties			Flexural Properties*		Compressive Properties*		Sample Thickness(4)
				Tensile Strength(1)	% Elongation	Modulus of Elasticity(2)	Flexural Strength(1)	Flexural Modulus(2)	Compressive Strength(1)	Compressive Modulus(3)	
3GWR130-3	50	50	Asbestos	3950	1.8	3.86	9,000	7.96	16,900	2.31	.056
3GWR130-2			3GWR120	6475	2.7	3.70	12,290	7.14	27,480	2.52	.058
4GWR16-1			3GWR106-1	4620	1.1	7.5	33,940	78.8	24,950	7.55	0.67
3GWR130-5	45	55	Asbestos	6560	2.1	4.35	10,950	10.5	19,540	2.96	.068
3GWR130-4			3GWR120	7800	5.9	3.33	13,090	7.49	27,600	2.78	.069
3GWR130-7	40	60	Asbestos	6680	3.4	3.80	10,430	6.20	20,370	2.64	.073
3GWR130-6			3GWR120	7485	2.8	3.61	12,360	5.99	23,880	2.59	.075
4GWR16-3			3GWR10601	5290	1.3	7.80	44,430	41.2	24,450	7.17	.086
3GWR130-9	35	65	Asbestos	8325	2.4	4.50	14,360	10.0	26,350	2.94	.087
3GWR130-8			3GWR120	6550	3.3	3.18	12,270	7.04	23,730	2.83	.090
4GWR16-4			3GWR106-1	5115	1.0	6.63	43,090	43.9	24,280	7.10	.097
3GWR130-11	30	70	Asbestos	7800	5.3	3.50	14,120	8.34	19,620	3.12	.111
3GWR130-10			3GWR120	7065	4.8	2.68	13,210	6.68	22,240	2.90	.104
4GWR16-5			3GWR106-1	4860	1.3	5.31	23,470	17.5	23,800	6.99	.118

* Flexural and Compressive properties were determined with unconventional samples. The data is reliable only for internal comparison.

(1) psi

(2) psi x 10^5

(3) psi x 10^4

(4) Sample thickness is inversely proportional to density. Flexural and compressive properties should have higher values with increased density or decreased thickness.

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