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UCC - RESIN-GRADE 144 ASBESTOS

A WHISKER REINFORCEMENT
FOR THERMOPLASTIC RESINS

by

R. E. Byrne, Jr.

August 25, 1967

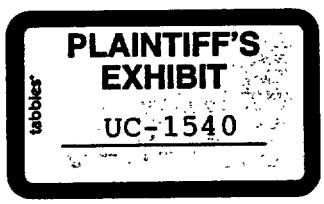
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Group Manager - R. G. Woolery

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Niagara Falls, New York
August 25, 1967

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INTRODUCTION

While composite and fiber reinforced structures are thousands of years old, only in the last two decades has technology become available for synthesizing and optimizing new materials from dissimilar elements to tailor a material for new uses. Growth of this industry, largely in the past 10 years, has resulted in total annual sales in 1966 of over 4 billion dollars.

In fiber reinforced structures, the fiber has the major role of carrying load. The matrix serves to bind the fibers in a fixed spatial arrangement, to transmit and distribute load to the fiber and to protect the fiber, in some cases, from hostile environments.

One of the latest concepts in this field is that of whisker reinforcement(1). W. P. Mulvaney has recently demonstrated the applicability of the theories of whisker technology to the data obtained on asbestos fiber reinforced vinyl resins(2).

This report presents data on the reinforcement of several thermoplastic resins with R-G144 asbestos. While the data are intended to be cursory in nature, they agree, in general, with Mulvaney's conclusions. Work is in progress, both at Niagara Falls and Bound Brook, on the reinforcement of nylon molding compounds, polysulfone, and rigid vinyl pipe compounds. A report on the properties of reinforced Nylon 6 has recently been issued by W. P. Mulvaney(6).

SUMMARY

UCC Resin-Grade 144 asbestos (R-G144) is hydraulically refined chrysotile mineral with a purity and degree of fiber liberation not previously available. It contains from 2 to 3 times as much fully liberated asbestos (free fibers) as does a conventional asbestos. The chrysotile fibers in R-G144 are of smaller diameter and narrower diameter distribution than a Canadian chrysotile. For these reasons, it provides reinforcing effects in synthetic resins which are different from those normally associated with asbestos. R-G144 may be considered a true reinforcing whisker and should not be considered as a filler.

Data are presented showing the improvement in tensile properties, heat distortion temperature, and, in some cases, impact resistance resulting from the reinforcement of several resins with R-G144. Comparative data show the superiority of R-G144 over Canadian chrysotile in a clear vinyl compound. The properties of R-G144 reinforced high density polyethylene compare quite favorably with polypropylene.

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CONCLUSIONS AND RECOMMENDATIONS

From the work presented here, the following conclusions may be drawn:

1) R-G144 is a unique whisker reinforcement for synthetic resins.

2) New classes of polymers, with new levels of performance, can be prepared from R-G144 and standard resins.

3) Resins which have a chemical affinity for chrysotile (hydrated magnesium silicate) benefit most from R-G144 reinforcement.

It is recommended that work be continued to explore R-G144 reinforcement of thermoplastic resins, particularly those with available functional groups, such as polysulfone, polycarbonate, C-4, phenoxy, and acrylics. Chemical modification of R-G144 should be examined as a means of increasing its reinforcing efficiency in less reactive polymers. The reinforcement of epoxy and phenolic resins with high levels of R-G144 should also be investigated.

DISCUSSION

General

UCC Resin-Grade 144 asbestos represents a manufacturing improvement on the natural mineral whisker, chrysotile asbestos. Because of increased product purity and the higher content of individual fibrils (whiskers), R-G144 reinforced plastic materials are superior to those obtained with conventional chrysotile products.

Chrysotile is one of a group of six different types of asbestos fibers commercially available. Table I shows the physical characteristics of the six commercially important asbestos minerals. As shown in the table, chrysotile is a tubular, fibrous hydrated magnesium silicate, $Mg_6(OH)_8Si_4O_{10}$, generally believed to be hollow. It makes up about 90% of all asbestos used in the United States, most of which is mined and processed in Canada and is known, consequently, as Canadian chrysotile. (A comprehensive treatment of the mineralogy of chrysotile, its basic fiber properties, and the rheology of aqueous suspensions can be found in a recent report by F. A. Mumpton, et al.)(3)

Canadian chrysotile occurs in low yield (10-15%) as a cross or slip fiber of varying length in serpentine rock. It is refined by crushing and subsequent air separation to remove waste material. It is then graded according to fiber length, from Grade 3 (the longest) to Grade 7. R-G144 is similar in fiber length to Grade 7. As it is normally sold, however, Grade 7 chrysotile asbestos contains only 60% asbestos and 40% serpentine rock dust with the asbestos fibers agglomerated in bundles of varying size. In this respect it differs from R-G144 which is refined hydraulically to contain not less than 99% asbestos and to fully liberate the asbestos fiber to its fundamental particle diameter. R-G144 also contains less than 0.5% magnetite, whereas it may run as high as 3% in a good Grade 7 product.

R-G144 is mined from a massive asbestos deposit near Coalinga, California. The ore yields 40-60% asbestos and is texturally different from most Canadian-type deposits. The favorable mineralogy and hydraulic refining result in R-G144 containing

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TABLE I

Physical Properties of Asbestos Minerals*

Property	Chrysotile	Anthophyllite	Crocidolite	Actinolite	Tremolite	Amosite
Composition	$Mg_3Si_2O_5(OH)_4$	$Mg_7Si_8O_{22}(OH)_2$	$Na_2Fe_3Fe_2Si_8O_{22}(OH)_2$	$Ca_2Fe_5Si_8O_{22}(OH)_2$	$Mg_5Ca_2Si_8O_{22}(OH)_2$	$(FeMg)_7Si_8O_{22}(OH)_2$
Crystal Habit	Fine, thin, easily separable fibers	Prismatic crystals and fibers	Long brittle fibers	Prismatic crystals and fibers	Prismatic crystals and fibers	Prismatic crystals and fibers
Color	White, gray, greenish	Gray-white	Blue	Green	White, gray-white, greenish	Ash gray or brown
Luster	Silky	Vitreous to pearly	Silky to dull	Silky	Silky	Vitreous to pearly
Occurrence	Altered ultrabasics and intruded limestone	Crystalline schists and gneisses	Fe-rich, argillaceous schists	Metamorphosed limestones and crystalline schists	Metamorphosed limestones and Mg-rich rocks	Crystalline schists
Veining	Cross-fiber, Slip-fiber, Massive fiber	Slip-fiber Massive fiber	Cross-fiber	Slip-fiber Massive fiber	Slip-fiber Massive fiber	Cross-fiber
Hardness	2.5-4	5.5-6	4	6	5.5	5.5-6
Specific Gravity	2.4-2.6	2.8-3.1	3.2-3.3	3.0-3.2	2.9-3.2	3.1-3.3
Refractive Index (mean)	1.51-1.55	1.61	1.7	1.63	1.61	1.64
Texture	Soft to harsh also silky	Harsh	Soft to harsh	Harsh	Harsh	Harsh
Tensile Strength (psi)	80,000-100,000	<4000	100,000-300,000	<1000	1000-8000	16,000-90,000
Electric Charge	Positive	Negative	Negative	Negative	Negative	Negative
Resistance to Acids and Alkalis	Poor	Very good	Good	Fair	Good	Good
Flexibility	Very good	Poor	Good	Poor	Poor	Good
Impurities Usually Encountered	Magnetite, chromite, calcite	Magnetite	Magnetite	Calcite	Calcite	Magnetite

*Reproduced from "Properties of Union Carbide's Chrysotile Asbestos" by F. A. Mumpton, S. Chwastiak, and K. Park, dated May 31, 1967, Chemicals & Plastics Division

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a much higher concentration of individual fibrils and fewer fiber bundles than the Canadian chrysotile. As shown in Figure 1, the average diameter of the UCC fibril is about 260 Angstroms and varies over a narrower range than a typical Grade 7 asbestos which averages about 350 Angstroms. The average aspect ratio (length to diameter) of an R-G144 fibril is about 200 which is well above its critical value for optimum reinforcement as shown in Mulvaney's report(2).

The higher purity, larger number of individual fibrils, and smaller average fibril diameter greatly enhance the reinforcing efficiency of R-G144 asbestos. For the same reasons, R-G144 is more efficient for viscosity build-up and thixotropy in liquid resin systems which has been demonstrated by J. F. Bliss and C. Pitt(3) at Bound Brook.

Vinyl Resins

R-G144 asbestos, with its strong cationic surface charge, has a natural affinity for and is well wetted by vinyl chloride polymers. Since one of the criteria for good whisker reinforcement is a strong bond between fiber and matrix, it is not surprising that excellent mechanical properties result. In addition, with the proper choice of stabilizers, a compound results which retains excellent see-through even at relatively high (30 phr) asbestos loadings.

Table II shows test data on compression molded samples of VYNS (PVC-PVa copolymer) compounded on a differential speed, two-roll mill. The data show that the optimum combination of strength and rigidity occurs at about 15 phr of R-G144.

TABLE II

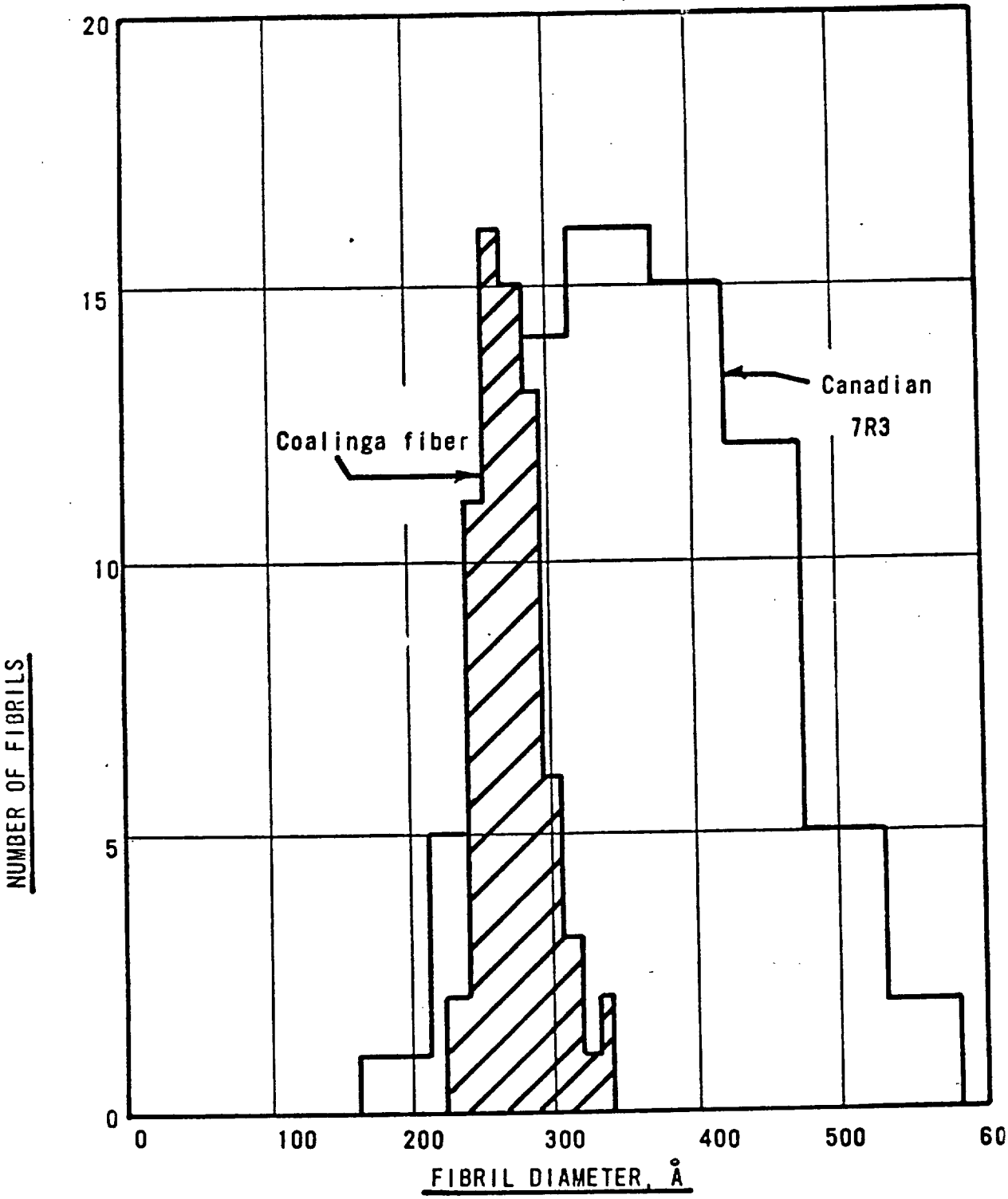
Reinforced VYNS*

R-G144, phr	0	5	10	15	20	25
Tensile Strength, psi	7600	8800	9000	8600	6700	6000
Tensile Modulus, psi x 10^{-3}	396	430	531	542	540	551
Elongation, %	2	3	3	4	2	2
Izod Impact, ft.-lb./in.	0.6	0.5	0.5	0.5	-	-
Heat Distortion Temp., °C.	63.0	-	69.9	-	-	-

*Formulation	Parts
VYNS	100
Temex 5	1.2
Advance CH-90	0.5
" ABC-18	0.75
Stearic acid	1.0
R-G144	0-25

At this level, neither elongation nor impact strength is adversely affected and a significant improvement in heat distortion temperature (HDT) is apparent. Except for the optimum level, these effects are also reported by Mulvaney(2). It should be noted that the presence of chrysotile in a vinyl compound can result in resin degradation unless suitable stabilizers are added. This degradative effect is more pronounced as the asbestos level increases, but small amounts of Mark C, Advastab CH-90, and similar chelating stabilizers have been found to be effective in overcoming degradation at levels up to 50 per cent by weight R G144.

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HISTOGRAM OF A TYPICAL FIBRIL DIAMETER DISTRIBUTI

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The properties of R-G144 reinforced rigid vinyls are also influenced by the degree to which the asbestos is dispersed in the system. Dispersion is not difficult, but processing variables can influence the product properties. In some cases, these variables are as important as the critical fiber volume. It has been observed that the critical volume is from about 5 to 15 phr R-G144. Mulvaney[2], by mathematical analysis of test results in plasticized PVC samples, has calculated this volume to be from 11-17 per cent.

Table III shows data on QYTQ (PVC homopolymer) reinforced with R-G144. In general, the effects are the same as those noted with the copolymer except that optimum loading is somewhat higher. The apparent increase in Izod impact strength is worthy of special note.

Two levels of plasticization with dioctyl phthalate (DOP) are also shown in Table III. The same reinforcing effects are shown in plasticized samples with no significant increase in hardness (Durometer). In the plasticized samples there is no marked decrease in elongations up to 20 phr R-G144.

TABLE III

Reinforced QYTQ

R-G144, phr	Tens., psi	Elong., %	Mod., psi x 10^{-3}	Izod, ft-lb./in.	H.D.T., °C.
0	8100	127	430	0.52	69.4
5	7900	8	462	0.77	70.2
10	8100	54	467	1.93	71.9
20	8400	4	548	1.10	71.4
		- With 20 phr DOR -			
0	4250	172	177	0.46	31.5
5	4700	167	161	0.87	37.6
10	5000	182	177	1.05	38.7
20	4400	189	178	1.06	37.9
		- With 40 phr DOP -			Durometer Hardness
0	2900	293	4.5	-	90
5	3300	197	4.7	-	91
10	3200	260	8.0	-	90
20	2700	240	8.0	-	92
		- With 60 phr DOP -			
0	2400	203	1.3	-	76
5	2300	337	1.3	-	79
10	2300	283	1.7	-	79
20	2000	253	3.9	-	83

The superiority in a typical vinyl formulation of R-G144 over Canadian chrysotile is shown in Table IV which includes data for samples prepared from Carey 7RF9 and Johns-Manville 7R06 asbestos.

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TABLE IV

Comparative Data with Competitive Asbestos in VYNS

(10 phr Asbestos)

	None	R-G144	Carey	JM
Tens. Strength, psi	7600	9000	7700	7800
Tens. Mod., psi x 10^{-3}	396	531	470	490
Elong., %	2	3	16	6
Izod, ft-lb./in.	0.6	0.5	0.5	0.5
Heat Dist. Temp., °C.	63.0	69.9	64.6	63.3
Color	Lt. Gray	Lt. Tan	Dk. Gray	Dk. Gray
Clarity	Clear	Clear	Opaque	Opaque

Formulation:

VYNS	100 parts
Temex 5	1.2 "
Advastab CH-90	0.5 "
" ABC-18	0.75 "
Stearic acid	1.0 "
Asbestos	10.0 "

Union Carbide's rigid PVC pipe compound QGPB-9311, which is based on QYTQ-7, is markedly improved in tensile strength, modulus, and Izod impact strength by the addition of R-G144. These data in Table V, do not show the increases in HDT which have been seen in other compounds and which have been reported by L. Robeson(5) to be as high as 80°C. with 40 per cent R-G144. In most cases the samples containing 30-40% R-G144, were severely degraded and are not included in the tables for this reason. Further work with QGPB-9311, including extrudability, is being done in Bound Brook.

A sample of calendered, rigid sheet based on VYNS and containing 20 phr R-G144 has been submitted to Polyplastex United. This material, known as ZCA-0511, is being evaluated as a fire-resistant structural substrate for rigid aircraft interior parts. According to Polyplastex, this is the only material which passes a new FAA burn-through test requirement for new aircraft interior parts. R-G144 asbestos-containing compounds similar to KDA-2618 and KDA-2034 are also reported by Polyplastex to have sufficiently low flame spread rating to be utilized in aircraft interiors. Other vinyl compounds containing R-G144 are currently under evaluation at Bound Brook and Wayne, New Jersey, and Ottawa, Illinois.

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TABLE V

QGPB-9311

R-G144, %	Tens., psi	Elong., %	Mod., psi x 10^{-3}	Izod, ft-lb./in.	H.D.T., °C.
0	8000	152	410	0.60	72.2
3	8000	139	445	0.70	71.2
5	8200	115	479	0.83	71.6
8	8300	7	-	0.60	71.4
10	8200	41	490	0.85	72.4
12	8400	11	-	0.60	72.6
15	8800	5	599	0.65	70.4
20	8800	4	567	0.70	71.2

Styrene Resins

R-G144 provides a means of producing higher modulus, tougher styrene compounds. The crystal polystyrenes, SMD-3500, are stiffened and improved in HDT, as shown in Table VI. The same magnitudes of tensile strength increase with vinyl polymers is not obtained in the polystyrenes, probably because of a lack of compatibility with the chrysotile mineral. Modification of the chrysotile fiber to render it less electropositive produces better reinforcement of polystyrene. For example, a 10% increase in tensile strength can be realized by treatment of R-G144 with Tergitol 04, an anionic surfactant.

TABLE VI

Polystyrene, SMD-3500

R-G144 phr	Tens. Str. psi	Elong. %	Tens. Mod. psi x 10^{-3}	H.D.T. °C.	Izod ft-lb./in.
0	5700	1.2	452	83.4	0.39
5	5500	1.2	462	84.5	0.35
10	5100	1.1	483	84.9	0.38
15	4400	0.8	510	86.9	0.24
20	4600	0.7	535	85.4	0.27
25	3700	0.6	570	88.3	0.26
40	4400	0.5	720	90.7	0.32
10*	5600	1.0	475	84.2	0.33

*R-G144 treated with 5% Tergitol 04

Styrene-acrylonitrile copolymer, RMD-4511, which is somewhat more ionic in nature than SMD-3500, has R-G144 reinforced properties which are more favorable. Typical property values are shown in Table VII. As is the case with all the styrene polymers, a brown coloration occurs which intensifies with increasing R-G144 content. The data show modulus increases, heat distortion improvement, and slight increases in tensile strength up to 10 phr asbestos. Chemical modification of the asbestos fiver can provide higher levels of reinforcement.

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TABLE VII

Styrene-Acrylonitrile, RMD-4511

R-G144 psi	Tens. Str. psi	Elong. %	Tens. Mod. psi x 10^{-3}	H.D.T. °C.	Izod ft-lb./in.
0	8800	1.9	507	88.8	0.28
5	8400	1.7	540	90.5	0.37
10	9100	1.9	611	91.6	0.30
15	7700	1.9	605	92.8	0.40
20	6700	1.8	667	93.6	0.32
25	6500	1.7	720	91.3	0.32
40	7600	0.9	1210	98.0	0.40
10*	9500	1.7	667	95.3	0.25

*R-G244, chemically modified asbestos

Attempts to reinforce ABS compounds have shown that even low levels of R-G144 cause a loss in tensile strength, elongation, and Izod, but the expected increases in modulus and HDT. Some preliminary work has shown that chemical modification of R-G144 effects improvement in ABS strength and toughness such as that shown with RMD-4511.

Further work should be done to explore the possibility of devising a tougher, more heat resistant ABS material.

Polyolefins

The data shown in Tables VIII and IX show the improvements in strength, modulus, and heat resistance of polyethylene compounds containing R-G144. These property improvements are more pronounced in the high density DMD-7000, approaching the values normally associated with polypropylene. Optimum reinforcement occurs between 10 and 25 phr asbestos in both high and low density resins.

TABLE VIII

Low-Density Polyethylene, DYNH-4

R-G144, phr	0	5	10	15	20	25	40
Density, g./cc.	.9164	.9465	1.009	1.047	1.048	1.083	1.267
Tensile Strength, psi	1460	1460	1390	1160	1370	1390	1540
Elongation, %	538	505	532	270	58	53	8
Tens. Modulus, psi x 10^{-3}	18.1	24.1	32.2	35.3	44.3	51.1	67.9
Tens. Impact, ft-lb./in.^{3}	218	114	82	66	60	60	35
Melt Index, Dg./min.	1.69	1.52	1.43	1.15	.65	.32	.14
Heat Dist. Temp. °C. (66 psi)	53.6	51.9	53.2	63.3	68.4	71.4	72.5

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TABLE IX

High-Density Polyethylene, DMD-7000

R-G144 phr	0	5	10	15	20	25	40
Density, g./cc.	.9699	1.004	1.032	1.068	1.098	1.136	1.262
Tensile Strength, psi	3200	3600	3700	3900	3600	3600	3400
Elongation, %	38	11	11	10	4	3	1
Tens. Modulus, psi x 10^{-3}	177	192	208	225	246	257	304
Tens. Impact, ft-lb./$in.^3$	81	43	25	35	18	11	11
Melt Index, Dg./min.	4.85	3.56	2.50	1.78	1.04	.52	.08
Heat Dist. Temp., °C.	49.6	50.2	54.3	52.6	59.0	62.5	65.9

In both cases, there is a drop in elongation and impact resistance with increasing asbestos content. Melt flow decreases with increasing fibrous reinforcement. Tests with ethylene copolymer containing polar groups such as acrylic acid indicate that even higher levels of reinforcement are readily attainable.

The data indicate that, by proper resin selection and possibly by suitable pretreatment, the lower performance resins can be upgraded for use in areas requiring higher modulus and heat resistance. At the same time, improvements in fire resistance and dimensional stability are coincident with asbestos reinforcement, as is the case in any resin system.

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REB:dmp

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