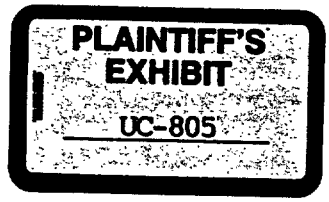
WV-0001 #-7

STATUS REPORT



NEW ENTERPRISES

ASBESTOS-REINFORCED RESINS

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L. C. Shriver

Date: October 7, 1963

Project No.: 161W21

File No.: 1342

SUMMARY Chrysotile asbestos and aqueous acids react in two ways: the acid is neutralized by a magnesium hydroxyl group and is retained in the asbestos; the acid is neutralized, and the magnesium salt is dissolved or precipitated in the water layer. Very weak acids, such as magnesium dihydrogen diphosphate, give the first effect. Intermediate acids, such as acetic acid, give both effects and incomplete reaction. Strong acids, such as hydrochloric acid, give the second effect which is stoichiometrically complete.

Dibasic and tribasic acids, which have a wide spread in ionization constants, have been used as cross-linking agents for asbestos. These materials, however, disrupt the asbestos structure by extracting magnesium prior to cross-linking through the weaker acid groups. The effect on resin properties of partially neutralizing these acids before mixing with asbestos will be investigated. Since water is required in these reactions, more satisfactory techniques for molding and curing must be sought.

STRUCTURE OF ASBESTOS In the last report the re-occurring formula unit of asbestos was given as $Mg_6(OH)_8Si_4O_9$. The magnesium-hydroxyl attack points on the molecule were considered to be six (≥Si-OMgOH) groups per re-occurring asbestos unit. In view of more enlightened information since obtained from Sterling Forest and elsewhere on the structure of asbestos, this assumption is not strictly true. Originally it was supposed that the siloxane bulwark of the molecule was a chain of connected duodecagons of the structure shown in Figure I. This configuration leaves six unsatisfied silicon bonds to carry the six (OMgOH) groups. Actually, however, the siloxane nucleus is not a chain polymer as shown but a "sheet" polymer of interlocking duodecagons, as indicated in Figure II. It can be seen with this configuration only one valence of each silicon is unsatisfied, or four bonds per re-occurring formula unit are available to hold 6-Mg's, 5 extra O's, and 2 extra OH's. (8-6). It is obvious then that conventional full valence bonding cannot be applied here and apparently the coordinate bonding of magnesium is involved. It also appears that magnesium atoms, holding

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two hydroxyls must be part of the molecule. This rather loosely bound structure would explain, in part at least, the ease and rapidity with which magnesium is cleaved from the asbestos molecule by the action of even relatively weak acids. This does not change the fundamental conception that only six hydroxyls per formula weight of asbestos are neutralizable with acid and that approximately twelve equivalents of H^+ are necessary to cleave all the magnesium from the asbestos molecule.

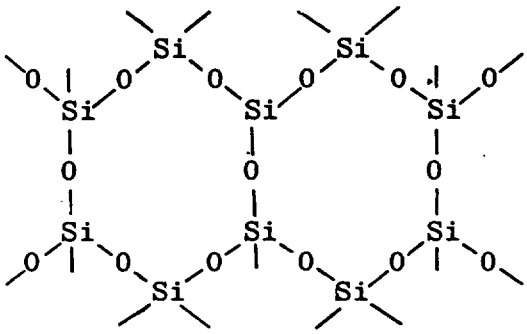


FIGURE I

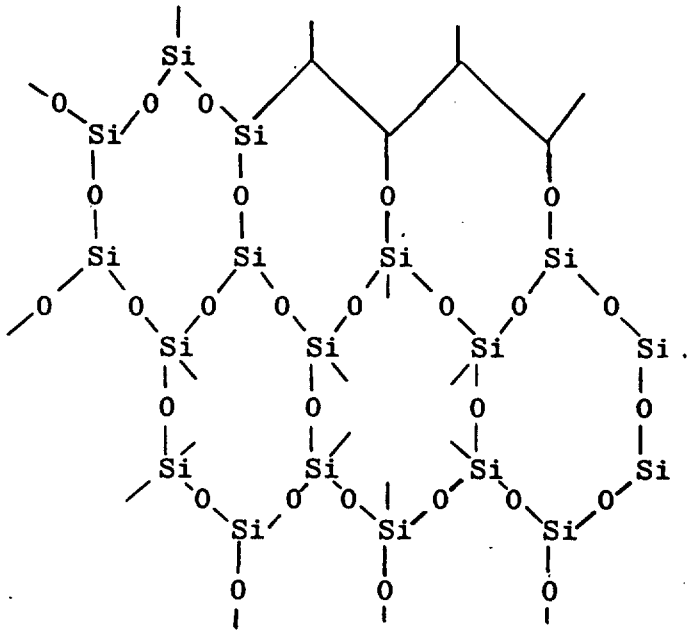


FIGURE II

The structure of asbestos, from the geologist's point of view, is envisioned as "layers" of molecules, that is progressive "layers" of oxygen, silicon, oxygen and hydroxyl, magnesium and finally hydroxyl on top. The thickness of this molecular "layer" is calculated to be 7.13A. Six to ten of these molecular layers form the walls of the hollow tubes, the form in which the chrysotile asbestos occurs. These tubes are roughly 250A in outside diameter, and if an average eight layers of 7.13Å is assumed, the inside diameter would be approximately 140Å.

AQUEOUS ACID REACTIONS Reaction of Coalinga asbestos with various aqueous acids at 25°-108°C. was studied. In each reaction, quantitative measurement of acid consumption and magnesium leaching at various time intervals was made. From the data obtained, the course of reaction was determined.

1. <u>"Strong" Acids (Dissociation Constants 1.0 x 10^{-3} or Higher)</u>

Data obtained for the reaction of hydrochloric acid with asbestos are shown in Tables I and II. As shown by these data, strong acids will cleave magnesium from the asbestos molecule in essentially stoichiometric amounts based on the quantity of acid which has reacted at any given time. If as much as 12 equivalents

of acid per formula weight of asbestos $Mg_6(OH)_8Si_4O_9$ is present, this reaction will continue until all the magnesium has been removed and only a siloxane residue remains. If less than 12 equivalents of acid per formula weight are present, however, the reaction will continue until (1) all the acid is neutralized, (2) the atoms of magnesium solubilized will be one-half the equivalents of acid reacted and (3) the remaining magnesium atoms and their accompanying hydroxyl groups will be left in the asbestos molecule untouched. In short, the reaction of "strong" acids with asbestos can be considered as their essentially instantaneous action of $2H^+$ ions to remove a magnesium atom from the molecule. This group includes, in addition to the totally ionized acids, other polybasic acids whose "first hydrogens" are relatively strong such as maleic (1.4×10^{-2}) and phosphoric acid (7.5×10^{-3}). Data obtained using maleic acid are shown in Table IV and V and for phosphoric acid in Table III.

2. Acids in the 10^{-5} Range of Dissociation Constant

The conventional straight chain organic acids (acetic, butyric, adipic, succinic, etc.) are included in this group. Their chemical action on asbestos departs markedly from that of the strong acids and (based chiefly on the behavior of acetic acid) may be characterized as follows:

(1) Their reaction with asbestos is never complete even when very high excess concentrations of acid and temperatures of 100-108°C are employed. Reaction of 40-50% of the magnesium is easily and quickly obtained at concentrations of 6-24 mols of acid per formula weight of asbestos. As concentration of acid is increased the maximum reaction point rises slowly until at 60 mols acid concentration 70-75% reaction of magnesium is obtained. Data for these various concentrations of acetic are given in Table VI.

(2) While substantial magnesium cleavage does occur in reactions with these acids, it approaches stoichiometric quantities only when large excesses of acid are employed and is relatively low when less than theoretical concentrations are employed. For example with acetic acid, when 6.0 mols of acid per formula weight of asbestos is used, only 14% of the magnesium reacted is cleaved from the asbestos molecule.

These data for acetic acid are summarized in Table VII. These data, together with other fragmentary data obtained at lower temperatures, suggest that, with the proper selection of acid concentration, time and temperature, considerable pendant group attachment might be accomplished with a minimum of magnesium cleavage. More data will be obtained on this important point.

From these data for the action of acetic acid, a wide difference in reactivity of magnesium atoms (or probably more correctly their attached hydroxyls) is indicated, since roughly 40-50% of the magnesium is attacked rather readily, but approximately 25% can probably not be attacked at all. It is also evident that

the cleaving reaction by the "second" mol of acid lags considerably behind the reaction of the "first" mol which simply couples by neutralization.

3. Acids in the 10^{-7} to 10^{-8} Range of Dissociation Constant

When the dissociation constants of acid groups are in the low range of 10^{-7} to 10^{-8}, reaction will occur with the more reactive asbestos hydroxyl without any discernible magnesium cleavage. This conclusion is based on data collected for the action of the "second" H^+ ions of maleic ($8{,}6 \times 10^{-7}$) and phosphoric (6.2×10^{-8}) acids in the cross-linking of asbestos. A more detailed discussion will appear later in the report. (See Tables III, IV, and V.)

NONAQUEOUS ACID REACTIONS Limited investigation of the reaction of maleic acid with asbestos in refluxing ketones (80-140°C.) as solvents indicates very low reaction rates and maximum reactions of only 15-20%. In addition, magnesium is cleaved in stoichiometric quantities. This approach, therefore, is not promising. Data obtained in methyl ethyl ketone is shown in Table VIII and in cyclohexanone in Table IX.

CROSS-LINKING OF ASBESTOS WITH DIBASIC ACIDS From the foregoing discussion of the action of "strong" acids on asbestos it is evident that in the cross-linking of asbestos with either maleic or phosphoric acids, the "first" H^+ ions can only cleave magnesium from the molecule. It follows then that the cross-linking must be accomplished by the "second" H^+ ions of the acid salts formed by the cleavage reaction. With maleic acid, the acid salt would be magnesium dihydrogen dimaleate, $Mg(OOCCH{=}CHCOOH)_2$ and for phosphoric acid, magnesium tetrahydrogen diphosphate $Mg(H_2PO_4)_2$. Chemical analyses made during actual cross-linking experiments with the two acids confirmed this conclusion. This consideration lead to the attempted preparation and isolation of the two salts for their subsequent use as cross-linking agents. Although the $Mg(H_2PO_4)_2$ was not isolated, a hydrated form of the maleic salt was obtained and employed in several cross-linking experiments. This cross-linking method has the advantage over the use of the acid and asbestos directly, of bringing the more reactive hydroxyls into play in the cross-linking reaction. Otherwise these reactive hydroxyls are wasted in making the magnesium salt by cleavage before cross-linking occurs.

In one instance a highly cross-linked product (97.7% of carboxyl reacted) was prepared in the form of a patty by this method. The ratio of carboyl/unit formula of asbestos was 1.33 or 4.5 hydrols to each carboxyl. This product was extremely hard and had fair water resistance. Other attempts using the same ratios but different curing conditions were not as successful, although one sample, prepared in the form of a cylinder (68% of carboxyls reacted) showed 1900 lbs/sq.in. compressive strength. The rate of temperature rise (with the resulting removal of water) versus the rate of cure is optimum within narrow limits for this reaction, due to the limited solubility of the salt in water (approximately 5%

at 25°C and probably 25% at 80°C.). The large amount of water which must eventually be removed from the cured specimens (50-65%) makes it difficult to maintain formed shapes during curing. This disadvantage, because of the lower water content, is not so pronounced in the phosphoric acid reaction and further work is planned with this acid employing an acid salt prepared and left in solution.

In summarizing acid cross-linking, it might be pointed out that the products prepared from either maleic or phosphoric acids are rock-like in character and have considerable breaking strength. This was particularly true of the sample prepared from maleic salt which was almost completely cross-linked. This sample required repeated heavy hammer blows to break it. Lack of water resistance is a major problem with these products. Samples vary from fast disintegration in cold water in one hour, to slow surface disintegration after overnight soaking. At present the lack of equipment here to form definite shapes (as cylinders for compression testing), which do not contain numerous voids, is a definite handicap in completely evaluating the cross-linked products.

CONCLUSIONS The rate of reaction of an aqueous acid with asbestos varies directly with temperature, concentration, time, and acid ionization constant. Only strong acids (ionization constants of 10^{-3} or higher) react appreciably at 25°C. and stoichiometrically in boiling aqueous solutions. Strong acids serve only to cleave magnesium from asbestos. Only weak acids (ionization constants of 10^{-5} or lower, and preferably about 10^{-7}) are useful for attacking pendant groups and cross-linking. Even weaker aicds (e.g., phenols) may be capable of reaction. The minimum strength required for reaction is not yet known.

Although acids will react in the absence of water, reaction is appreciably facilitated by the presence of water.

The mechanism of cross-linking with dibasic acids having one strong and one weak acid group (e.g., maleic and phosphoric acids) involves 1) cleavage of magnesium to form a dibasic magnesium salt (e.g., $Mg(OOCCH{=}CHCOOH)_2$) and 2) neutralization of the acid groups of this salt by reaction with the remaining - MgOH groups of the asbestos. In order to prevent magnesium cleavage, it is advantageous to prepare the dibasic magnesium salt from magnesium hydroxide.

As a result of this study, several possible routes are suggested to the preparation of asbestos-containing compositions for use as pipe, formica-type laminates, building panels, printed circuits, and auto body patch kits. These reactions, which would cross-link the asbestos, are outlined via the following list of reactants:

1. Polybasic acids (e.g., $Mg(H_2PO_4)_2$, magnesium dimaleate, dimer acid, etc.).

2. Styrene + unsaturated acids (e.g., magnesium dimaleate. acrylic acid and a carboxyl-capped polyester).

3. Polyphenols.

4. Diepoxides + polybasic acids.

5. Diepoxides (e.g., EP-206 with ammonium fluoborate catalyst).

6. Styrene + neutral esters of unsaturated acids (e.g., acrylic, methacrylic, and maleic).

7. Diisocyanates.

Other potential areas of application for asbestos are:

8. As coatings, modifiers for latexes, and molding powders after reaction with either a drying oil acid or acrylic acid.

9. Acid scavengers (e.g., as an HCl acceptor)for chemical reactions.

10. Soil conditioner for slow release of Mg into soil.

11. Fertilizer after reaction with $NH_4H_2PO_4$.

12. Flame-proof foams (taking advantage of the hydroxyl functionality of asbestos rather than using as an inert) by reaction with isocyanates.

EXPERIMENTAL In the study of the activity of acids in aqueous digestions, 30.0 gms. of asbestos in 700 cc of acid solution was employed. In the ketone digestions a ratio of 40 gms./ 500 cc was employed. With cross-linking experiments using phosphoric acid a recipe of asbestos 100 parts, 87% phosphoric acid 80 parts and water 25 parts, was employed. In maleic acid cross-linkings various ratios of materials were used but all within the following limits: Water 6-8 gms., maleic acid 12 gms and asbestos 16.3 to 30 gms. In the maleic salt cross-linking reactions a single recipe of water 90 gms., maleic salt 20 gms. and asbestos 51.0 gms. was used. The mixes in the cross-linking experiments were worked by hand and formed into "patties" for curing, except in one case where cylinders were formed by packing in glass tubes.

ANALYTICAL Magnesium content was determined by the method outlined in the report of April 8, which involves determining the amount of standard alkali necessary to precipitate the magnesium as hydroxide. "First" H^+ ion was determined by titrating with methyl red (pH range 4.4-6.2) as indicator; and "second" H^+ ion by finishing the titration with Phenolphthalein (pH range 8.3-10) as indicator.

lw

ATTACHMENTS: 9 Tables

L. C. Shriver/PLS

TABLE I

REACTION OF ASBESTOS WITH

AQUEOUS HYDROCHLORIC ACID AT 102°C.

(500 cc acid solution/30.0 gms asbestos. Equivalent data for acid given below are per formula weight of asbestos-554.)

Reference Number	Reaction time, hrs	Mols HCl Initially	Mols HCl At Reaction Completion	Mols HCl Reacted	Atoms Mg Solubilized	Mg x2
102LCS23-2	1.5	2.00	0	2.00	0.96	1.92
23-1	1.0	4.06	0	4.06	2.00	4.00
23-3	1.5	8.21	0	8.21	4.06	8.12
27	2.0	7.53	0.08	7.45	3.97	7.94
31	2.0	12.00	0.326	11.67	5.80	11.60

TABLE II

REACTION OF ASBESTOS WITH AQUEOUS HYDROCHLORIC ACID AT AMBIENT TEMPERATURES

(550 cc acid solution/40 gms. asbestos. Equivalent data for amounts of acid given below are per formula weight of asbestos-554)

REF. No. 102LCS43

Reaction Time, hrs	Mols HCl Unreacted	Mols HCl Reacted	Atoms Mg Solubilized	Mg x2
0	13.35	0	0	0
17.75	4.40	8.95	3.52	7.04
45.5	2.79	10.56	4.93	9.86
89.5	1.72	11.62	5.69	11.38
100.5	1.64	11.71	5.75	11.50

TABLE III

REACTION OF ASBESTOS WITH AQUEOUS PHOSPHORIC ACID AT BOILING TEMPERATURE (103°C.)

(500 cc aqueous phosphoric acid solution/30 gms. asbestos. Acid equivalent data given below are per formula weight of asbestos-554. Initial concentration of acid-6.065 mols acid/formula weight asbestos).

Ref. No.	Reaction Time Hrs.	Equivalents 1st H^+		Equivalents 2nd H^+	
		Unreacted	Reacted	Unreacted	Reacted
	0	6.065	0	6.065	0
	2.75	1.76	4.30	5.42	.64
	5.25	0	6.065	4.02	2.04
	10.75	0	6.065	2.83	3.23
	13.75	0	6.065	2.71	3.35

TABLE IV

REACTION OF ASBESTOS WITH AQUEOUS MALEIC ACID AT BOILING TEMPERATURE (103-106°C)

(500 cc maleic acid solution/30 gms asbestos. Acid equivalent data given below are per formula weight of asbestos-554.)

Reaction Time Hrs.	Equivalents 1st H^+ Unreacted	Equivalents 1st H^+ Reacted	Equivalents 2nd H^+ Unreacted	Equivalents 2nd H^+ Reacted	Atoms Mg Solubilized	Mg x 2
	102LCS14-A. Initial Concentration-6.01 mols maleic acid					
0	6.01	0	6.01	0	0	0
3	2.27	3.74	5.82	0.19	1.94	3.88
8	0.00	6.01	5.60	0.41	2.97	5.94
11	0.00	6.01	5.31	0.70	2.91	5.82
14	0.00	6.01	5.04	0.97	3.05	6.10
	102 14-B-Initial Concentration 4.25 Mols.					
0	4.25	0	4.25	0	0	
3	1.62	2.63	4.01	0.24	1.24	2.48
8	0.19	4.15	3.93	0.32	1.79	3.58
11	0.00	4.25	3.56	0.69	2.01	4.02
14	0.00	4.25	3.45	0.80	1.89	3.78

TABLE V

REACTION OF ASBESTOS WITH AQUEOUS MALEIC ACID AT AMBIENT TEMPERATURE.

(700 cc maleic acid solution/30 gms. asbestos. Acid equivalent data given below are per formula weight of asbestos-554.

REF. NO. 102LCS25
Initial Concentration 6.08 mols maleic acid.

Reaction Time, hrs.	Equivalents 1st H^+ Unreacted	Equivalents 1st H^+ Reacted	Equivalents 2nd H^+ Unreacted	Equivalents 2nd H^+ Reacted	Atoms Mg Solubilized	Mg x 2
0	6.08	0	6.08	0	0	0
3.25	5.32	0.76	6.03	0.05	0.52	1.04
22.5	4.25	1.83	6.07	0.01	0.89	1.78
53.5	2.93	3.15	6.05	0.03	1.61	3.22
75.0	2.19	3.89	5.70	0.35	2.09	4.18
99.5	1.36	4.72	6.08	-0.03	2.29	4.58

REF. NO. 102LCS45
Initial Concentration 11.73 Mols Maleic Acid.

0	11.73	0	11.73	0	0	
17.25	8.71	3.02	11.59	0.14	1.36	2.72
43.75	6.76	4.97	11.73	-0.20	2.14	4.28
60.5	4.01	7.72	11.64	0.09	3.41	6.82

TABLE VI

REACTION OF ASBESTOS WITH BOILING ACETIC ACID SOLUTIONS

(700 cc acetic acid solution/30 gms. asbestos)

Ref. No.	Reaction Time, Hours	Reaction Temp. °C.	Initial Conc. of Acid Mols/ Formula Weight Asbestos	Mols Acid Used/Formula Wt. Asbestos	Atoms Mg Solubilized Formula Wt. Asbestos	Mg x2
102LCS51	2.0	100	1.09	0.40	--	--
"	4.25	"		0.45	--	--
"	7.0	"		0.52	0.13	0.26
"	10.8	"		0.69	0.14	0.28
102LCS52	1.67	101	2.95	0.90	0.19	0.38
	4.25			1.19	0.33	0.66
	7.08			1.45	0.33	0.66
	11.00			1.64	0.35	0.70
	16.00			1.70	0.36	0.72
102LCS29	16.0	Ambient	6.03	0.39	0	0
"	5.75	102		3.23	0.37	0.74
"	10.0	102		3.48	0.745	1.49
102LCS37	3.0	103	12.0	4.30	1.80	3.60
"	8.0	103		4.48	1.95	2.90
102LCS38	3.0	105	24.0	5.14	2.55	5.10
	8.0	"		6.23	3.14	6.28
	16.0	"		6.35	3.20	6.40
102LCS39	6.0	108	60.0	7.35	3.68	7.36
"	22.0	"		8.10	3.85	7.70

TABLE VII

REACTION OF AQUEOUS ACETIC ACID

WITH ASBESTOS AT BOILING TEMPERATURE (100-108°C)

(700 cc of acetic acid solution/30 gms. asbestos)

Ref. No.	Approx. Time For Reaction Maximum Hrs.	Reaction Temp. °C	Initial Conc. Of Acid Mols/formula Wt. Asbestos	% Magnesium Attacked	% Mg Cleaved	Mg Cleaved / Mg Attacked %
102LCS51	10.8	100	1.09	9.6	2.3	24.0
52	16.00	101	2.95	22.2	6.0	27.0
29	5.75	102	6.03	47.7	6.2	13.0
37	3.0	103	12.0	41.8	30.0	72.0
38	8.0	105	24.0	51.5	47.3	92.0
39	6.0	108	60.0	71.0	64.1	90.2

TABLE VIII

REACTION OF MALEIC ACID IN NON-AQUEOUS MEDIUM (METHYL ETHYL KETONE) AT 80°C

(550 cc maleic acid solution/40 gms. asbestos. Acid equivalent data below are per formula weight of asbestos-554. Initial concentration of acid on this basis-6.02 mols. Ref. No. 102LCS42.).

Reaction Time, Hrs.	Equivalents 1st H^+ (Methyl red indicator)	
	Unreacted	Reacted
0	6.02	0
17.25	5.68	0.34
41.75	5.33	0.69
65.75	5.08	0.94
89.75	5.07	0.95
113.75	5.07	0.95

Titrations with phenolphthalein compared with methyl red indicated practically no 2nd H^+ reaction. Analysis of water soluble portion of residue from reaction indicated 0.34 atoms of Mg/formula weight of asbestos solubilized as magnesium salt.

TABLE IX

REACTION OF ASBESTOS IN NON-AQUEOUS MEDIUM (CYCLOHEXANONE) AT 140°C.

(700 cc. of maleic acid solution/40 gms. asbestos, Acid equivalent data below are per formula weight of asbestos-554. Initial concentration of acid on this basis-5.77 mols.)

Reaction Time, Hrs.	Equivalent 1st and 2nd H^+ (Phenolphthalein indicator)	
	Unreacted	Reacted
0	5.77	0
2.17	4.85	0.82
7.17	4.64	1.03
13.17	4.65	1.02

Titrations with methyl red indicator were not sharp in this instance so that differentiation of reaction of 1st H^+ and 2nd H^+ was not obtained.

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STATUS REPORT

POLYPROPYLENE RESILIENCY STUDIES:

DYNAMIC MECHANICAL PROPERTIES OF POLYPROPYLENE, ASBESTOS-FILLED POLYPROPYLENE, AND NYLON 66

Authors: J. A. Faucher
G. M. Bryant
J. V. Koleske

Date: December 11, 1963

Project No.: 161E19

File No.: 1803

SUMMARY The mechanical loss, which may be considered as an inverse measure of resiliency, and the components of the complex shear modulus of polypropylene, dyeable polypropylene, asbestos-filled polypropylene and nylon were investigated as a function of temperature with the torsion pendulum. Temperatures ranged from -180 to 240°C. depending on the material investigated. Orientation, annealing, and moisture content when applicable were utilized as variables.

The UCC dye assistant has little effect on the dynamic mechanical properties of polypropylene except at elevated temperatures. Annealing polypropylene improves its properties with the mechanical loss significantly improved (decreased) in the room temperature zone. Oriented specimens showed an increase in mechanical loss with the magnitude of the loss about equal in the orientation direction and normal to it. The glass transition peak of polypropylene was obscured by orientation. The components of the complex shear modulus were increased in and normal to the draw direction, but the increases were markedly different in the two directions.

Dyeable U. S. Rubber, Herculon (melt dyed), and dyeable Shell polypropylene were compared. It was not possible to definitely assign any secondary peaks to the dye or dye assistants. Little difference was found in the overall character of the mechanical loss for these polymers except for the height of the major loss peak. The peak was highest for the melt dyed Herculon and lowest for the dyeable Shell polymer. The Shell and U. S. Rubber polypropylenes had very similar properties in the room temperature zone.

Asbestos filler (Chrysotile) in the amount of 10, 20 or 30% had little effect on the mechanical loss of polypropylene. This filler increased both components of the complex modulus. Moderate annealing times improved the loss and modulus of

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asbestos-filled polypropylene. Long annealing times (19 hrs. at 130-140°C.) resulted in poor mechanical properties which have been attributed to a degradation of the polypropylene catalyzed by the Chrysotile. Orientation of the filled polymer increases the mechanical loss and the components of the complex modulus measured normal to the orientation direction. In the orientation direction the shear properties are poorer than those obtained with the unoriented polymer. Young's modulus is largest in the draw direction, and it decreases to a minimal value normal to the draw direction. The highly oriented asbestos-filled polymer is easily fibrillated and may hold some promise as a fibrillating fiber..

Molded Nylon 501 carpet yarn and Zytel 101 (both are nylon 66) were examined and compared with polypropylene. In the room temperature zone dry nylon has far superior loss properties to those of polypropylene. However, when conditioned at constant temperature and humidity, the nylon shows a shift of its major loss peak to the room temperature zone or a new loss peak near room temperature. In the moist conditions employed, which are closer to use conditions than the dry condition mentioned above, the loss properties are about equal to or poorer than those of polypropylene near the temperatures which are important to carpet resilience.

INTRODUCTION The torsion pendulum provides a simple, rapid method for obtaining the mechanical loss, Q^{-1}, and the real and imaginary or loss components of the complex shear modulus of polymeric materials. A torsion pendulum[1] is set into oscillation and it continues to oscillate with a constant frequency and a gradually decreasing amplitude. The log decreament, Δ, is determined from the natural logarithm of the ratio of two successive amplitudes, and from it the mechanical loss can be calculated by means of

$$Q^{-1} = \Delta/\pi. \qquad (1)$$

The mechanical loss is related to the energy stored and the energy lost per cycle by

$$Q^{-1} = \pi \left\{ \frac{\text{Energy lost/cycle}}{\text{Energy stored/cycle}} \right\}. \qquad (2)$$

This, of course, is related to the resilience of a material which may be defined[2] as the ratio of the work recovered to the work absorbed by a deformed material.

With Q^{-1} known it is possible to calculate the real and imaginary components, G' and G" respectively, of the complex shear modulus by the relationships

$$G' = (K/4)f^2\left[4.0 \pm (Q^{-1})^2\right] \quad (3)$$

and

$$G'' = Kf^2Q^{-1} \quad (4)$$

where f is the frequency and K is a constant that depends on the geometry and dimensions of the specimen, the moment of inertia of the system, and certain constants that enter when the differential equation for the motion of the torsion pendulum is solved. The minus sign in the bracket term of Equation 3 is used if the complex shear modulus, G*, is independent of frequency, and the plus sign is used if the dynamic viscosity is independent of frequency. In the work reported on, the dynamic viscosity was assumed to be the frequency independent factor. However, it should be noted that the small values of Q^{-1} encountered with polypropylene result in $(Q^{-1})^2$ being almost negligible compared with 4.0 throughout most of the temperature range covered. From Equations 3 and 4 it can be seen that at small values of Q^{-1} the mechanical loss is given by the ratio of G" to G'. It should be noted at this point that Q^{-1} does not depend on sample dimensions or geometry except in the manner that they affect the frequency; however, both G' and G" do depend on these physical parameters.

In brief, the two components of the complex shear modulus may be thought of in the following manner. When a specimen is loaded in a torsion pendulum, two mechanisms respond to the oscillatory motion. G' comes into being through the distortion mechanisms that respond in phase with the applied load, while G" arises through the distortion that is 90° out of phase with the applied load. These components are related to the complex shear modulus by

$$G^* = \left[(G')^2 + (G'')^2\right]^{1/2} \quad (5)$$

G* was not calculated in this work.

EXPERIMENTAL A recording torsion pendulum similar to that described by Nielsen[1] was used to obtain the mechanical loss as a function of temperature from -180 to 240°C. Various isotactic polypropylenes, nylon 66, ethylene/N-methyl-N-vinyl acetamide (ethylene-MeVA), polyethylene, and asbestos-filled polypropylene were investigated.

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Unoriented, unannealed specimens were in an "as molded" condition. This involved molding under pressure near the melting point and then quenching the molded plaque in the press. The plaques were stored at room conditions, unless otherwise noted, for at least 48 hours prior to testing. When specimens were annealed, they were placed in an oven set at the annealing temperature. Unless otherwise noted, at the end of the annealing period the oven was turned off and the specimens were oven cooled to room temperature. Oriented specimens were drawn in an Instron tensile tester to the desired draw ratio. To minimize voiding of oriented specimens, the elongations were carried out at elevated temperatures.

DISCUSSION

Frequency Dependence of Dynamic Mechanical Properties

The mechanical loss, G', and G" are dependent on temperature and on frequency of oscillatory loading. Therefore to fully describe the dynamic mechanical properties of a material, it is necessary to examine both dependent variables and to represent the property-temperature-frequency information in a three-dimensional plot. With the freely oscillating torsion pendulum only the temperature is controlled and the frequency varies with the response of the sample. Thus, what one actually views in a property-temperature plot is a diagonal slice through the three-dimensional plot rather than a true plot at constant frequency. Usually it is assumed that the frequency variation encountered with a torsion pendulum is small, a few cycles over a large temperature range, and does not cause an appreciable shift in dynamic properties. In the case of polypropylene the shift is readily apparent at the temperatures of particular interest in this study.

Since certain data taken with polypropylene on the torsion pendulum seemed anomalous, it was decided to investigate the frequency dependence of Q^{-1}. Specimens of various dimensions and different moments of inertia were used to vary the frequency about one and a half decades over the low frequency range of fractional cycles to almost ten cycles per second. The temperature range of -40 to 60°C., which included the glass transition of polypropylene, was covered. The results for certain temperatures are shown in Figure 1 for Shell Type 5820 polypropylene. Although there is scatter in the data, a noticable dependence on frequency exists. Similar plots were made for G' and G" but are not shown. A less extensive investigation was made with (ethylene-MeVA), and the results are shown in Figure 2. From viewing Figures 1 and 2 it would seem imperative that the frequency be stated along with the values of Q^{-1}, G', G" or Tg for these polymers.

With the frequency dependence of Tg readily available from the above investigation, it was possible to approximate the activation energy for the transition by a method described by Ke[3]. At the point of maximum mechanical loss, i.e., at Tg,

$$\tau\omega = 1 \qquad (6)$$

where τ is the relaxation time and ω is the angular frequency in radians per second. This method assumes that a single relaxation time exists. Since the temperature dependence of the relaxation time is represented by

$$\tau = \tau_o \exp(\Delta H/RT), \qquad (7)$$

where ΔH is the activation energy, R the gas constant, T the absolute temperature, and τ_o a constant, it is a simple matter to calculate τ from Equation 6 and make the Arrhenius type plot implied by Equation 7. This plot is shown in Figure 3 for Shell 5820 polypropylene and for ethylene-MeVA. The activation energy of 40.6 kcal. per mole for polypropylene is in the neighborhood of the 47.3 kcal. per mole obtained for the stress relaxation process[4] with dyeable Shell 5820 polypropylene.

Polypropylene

Samples of Shell Type 376 and 5820 and Hercules Type 6420 polypropylene with and without the UCC dye assistant (10% of the ethylene-MeVA copolymer) were examined. The results for the Shell Type 376 are shown in Figures 4 and 5. Near room temperature, which is of importance to carpet resiliency, the mechanical loss was little affected by ethylene-MeVA. Above 30°C. the ethylene-MeVA causes an increase in the mechanical loss except in the case of the Shell Type 5820 polymer, not shown, which had about equivalent loss with and without ethylene-MeVA until temperatures of about 120°C. were reached. By examining the frequency, Figure 4, it can be seen that the lower frequency and with the dyeable polypropylene would cause the results to be somewhat high (also see Figure 1). If a correction for the frequency difference were made, the curves would have better agreement. The general character and magnitude of G' and G'' are not significantly altered by the ethylene-MeVA as shown in Figure 5.

If two polymers had quite different glass transition temperatures, they would be considered incompatible if both loss peaks were apparent when examining a mixture of the materials. If a single loss peak were obtained for the mixture, the polymers would be considered compatible. The loss character of ethylene-MeVA is compared with that of the polypropylene and dyeable polypropylene in Figure 4, and it is readily apparent that the polymer

has a pronounced loss peak at about 0°C. (Here the frequency dependence is such as to exaggerate the loss differences.) Unfortunately, the loss maximum for both polypropylene and EMeVA occurs at about 0°C., which does not allow a great deal to be said about the compatibility of the materials.

Molded plaques of polypropylene were annealed following the schedule shown in Table I. The mechanical loss data for the Shell Type 376 polypropylene are shown in Figure 6.

TABLE I

ANNEALING SCHEDULE AND PROPERTIES OF POLYPROPYLENE

(ALL ANNEALED SAMPLES WERE OVEN-COOLED)

Type Polypropylene	Annealing Time, min.	Annealing Temp., °C.	Density	(Loss Max.) Tg °C	Frequency at 0°C., c.p.s.
Shell 376	0	---	0.9108	8	4.7
Shell 376	80	120-130	0.9156	3	2.2
Shell 376	180	130-140	0.9206	3	2.3
Shell 302	0	---	0.9166	7	5.0
Shell 302	300	130-140	0.9226	5	2.7
Shell 5824*	0	---	0.9084	2	2.1
Shell 5824*	1200	130-140	0.9112	2	2.4

* Shell Type 5824 contained a nucleating agent.

As expected, the value of Tg was not significantly affected by annealing (the higher Tg values shown in Table I for the unannealed samples are probably due to the measurements being made at a higher frequency than for the annealed samples). Above Tg there is a marked decrease in loss for the annealed samples indicating that the materials are more resilient until elevated temperatures are reached. Although the spectrum of frequencies is not shown, the unannealed specimen was run at higher frequencies than the annealed specimens which results in the values being somewhat low for direct comparison. Except for the introduction of secondary loss maxima, annealing has little effect below Tg. No attempt will be made to explain these secondary peaks, except to say that it is unlikely that they are caused by oxidation.

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The calculated values of G' and G" for the annealed Shell Type 376 are shown in Figures 7 and 8. The position of the maximum in G" is unchanged by annealing, although the value of Tg has decreased slightly, as would be expected, from that obtained by the mechanical loss data. Above Tg a plateau region becomes more prevalent as the annealing time is increased. This probably is due to an increase in crystallinity or a perfection of crystallities effected by annealing. Below the Tg region, G" is affected in a more complex manner than it is above Tg. At the shorter annealing time G" is increased and at the longer time it is decreased. Here again the secondary peaks are apparent. Values of G' are increased by annealing as would be expected; however, in the region of Tg the increase is very slight. Below Tg the effect of annealing time is similar to that found for G" although it is quite possible that the difference between the two annealed samples is within experimental error. As previously noted, the sample size and shape are taken into account in calculating G' and G", and thus the values obtained at high temperatures may be in error due to a change in one of these parameters. Overall, it can be concluded that annealing does enhance the resilience of polypropylene in the temperature zone important to carpet use and at temperatures above Tg.

To obtain an insight on the effect of nucleating agents, Shell Type 5824 polypropylene (melt flow 13.8), which contained a nucleating agent added by Shell, was examined in an as molded condition and after annealing. The results were then compared to those obtained with Shell Type 5820 polypropylene (melt flow 11.5) which supposedly was very similar to 5824 except that it did not contain a nucleating agent. The mechanical loss and appropriate frequencies are shown in Figure 9. Since these results are taken at almost the same frequencies, they are directly comparable. Before annealing, the nucleated polypropylene, density 0.9084, is somewhat less resilient than the non-nucleated polymer, density 0.9242. However, after annealing for 20 hours at 130-140°C., the nucleated polymer, density 0.9112, has a marked decrease in mechanical loss above Tg indicating that there should be improved resilience in and above the room temperature zone. The temperature dependence of G' and G" shown in Figure 10 indicates that the decreased loss of the annealed, nucleated polypropylene is brought about principally by a large decrease in the loss component along with a smaller increase in the real component of the shear modulus (see Equations 3 and 4).

Since orientation effects were thought to be of significant importance to resiliency, several oriented specimens were examined and a typical example is discussed. Shell Type 5820 polypropylene was molded and a plaque was drawn 9:1 at 105°C. The density before orientation was 0.9242 and after

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orientation was 0.9092 indicating that some voiding occurred during orientation. Measurements of the loss and frequency are shown in Figure 11. For the oriented polymer the shearing force was applied both normal to the draw direction (specimen mounted in the apparatus parallel to the draw direction) and parallel to the draw direction (specimen mounted normal to the draw direction). From Figure 11, it can be seen that the loss is greater for the drawn specimens. To compare the curves at equivalent frequencies, the curve for the unoriented polymer would be shifted to slightly higher loss values throughout most of the temperature range investigated. The increase in loss after orientation may be due to the presence of voids in the drawn polymer. It should be noted that little difference exists in the magnitude of the loss for the oriented polymer in the two directions except between 80 and 110°C.

Both components of the complex shear modulus, in each of the directions examined, are markedly increased by drawing as shown in Figures 12 and 13. At 0°C. and 20°C. the magnitude of G' and G'' are about 10-20 times greater normal to the direction of orientation and about 2-3 times greater parallel to the direction of orientation than those of the unoriented polymer. The character of the properties is significantly altered by orientation in all instances, though not in the same manner, except for G' of the polymer parallel to the draw direction which retains a resemblance to G' of the unoriented polypropylene. Although there is considerable variation in the magnitude and character of the properties of polypropylene when oriented, the mechanical loss or ratio of the components of the complex shear modulus in the two directions is nearly the same.

It is possible to attempt an explanation for the magnitude of the changes in the complex shear modulus. The oriented polymer has its molecular chains oriented to a greater degree parallel to the draw direction. When the shearing force is applied normal to the draw direction the primary bonds of the polymer chains are in a position to resist the force to a greater degree than they did in the unoriented polymer with the result being a very marked increase in modulus. When the shearing force is applied parallel to the draw direction the weaker secondary bonds between the chains become the force resisting components. In this latter case one would expect a lower modulus than that obtained for the unoriented polymer. However, it is possible that the order, and therefore cooperative secondary bonds, created by orientation is more important than the contribution of the chains or chain segments aligned in any given direction in the unoriented polymer. That is, the orientation creates cooperative secondary bonds that have a larger force resisting capacity than the random secondary bonds

and primary bonds that exist in any direction in the unoriented polymer. This latter factor would allow for an increase in modulus, as was obtained in this instance, in the parallel direction even though the secondary forces come into play to a greater degree than do the primary bonds.

It is interesting to note that Wakelin, et. al.,[5] who examined the torsional, stress-strain, and bending moduli of nylon 66 and Dacron filaments, found that while the stress-strain and bending moduli showed marked increases with increasing draw ratio, the torsional modulus was only slightly increased by drawing. To account for this difference, it was thought that the drawing process may increase the torsional modulus near the core of the filament and has little effect on the modulus of the material near the surface. Since the specimens used in the work being reported on were entirely oriented and no torsion measurements were made on filaments, it is not possible to substantiate or to refute this theory. The manner in which a polymer in a carpet responds to the various forces applied during normal, everyday use probably encompasses all of these moduli in a complex fashion.

Recently U. S. Rubber Company announced a new dyeable polypropylene and Hercules Powder Company has been marketing a melt-dyed polypropylene under the trade name Herculon. Yarns of these two materials were molded into plaques and examined with the torsion pendulum to see if the added materials affected the dynamic properties in any significant manner. The results were compared to those obtained with dyeable Shell Type 5820 polymer and are shown in Figure 15. The frequencies are about equivalent for the three polymers so the results may be directly compared.

In general, there is little difference in the overall character of the mechanical loss for these three polymers. The Shell polymer has the best overall properties, but in the room temperature zone which is important to carpet resilience there is no difference between the Shell and U. S. Rubber polymers. The height of the glass transition peak shows marked differences. How this would affect the final properties of the polymers is not known; however, it seems probable that the lower the peak value, the more resilient will be the final product. There is an indication of a secondary transition at about -60°C. with the Herculon that may be due to the melt-dyeing agent, but this is very slim evidence. In addition, sometimes polypropylene shows a peak at about this temperature as shown in Figure 6. The U. S. Rubber polymer has a definite peak at 80°C., but it does not seem reasonable to assign this to the dye assistant which supposedly is of low molecular weight. Here again, some

polypropylenes show a small peak or inflection point at about 70°C. that has been attributed to the onset of crystallite melting.

Asbestos-Filled Polypropylene

To determine the effect of a filler on resilience, blends of Shell Type 5820 polypropylene containing 10, 20, and 30% asbestos fiber were prepared by milling the two materials at 165-170°C. for 5-10 minutes. The asbestos used was chemically refined, Grade 7 Chrysotile obtained from the Nuclear Division. The asbestos appeared to be well dispersed in the milled mixture; but when plaques were molded, the 20% and 30% asbestos blends had a high concentration of asbestos near the edge and center of the plaque. Twenty per cent of the filler increased the density from 0.9242 to 1.039.

The mechanical loss data shown in Figure 16 indicated that the filler has little effect on the resilience of polypropylene except at elevated temperatures. The 20% blend appears to have the best characteristics above room temperature; however, it should be kept in mind that the asbestos was not well dispersed in this sample and the concentration of filler is only approximate. In addition, the data for the 20% blend was taken at frequencies that were about 20% higher than the other filled polymers which would have the effect of decreasing the loss values. The Tg was not changed by addition of filler, but there is evidence of a secondary loss peak in the 80-110°C. temperature range. (Note: Hercules Powder Company recently placed an asbestos-filled polypropylene, Pro-fax 66F1, on the market for use in extrusion and injection molding applications. Their material is said to retain or augment several desirable properties of unmodified polypropylene. From certain properties listed in the data sheet[6], it would seem that they use Crocidolite rather than Chrysotile for the filler.) The values of G' and G'' are shown in Figure 17. The real component is increased by increasing the filler content except for the 20% blend which shows a lower modulus below room temperature. Only the 30% asbestos blend shows pronounced effects of the filler. Since the asbestos filler should have good mechanical loss properties but did not enchance those of polypropylene, it is quite possible that the filler inhibited perfection of crystalline regions or crystallization of the polymer. Thus the loss improvement obtained from addition of filler is balanced by an increase in the amorphous character of the polypropylene.

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To test the postulation that the filler inhibited the crystallization of the polymer, specimens of the 20% blend were annealed at 130-140°C. for 2.5 hours and for 19 hours. The density after 19 hours annealing was 1.081 compared with 1.039 for the unannealed filled polymer. There was insufficient 2.5 hour material for a density determination. The surface of the specimen annealed for 19 hours was crazed. Viewing the cross section of this specimen revealed a thin cream colored perimetric region that seemed to be quite porous. This specimen was brittle and poor in strength properties.

The mechanical loss measurements are shown in Figure 18. The moderately annealed material has improved resilience as indicated by the generally lower mechanical loss. The glass transition temperature has been shifted to a lower temperature and the possibility of a secondary loss peak near 110°C. still exists after annealing. The long annealing time produced a marked increase in Q^{-1} and a much less resilient material in the temperature range investigated than the un-annealed or moderately annealed filled polymer.

The components of the complex shear modulus are shown in Figure 19. The real component increased for the moderately annealed specimen and severely decreased for the 19-hour annealed specimen. The imaginary component decreased with annealing time. Since Q^{-1} is related to the components of the complex modulus by $Q^{-1} = G''/G'$, the decrease in G'' is not sufficient to compensate for the decrease in G' for the 19 hour specimen and much poorer resilience resulted.

Since moderate annealing improved the mechanical properties, the initial postulate seems to be confirmed. The effect caused by long annealing times is evidentally a severe degradation of the polypropylene. In a recent Avisun Corporation patent[7], it is shown that asbestos in all forms except Anthophyllite in the presence of particular inhibitors catalyzes the heat degradation of polypropylene.

The 20% asbestos fiber blend was drawn 4:1 and 12:1 at 145-155°C. in an Instron tester and examined with the recording torsion pendulum. The density decreased from 1.039 for the unoriented material to less than 0.804 (the limit of the density gradient used) for the oriented materials. The mechanical loss properties are shown in Figure 20. Orientation has little effect on the glass transition temperature except for a slight decrease with the 12:1 draw-ratio material. Below Tg the loss increases with increasing orientation, but above Tg the increase in loss is independent of draw ratio except for the 4:1 and 12:1 draw ratio materials tested normal to the draw direction at the higher temperatures where a possibility of a secondary transition exists. In the orientation direction the loss is

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higher than it is normal to it throughout the temperature range investigated. The increase in loss with orientation is not too surprising when one considers that a large amount of voiding must have taken place on orientation to account for the extreme decrease in density. The voids probably act as amorphous material which causes an increase in loss at any given temperature. It is quite certain that annealing the oriented specimens would decrease their mechanical loss. The frequencies have been noted at two temperatures in Figure 20, and it should be kept in mind that this difference in frequency is such as to accentuate any real differences in the materials being compared.

The components of the complex shear modulus normal to the draw direction are shown in Figure 21. The real component increases with increasing orientation except for the unexpected decrease above 40°C. for the 4:1 draw-ratio material. The imaginary component increases with increasing orientation. In addition, the G" curve for the 12:1 drawn material shows evidence of several secondary loss peaks. The marked increase in complex modulus with orientation seems quite dramatic when one considers that the increases came about even though the density of the material decreased about 20% on orientation.

Figure 22 shows the components of the complex shear modulus in the direction of orientation and normal to it for the 12:1 drawn material. As discussed above G' and G" are increased normal to the draw direction on orientation as one would expect. In the draw direction G' has a very low value and G" is increased below the vicinity of Tg and decreased above the vicinity of Tg. Thus it seems that the secondary bonds in the direction of orientation are weak and in large part their formation or perfection may have been inhibited by the presence of the asbestos. These highly oriented filled materials were easily fibrillated and may hold some promise as a fibrillating fiber that contains hydrophilic and hydrophobic groups. R. G. Curtis attempted to dye the asbestos in a 5 mil. plaque of the 20% blend and had good success with 2% Celliton Fast Red, GGA. However, little or no dyeing took place with 2% Zylene Milling Blue, GL, with 4% sulfuric acid or with 2% Calcodin Blue, 4 GL, with 20% sodium chloride.

Utilizing specimens of the 20% blend that had been drawn 8:1 at 160°C., Young's modulus was determined from stress-strain data at room temperature to be 1.3×10^{10} in the draw direction, 0.33×10^{10} at 45° to the draw direction and 0.13×10^{10} dynes/cm^2 normal to the draw direction.

Nylon 66

Nylon performs well as a carpet yarn, as evidenced by its rapid growth in this textile application. For this reason its dynamic mechanical properties were examined and used as a reference material of good resiliency. Zytel 101, a molding grade of nylon 66, was used for most of the investigation. Textured Nylon 501 carpet yarn, nylon 66, that had been molded into a plaque has essentially the same properties as Zytel 101. Since nylon is moisture sensitive, it was examined at various moisture contents. Dry nylon, 0% humidity, was obtained by drying the plaque in a desiccator over anhydrous $CaSO_4$ for at least 48 hours prior to use. Since dry nitrogen at various temperatures is used as a heat transfer agent in the torsion pendulum apparatus, the dried specimens should have remained at low moisture contents throughout the runs. Nylon was also conditioned at constant temperature and humidity (73.4°F. dry bulb and 61.6°F. wet bulb) for two weeks prior to measurement. Below 0°C. the dry nitrogen heat transfer agent should have had little effect on the moisture content of the conditioned nylon, but above 0°C. undoubtedly some loss of moisture took place. The 100% relative humidity conditions were obtained by suspending the nylon specimen over water in a closed system at room temperature for 24 hours prior to use. Below 0°C. no attempt was made to control the humidity of the heat transfer agent, but above this temperature the dry nitrogen was bubbled through water before being sent to the mounted specimen.

The mechanical loss of dry nylon 66 is compared with that of polypropylene in Figure 23. The loss curves show the three characteristic loss peaks associated with nylon and the single peak associated with polypropylene. Near room temperature dry nylon has extremely low loss implying a high degree of resiliency. However, if Figure 24, which shows the loss curves for nylon at various moisture contents, is examined, one finds a different behavior. The loss curves for nylon in the presence of moisture have been significantly altered in the room temperature zone. This alteration is such that nylon now has about the same or higher loss than polypropylene. Thus under conditions that would be more similar to room conditions (the constant wet and dry bulb conditions) the nylon is no better than polypropylene in an "as molded" state. Of course, the effect of orientation and/or annealing on properties at various moisture contents may have an important influence on a final product as nylon carpet yarn. In addition, the texturing method used on a particular yarn may significantly alter some or all properties studied from a basic standpoint.

Under the constant temperature and humidity conditions, Figure 24, it would seem that nylon has been plasticized, for the major loss peak that occurred at about 70°C. in the dry nylon has shifted to a temperature of about 20°C. This behavior is similar to that reported by Woodward, et. al.,[8] for nylon 66 held at 100% relative humidity for 3 weeks except that the height of the peak was increased in their work. The odd behavior, indicated by the short plateau between 30 and 60°C., of the loss for the conditioned specimen may be due to a change (decrease) in moisture content which could become appreciable in this temperature range. The lowering of the moisture content with temperature is verified by the fact that the conditioned specimen's loss curve approaches that of the dry nylon at the higher temperatures.

The curve for nylon at 100% relative humidity shown in Figure 24 indicates a different behavior. A new peak is apparent at about 0°C. and there has been only a slight shift in the major loss peak. It should be kept in mind that in this instance the specimen was not dried by heat transfer agent since moist nitrogen was used above 0°C. These differences can be seen more clearly in Figure 25 which shows the imaginary portion of the complex modulus.

Although the data presented on the effect of water on nylon are meager, some attempts at explanation of the phenomena can be made. It is possible that a stoichiometric relation exists between water and nylon before plasticization takes place. Severe deviations from the proper ratio result in the water and nylon acting independently. Of course without more data, an explanation such as this is only speculation. Another possibility could be that the slow drying caused by the heat transfer agent in the case of the constant dry and wet bulb conditioned nylon produced an apparent blending of the two separate peaks that were observed with the 100% relative humidity specimen. This possibility would be more secure if the short plateau region (30-60°C.) extended to higher temperatures, say about 100°C. A third way of looking at the data is to assume that unbound water was present in the 100% relative humidity conditioned specimen and melting of ice at 0°C. caused the secondary loss peak (here the possibility would exist that the unbound water had been vitrified and one observes the devitrification and subsequent melting of ice in this region). However, although this may seem plausible, one must keep in mind that the nylon was not "wet to the touch" and it should take a relatively large amount of unbound water melting or devitrifying to cause the distinct peak seen at 0°C. Actually the work of Woodward, et. al.,[8] does not help in these explanations, for there was no mention of whether or not humidity conditions were controlled during the time their data was taken.

A specimen of molded Nylon 501 carpet yarn was oriented to a draw ratio of 3.5:1 in an Instron tensile tester at 220-225°C. The oriented specimen was examined only by applying the shear stress normal to the orientation direction. The results shown in Figures 26 and 27 are in general agreement with those obtained with polypropylene. The mechanical loss and the components of the complex modulus increase when the specimen is oriented. It should be mentioned that Marlex 6050 (polyethylene) was also examined in an as molded and in an oriented state and similar results were obtained.

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5614-JVK; 29 through 35-JEP; 37, 38, 39-JEP

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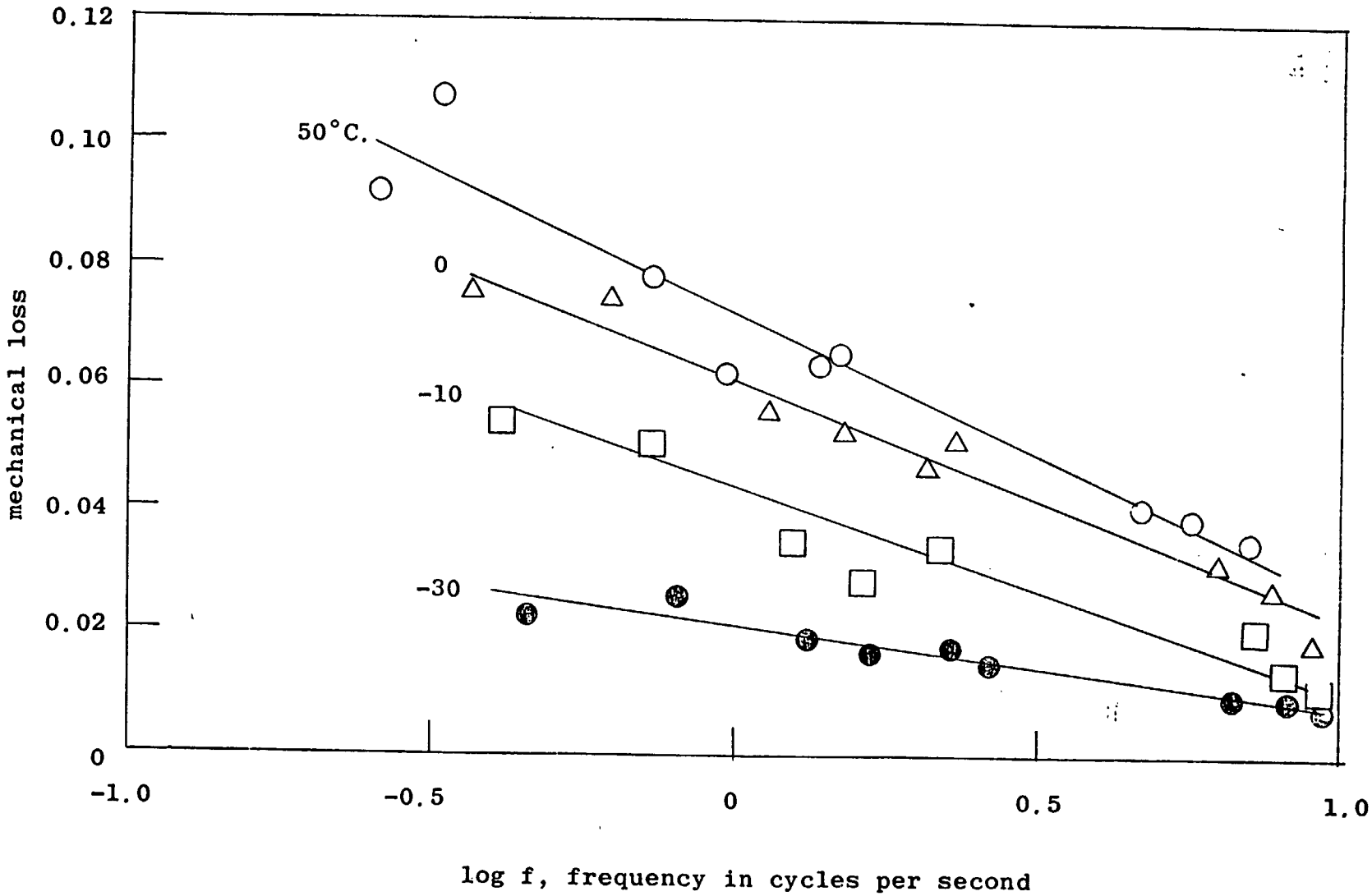
Joseph V. Koleske

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ATTACHMENTS
27 Figures

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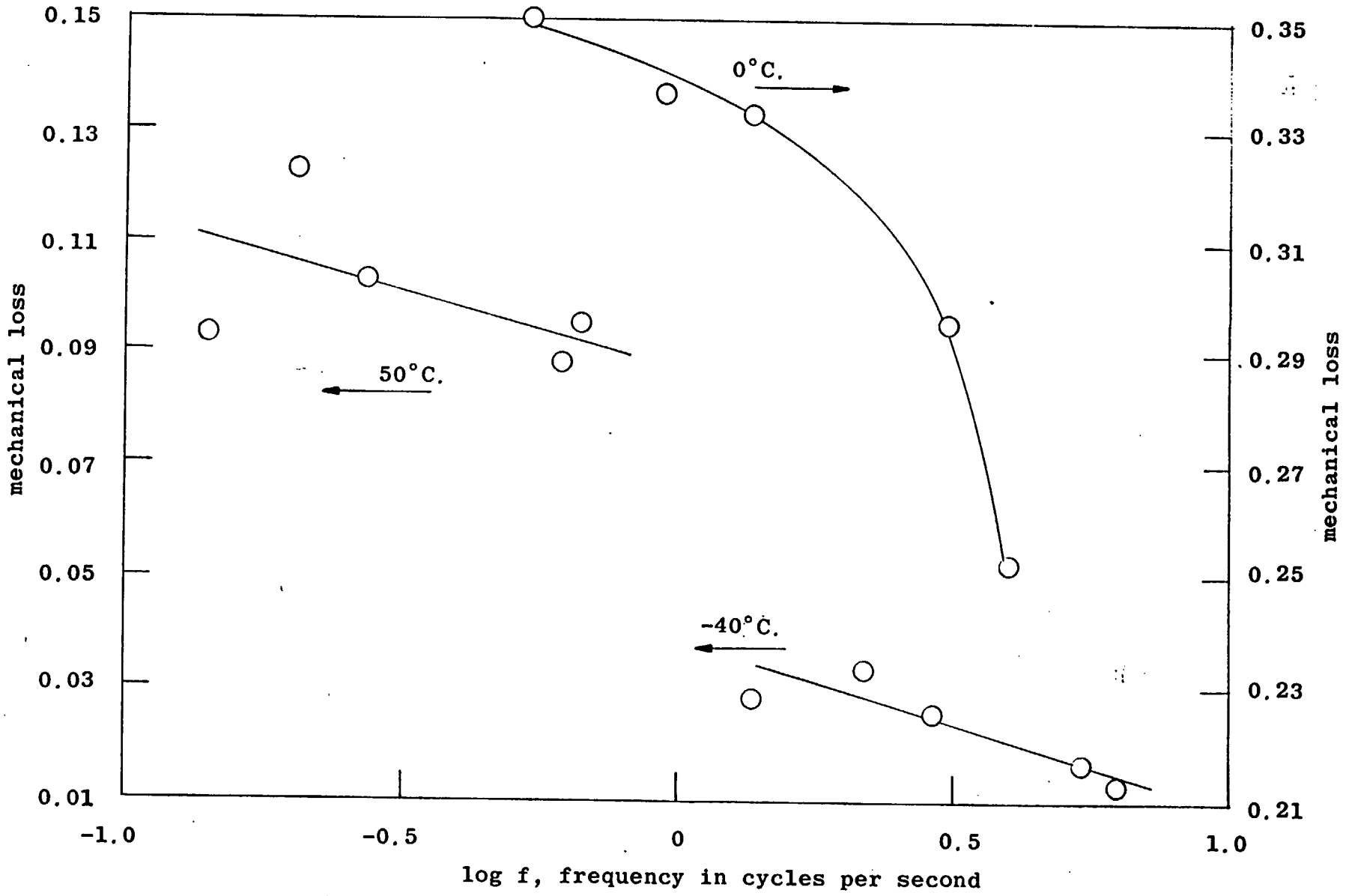
FIGURE 1. FREQUENCY DEPENDENCE OF THE MECHANICAL LOSS OF SHELL 5820 POLYPROPYLENE.



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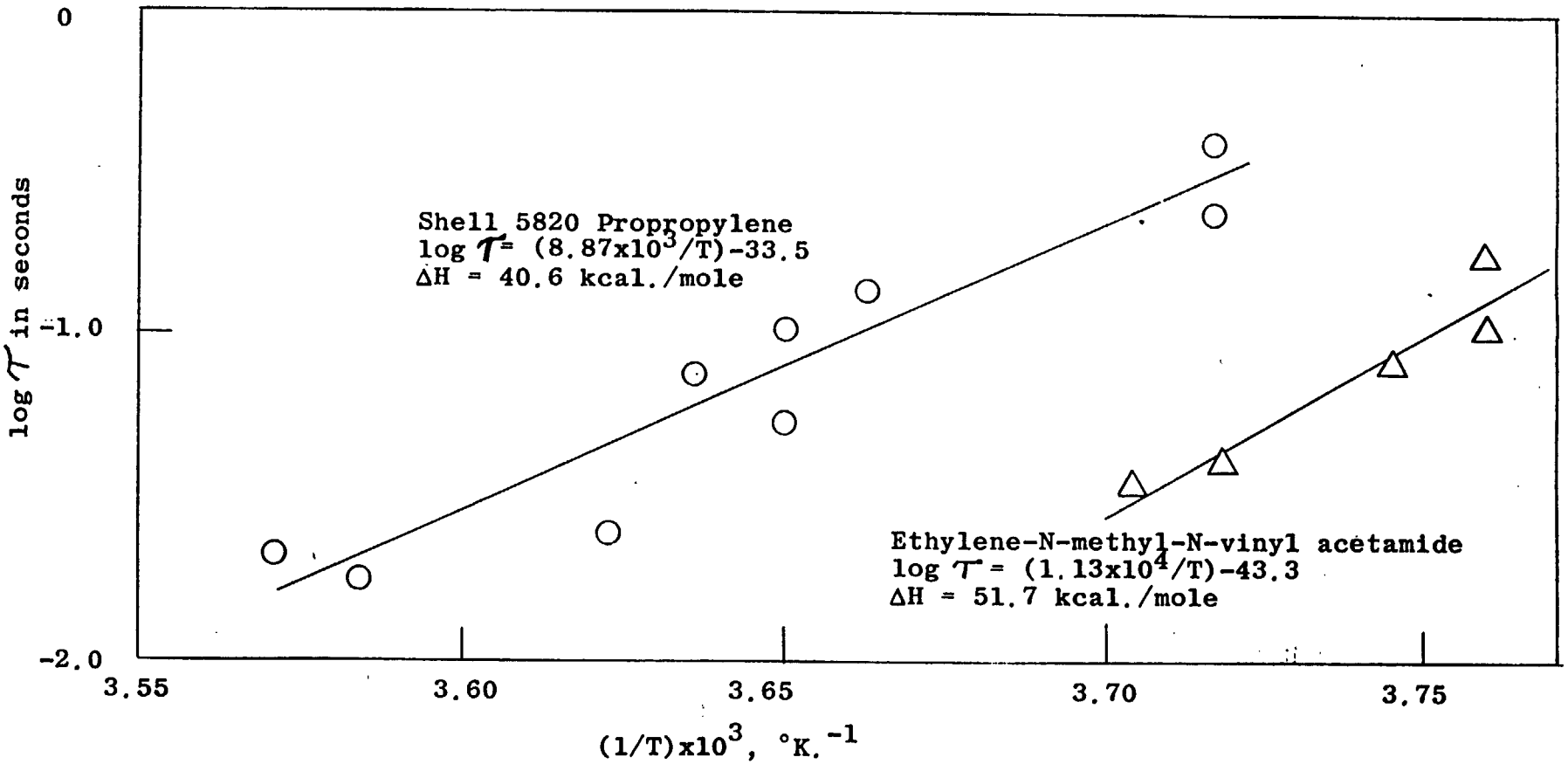
FIGURE 2. FREQUENCY DEPENDENCE OF THE MECHANICAL LOSS OF ETHYLENE/ N-METHYL-N-VINYL ACETAMIDE (LOT 1433, STIRRED AUTOCLAVE)



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FIGURE 3. ARRHENIUS TYPE PLOT FOR POLYPROPYLENE AND ETHYLENE/N-METHYL-N-VINYL ACETAMIDE. LINES REPRESENT A LEAST SQUARES FIT OF THE DATA.



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FIGURE 4. MECHANICAL LOSS AND FREQUENCY FOR SHELL TYPE 376 POLYPROPYLENE WITH AND WITHOUT ETHYLENE-MeVA AND ETHYLENE-MeVA LOT 1433, STIRRED AUTOCLAVE, 25% MeVA.

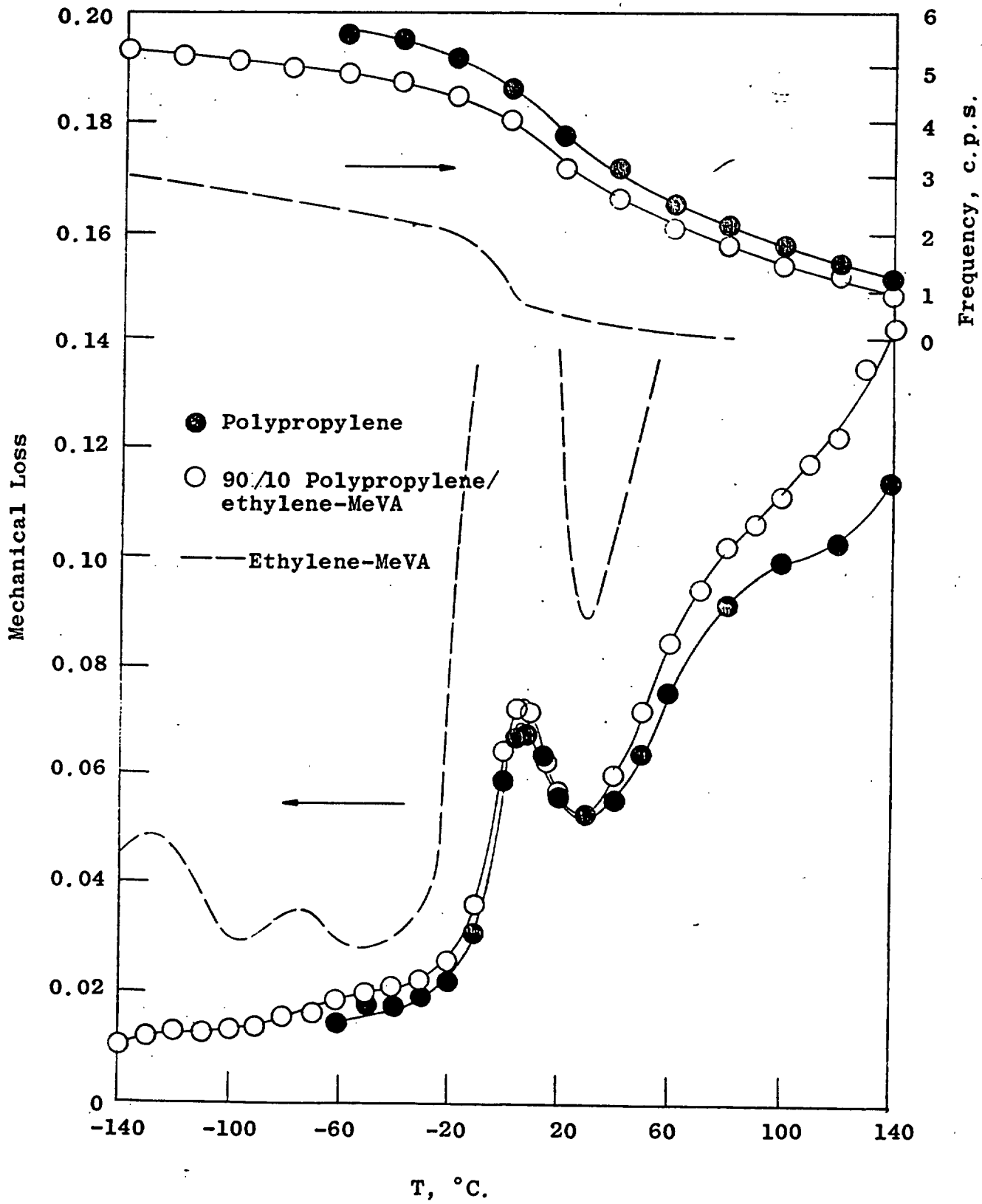


FIGURE 5. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH AND WITHOUT THE U.C.C. DYE ASSISTANT.

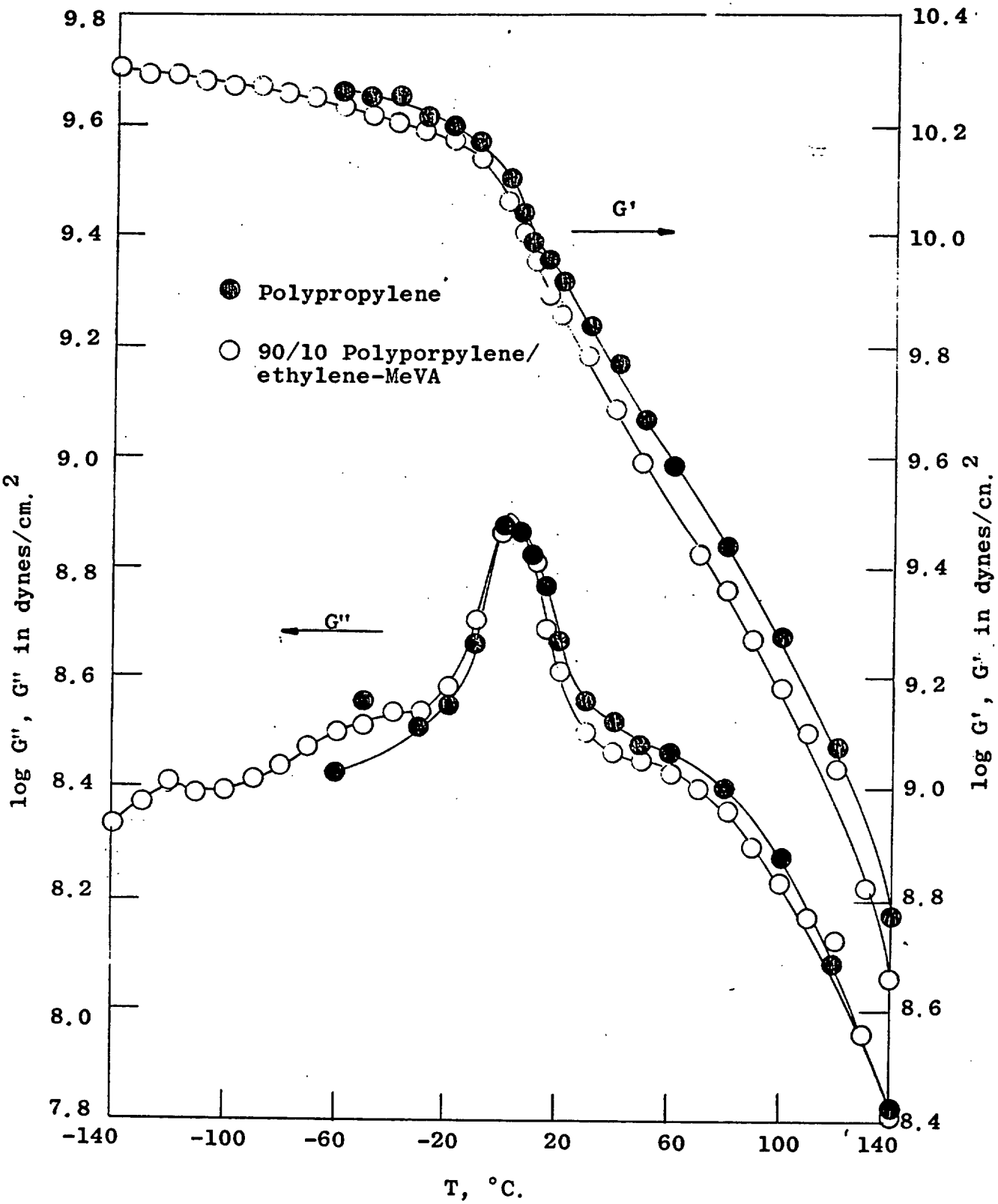
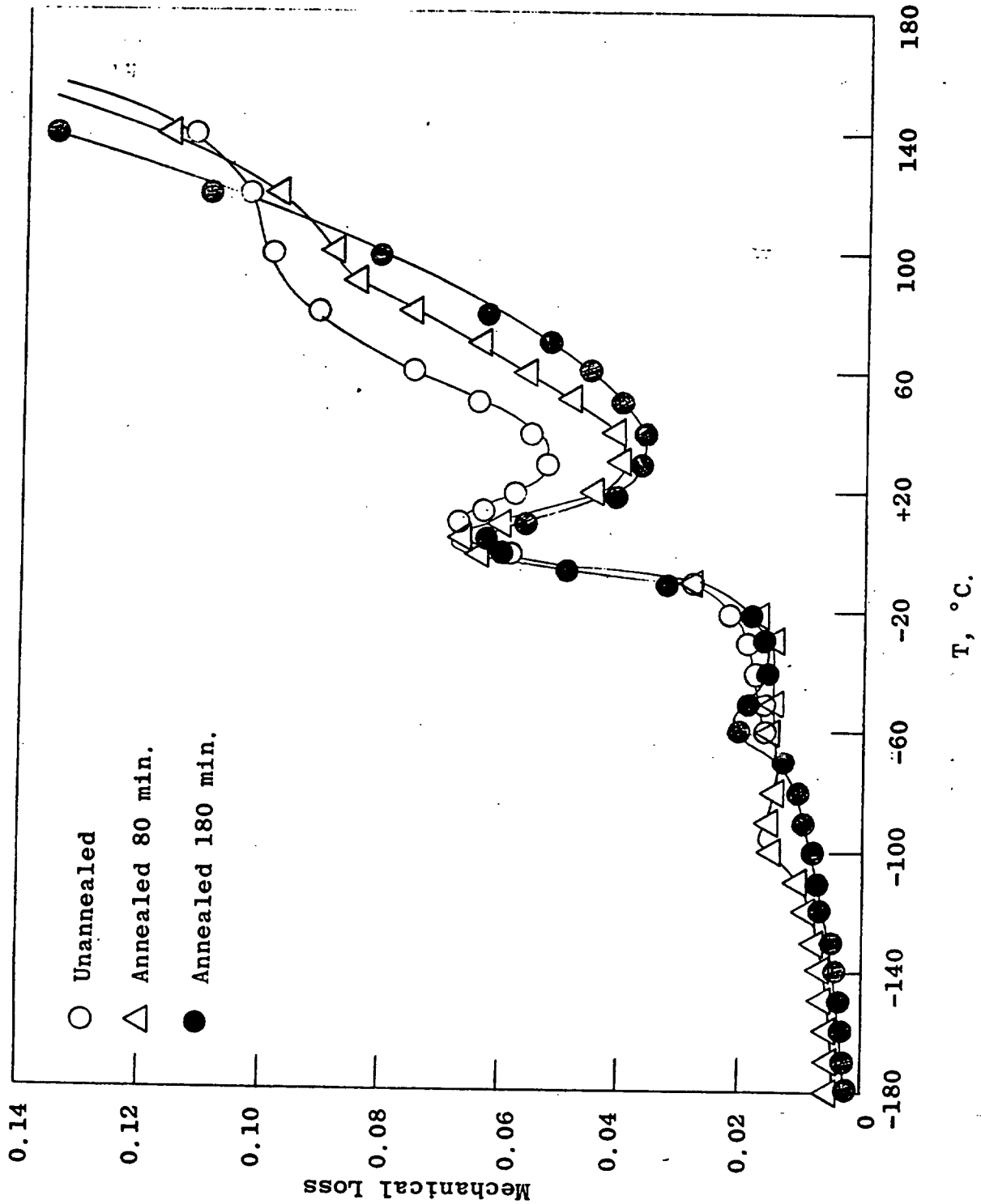
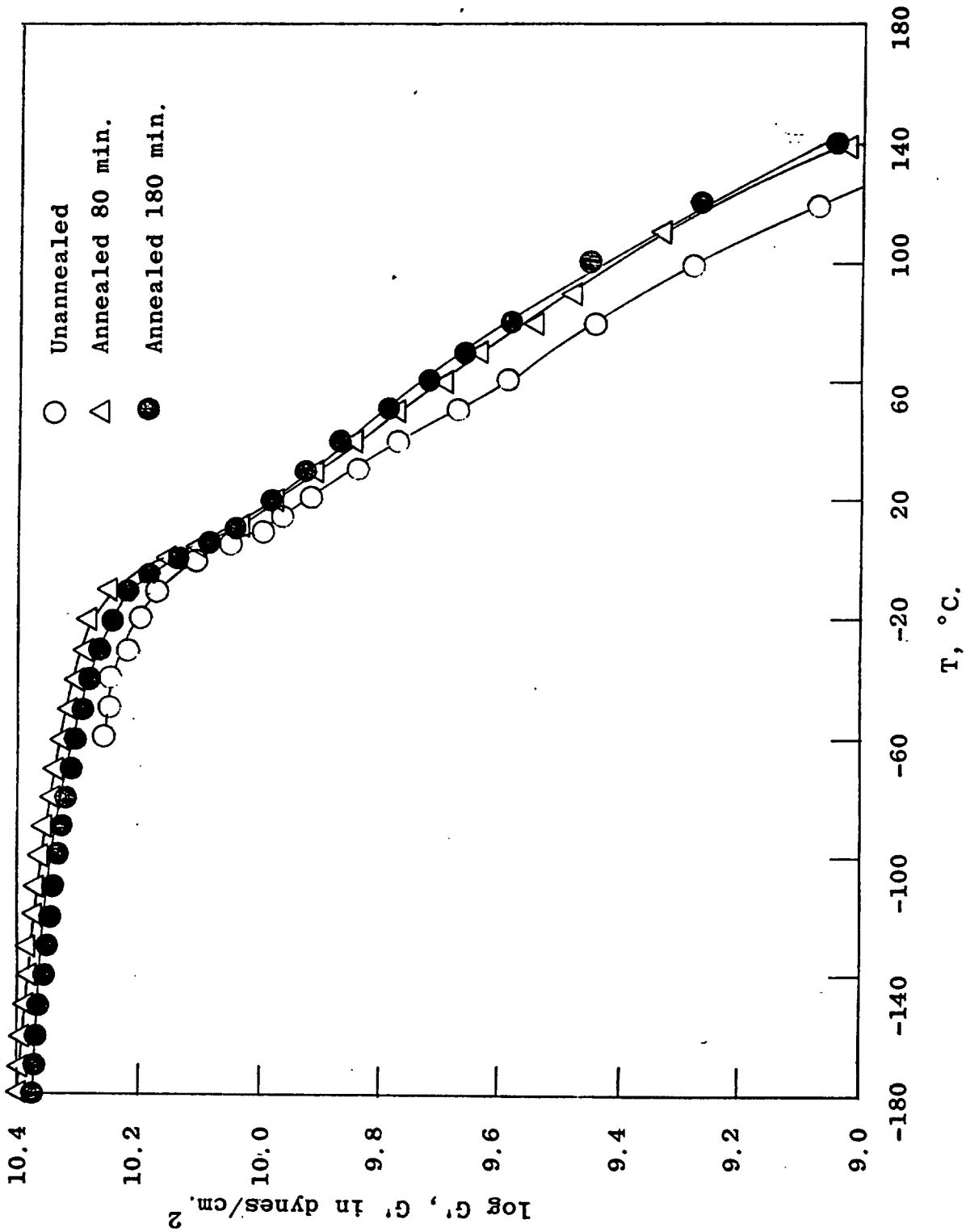


FIGURE 6. MECHANICAL LOSS FOR UNANNEALED AND ANNEALED SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS



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FIGURE 7. REAL COMPONENT OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS



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FIGURE 8. IMAGINARY COMPONENT OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS.

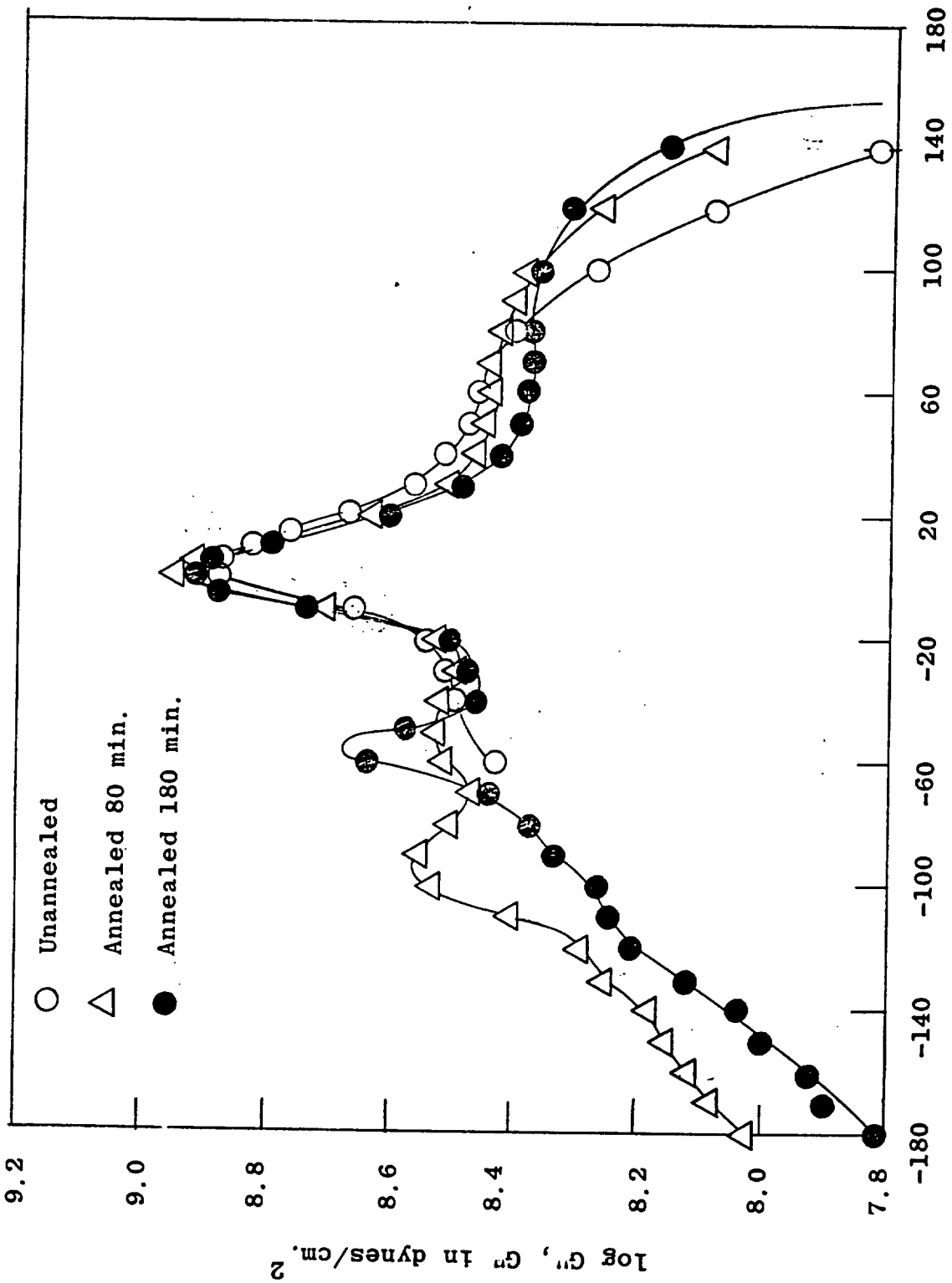
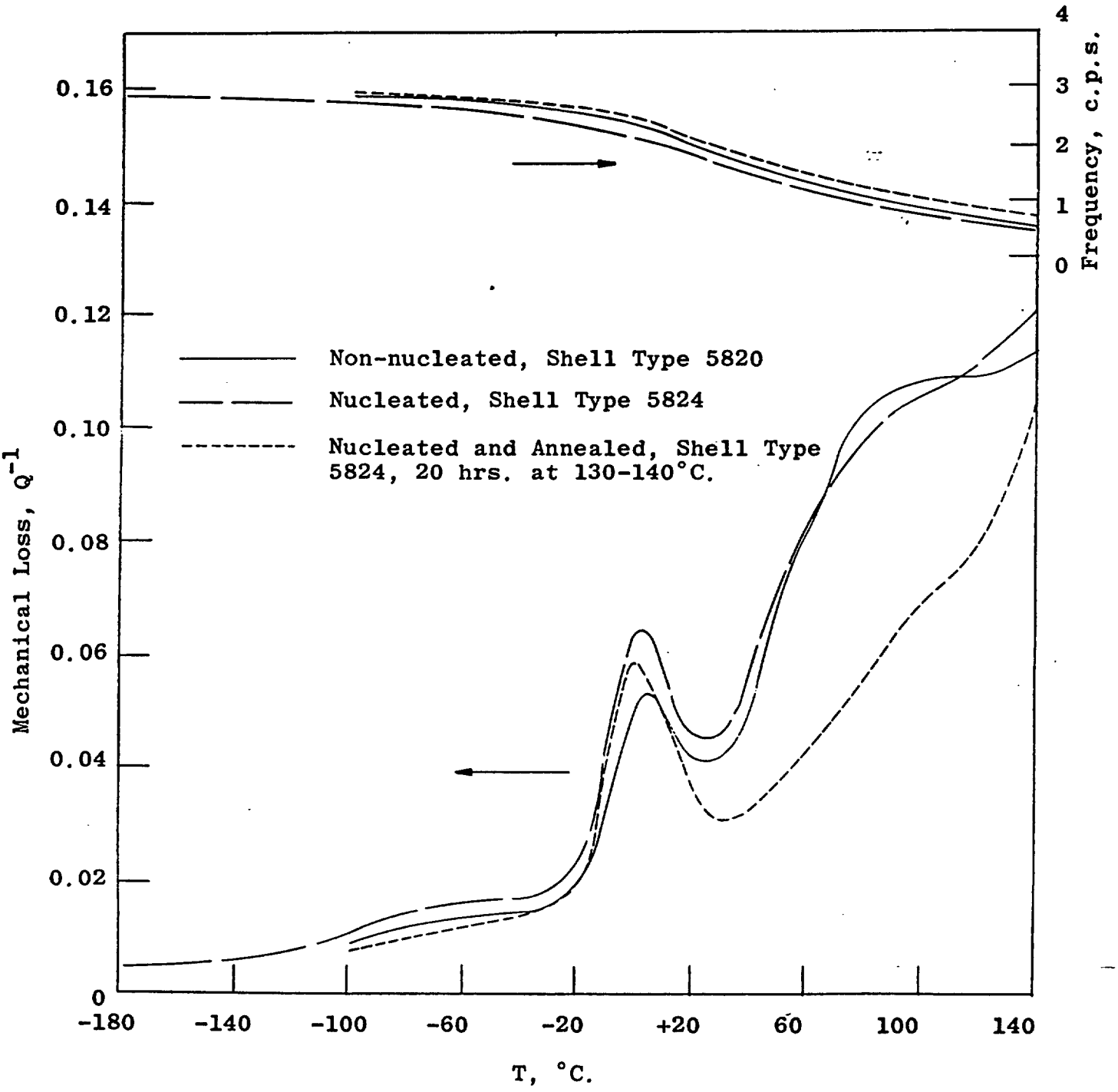


FIGURE 9. MECHANICAL LOSS FOR NON-NUCLEATED AND NUCLEATED POLYPROPYLENE



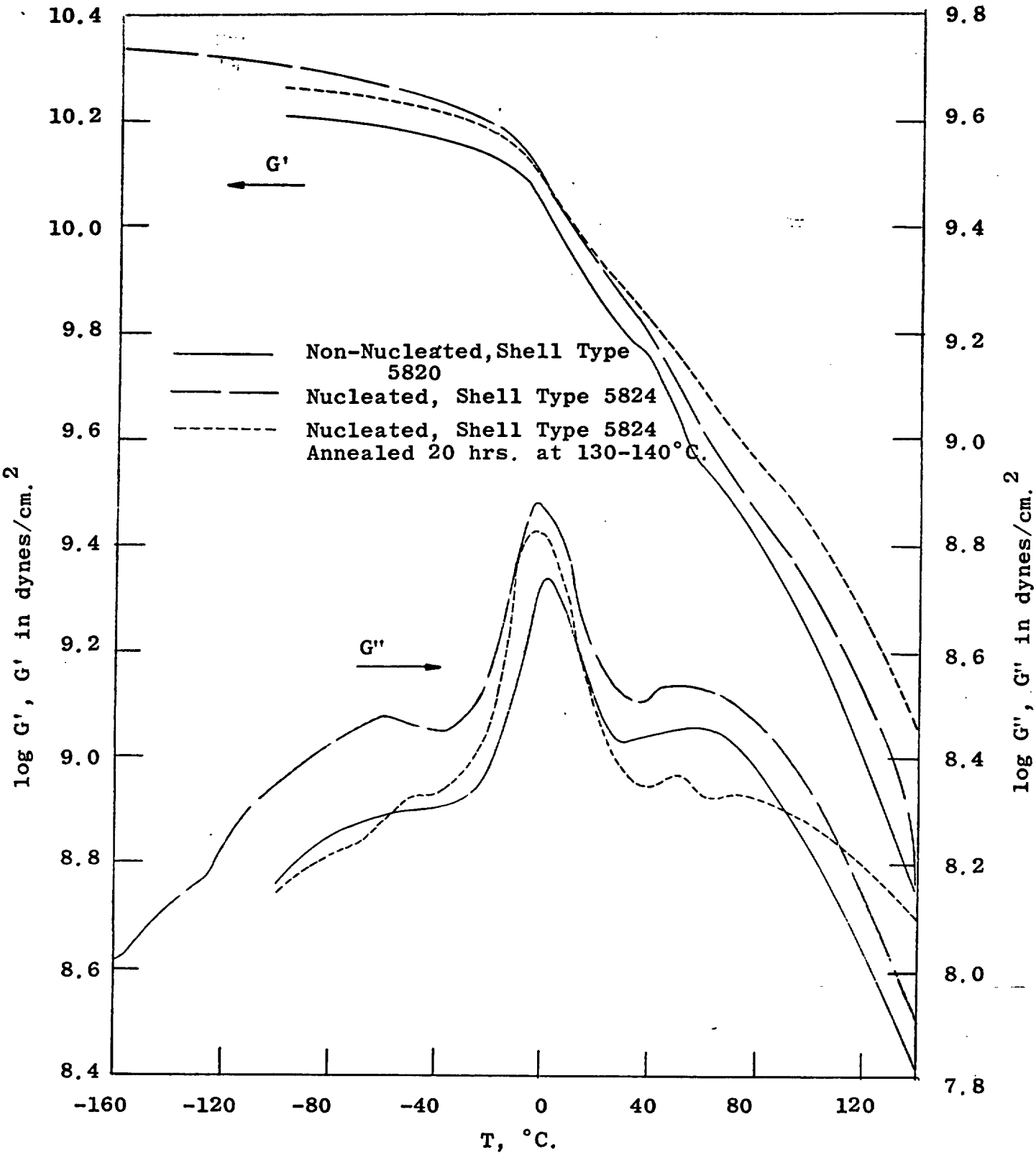


FIGURE 10. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR NON-NUCLEATED AND NUCLEATED POLYPROPYLENE

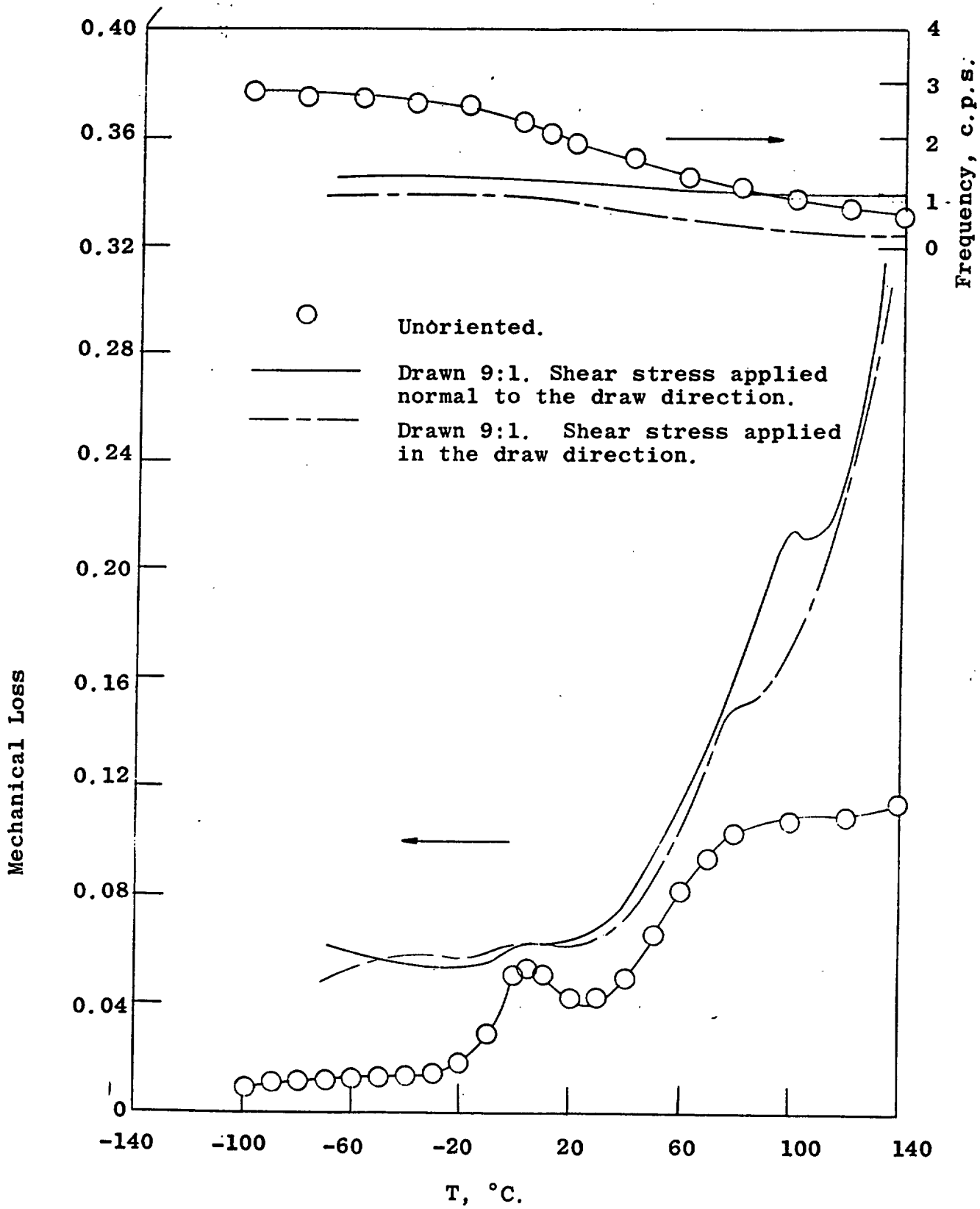
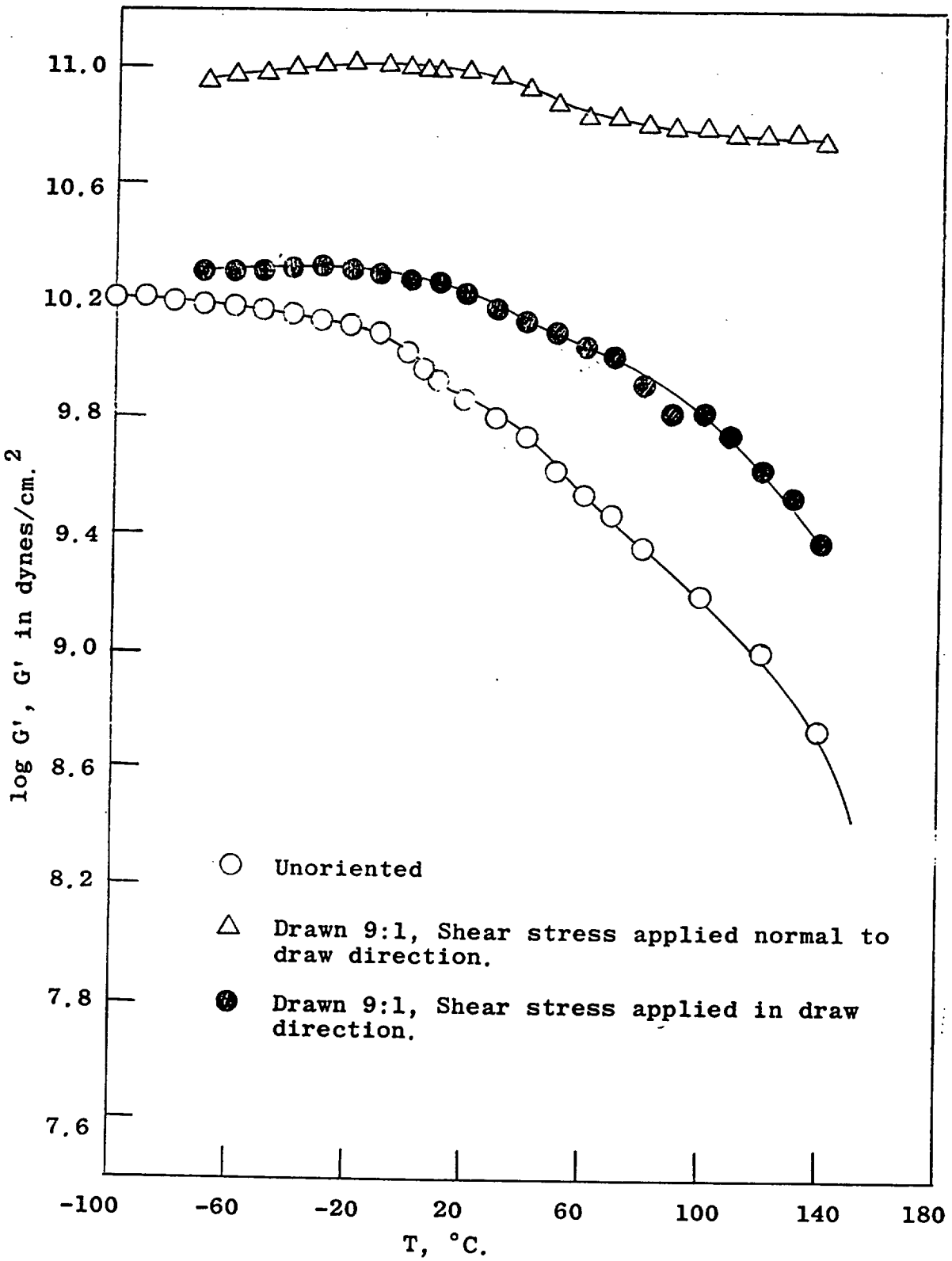


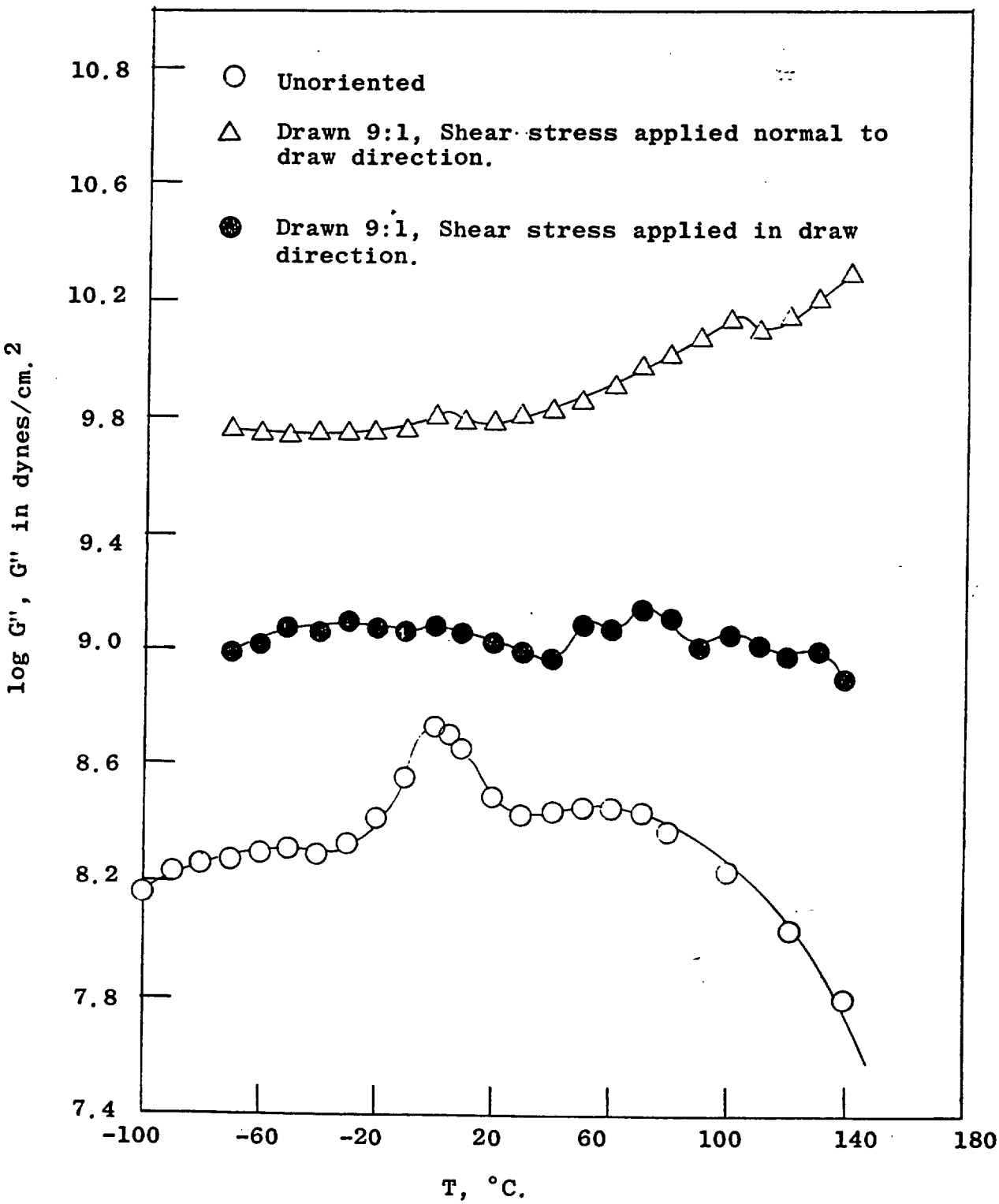
FIGURE 11. MECHANICAL LOSS AND FREQUENCY OF MEASUREMENT FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE.

FIGURE 12. REAL COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE



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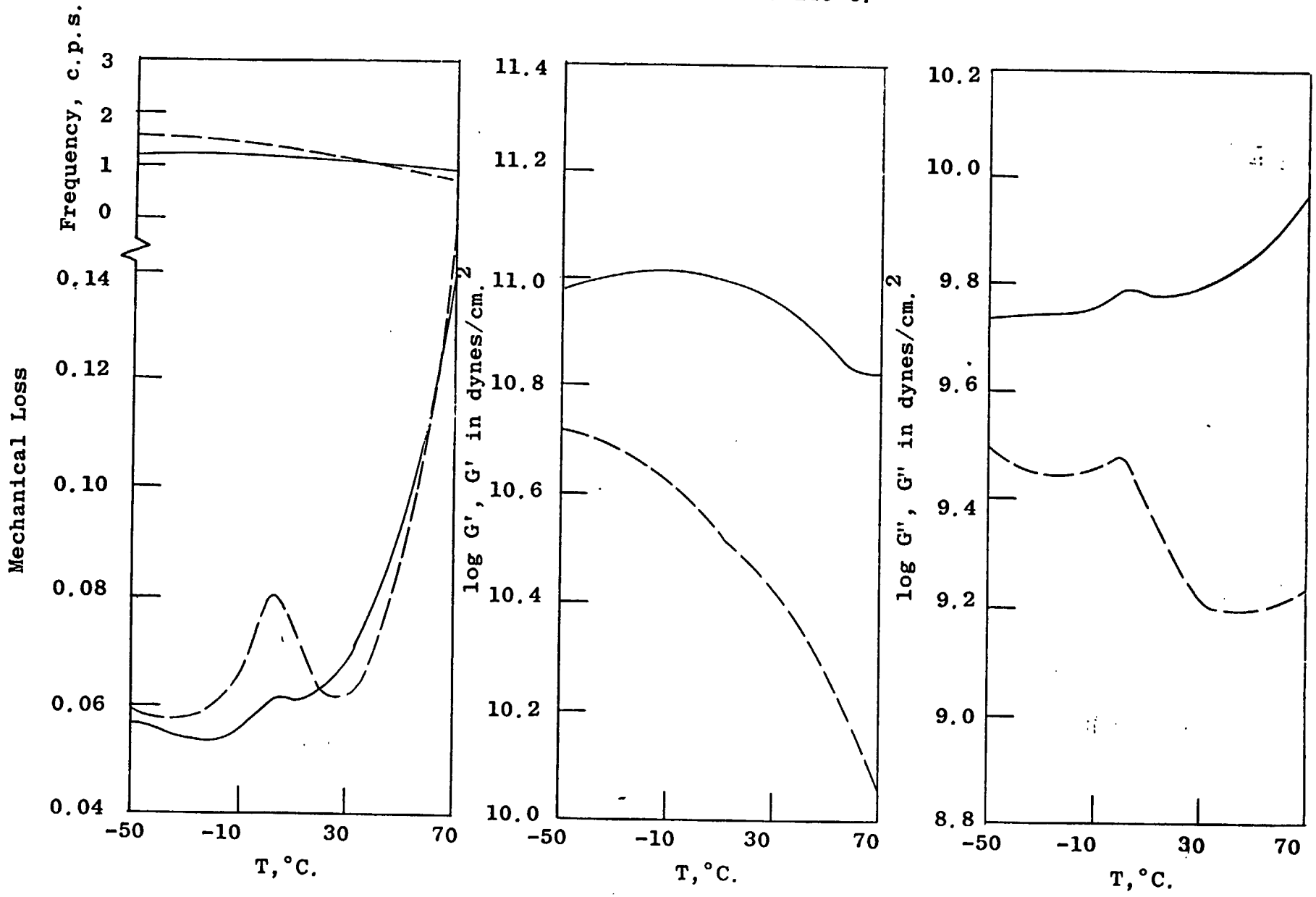
FIGURE 13. IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE



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Union Carbide trial exhibit UC-805: Union Carbide Research and Development Status Reports on Asbestos-Reinfo...
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FIGURE 14. MECHANICAL PROPERTIES FOR SHELL TYPE 5820 POLYPROPYLENE. SHEARING STRESS APPLIED NORMAL TO THE DRAW DIRECTION. —— DRAWN 9:1, — — — DRAWN 9:1 AND ANNEALED 40 MIN. AT 130-140°C.



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FIGURE 15, COMPARISON OF MECHANICAL LOSS FOR COMMERCIAL DYEABLE POLYPROPYLENES

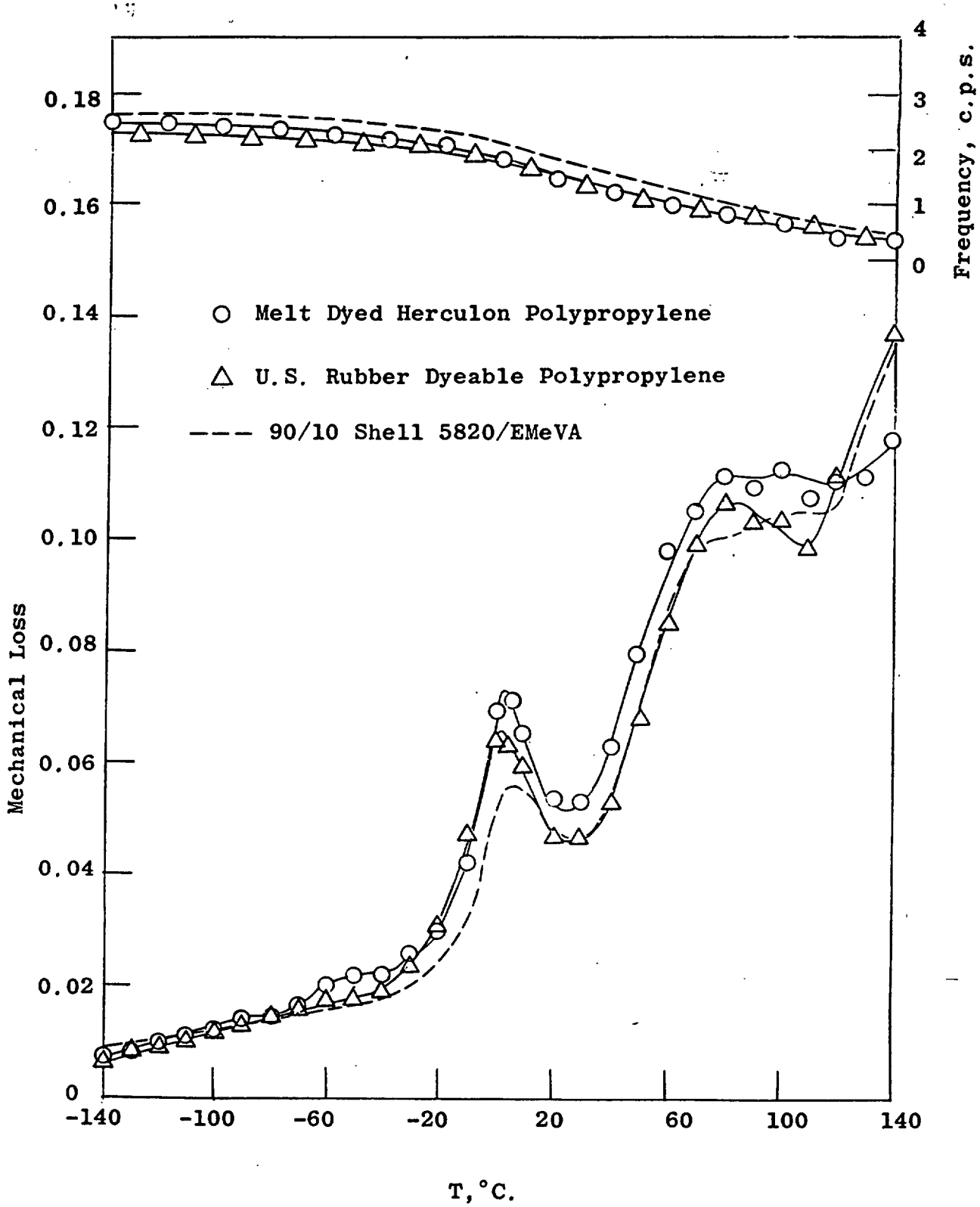
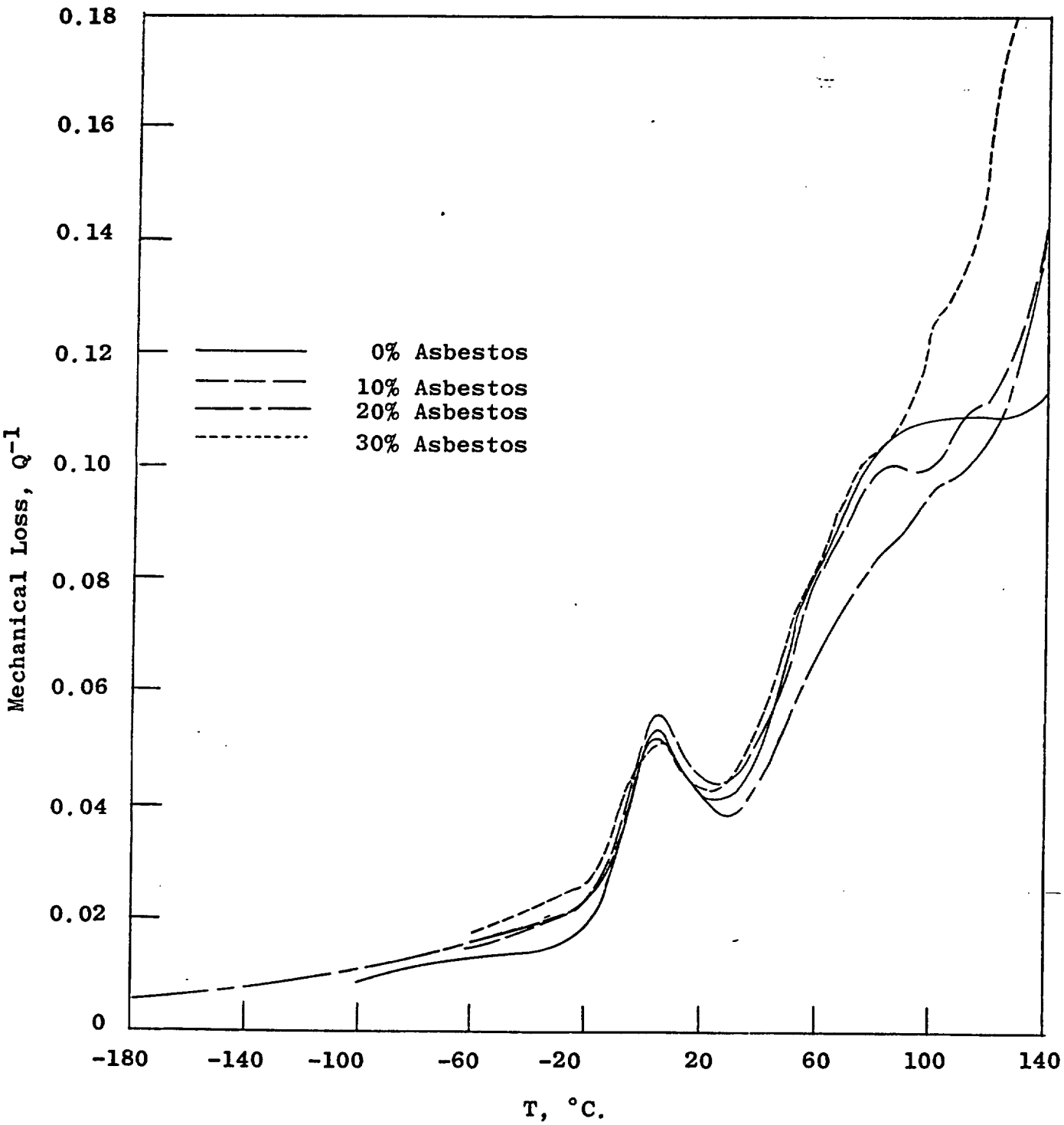


FIGURE 16. MECHANICAL LOSS FOR SHELL TYPE 5820 POLYPROPYLENE WITH AND WITHOUT AN ASBESTOS FILLER



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FIGURE 17. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF SHELL TYPE 5820 POLYPROPYLENE WITH AND WITHOUT AN ASBESTOS FILLER

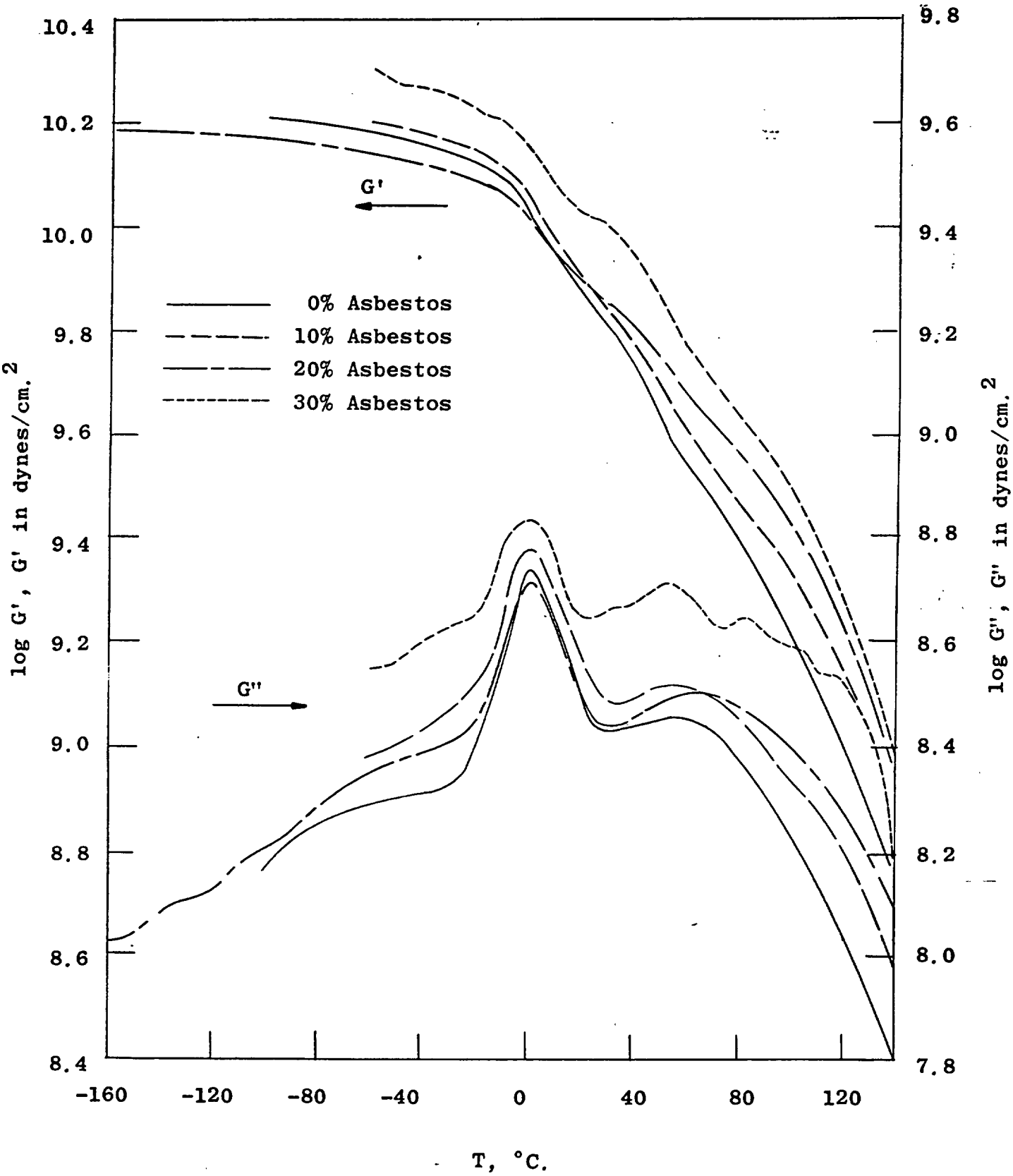
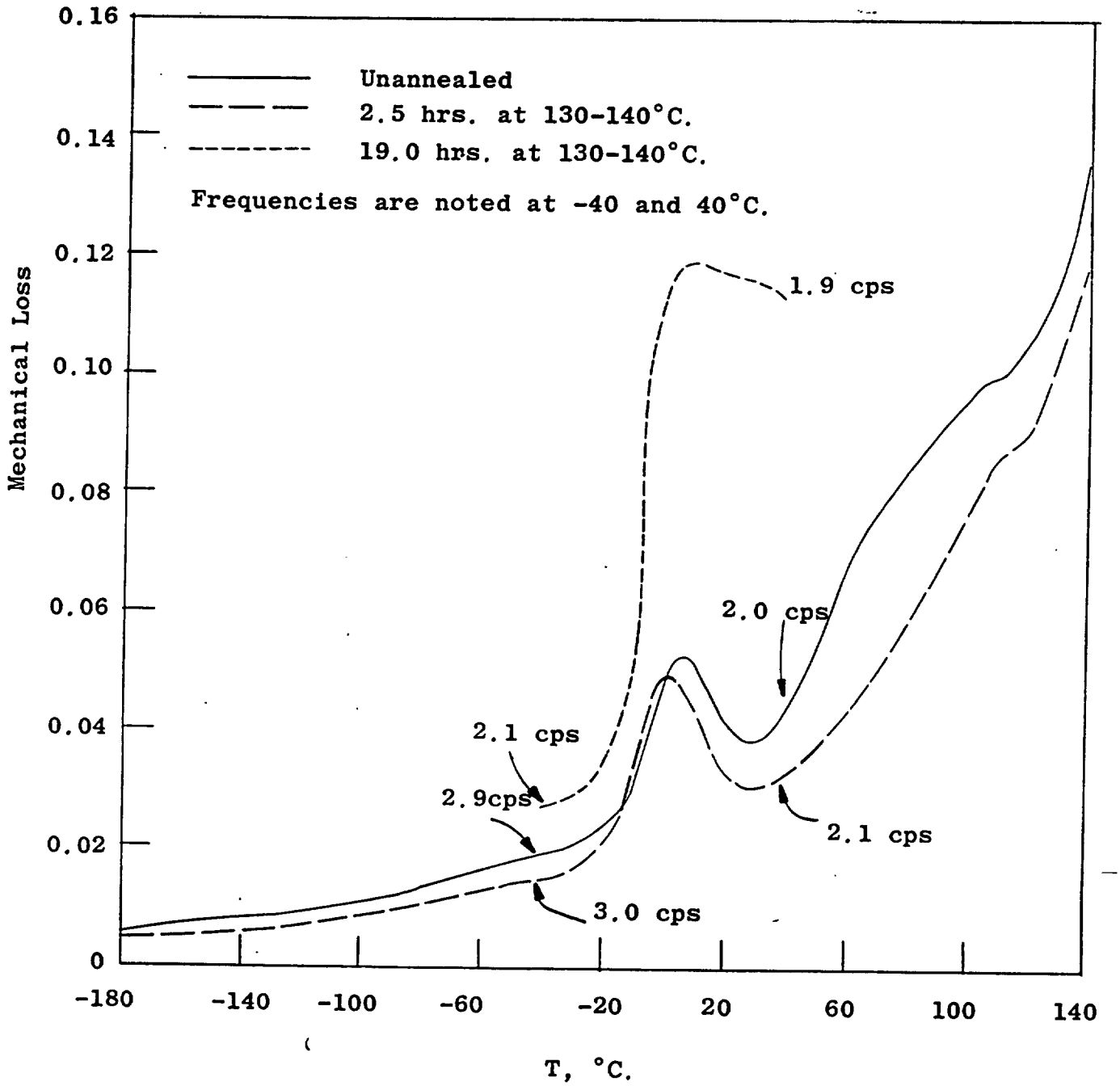
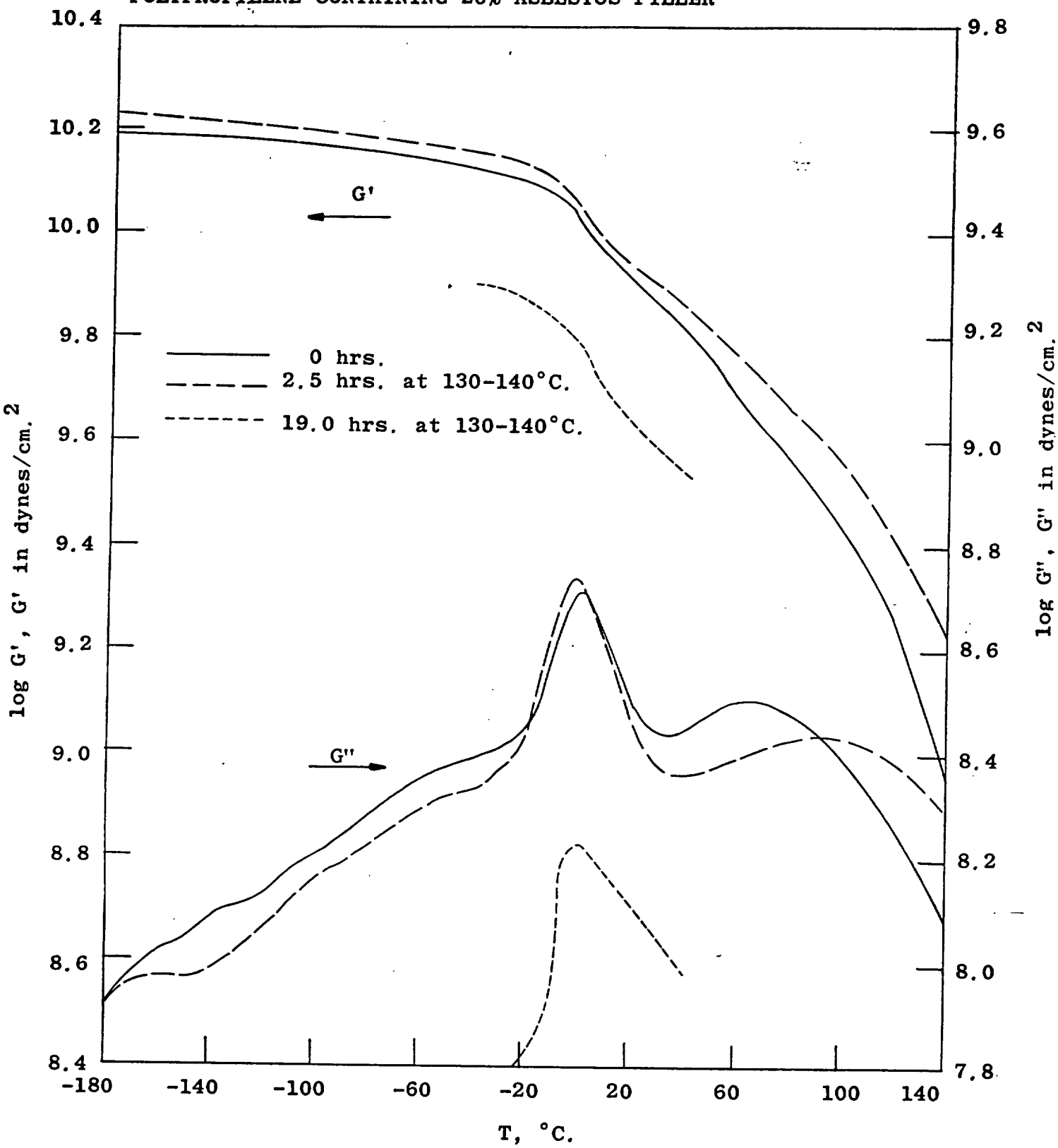


FIGURE 18. MECHANICAL LOSS OF ANNEALED AND UNANNEALED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS FILLER



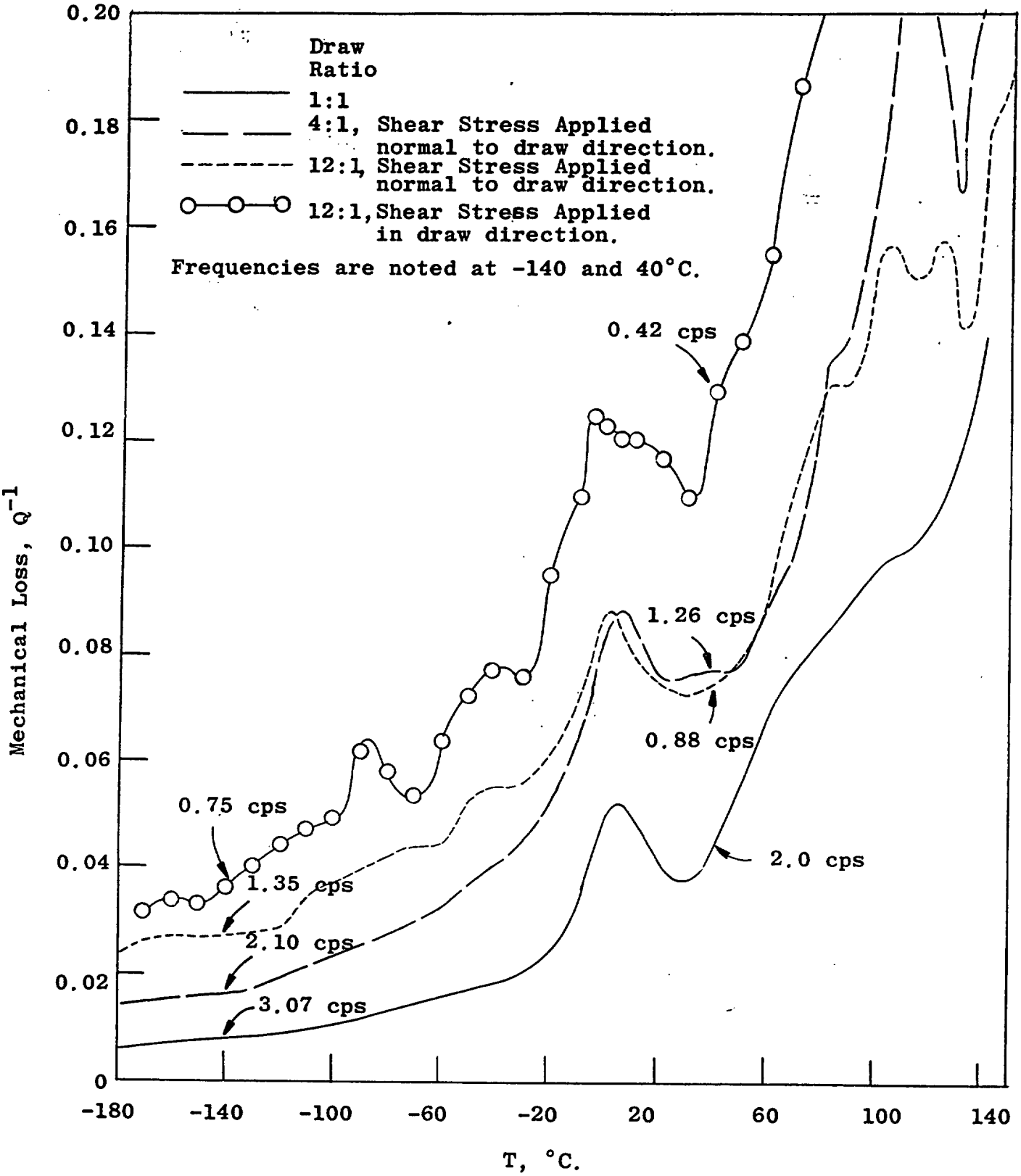
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FIGURE 19. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF ANNEALED AND UNANNEALED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS FILLER



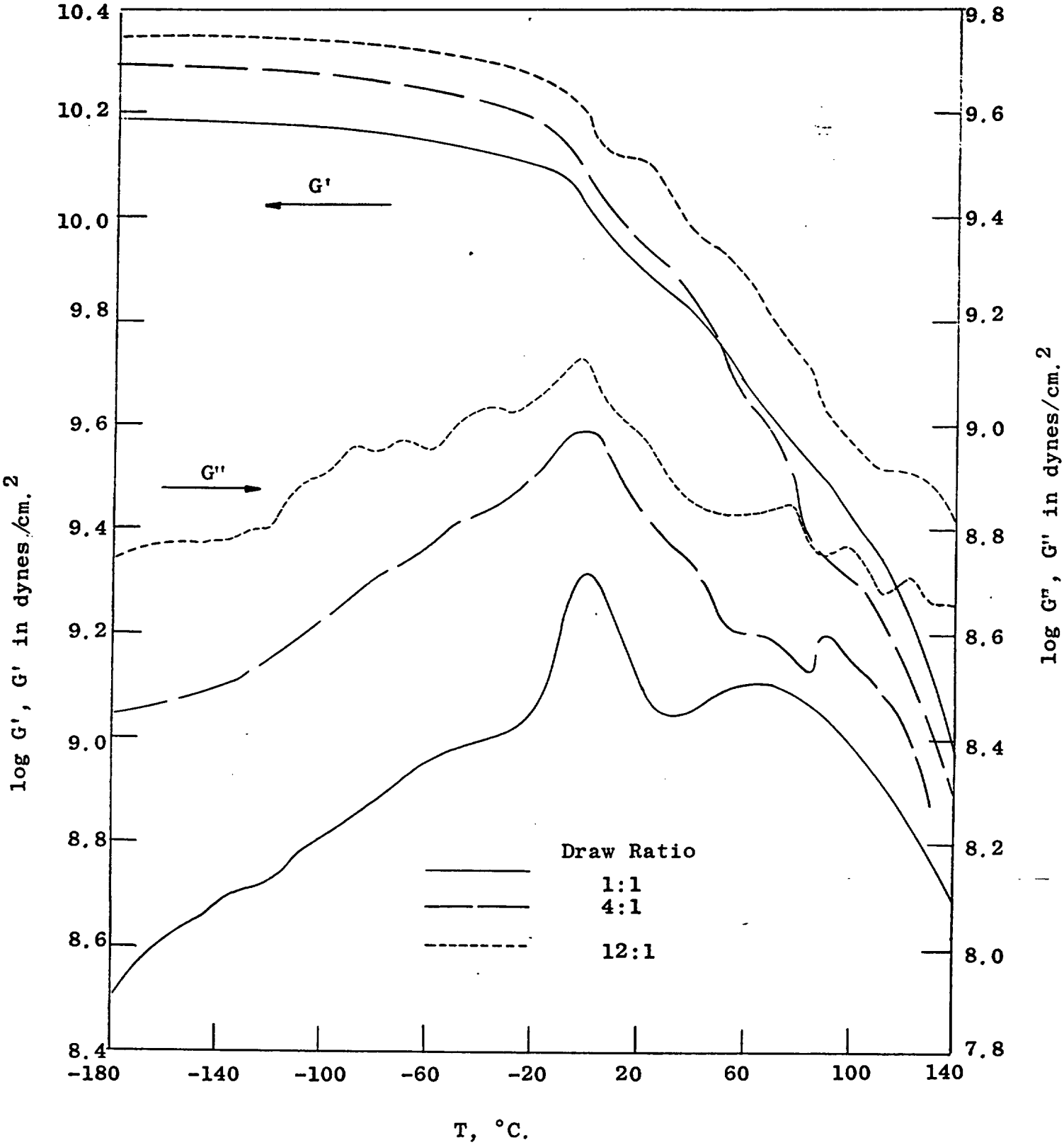
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FIGURE 20. MECHANICAL LOSS FOR ORIENTED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS



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FIGURE 21. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF ORIENTED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS. SHEAR STRESS APPLIED NORMAL TO DRAW DIRECTION FOR ORIENTED SPECIMENS.



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FIGURE 22. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS IN AND NORMAL TO DRAW DIRECTION FOR SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS

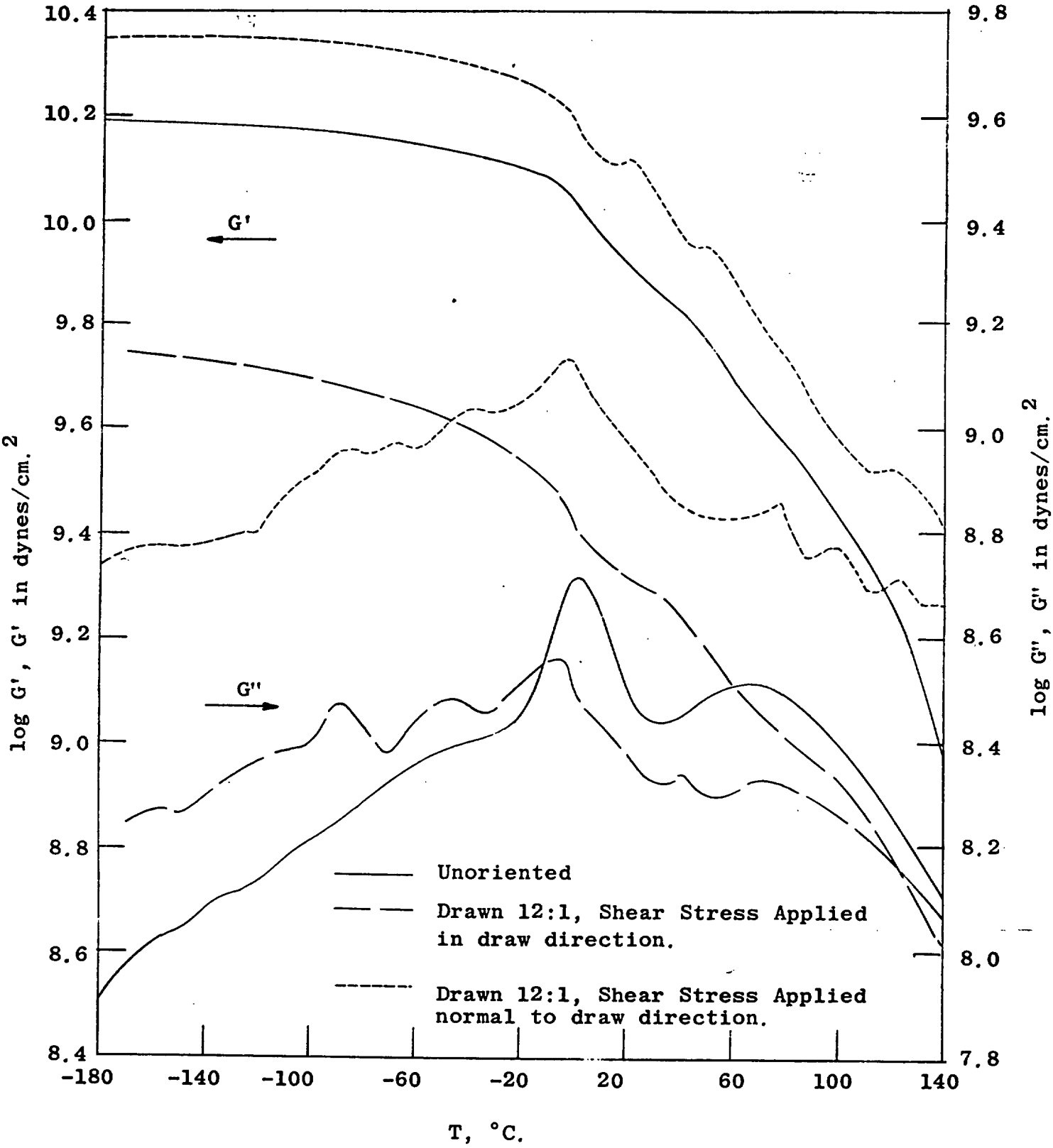


FIGURE 23. COMPARISON OF MECHANICAL LOSS FOR SHELL TYPE 5820 POLYPROPYLENE AND DRIED ZYTEL 101 (NYLON 66). THE NYLON WAS DRIED FOR 48 HOURS IN A DESICCATOR OVER $CaSO_4$.

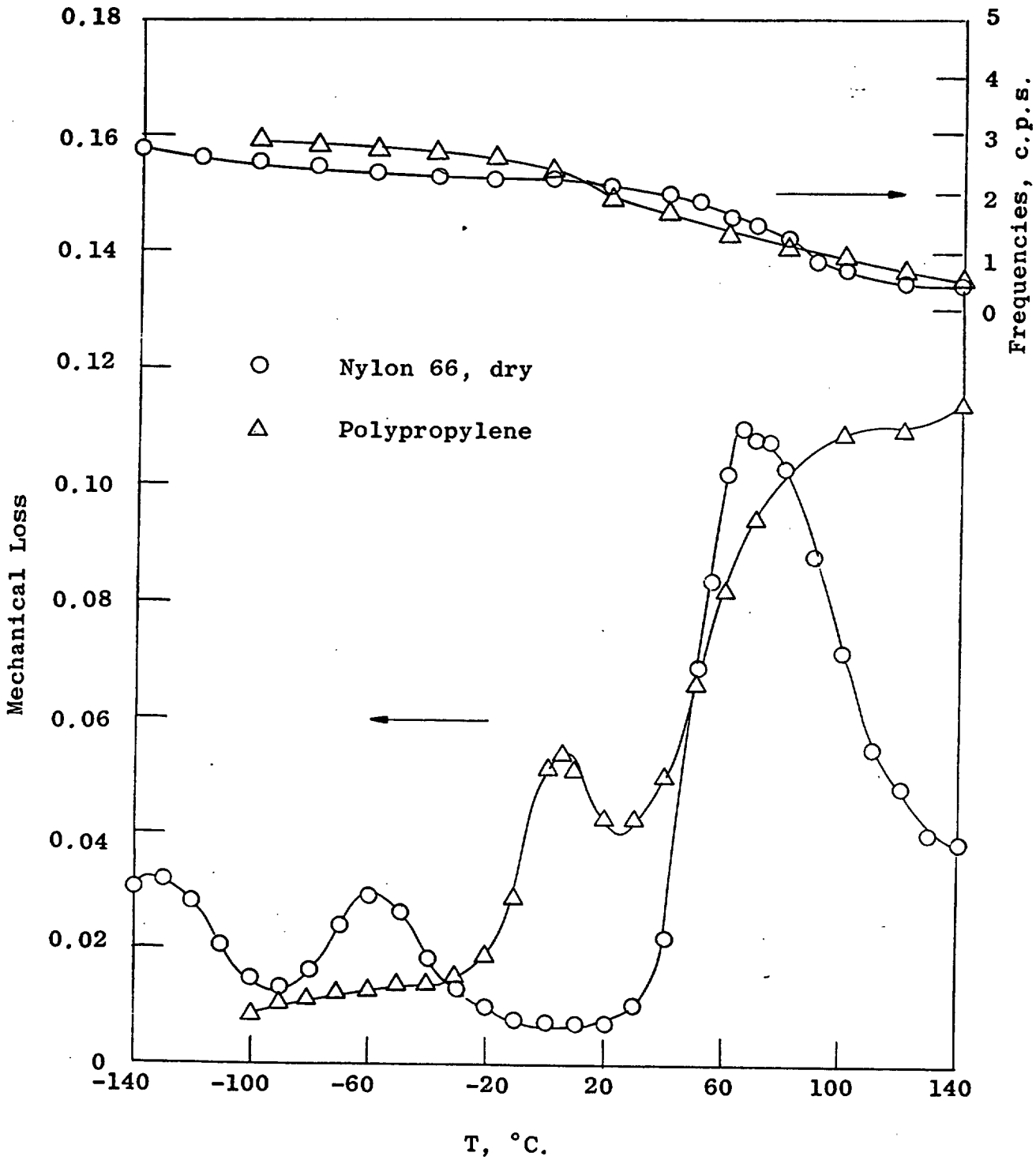
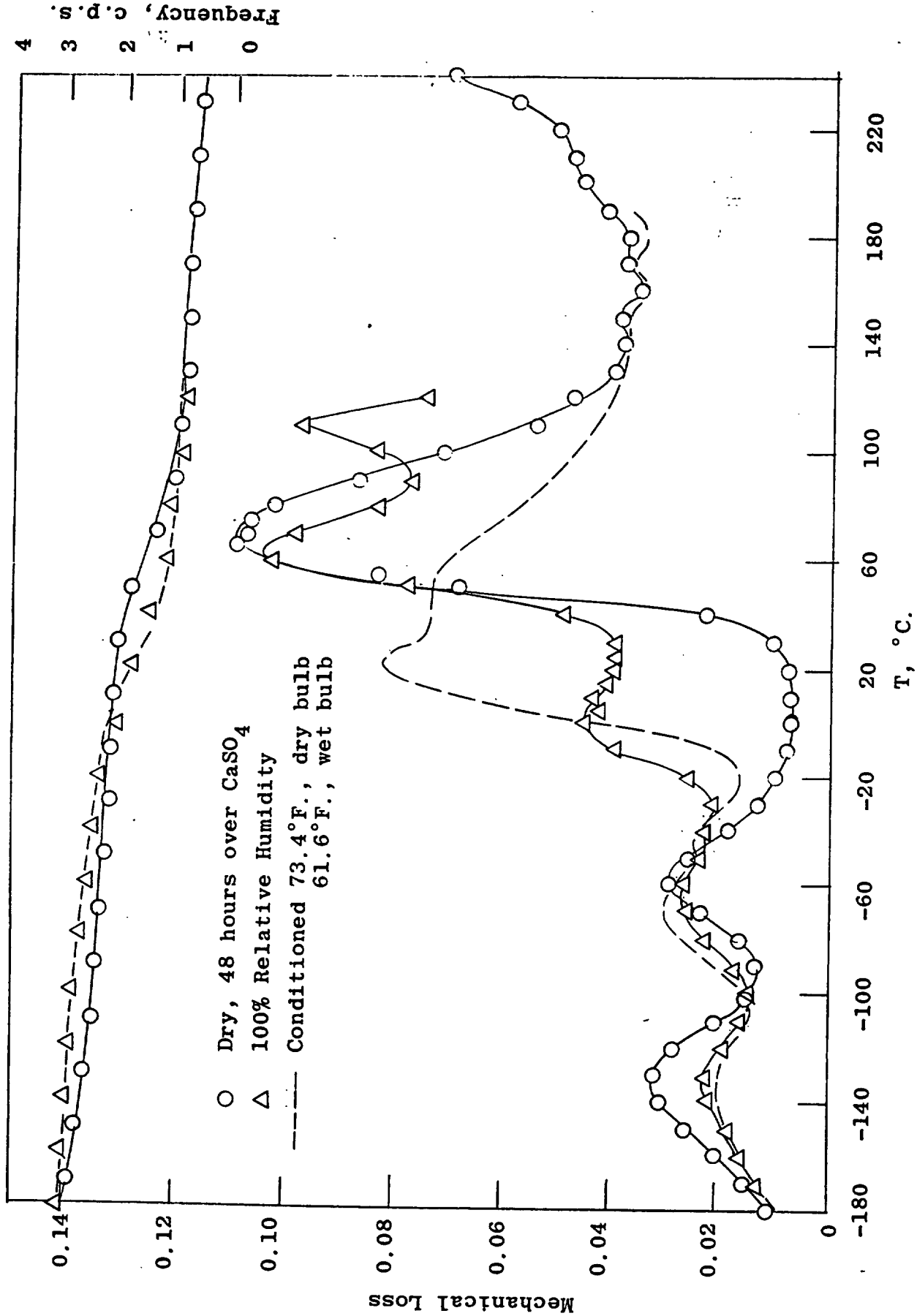
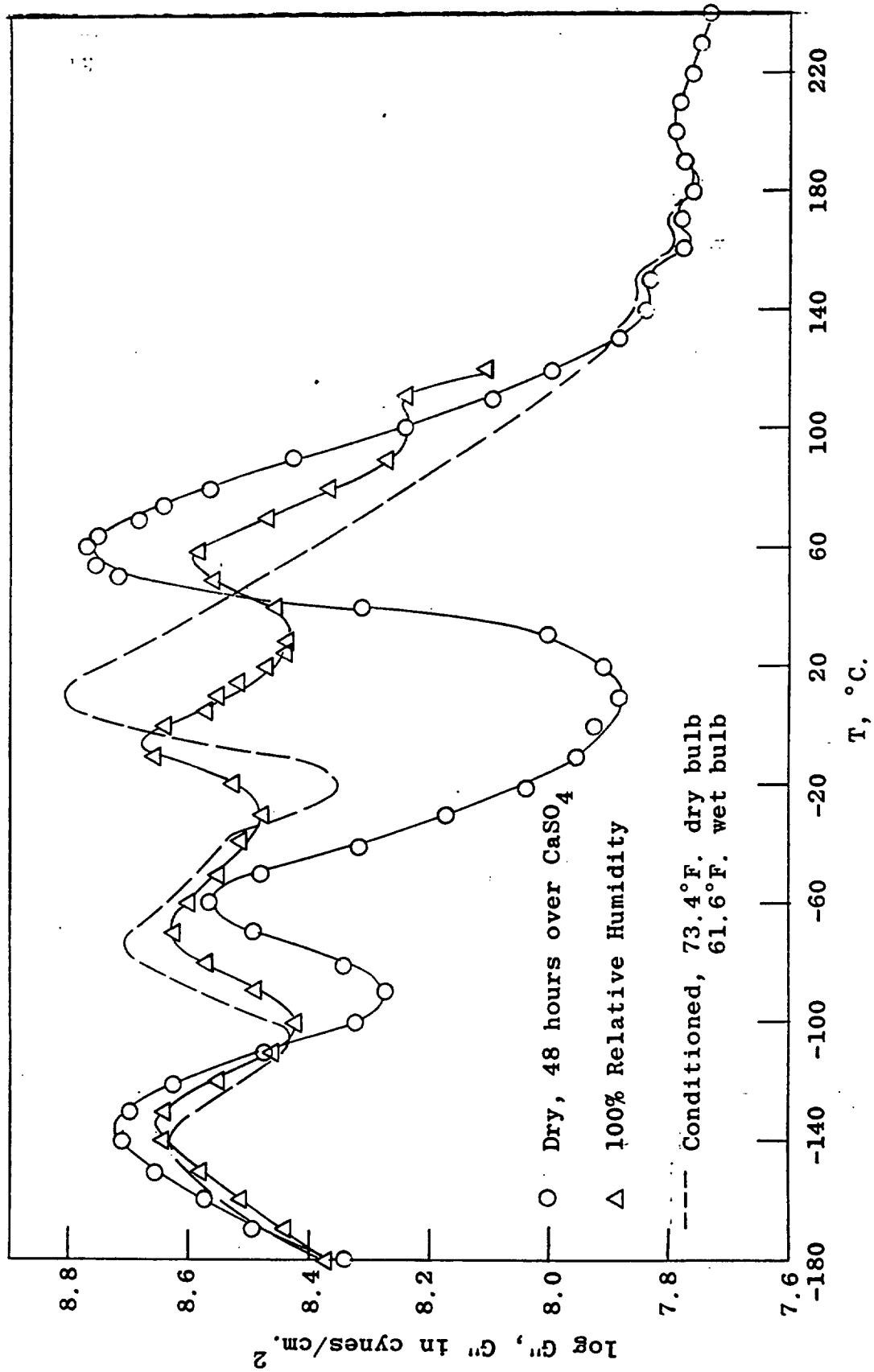


FIGURE 24. MECHANICAL LOSS FOR ZYTEL 101 (NYLON 66) AT VARIOUS HUMIDITIES



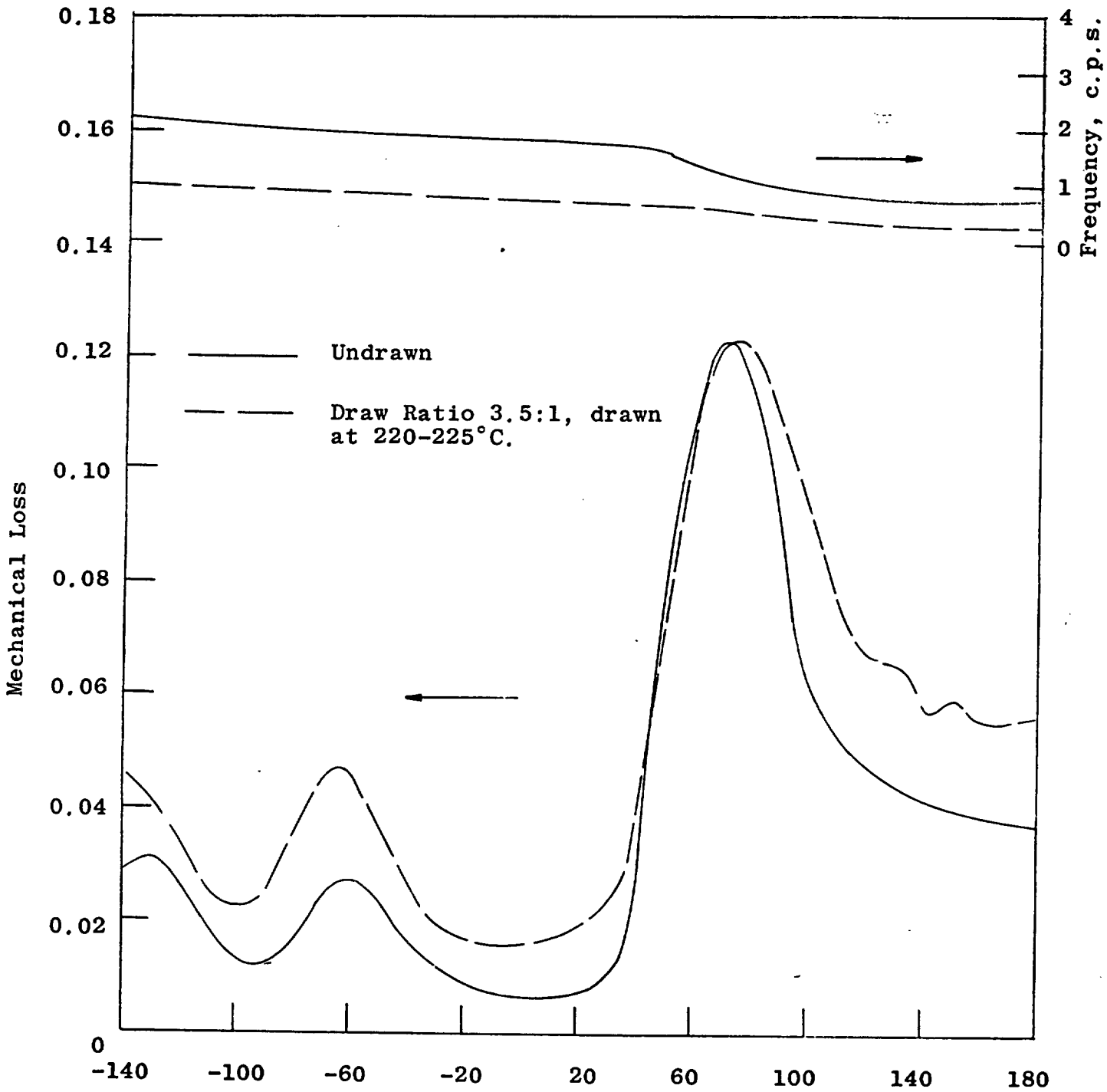
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FIGURE 25. IMAGINARY COMPONENT OF COMPLEX SHEAR MODULUS FOR ZYTEL 101 (NYLON 66) AT VARIOUS HUMIDITIES



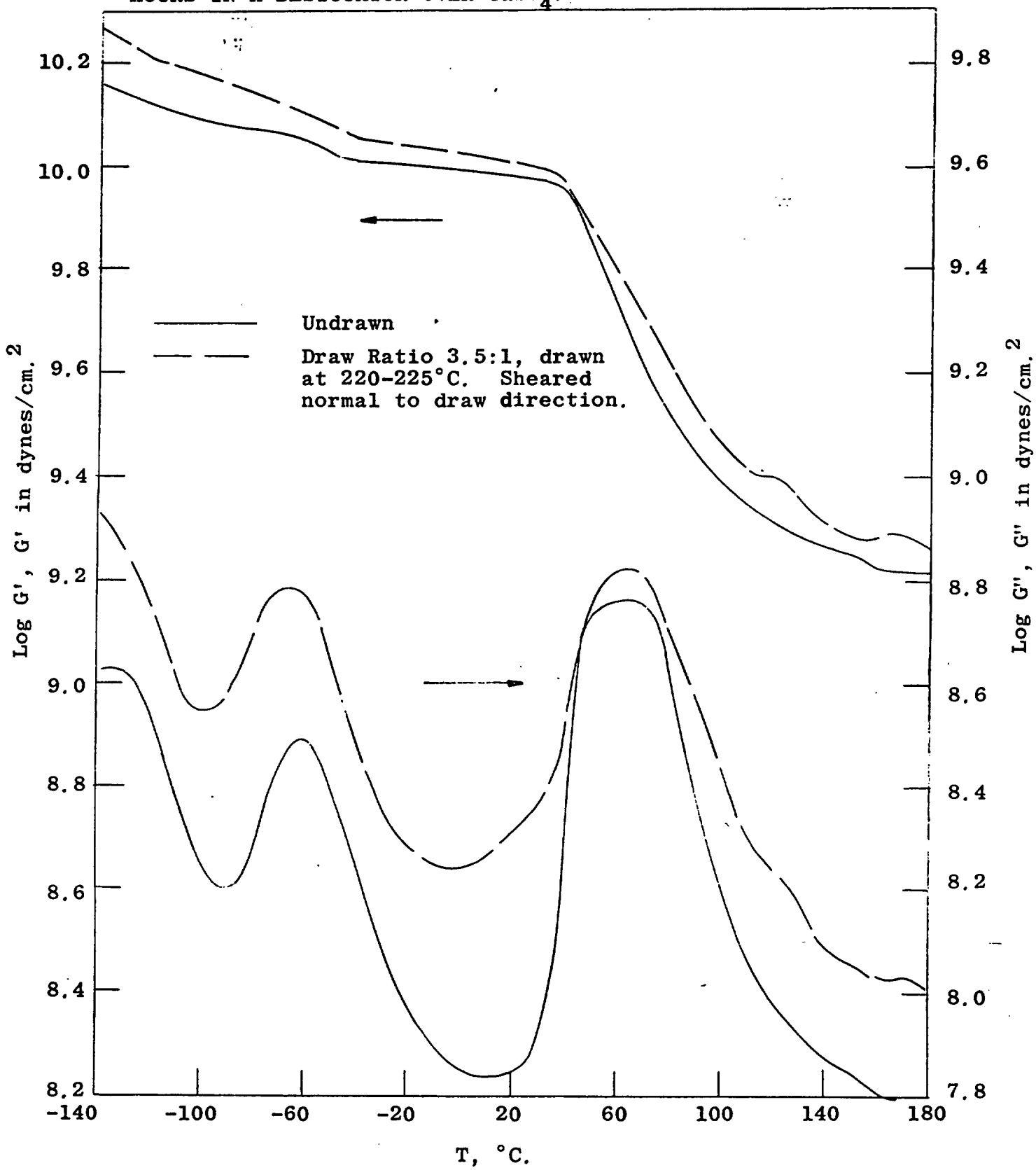
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FIGURE 26. EFFECT OF ORIENTATION ON MOLDED NYLON 501 YARN (NYLON 66). DRIED FOR 48 HOURS IN A DESICCATOR OVER $CaSO_4$. DRAWN SPECIMEN WAS SHEARED NORMAL TO THE ORIENTATION DIRECTION.



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FIGURE 27. EFFECT OF ORIENTATION ON THE COMPONENTS OF THE COMPLEX SHEAR MODULUS OF MOLDED NYLON 501 YARN (NYLON 66). DRIED 48 HOURS IN A DESICCATOR OVER $CaSO_4$.



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NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

Authors: C. W. McGary
G. W. Rausch

Date: July 7, 1964

Project No.: 162D21

File No.: 2746

SUMMARY Chrysotile asbestos, which has the formula $Mg_6(OH)_8Si_4O_{10}$, has been described as a crystalline hydroxymagnesium silicate polymer; it may be looked upon as mechanically bonded layers or sheets of silicon-oxygen tetrahedra chemically condensed onto magnesium hydroxide layers. The greater bond length of the brucite layers, $(Mg(OH)_2)$ on the outside result in a curvature of the layers to form a spiral "wrapping" or fiber. The gross chemical properties are determined by these surface brucite layers.

The purpose of this report is to define the possible chemical reactions of asbestos and to qualitatively summarize the results obtained with broad classes of reactants; for example, the basic property of chrysotile can be utilized by reaction with acidic organic compounds and by chemisorption. Other reactions of potential utility are base catalyzed ring openings and the addition of asbestos to multiple bond systems.

All the above reactions should be suitable for modification of asbestos fiber surfaces resulting in fibers with different properties such as acid resistance, lubricity, organophillicity, and better cohesion. Asbestos can be looked upon as a cross-linking agent if it is incorporated as a coreactant in the formation of a high organic polymer.

Work completed indicates that carboxylic acids containing other functional groups can be employed to provide an organic surface on asbestos suitable for further reaction. Polymers containing Lewis acid functional groups are strongly adsorbed on asbestos. Future work will exploit these reactions to produce new and potentially useful materials.

INTRODUCTION In 1963 over 700,000 tons of short fiber chrysotile asbestos was consumed in the United States in applications like plastics reinforcement and filler, floor tile, paper treatment, asphalt shingles, molded brake linings, and masonery products such as asbestos cement and acoustical tile.

Research and Development Department
Chemicals Division
Union Carbide Corporation

Union Carbide Nuclear Division has a new wet refining process capable of producing high purity dispersed asbestos at a price of $80-120/ton or conventional short fiber grades of asbestos at $50-60/ton. The Nuclear Division has at least a 100 year reserve of short fiber chrysotile asbestos. However, most short fiber asbestos markets like those listed above are captive markets in established product lines and either new uses for asbestos or improved products employing large quantities of asbestos are necessary to provide a proprietary position for Union Carbide.

The object of the Chemicals Division program is to investigate and establish the chemical reactions of asbestos and to determine whether derived products of asbestos are worthy of specific end-use applications. The quality of products encorporating asbestos is highly dependent on fabrication techniques; hence a considerable research outlay is required to merely enter existing markets. For this reason conventional applications are not being emphasized until truly promising new products are developed.

Chrysotile asbestos has the general formula $Mg_6(OH)_8Si_4O_{10}$. The structure has been described as a crystalline hydroxymagnesium silicate polymer and is now looked upon as simply layers or sheets of silicon-oxygen tetrahedra chemically condensed onto magnesium hydroxide layers[1] with mechanically interlocking between successive layers. The greater bond lengths of the brucite layers, $(Mg(OH)_2)$, on the outside, result in a curvature of the layers to form a spiral "wrapping" or fiber. Gross chemical properties are determined by the brucite layers on the surface with asbestos ordinarily having chemical properties similar to magnesium hydroxide. Neutralization of the magnesium hydroxide with strong acid solubilizes the magnesium leaving a fibrous silica structure behind. If it is assumed that each magnesium atom in a recurring unit of $Mg_6(OH)_8Si_4O_{10}$ is bound to the silica layer, a total of six -MgOH groups are present for reaction. The other two hydroxyl groups then represent one molecule of water hydrating the silica as two -SiOH groups. It is more likely that the two hydroxyl groups are paired with two magnesium ions existing as adsorbed magnesium hydroxide[2].

Since a structural chrysotile fiber contains 6-10 layers of brucite and silica, the availability of all the OH groups for reaction is uncertain. With strong acids magnesium is extracted stoichiometrically leaving fibrous silica. The first molecule of water (2 OH) is lost at temperatures from 130-370°C. Coalinga CMS grade asbestos is a short fiber dispersed chrysotile corresponding to Quebec number 6 and 7 grades and is composed of bundles of individual fibers.

Chemical modification of asbestos can be directed toward three types of products. First, the asbestos itself can be chemically degraded to useful materials such as magnesium salts and silica.

Since chemical properties of asbestos are determined by surface effects, surface modification of the asbestos can result in significant changes in chemical properties.

Finally, since asbestos is a high inorganic polymer, cross-linking of polymer molecules could lead to strong solid products. The ordinary concept of chemical cross-linking may be inadequate in this context because molecular cross-linking of a comparatively large asbestos fiber may mean only surface modification resulting in stronger fiber interaction and better cohesion. The geometry of the fibers is such that a random packing of fibers will leave spaces larger than molecular dimensions. However, chemical reaction of a very high molecular weight organic polymer with asbestos could result in fiber cross-linking. Asbestos then becomes the minor component and might be considered a cross-linking agent for the organic polymer.

DISCUSSION Three general reactions may be envisioned as potential routes to modified asbestos. First, acids, acid-forming compounds, or acid derivatives may react with asbestos to form simple salts. This reaction is known to occur readily and is accompanied by extraction of magnesium as a magnesium salt.

A second potentially useful reaction is the addition of pendant hydroxyl groups to unsaturated or cyclic compounds. Rings like oxiranes which open under basic conditions are likely candidates.

Finally, chemisorption can result in strong adhesion of polar groups to either acidic or basic sites on the asbestos structure.

POTENTIAL REACTIONS AND PRIOR ART

Inorganic Salts of Asbestos

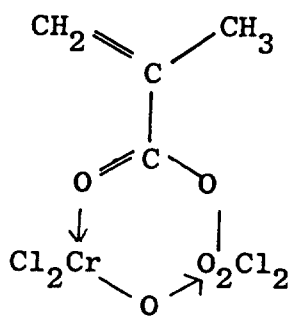
Weak acids will partially add to asbestos by salt formation to modify the asbestos surface or cause cross-linking whereas strong inorganic acids are completely neutralized by asbestos with extraction of magnesium. Patents describe solid products of asbestos bound with fluosilicic acid[4] and alumina sol[5] as well as corrosion resistant coatings from silica sol and asbestos[6]. Asbestos cross-linked with dibasic acids or

polybasic polymeric acids is in reality a high inorganic polymer. Boric acid combines with magnesium carbonate at high temperatures to form a high strength brick[7] and may be a suitable binding or cross-linking agent for asbestos.

Inorganic anhydrides, esters, and acid halides would react with asbestos and produce products similar to those derived from the corresponding acids. The reaction of esters might be useful in lowering magnesium extraction but in aqueous solution, if sufficient reaction time is allowed, hydrolysis of the acid salt would result in equilibrium between the acid and salt as is found on acid addition, and the free acid could extract magnesium. With anhydrides magnesium extraction should parallel that found with acids. Acid halides should cause more extensive magnesium extraction by the hydrogen halide by-product. Alkoxy silanes and halosilanes were reported to provide a reactive asbestos surface by reaction with OH groups[8]. Improved asbestos filled polyethylene can be produced by irradiation of asbestos modified by vinyl silanes[17]. Amino alkyl silanes should be suitable for modifying asbestos prior to cross-linking or condensation polymerization.

$$X_3Si(CH_2)_nNH_2 + YOMgOH \longrightarrow (YoMgO)_3Si(CH_2)_nNH_2$$

A similar surface modifier is methacrylatochromic chloride (I)

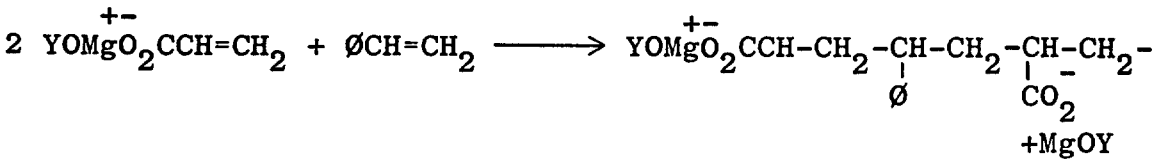


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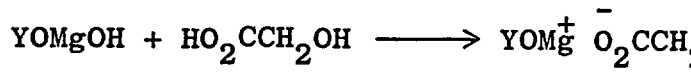
Most inorganic acids and derivatives have ionization constants that are either too large, causing magnesium extraction, or too small, and apparently insufficient for reaction. However, reactivity of very weak acids with asbestos is not clearly defined.

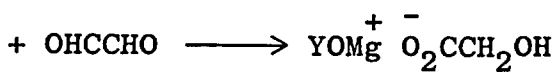
Asbestos Reaction with Organic Acids

Organic acids offer promising candidates for salt formation with asbestos since their ionization constants fall in an intermediate range, making them reactive toward asbestos, but allowing at least some acid addition without total magnesium extraction. Oxalic acid and oxalate salts have been used to treat asbestos paper for high strength properties[11], apparently by cross-linking the fibers. Similar cross-linking should also be observed with polymeric carboxylic acids such as polyacrylic acid. Acrylic acid (or other unsaturated acids) could be applied to asbestos and then copolymerized to provide cross links in a technique like that employed with polyester resins. Thermal



polymerization of the adsorbed acrylate ion could also result in cross-linking. A suitable reactive substrate for condensation polymerization may be achieved by similar reaction of asbestos with glycolic acid or glyoxal:





Various carboxylic acid derivatives or thiocarboxylic acid derivatives may be employed to produce similar products. Carboxylic anhydrides should behave much like the corresponding acid. Ketenes could be expected to add readily at low temperature, perhaps with little magnesium cleavage. Isocyanates also should react. Simple carboxylic esters offer no advantages over acids but lactones, adding as either monomer or polymer would provide a reactive organic hydroxyl group for cross-linking or further polymerization.

Carboxylic acid chlorides have not been studied since evolution of hydrogen chloride can be expected to cause massive leaching of magnesium.

Simple amides and nitriles are relatively stable to hydrolysis and would offer the same problem of slow hydrolysis observed with esters. By-product amines or ammonia could maintain a higher pH so as to minimize magnesium extraction.

Lactams do not undergo ring opening as readily as do lactones but are hydrolyzed much easier than simple amides. Polyvinylpyrrolidone has been used as a binder in strong asbestos paper[14,15] and it is possible that some cross-linking may have occurred by ring opening.

Cyanuric acid has a first ionization constant of 1.8×10^{-7} and should add easily to asbestos with little magnesium extraction. Cross linking might then be effected by partial pyrolysis of the dry, treated asbestos. Any acidic organic material with an ionization constant in the range 10^{-7}-10^{-8} could be a candidate for asbestos treatment.

Other organic acids that might be considered are sulfonic, sulfinic and phosphonic acids. Their high acidities would result in considerable magnesium extraction along with addition. Sultones may add polymerically like caprolactone.

Alcohols and mercaptans are normally very weakly acidic and only highly activated molecules can be expected to add to asbestos. Acetylenes likewise are too weakly acidic to be expected to react. Alkyl halides could react by nucleophillic substitution or by elimination of hydrogen halide. By either reaction the hydrogen halide by-product will extract magnesium.

Addition of Unsaturated Compounds and Cyclic Compounds to Asbestos

The addition of multiply-bonded organic molecules to asbestos would have to take place by addition of hydroxide ion to the multiple bond since magnesium hydroxide is not amphoteric and incapable of yielding a proton even with strong base catalysis. Steric crowding and unfavorable equilibria would certainly make such addition difficult:

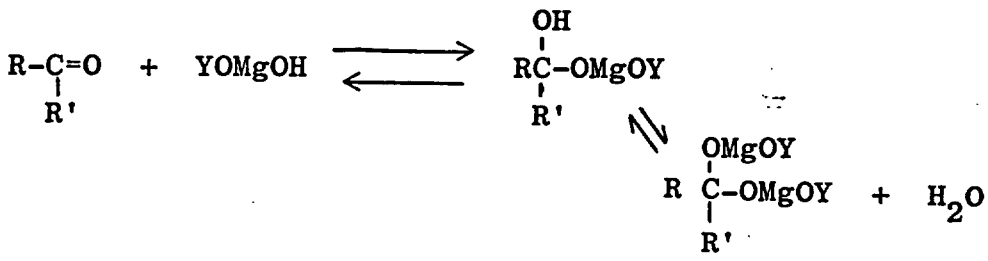
$$YO\overset{+-}{M}gOH + CH_2{=}CHX \longrightarrow HOCH_2\underset{\underset{MgOY}{|}}{CHX}$$

where X = CN, CO_2R, $\overset{\overset{O}{\|}}{C}R$, etc.

Y = asbestos

If -SiOH groups are present on asbestos addition should occur more readily. This problem is further complicated by the tendency of activated vinyl compounds to polymerize. Unactivated vinyl compounds and acetylenes should be unreactive toward hydroxide addition.

The addition of carbonyl compounds may be postulated by the following route:

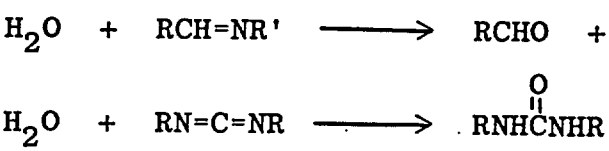


R, R' = alkyl, aryl, H

Y = asbestos

Such reactions are normally acid catalyzed and equilibrium will be far in the direction of the aldehyde or ketone.

Multiply-bonded carbon-nitrogen compounds should resemble carbonyl compounds in reactivity. Schiff bases and carbodiimides are likely to cause asbestos dehydration:



Ring opening of epoxides by asbestos could yield a monomagnesium salt of a glycol or a polyalkylene oxide bonded to asbestos. The treatment of asbestos with a polyamide epoxy resin to produce fiber mats of improved interfiber bonding is described in a patent[16]. Epichlorohydrin could be used as a difunctional molecule if magnesium extraction by byproduct hydrogen chloride is permissible.

Thiuranes should undergo ring opening like oxiranes, but alkyleneimines are usually stable to ring opening under basic conditions as are higher cyclic ethers like tetrahydrofuran.

Chemisorption

Asbestos is definitely basic but can have both acidic and basic sites on the polymer spine. Acids should be readily adsorbed on the hydroxyl surface. This is evident in the reaction of carboxylic acids where the rate of adsorption of acid from solution is several times as great as the rate of neutralization of the acid. Polymers containing Lewis acid functional groups

such as ketones, acetals, and nitriles could be adsorbed on the brucite surface of asbestos and behave like graft copolymers of asbestos and organic material. The organic loading on such "grafts" could be controlled by selective extraction of lower molecular weight material through solvent choice. Both addition and condensation polymers could be added to asbestos this way.

Chemisorption could take place at acid sites on asbestos as well as on the brucite surface. However, such sites are much less numerous and chemisorption of bases is likely to be quite weak. If very high molecular weight bases were employed, a noticeable adsorption might be observed.

UNION CARBIDE CHEMICALS DIVISION PROGRAM

The Chemicals Division became actively engaged in asbestos research in 1963 when P. L. Smith and L. C. Shriver began studying the effects of acid on asbestos.

The work thus far has largely ignored product application or evaluation of potentially useful materials and reactions of "unmasked" asbestos, ie, the silica residue after acid extraction of magnesium. This approach will be continued but any reactions that promise ultimate utility and good economics will be thoroughly investigated and the products will be evaluated as commercial materials.

Smith and Shriver found that acid addition to asbestos is in competition with magnesium extraction and that dibasic acids react by both mechanisms to "cross link" asbestos in a solid inorganic product. For example, phosphoric acid (and presumably other strong acids with similar first and second ionization constants) reacts first with asbestos to extract magnesium ion and the magnesium dihydrogen phosphate then acts as a difunctional acid which adds to the asbestos surface[3].

Smith and Shriver also studied maleic and acetic acid[10] and found that magnesium extraction occurs simultaneously with acid addition in the acetic acid reaction. Maleic acid acts as a strong acid to extract magnesium to form magnesium hydrogen maleate which then reacts further by addition to asbestos. Direct addition of magnesium dihydrogen phosphate or magnesium hydrogen maleate solutions to asbestos can also be used to form solid rock-like products. If the strength properties of these products is due to increased cohesion through surface effects, boric acid could prove to be a better and more economical binder than either phosphoric acid or maleic acid.

The addition of acids to asbestos seems to depend on acid strength or pH with carboxylic acids falling into an acidity range capable of both acid addition and magnesium extraction. Polymeric carboxylic acids should be better cross-linking agents than dibasic acids like maleic acid because extracted magnesium can cross-link the organic reagent and a larger molecule is better suited to bridge the large distance between two asbestos fibers. The Plastics Division has reported some success in "cross-linking" asbestos by milling it with an ethylene-acrylic acid copolymer[12]. Aqueous polyacrylic acid is slow to add to asbestos, probably because of molecular bulk and slow diffusion. Current work indicates that a high loading of acrylic acid can be made on asbestos. The product is hydrolytically unstable but might be incorporated in a vinyl resin. This work is being continued to elucidate the structure of the reaction product, to develope an efficient process, and to investigate the utility of the product as a comonomer in vinyl resins and vinyl cured polyesters.

Unsaturated fatty acids should also be investigated. Asbestos with an unsaturated fatty salt surface might be an excellent thixotropic agent and coating filler capable of vinyl cross-linking reactions.

A few acid derivatives have been examined for reactivity with asbestos. Maleic anhydride, as expected, acts much like maleic acid[3], ultimately forming a hard, cross-linked resin. Toluene diisocyanate reportedly cross links asbestos[13] but in repeating the work, Shriver found that only the surface of the solid product had reacted completely, quite likely by hydrolytic polymerization of the isocyanate to a polyurea[3]. Isocyanate-capped polyether prepolymers also seem to react with asbestos but the evidence is inconclusive. Asbestos does catalyze the dimerization of phenyl isocyanate. A study of catalyzed reactions between asbestos and isocyanates could perhaps be justified, but the chances of successful reaction are poor.

Carboxylic esters are very slow to hydrolyze and quite ineffective in adding carboxylate ion to asbestos. Shriver found little acetate addition on heating aqueous solutions of ethyl acetate or 2-ethylhexyl acetate with asbestos. Heating of dry carbitol acetate with asbestos at 180° for 12 hours gave less than two percent addition of organic material. Ester hydrolysis must be fast to offer any advantages over acid addition since after sufficient time, hydrolysis of the salt results in the same equilibrium whether acid or ester is the starting material and magnesium extraction can still occur.

It is possible that activated esters may be sufficiently more reactive than acetates to allow rapid hydrolytic addition of carboxylate ion. Dialkyl maleates should be investigated because only one ester group is highly activated and could provide a handle for attachment of a vinyl surface to asbestos.

Lactone rings are easily opened in basic solution. Caprolactone added readily to asbestos as polycaprolactone in both aqueous and organic solvents. Magnesium extraction is low, but the rate of caprolactone polymerization was several times faster than the rate of addition to asbestos on a weight basis and organic loading was only 4-8% by weight. The products were hydrolytically unstable. Higher organic loading of asbestos may be possible and the caprolactone polymer byproduct may also add. Other lactones including sultones must be investigated.

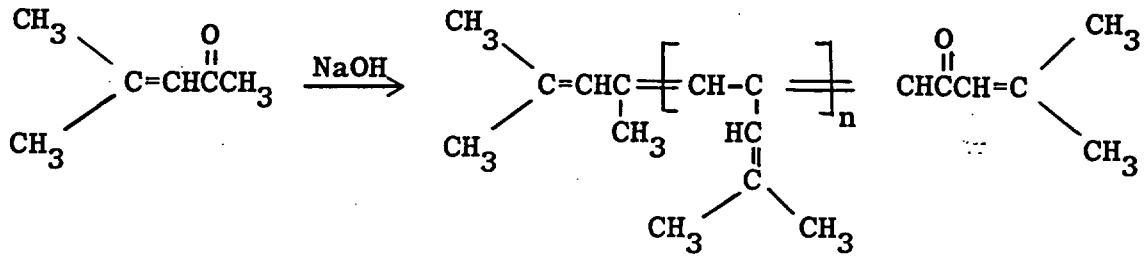
To complete the work on lactones, lactams should also be added to asbestos. Caprolactam does not add under conditions similar to those employed with caprolactone, but the use of a strong base catalyst could result in addition of polymerized material.

Phenol is apparently too weak an acid to react with asbestos. Heating of aqueous phenol with asbestos to 105° and anhydrous phenol with asbestos to 220° lead to no product. It is very likely that strongly activated phenols will react with asbestos. The necessary acidity can be determined by attempting the reaction with various phenols of known ionization constant.

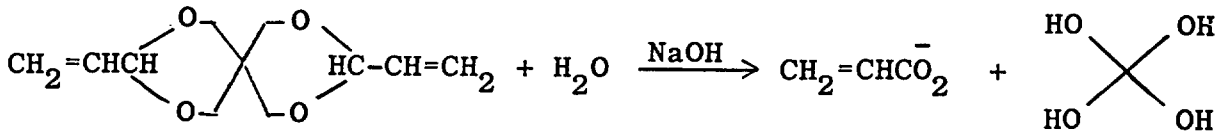
The ionization constant of cyanuric acid makes it ideal as an asbestos modifier. "Asbestos cyanurate" could act as a thermosetting molding powder.

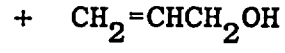
It is unlikely that alcohols can be added to asbestos. 2,6,8-Trimethyl-4-nonanol undergoes dehydration exclusively on being heated with asbestos at 200°.

Attempts to add multiple bonded organic molecules to asbestos have met failure. The addition of asbestos to the double bonds of acrylonitrile, divinyl spirobi-(m-dioxane), and mesityl oxide was attempted in inert solvents. Without catalyst no reaction ensued. In a fashion analogous to conventional cyanoethylation procedures, a solution of acrylonitrile was heated with asbestos and a catalytic amount of powdered sodium hydroxide. The product was asbestos containing 7.5% by weight of polyacrylonitrile strongly adsorbed on the surface. The same procedure was then attempted with mesityl oxide, resulting in a higher aldol condensation product adsorbed on asbestos.



Divinyl spirobi-(m-dioxane) also added to asbestos under sodium hydroxide catalysis, yielding an asbestos acrylate salt containing 8.6% organic material. A disproportionation can be envisioned:





The use of activated vinyl compounds such as divinyl sulfone that are unreactive toward bases is necessary to conclusively determine whether addition of asbestos to carbon-carbon double bonds can take place.

Asbestos modified by polyacrylonitrile, mesityl oxide aldol condensate, or polycaprolactone could not be successfully compression molded. The poor adhesion of the moldings could be due to insufficient organic material or to cross-linking of the organic resin before molding.

One non-acid ring opening was investigated in this program by L. C. Shriver. When propylene oxide is heated with asbestos under high pressure, the starting material is polymerized and apparently some of the polyether is bound to the asbestos either as a magnesium alkoxide or through chemisorption. Such polyether grafted asbestos might be useful as a compatible filler. However, evidence of actual formation of the modified asbestos is inadequate and the product will not be hydrolytically stable.

Chemisorption of acidic species occurs on asbestos as expected. Polyacrylonitrile is strongly adsorbed on asbestos when formed in situ. Polyaldol condensation of mesityl oxide or acetaldehyde on asbestos results in a product that also appears to be due to chemisorption. Other suitable polymers might be formed in situ on asbestos by initiation of vinyl polymerization with ionizing radiation or adsorbed initiator.

The chemisorption of basic compounds by asbestos is questionable. We have found that pyridine when refluxed with dry asbestos and extracted with anhydrous ether, does not adhere to asbestos. A high molecular weight polyamine or polyether might be chemisorbed and would be easily detectable but the value of examining such systems is debatable.

UNION CARBIDE PATENT POSITION

Few patents have been issued on the chemical modification of asbestos. In general, the various patented compositions of matter containing asbestos describe the use of binders and adhesive matrices to produce cohesive products.

Specific patents covering possible reaction products of asbestos include compositions of asbestos and hydrous metal oxides[5], silica sol[6], and fluosilicic acid[4]. Silane modified asbestos is well known and it is likely that only process patents and specific compositions patents for resins filled with silane-modified asbestos are attainable. Such a patent has been issued for the treatment of polyethylene and vinyl triethoxy silane-modified silica with ionizing radiation[19].

Composition of matter patents on carboxylate-modified asbestos include a patent on fibrous sheets from asbestos treated with oxalic acid[11] or a polymer containing carboxyl and carboxamide groups[20]. The use of polyvinyl pyrrolidone[14,15] and an epoxy-polyamide thermosetting resin[16] in high strength asbestos mats and papers have been patented. The addition of metal soaps to disperse asbestos[5,21,22] by formation of a protective colloid is a form of chemisorption.

It appears that any specific new compositions of matter based on asbestos modified by acids or by chemisorption of polymeric materials can be considered patentable. The broad classes of carboxylate or chemisorption-modified asbestos are partly disclosed, limiting patent claims. For example, compositions of asbestos modified by polymerized lactones might be patented as a class. Another patent might cover asbestos modified by unsaturated carboxylic acids. The processes for the production of these materials are also patentable.

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UV-0001 # 22

STATUS REPORT

RIGID FOAMS, NEW RAW MATERIALS, EXPLORATORY

POWDERED ASBESTOS AS A RIGID FOAM FILLER

ORIGINAL COPY

Authors: E. F. Cox
W. C. Kuryla

Date: May 21, 1965

Project No.: 127G16

File No.: 4095

SUMMARY No improvements in rigid foam properties were observed as a result of incorporating a powdered asbestos filler into NIAX Foam System T-248/T-600. The foam compression properties were severely degraded at a 10 phr asbestos level, and the asbestos filler did not improve flammability properties.

Differences in asbestos-resin mixing methods, wherein a high shear 3-roll paint mill was compared with a low shear laboratory stirrer, were not observed in the properties of the foams made with each of these respective solid-resin mixtures.

While the present study is somewhat disappointing in its findings, work now underway with other solid fillers such as zinc borate may be more encouraging and will be reported in the near future.

INTRODUCTION One of the objects of this study was to determine the effect of an asbestos filler on rigid foam properties. Another was to determine what effect the nature of the mixing process (i.e., mixing the asbestos into the polyol system), would have on the foam properties. In the latter study a low shear air-driven laboratory stirrer was compared with a high shear 3-roll paint mill.

Previous studies in the area of powdered fillers in rigid polyurethane foams include the work of Kessell and James(1), who found that inert fillers did not improve the shear modulus properties of the rigid foams under study. These workers also observed that powdered fillers depressed the compressive strength properties of foams, which is in accord with the findings of the present study.

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(1) F. Hostettler, W. R. Proops, E. L. Kessel, R. VanCleve, R. H. Harding, and B. F. James, "Polyurethanes: Rigid Foam Application and Evaluation; Influence of Powdered Fillers on Modulus of Rigidity", Research Dept. Project Report, May 1, 1961.

Research and Development Department
Chemicals Division
Union Carbide Corporation

DISCUSSION In the coatings field there is considerable evidence which indicates the necessity of a high shear mixing process (i.e., mixing certain solids into a paint system), for the realization of optimum coating properties. It was of interest to ascertain whether or not an improvement in rigid foam properties would be obtained by the high shear mixing of asbestos powder into the polyol side of a foaming system.

The data of Table I indicates that, in the T-248/T-600 system of the present study, there is no signficant difference between the low and high shear mixing techniques. Furthermore, the data strongly indicates that there is nothing to be gained in foam properties with the use of asbestos powder as a filler. In fact, the foam compression properties rapidly degrade with increasing amounts of filler. Likewise, no improvement is indicated in the flammability properties of asbestos containing foams.

The foam system used in this study was NIAX Resin T-248 (80 parts of BE-320, 16 parts of RO-350, 4 parts KM-1, 26 parts of U-11B, and 1.0 parts of propylene oxide), and NIAX Activator T-600 (98.5 parts of PAPI and 1.5 parts of Silicone L-5310). The procedure used for mixing the asbestos powder into the resin is described in the Experimental section. The powdered asbestos filler was obtained from Mr. N. J. Setter of the Mining and Metals Division (High Purity No. 7 Grade, Chrysotile asbestos).

While the present study is somewhat disappointing in its findings, work now underway with other solid fillers such as zinc borate may be more encouraging in that higher levels of additive do not severely depress the compression properties of the foams having the filler incorporated therein. This work will be reported in the near future.

EXPERIMENTAL

Low Shear Mixing

The asbestos powder was mixed into the T-248 resin system using an air driven laboratory stirrer, over a 1 to 2 minute time period. The fluorocarbon which had volitilized was then re-added, and the T-248/asbestos mixture foamed in a standard manner using T-600 as the activator in the following formulation.

Formulation

T-248 Resin	127 parts
T-52N Catalyst	1.0 parts
U-11B	13 parts
T-600 Activator	82 parts
Asbestos Filler	Indicated in Table I

High Shear Mixing

The asbestos powder was first mixed into the T-248 resin system by the use of a bread dough mixer, and stirred for a period of 5 minutes. This "pre-mix" was then passed three times through a 3-roll paint mill, over about a 2-1/2-hour period. The fluorocarbon which had been volitilized during this processing was then re-added, and the T-248/asbestos mixture foamed in exactly the same manner as described above.

Experimental Discussion

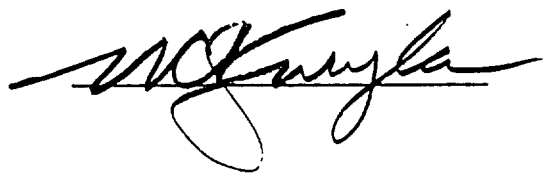
The mixing of asbestos powder into a T-248 resin system at the 5 phr level (parts per 100 parts of polyol blend) gave no particular difficulty in either the actual mixing operation or subsequent foaming of the mixture. However, at higher additive levels the mixtures were increasingly more viscous, and, in fact, mixtures containing 15 phr asbestos were semi-solid in consistancy. These 15 phr mixtures were extremely difficult to foam and a good mixing of activator with the mixture could not be accomplished.

The asbestos-containing foams were all friable or "punky", this property being generally proportional to increasing asbestos content and reflected in the compression properties of the foam (Table I).

Additional work is planned for hydrophobic and chemically modified asbestos for use as fillers in rigid foams.

NOTEBOOK REFERENCE: 8WCK-21

ATTACHMENT: 1 Table



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ACL Doc 16028 · Page 78 of 177

TABLE I

PHYSICAL PROPERTIES OF ASBESTOS CONTAINING FOAMS

(SYSTEM = T-248/T-600)

Asbestos Content (PHR)	0	5**	5*	10**	10*
Foaming Data:					
Cream Time (sec.)	30	28	30	28	30
Rise Time (sec.)	140	110	135	115	115
Tack Free Time (sec.)	105	90	90	90	85
Properties Data:					
Appearance	122.	122.	122.	123.	123.
Core Density PCF	1.65	1.60	1.77	1.81	2.03
Closed Cells PCT	87.	85.	87.	70.	82.
Cell Volume .0001 cc.	0.0	0.0	0.0	0.0	0.0
Compressive Strength					
25C PSI PARL	33.	20.	24.	7.	10.
PERP	8.	7.	8.	4.	6.
100C PSI PARL	25.	14.	18.	5.	11.
PERP	9.	9.	11.	0.	10.
Retention PCT	92.	101.	109.	0.	140.
Cold Aged PSI	0.	19.	23.	6.	10.
Dry Aged PSI	38.	18.	21.	21.	12.
Humid Aged PSI	20.	10.	13.	4.	8.
Cold Aging PCT Change					
Weight 14 Days	-9.6	-11.5	-9.0	-9.2	-8.2
Volume 2 Days	0.	0.	0.	0.	0.
14 Days	-49.	-23.	1.	-3.	1.
Dry Aging PCT Change					
Weight 14 Days	2.0	0.6	1.1	-6.6	0.7
Volume 14 Days	8.	10.	9.	19.	7.
Humid Aging PCT Change					
Weight 7 Days	0.0	0.9	5.3	-8.2	41.1
14 Days	-0.6	1.2	10.4	-8.7	-0.2
28 Days	0.3	7.0	1.1	-9.2	-2.1
Volume					
7 Days	34.	32.	23.	21.	19.
14 Days	44.	38.	27.	21.	22.
28 Days	47.	41.	33.	20.	21.
Flammability ASTM D1692					
Density PCF	1.60	1.52	1.68	1.82	1.95
Ignition Time, Sec.	15.	12.	13.	12.	12.
Extinguish Time, Sec.	33.	33.	31.	34.	37.
Burning Extent In.	1.2	1.3	1.2	1.2	1.4
Burning Rate In/Min	0.0	0.0	0.0	0.0	0.0

* Low Shear Mixing
** High Shear Mixing

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UV-0001 #24

STATUS REPORT

RIGID FOAMS, NEW RAW MATERIALS, EXPLORATORY:

"HYDROPHOBIC" ASBESTOS AS A RIGID FOAM FILLER

Authors: E. F. Cox
W. C. Kuryla

Date: August 18, 1965

Project No.: 127G16

File No.: 4470

SUMMARY Improvements in rigid foam properties were not observed as a result of incorporating a "hydrophobic" asbestos filler into NIAX Foam System T-248/T-600. The foam compression properties were severely degraded at a 10 parts "H"-asbestos level, and the filler did not improve either the flammability or shear properties.

Because of these results, and the findings of past studies which have clearly demonstrated the property-degratory effect of an asbestos filler, it is recommended that no further work be done with asbestos-based fillers in rigid polyurethane foams.

INTRODUCTION As part of the continuing program to investigate promising but inexpensive fillers in polyurethane rigid foams, "hydrophobic" asbestos powder was examined as an inert additive in NIAX Foam System T-248/T-600. A previous study[1] showed that asbestos powder, when incorporated into this foam system as an inert additive, not only severely degraded the compressive properties of the foams but failed to show any improvement in flammability properties as well.

It was felt by Mr. N. J. Setter of our Mining and Metals Division[2] that an asbestos which was chemically modified by its reaction with 10 wt.% stearic acid, and thereby rendered hydrophobic, would be significantly different in its chemical behavior to warrant its investigation as a rigid foam filler.

DISCUSSION Experimental:

A quantity of "hydrophobic" asbestos, which contained about 10 weight percent combined stearic acid, was

Research and Development Department
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received from Mr. N. J. Setter. This material was mixed into a T-248 Resin using an air-driven laboratory stirrer in levels of 5, 10, and 15 parts, just prior to foaming. The foaming of these resin-filler mixtures was done by the standard laboratory hand-batch technique, using open cardboard molds. Resin-filler mixtures which contained 15 parts of filler could not be successfully foamed due to the unworkably high viscosity of these mixtures.

Foam Results:

The "hydrophobic" asbestos-containing foams were all somewhat friable or "punky", but not to the same degree as those foams which contained the untreated asbestos(1).

The data of Table I indicate that, in the T-248/T-600 system of the present study, there is nothing to be gained in foam properties with the use of "hydrophobic" asbestos as a filler. The foam compression and shear properties rapidly degrade with increasing filler concentration. Likewise, no improvement is indicated in the flammability properties of "hydrophobic" asbestos-containing foams.

These findings are in full accord with those of a previous study whereby untreated asbestos was used as a filler(1); and are in general agreement with the work of Kessell and James(3), who found that inert fillers did not improve the shear modulus properties of the rigid foam systems under study.

CONCLUSIONS Because of the results of the present investigation, and the findings of past studies which have clearly demonstrated the property-degratory effect of an asbestos filler, it is recommended that no further work be done with asbestos-based fillers in rigid polyurethane foams.

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Notebook Reference: 8WCK-69, 73

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Attachments: Table 1

TABLE I

PHYSICAL PROPERTIES OF FOAMS CONTAINING "HYDROPHOBIC" ASBESTOS

(SYSTEM = T-248/T-600)

Formulation (Parts):						
"Hydrophobic" Asbestos	0	5	10	0	5	10
T-248	127	127	127	127	127	127
T-600	82	82	82	82	82	82
T-52N	0.6	0.6	0.6	0.8	0.8	0.8
U-11B	8	8	8	13	13	13
Foaming Data:						
Cream Time, Sec.	30	40	60	30	30	30
Rise Time, Sec.	250	190	140	120	140	120
Tack-Free Time, Sec.	170	140	140	125	100	90
Foam Properties:						
Appearance	122.	122.	122.	121.	121.	122.
Core Density PCF	2.01	2.17	2.18	1.70	1.75	1.80
Closed Cells PCT	90.	90.	87.	92.	88.	88.
Compressive Strength						
25C PSI Parl	44.	23.	14.	31.	21.	14.
Perp	20.	13.	9.	11.	9.	9.
Cold Aged psi	37.	27.	14.	-	22.	14.
Dry Aged psi	49.	26.	13.	34.	18.	12.
Humid Aged psi	23.	17.	9.	15.	12.	10.
Cold Aging pct Change						
Weight 14 Days	-5.0	-1.7	-7.3	-10.2	-8.4	-7.8
Volume						
14 Days	-16.	1.	2.	-38.	1.	2.
Dry Aging pct Change						
Weight 14 Days	0.9	0.2	-3.0	1.1	-3.5	-9.9
Volume 14 Days	3.	3.	4.	10.	8.	1.
Humid Aging PCT Change						
Weight 7 Days	4.8	5.0	3.5	-0.8	-1.1	-4.1
14 Days	2.9	7.0	4.1	0.8	0.0	-2.8
28 Days	4.0	9.6	17.8	-2.4	-4.0	-8.2
Volume						
7 Days	20.	13.	14.	35.	31.	30.
14 Days	29.	17.	20.	50.	34.	26.
28 Days	38.	23.	21.	62.	28.	23.
Flammability ASTM D1692						
Density PCF	1.93	2.10	2.06	1.70	1.75	1.80
Ignition Time Sec.	14.	16.	15.	15.	12.	14.
Extinguish Time Sec	39.	43.	39.	40.	34.	38.
Burning Extent In	1.1	1.0	1.2	1.0	1.1	1.2
Burning Rate In/Min						
Flammability ASTM E162						
Density PCF	2.09	2.25	2.22	-	-	-
Flame Spread Factor	36.7	41.8	37.0	-	-	-
Heat Evol. Factor	10.9	14.4	11.5	-	-	-
Flame Spread Index	399.	639.	426.	-	-	-
Burning Extent In.	15.0	15.0	15.0	-	-	-
Flame Penetration Test						
Density PCF	2.08	2.31	2.27	1.78	1.80	1.90
Penetr. Time Sec.	34.	23.	51.	26.	16.	22.
Weight Loss PCT.	13.8	8.8	12.3	13.2	11.3	20.8
Shear 25C 2. in PARL						
Density, PCF	2.01	2.19	2.22	-	-	-
Strength, psi	25.	13.	12.	-	-	-
Modulus, psi	271.	231.	267.	-	-	-
Shear 25C .5 in PARL						
Density, PCF	1.90	2.12	2.11	-	-	-
Strength, psi	33.	21.	14.	-	-	-
Modulus, psi	534.	593.	439.	-	-	-
Foam Ref., 8WCK-	73-1	73-2	73-3	69-1	69-2	69-3

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UV-0001 #85

STATUS REPORT

MECHANICAL PROPERTIES OF ESTANE-CHLOROBENZENE-ASBESTOS SYSTEMS

Authors: J. A. Faucher
J. V. Koleske

Date: November 10, 1965

Project No.: 399A50

File No.: 4858

SUMMARY Mechanical properties have been determined for blends of Estane polyurethane, chlorobenzene, and asbestos. The tensile properties of these systems are equivalent to or better than Estane at asbestos contents of up to 30%.

About 30-35% asbestos can be added to the Estane-chlorobenzene system and still obtain transparent molded plaques. Without the chlorobenzene, even 10% asbestos is readily visible in Estane. Since the additives are considerably cheaper than the elastomer, these systems or similar ones may be of commercial importance.

INTRODUCTION In a recent report (1) we commented on the fact that the addition of chlorobenzene to Estane 5701-F1 (a B. F. Goodrich Chemical Company polyurethane) had a marked effect on the tensile properties of the polymer. This improvement of tensile properties prompted an investigation of the effect of asbestos filler on the tensile properties of the Estane-chlorobenzene system.

EXPERIMENTAL Various amounts of chyrsotile asbestos (high purity, Coalinga) were milled into Estane containing 12-15% chlorobenzene at 120-150°C. for 5 minutes. (All percentages listed in this report are based on the Estane). Plaques of the milled material were molded at 150°C. and 1000-2000 psi (10 seconds). Room temperature tensile properties were obtained with an Instrom tester at a strain rate of 20 percent per minute. The real component of the complex shear modulus, G', and the mechanical loss were obtained as a function of temperature with the recording torsion pendulum.

Research and Development Department
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Union Carbide trial exhibit UC-805: Union Carbide Research and Development Status Reports on Asbestos-Reinfo... Published by AsbestosClaims.Law
ACL Doc 16028 · Page 85 of 177 asbestosclaims.law/library/16028/85

DISCUSSION The first point of interest was that the molded plaques were clear when up to 33% asbestos was added, i.e., no small particles of asbestos were visible. However, in the absence of chlorobenzene even 10% asbestos (the lowest asbestos composition investigated) was clearly visible in the molded plaques. It seemed that milling at 150°C. produced clearer plaques than those obtained by milling at about 120°C. Orientation of the clear plaques resulted in an opaque, white material.

In Figure 1 the mechanical loss spectra of Estane and of certain chlorobenzene-asbestos-Estane systems are shown. As might be expected, chlorobenzene causes a decrease in the glass transition temperature, Tg, of Estane. Addition of 23% asbestos resulted in an increase in Tg. If the asbestos were acting as an inert filler one would not expect a change in Tg, although the magnitude of the mechanical loss should decrease at the transition. Therefore, the increase we see in Tg probably reflects an interaction of the asbestos with the Estane-chlorobenzene system. The clarity of the molded plaques is another indication that an interaction exists. Figure 2 shows the real portion of the complex shear modulus as a function of temperature. It is interesting to note that even though the glass transition occurs at a lower temperature with the Estane-chlorobenzene system, above 0°C. the shear modulus is significantly higher (in keeping with the tensile data). Also, this system will be more flexible from -20 to 0°C. than Estane. Addition of asbestos caused the shear modulus to be markedly higher over the temperature range investigated.

The tensile properties of the systems studied are shown in Figure 3, 4, 5 and 6 as a function of the percent asbestos added. As a reference point, the tensile property of Estane containing no additives is shown on each plot. Young's modulus, Figure 3, increases as the amount of asbestos added is increased. The percent elongation, Figure 4, decreases as the asbestos content is increased, however, even with 30-40% asbestos the Estane-chlorobenzene-asbestos system has the same elongation as Estane without these additives. Thus, for an end use that requires a higher initial modulus along with the inherent elongation of the polyurethane, these blends may show some promise. In addition, it should be noted that two low cost materials can be added in fairly high amounts and still maintain the same properties in a rather expensive polymer.

The rupture energy, Figure 5, and the ultimate strength, Figure 6, of the asbestos systems decrease as the

asbestos content is increased. However, here again up to about 30% asbestos can be added to the Estane-chlorobenzene system and still achieve property values equal to that of Estane.

Joseph V. Koleske

References

1. Faucher, J. A. and J. V. Koleske, Informal Report, Tensile Properties of Estane with Various Additives, Project No. 399A50, 15 Sept., 1965.

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Attachments: 6 Figures

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Figure 1.

Mechanical loss of Estane and Estane plus additives

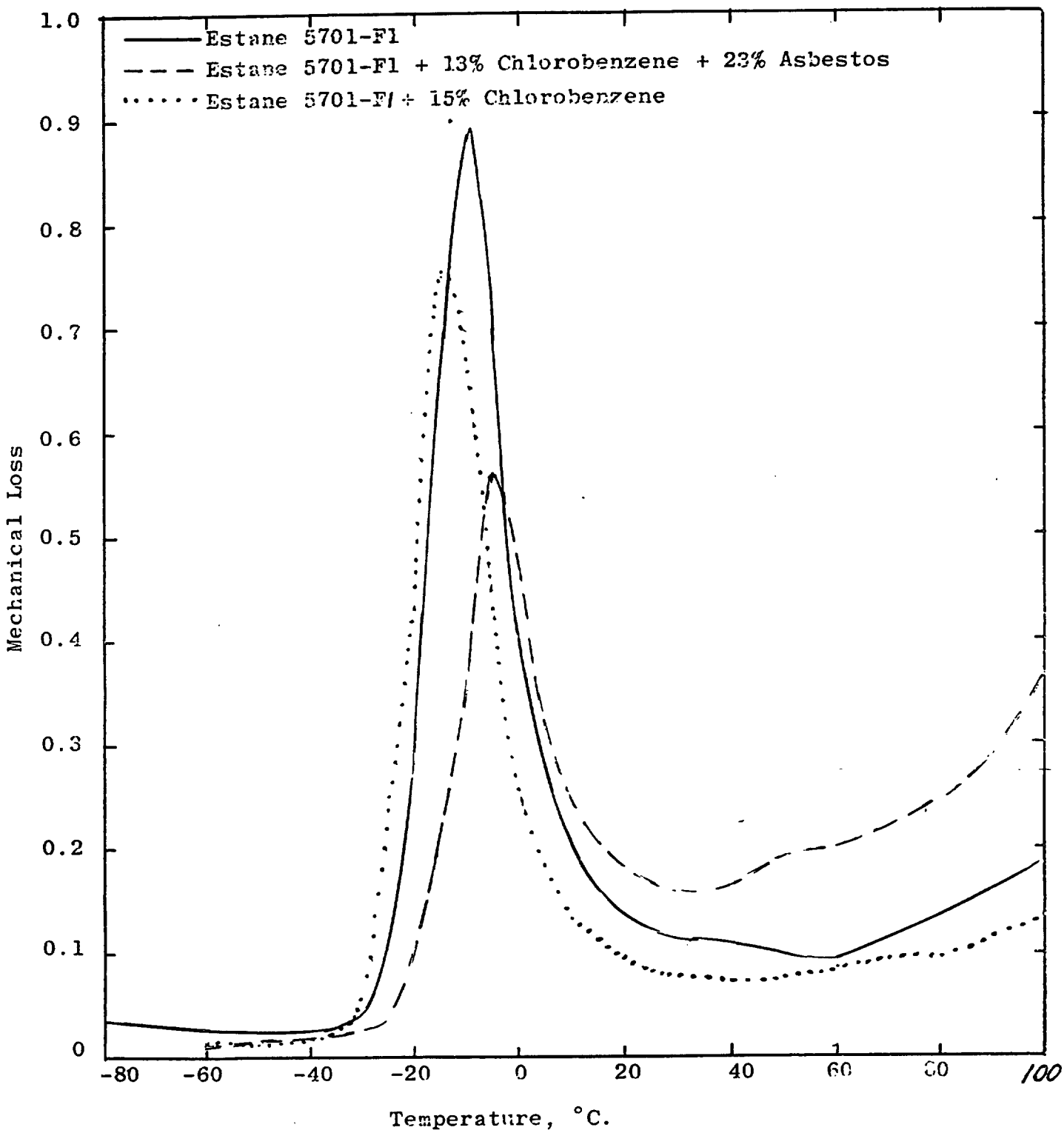
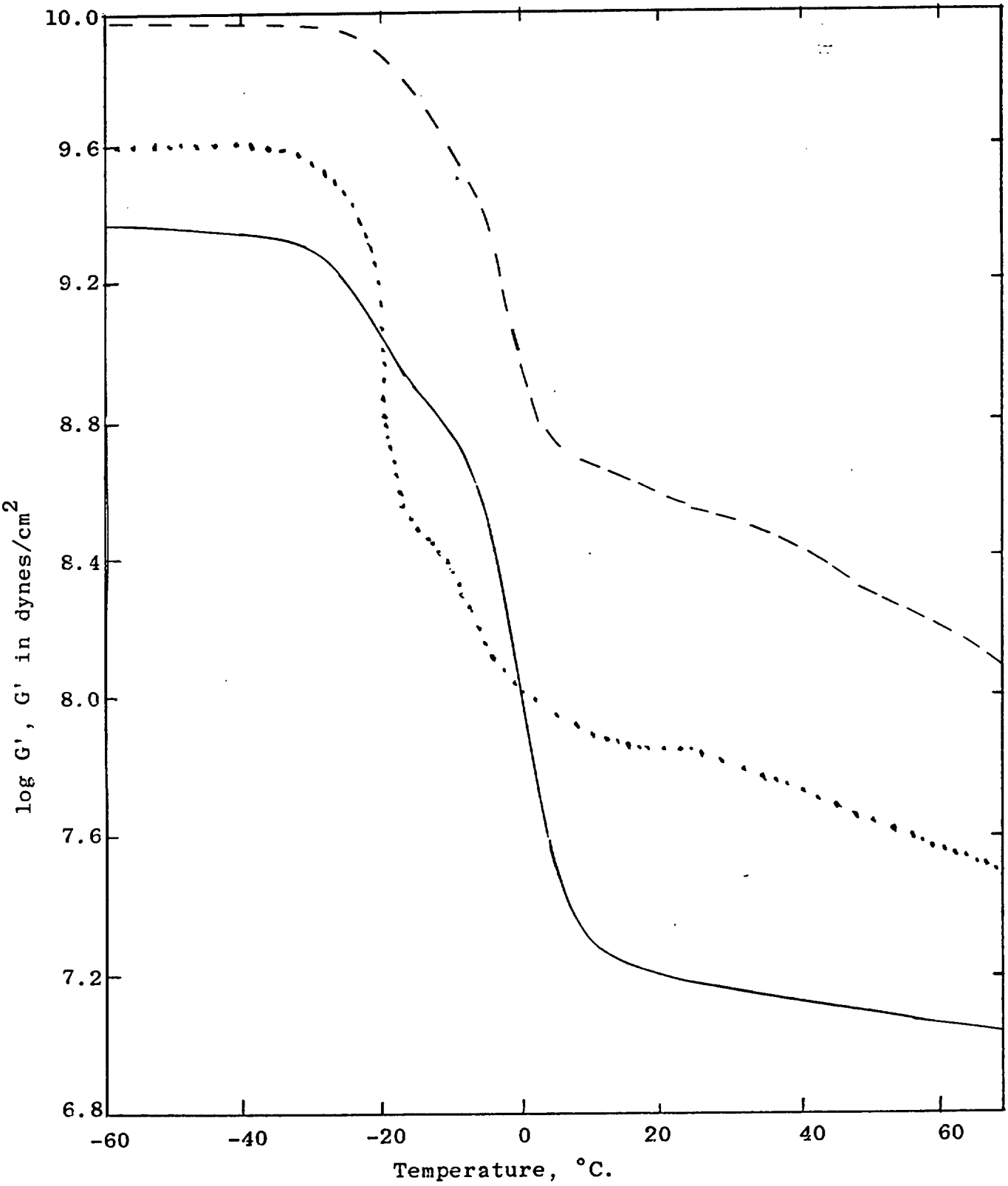


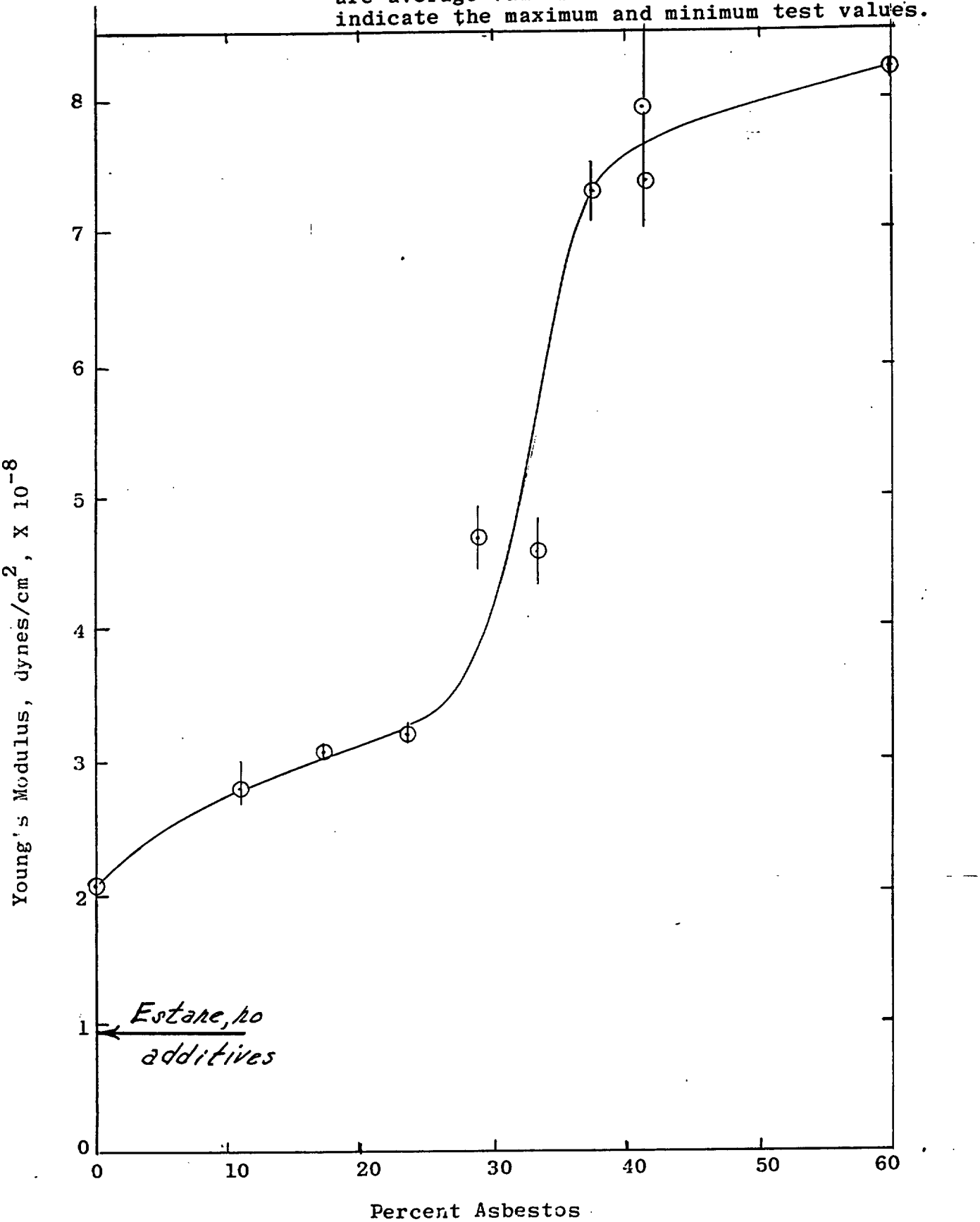
Figure 2

Real portion of the complex shear modulus, G' ,
for Estane ————, Estane + 15% Chlorobenzene ·····, and
Estane + 13% Chlorobenzene + 23% Asbestos ----



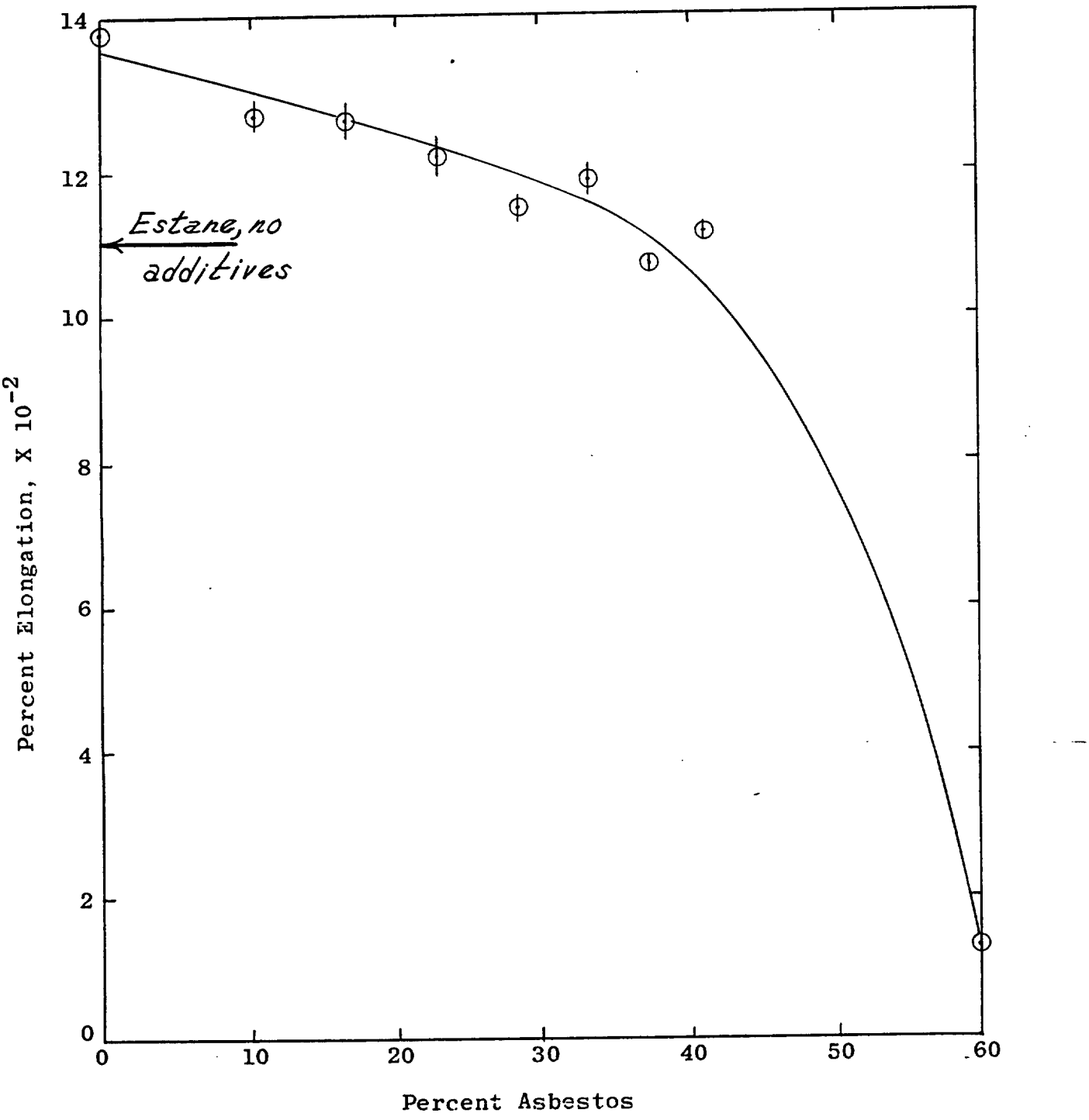
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Figure 3. Young's Modulus of Estane-Chlorobenzene-Asbestos Systems. Samples contained 12-15% chlorobenzene and indicated amounts of asbestos based on only Estane. Open circles are average values and the vertical lines indicate the maximum and minimum test values.



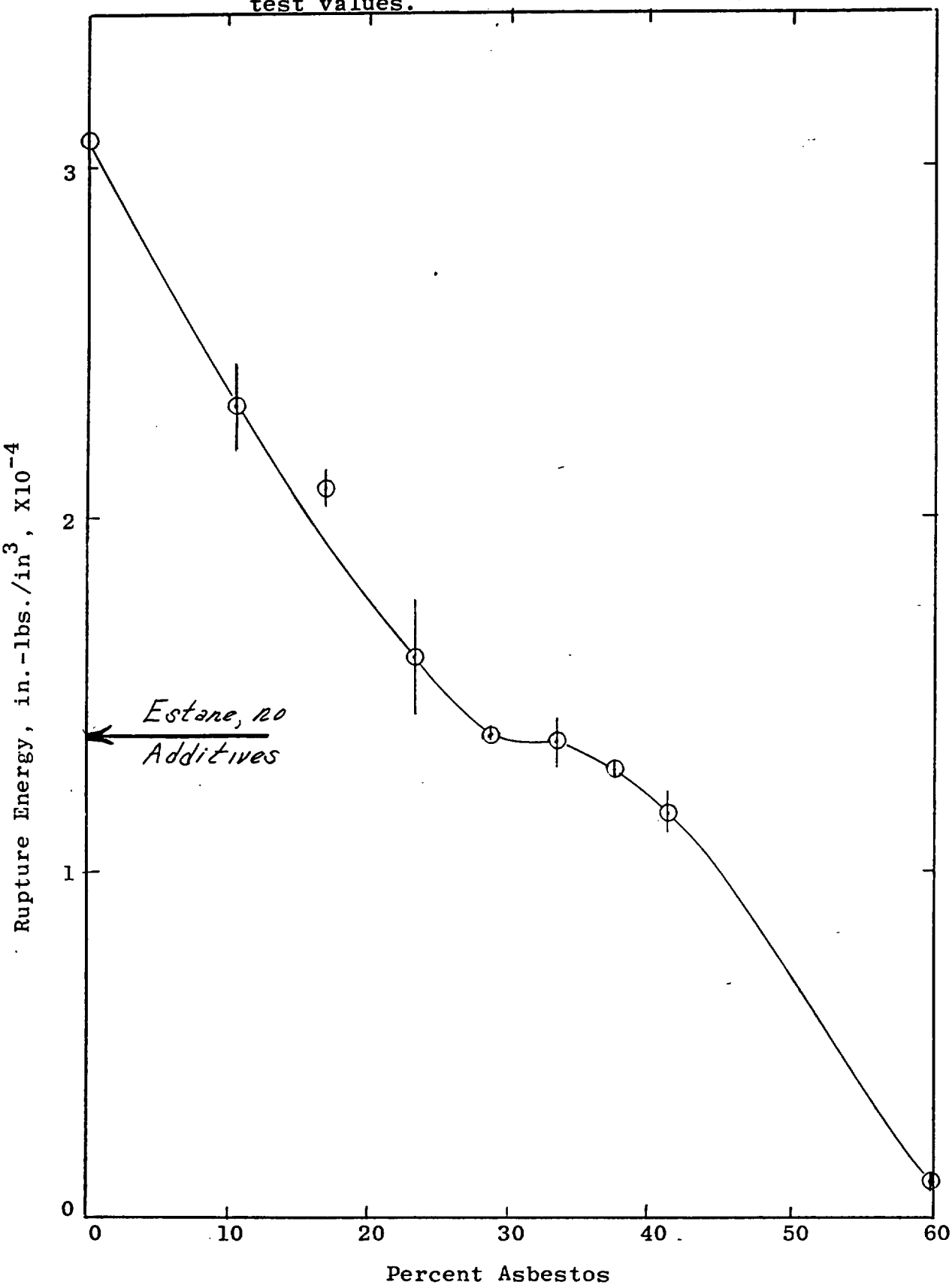
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Figure 4. Percent Elongation of Estane-Chlorobenzene-Asbestos Systems. Samples contained 12-15% chlorobenzene and indicated amounts of asbestos based on only Estane. Open circles are average values and the vertical lines indicate the maximum and minimum test values.



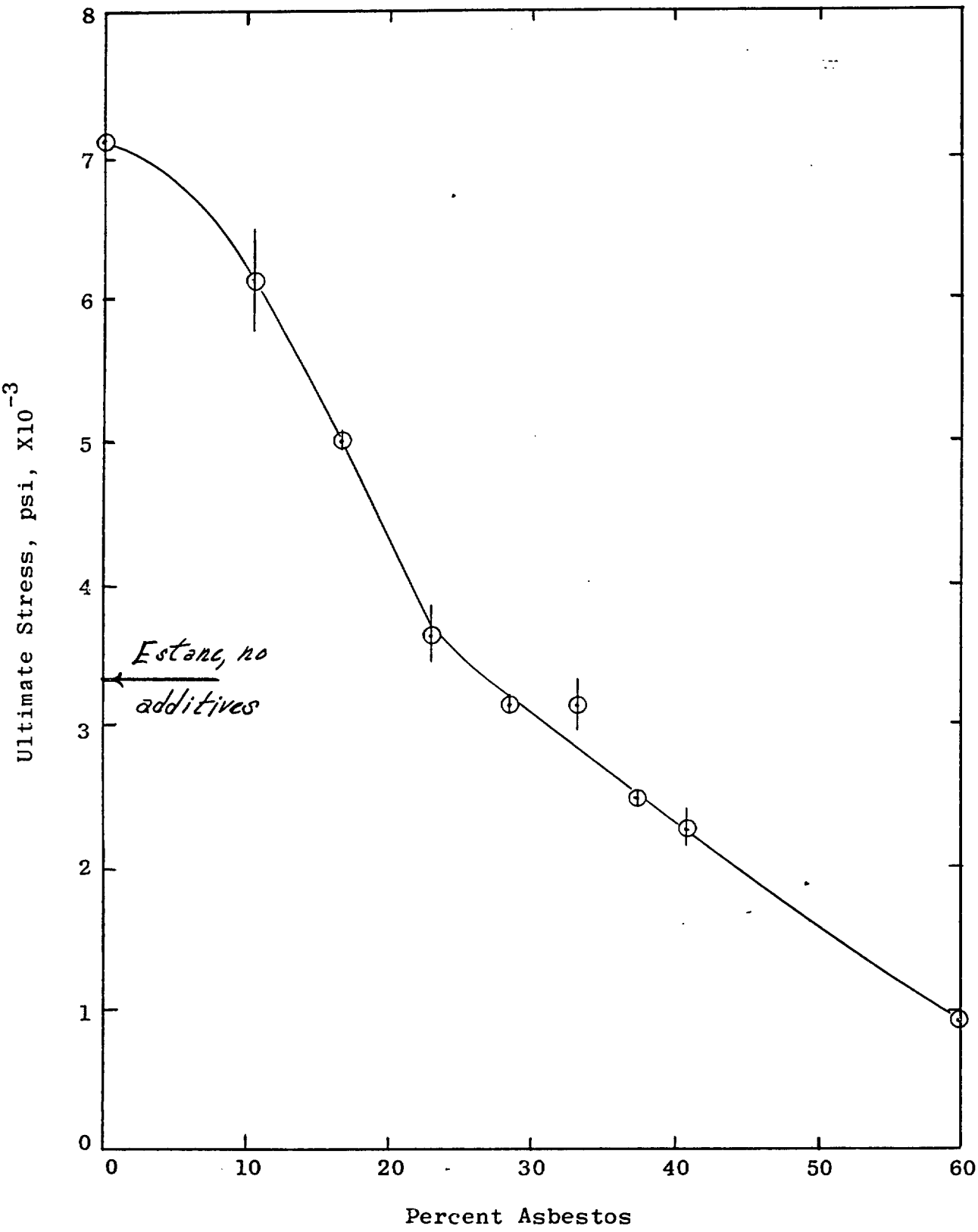
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Figure 5. Rupture Energy of Estane-Chlorobenzene-Asbestos Systems. Samples contained 12-15% chlorobenzene and indicated amounts of asbestos based on only Estane. Open circles are average values and the vertical lines indicate the maximum and minimum test values.



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Figure 6. Ultimate Stress of Estane-Chlorobenzene-Asbestos Systems. Samples contained 12-15% chlorobenzene and indicated amounts of asbestos based on only Estane. Open circles are average values and the vertical lines indicate the maximum and minimum test values.



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UC 2701 #5

STATUS REPORT

Formal

WATER-TREATMENT CHEMICALS

MISCELLANEOUS INDUSTRIAL WASTEWATER TREATMENT APPLICATIONS

AUTHORS: R. A. Conway
J. P. McGuire

DATE: June 24, 1963

FILE NO: 941

Project No.: 139E10

SUMMARY Laboratory tests have been conducted with several industrial waste samples using a variety of coagulants made by Union Carbide. The results of these tests indicate that these coagulants provide the capability to treat successfully several distinctly different types of industrial wastewaters. The wastes that were treated were from Glatfelter Paper Company, Champion Paper Company, Feldspar Corporation, and Union Carbide Nuclear Company. The coagulants used were POLYOX WSR 301, UCAR resin C-149, and the Nuclear Company's dispersed asbestos.

PROCEDURE

1. 500-ml samples were poured into each of six beakers and placed on a standard multiple mixer equipped with 1-in. by 3-in. paddles.

2. The coagulant was added as a dilute aqueous solution at various dosage levels during the rapid-mix (100 rpm) period of 30 seconds duration.

3. The samples were then mixed for 20 minutes at 25 rpm.

4. After a settling period ranging from 30 minutes to two hours, samples of supernatant liquor were collected for analysis.

DISCUSSION

Glatfelter Paper Company, Spring Grove, Pa.

A sample of this company's "green-liquor" wastewater was treated with UCAR resin C-149, alum, and dispersed asbestos.

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C-149 and a combination of C-149 and alum proved to be ineffectual. Dispersed asbestos proved to be quite successful. At a dosage of 50 mg/l the suspended solids concentration was reduced from an initial level of 230 mg/l to a final level of 77 mg/l (Table I).

Champion Paper Company, Canton, N. C.

A sample of plant effluent was treated with POLYOX WSR 301, dispersed asbestos, and C-149. Both dispersed asbestos and C-149 were ineffectual. Although the data were somewhat scattered, dosages of WSR 301 between 1 and 5 mg/l reduced the suspended solids content to a satisfactory level (Table II).

Union Carbide Nuclear Co., Rifle Mills, Col.

Tests made with a sample of a uranium-mining slurry obtained from the Nuclear Company's Rifle Mills mine showed that the only satisfactory coagulant in this application is POLYOX WSR 301. A resin dosage of 100 mg/l reduced the supernatant suspended solids to 50 mg/l (Table III). Since this dosage represents a cost of about $500 per million gallons, WSR 301 probably can't be considered for this application unless the dosage can be lowered through further test work.

Feldspar Corporation, Spruce Pine, N.C.

In these jar tests the pH of the samples was raised to 7.0 with lime, which is the intended operating procedure to be followed at Feldspar's treatment plant. This resulted in a supernatant suspended solids concentration of 104 mg/l in the raw sample. Since the requirement for suspended solids is about 100 mg/l or less and since all but the combination of C-149 and dispersed asbestos produced poorer results, there appears to be little sales potential in this application (Table IV). Some additional flocculation was obtained with the C-149-dispersed asbestos combination, although the suspended solids content was not lowered appreciably. This combination was also effective in treating the wastewater prior to the addition of lime.

CONCLUSION The two most promising applications of Union Carbide's coagulants that have been developed through this series of laboratory tests are at the Glatfelter Paper Company in Spring Grove, Pa. and the Champion Paper Company in Canton, N. C. These data have been forwarded to Mr. R. C. McQueen, who is following up these leads.

Attachments

4 Tables

hkh

J. P. McGuire

TABLE I

FLOCCULATION OF GREEN-LIQUOR SAMPLE FROM GLATFELTER PAPER COMPANY

Dispersed-Asbestos Dosage, mg/l	Supernatant Suspended Solids, mg/l (a)
0	230
50	77
100	59
150	33

(a) Difficulty was encountered in obtaining suspended solids measurements possibly due to growth of crystals in drying oven.

TABLE II

FLOCCULATION OF WASTEWATER FROM CHAMPION PAPER COMPANY

POLYOX WSR 301 Dosage, mg/l	Supernatant Suspended Solids, mg/l
0	104
0.1	124
1.0	24
2.0	84
5.0	34

TABLE III

FLOCCULATION OF SLURRY FROM RIFLE MILLS MINE OF UNION CARBIDE NUCLEAR COMPANY

POLYOX WSR 301 Dosage, mg/l	Supernatant Suspended Solids, mg/l
0	3260
50	2030
75	870
100	50

TABLE IV

FLOCCULATION OF WASTEWATER FROM FELDSPAR CORPORATION

Coagulant	Dosage, mg/l (a)	Supernatant Suspended Solids, mg/l
None	-	104
C-149	0.2	124
C-149	0.4	112
Dispersed asbestos	3.0	148
Dispersed asbestos	5.0	116
Dispersed asbestos and C-149	3.0/0.2	94

(a) pH of all samples was adjusted to 7.0 with lime.

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STATUS REPORT

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NEW ENTERPRISES

ASBESTOS REINFORCED RESINS

CHEMICAL REACTIONS OF ASBESTOS

AUTHORS: C. W. McGary
P. L. Smith
L. C. Shriver

DATE: April 8, 1963

FILE NO: 605

Project No: 161W61

SUMMARY The chemical modification of chrysotile asbestos (processed by the Nuclear Company) is being studied. The most likely point of attack for this type of asbestos is at pendant hydroxyl groups which can be represented by the fragmental formula: $\geqslant$Si-OMgOH. The reactions studied thus far have been with organic compounds containing groups known to be active with hydroxyls: anhydrides, acids (organic and inorganic), alkylene oxides and isocyanates. The work has followed an exploratory and fundamental pattern with each reaction being studied as quantitatively as possible by analyses, weight increases or losses of reaction product, etc. The results and information gathered for each reacting compound are summarized below. In no case should the information be considered as complete and further work is planned in all areas.

DISCUSSION Chrysotile asbestos is written empirically by various authorities as (1) $Mg_6(OH)_6Si_4O_{10}\cdot H_2O$ or (2) $Mg(OH)_8Si_4O_9$. (Formula weight - 554.2)

These formulas represent the constitution of the recurring unit in the chrysotile polymer. The exact configuration of the silicon-oxygen bonding in the polymer spine is not clearly defined, to the authors at least, but the important consideration is that, in each recurring unit (that is 554.2 formula weight), there are six (-O-MgOH) groups.

Aqueous Hydrochloric Reaction

This reaction, of course, has been known and studied elsewhere and is not novel. The purpose of the study here was to determine the speed of the reaction and the ultimate amount of acid required for our particular form of asbestos. The reaction can be

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represented as: $\equiv Si\text{-}OMgOH + 2\ HCl \longrightarrow MgCl_2 + H_2O + \equiv SiOH$. Reactions were carried out at boiling temperatures with 1.3-1.5 N starting acid. Data obtained showed that 11.6-11.7 mols of HCl were used for each formula weight of asbestos. Magnesium analyses at the same time indicated 5.6-5.85 atoms of magnesium were removed. The figures give good confirmation for the assumption of six (-MgOH) groups per formula weight. Sterling Forest has shown that the skeletal structure of the original asbestos polymer remains intact after acid treatment. Because of this fact, the residue should prove interesting for chemical modification and a relatively large amount is being prepared for this purpose.

Maleic Anhydride Reaction

The most desirable result of this reaction would be a product represented as:

$$\equiv SiOMgOOCCH=CHCOOH$$

This would give an asbestos product which might be visualized as giving chemically bonded filler for an epoxy/maleic/styrene resin system. Unfortunately, our work to date (all in organic solvent), indicates considerable cross-linking of the asbestos even with excess of anhydride. However, there is work underway with molten maleic anhydride in large excess reacting under pressure which may alter this picture.

Maleic Acid Reaction

The objective here, of course, is identical with maleic anhydride treatment. Reactions in molten maleic acid (mp 137-138°C) at 140-150°C and in boiling water solutions have given such large amounts of magnesium cleavage that this method of attack does not appear to have much merit. However, future work at lower temperatures might conceivably alter this picture.

Alkylene Oxide Reaction

Reactions at 150°C under pressure with propylene oxide at mol ratios of 167/1 have apparently produced, as might be expected, considerable amount of propylene glycols. However, in one experiment, where practically all of the oxide was reacted, there is considerable evidence that oxide was attached to the asbestos. Full evaluation of this product has not been completed, however.

Diisocyanate Reaction

The reaction with toluene diisocyanate in boiling methyl ethyl ketone solution (TDI/OH ratio 1:1) is quite rapid until it is terminated, apparently by cross-linking of the asbestos. This point occurs at approximately 1.4 mols diisocyanate/1.0 formula weight of asbestos. In another approach, a prepolymer of polypropylene glycol 425 and TDI (1.0/2.0 mol ratio) was prepared and then reacted at 135°C with asbestos (prepolymer/OH ratio 1:1). Weight increase of the product indicated 0.9 mols of the prepolymer had reacted with each formula weight of asbestos. The very interesting feature of this product was the fact that it was swollen considerably by organic solvents.

It is obvious that reactions using higher ratios of NCO/OH are in order and further work in this direction is planned.

ANALYTICAL In following acid/asbestos reactions, it is advantageous to follow analytically the stripping of magnesium from the asbestos molecule. Conventional analytical methods for the determination of Mg^{++} are tedious and time consuming. A rapid and sufficiently accurate method has been developed for our work, which involves the precipitation of the Mg^{++} ion from neutral solution with an excess of standard alkali solution. The precipitated magnesium hydroxide is allowed to settle and an aliquot of the supernatant liquid is back-titrated with standard acid and the Mg^{++} calculated from the alkali used for precipitation.

Leland C. Shores

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WV-0001
#2

STATUS REPORT
FORMAL

WATER TREATMENT CHEMICALS
CLARIFICATION OF GAS SEPARATION QUENCH WATER AT INSTITUTE

AUTHORS: R. A. Conway
G. T. Waggy

DATE: April 1, 1963

FILE NO: 460

Project No: 139E10

SUMMARY In cooperation with unit personnel, a bench-scale program to evaluate Carbide's coagulants for use in enhancing the clarification of quench water at the Institute Gas Separation Unit has been completed. High concentrations of suspended solids and oils in this cycle-water system have caused costly maintenance problems and reduced gas production. Preliminary testing at 25°C showed the use of UCAR resin C-149 to be economically attractive for this application. However, the effectiveness of C-149 varied inversely with temperature with this high-pH water. At the temperature range of 75 to 80°C encountered in the cycle system at the Institute unit, C-149 was virtually ineffective. However, the treatment of similar waste streams certainly offers potential markets for C-149 providing more favorable application conditions prevail.

DISCUSSION Continual build up of suspended solids and oils in the cycle water used to quench hot gases in the gas separation processes operated at our various plants usually results in both expensive maintenance problems and reduced gas production. At the request of Mr. R. L. Pecsok and Mr. R. A. Baxley of the Gas Separation Unit at the Institute Plant, laboratory testing was undertaken using Carbide's coagulants to enhance the clarification of the gas-quench water at this unit. Since the flow rate of this cycle system is 6,000,000 gallons per day, there is a sizable market for coagulants in this application, even at low dosage levels.

Initial bench-scale testing of UCAR resin C-149, dispersed asbestos, POLYOX water soluble resin WSR 701, CELLOSIZE hydroxyethylcellulose, and their combinations showed C-149 to be the most effective of these coagulants in this application.(1) Additional evaluation tests of C-149 were conducted on fresh quench-water samples, first at 25°C and subsequently at the elevated temperatures encountered in the actual cycle system. The results of these studies, which are presented in the attached table, show that the addition of 3 mg/l of C-149 at 25°C resulted in the removal of about 70 per cent of the organic matter and about 95 per cent of the suspended solids which did not settle out in the control samples.

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However, the coagulant's performance was greatly reduced as the temperature of the system was increased toward the required treatment temperature of 80°C. UCAR resin C-149 was found essentially ineffective for the clarification of the quench-water samples under these adverse application conditions of high pH (9-10) and extreme temperature.

Since the design of the Gas Separation Unit at Institute does not permit chemical treatment of the recycled water after the cooling towers, the use of C-149 in the cyclic system at this unit does not appear feasible. The substitution of C-149 for the ferrous sulfate which is presently used to enhance clarification of the relatively cool purge stream from this cyclic system should be considered if more efficient removal of organic matter from this purge stream becomes necessary. The treatment of similar quench-water systems definitely represents a potential market for C-149 providing the coagulant can be added to the system at a point where the temperature is lower than about 50°C. No additional work is planned on this application at this time.

Procedure

Preliminary coagulant evaluation studies were conducted by adding the coagulants in dilute aqueous solutions to 100-ml samples of quench water under gentle agitation. Visual observations were made of coagulant performance at various dosages. More refined testing was done on one-liter volumes of quench water treated with various dosages of C-149. Rapid (100 rpm) agitation was supplied by a multiple mixer during the two minutes while the coagulant solution was added to the individual beakers. Then, the agitation was reduced to 30 rpm for a period of 18 minutes, during which time the floc growth occurred. The flocculles were then allowed to settle for 40 minutes prior to withdrawing supernatant liquor for analysis. Studies were made at elevated temperatures by immersing the beakers of quench water in a constant temperature bath while the above coagulant application procedure was followed.

BIBLIOGRAPHY

(1) McGuire, J. P., Clarification of Gas Separation Quench Water At Institute, Research and Development Report, October 4, 1962.

NOTEBOOK REFERENCE: 5530-11GTW

Attachments:
1 Table

J. T. Waggy

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"UCAR" RESIN C-149

FLOCCULATION OF GAS SEPARATION QUENCH WATER

Date sample was collected	C-149 Dosage, mg/l	Temperature, °C	Quality of Supernatant Liquor[a]		
			Clarity, % trans (b)	Suspended Solids, mg/l (c)	COD, mg/l (d)
1-9-63	1	25	<10	160	2700
	3	25	<10	20	1100
	6	25	43	10	800
	9	25	46	10	870
1-9-63	1	75	<10	410	4500
	3	75	<10	550	3800
	6	75	<10	540	3900
	9	75	<10	620	4300
1-9-63	Control mixed	25	<10	600	5400
	Control settled	25	<10	450	3800
	Control filtered	25	94	1	770
12-18-62	1	50[e]	<10	120	1300
	3	50	<10	110	1100
	6	50	<10	150	1300
	9	50	<10	160	1500
12-18-62	Control mixed	50	<10	350	2500
	Control settled	50	<10	190	2200
	Control filtered	50	86	10	500

(a) Sample of supernatant withdrawn after forty-minute settling period.

(b) Clarity measured using a Fisher electrophotometer equipped with a 650A filter.

(c) Suspended solids determined by membrane filter procedure.

(d) Chemical oxygen demand was measured by the standard chromic-acid reflux procedure.

(e) These systems inadvertently cooled from 55°C at the start of the test to 45°C at the end.

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STATUS REPORT

INORGANIC POLYMERS, GENERAL
THE THEORY OF IMPACT STRENGTH, GENERAL DISCUSSION OF TRANSITIONS AND SOME PRELIMINARY EXPERIMENTAL RESULTS

Authors: J. A. Faucher
G. D. Jacobs

Date: December 3, 1963

Project No.: 161E17

File No.: 1730

SUMMARY The main objective of the inorganic polymers project is to find a way to confer impact strength or toughness on cheap, rigid inorganic materials which are polymeric in nature, such as cement, asbestos board, etc. Experience with the familiar organic polymers indicates that impact strength correlates well with the presence of low temperature "transitions" of a particular kind and which are easily detected by mechanical loss measurements. A similar correlation is being sought for inorganic materials. The various types of transitions known are discussed briefly; a method has been found to detect and measure some of these transitions by the convenient mechanical loss method. The possibility of incorporating tough organic polymers into inorganic materials is discussed and some experimental details are given.

INTRODUCTION

In June of this year a project on inorganic polymers was initiated with the stated objective of "imparting toughness to cheap inorganic materials which are rigid but brittle". Since this area is an unfamiliar one to most of the people in the department it was felt that a general orientation report would be useful to outline the thinking leading to the project, to give a survey of preliminary experimental results and to indicate possible directions for work in the near future.

General Considerations of Impact Strength in Organic Polymers:

In looking at the mechanical properties of conventional amorphous polymers one finds that they fall largely in two groups: 1) those which are very rigid but brittle (polystyrene, polymethacrylate) and 2) those which are very shock resistant but soft (rubber, polyisobutylene). The advent of the polycarbonate type polymers in the late 1950's brought an exceedingly interesting new class of polymers: materials which are both rigid and tough. This combination of properties had only been available before by additional processing, e.g. adding butadiene rubber to styrene to make "impact styrene" or further cross-linking of rubber to raise its stiffness. In either of these cases the combination of properties is nowhere near as outstanding as it is in the polycarbonates.

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Chemicals Division
Union Carbide Corporation

From the point of view of structure-property relations it immediately became of great interest to attempt to find the structural features, if any, which accounted for impact strength. A good indication was soon found by mechanical loss studies in the presence of characteristic low temperature transitions, or loss peaks. For details of the mechanical loss method and elementary interpretation see the Appendix. Our first report on this was in June, 1959.(1) Subsequent reports(2) of 1960 and 1961 dealt with polysulfonates, polyhydroxyethers, and poly(vinyl chloride).

The initial correlation was striking: polystyrene and poly(methyl methacrylate) (brittle) have no low temperature loss peaks; polycarbonate (tough) has a secondary transition at -100°C to -90, see Fig. 1. Furthermore, one can see in these terms why adding rubber to styrene helps the impact properties, since rubber has a low temperature peak at about -60°C. As a sort of naive working model one can look upon these low temperature peaks as "energy sinks". They determine the temperature region above which various small chemical groups of the polymer molecule can rotate or "wiggle" in some fashion. Consequently above such temperatures there is a built-in mechanism of energy dissipation. When a polymer has no such mechanism (polystyrene) then a sudden imput of energy leads to brittle fracture.

Such in brief are the working hypotheses built up over the past few years. To our knowledge the above explicit formulation is not to be found in the polymer literature as yet, although there are occasional references to the importance of low temperature loss peaks. Within the Corporation this type of correlation has been more thoroughly pursued at the Plastics Division laboratories. G. E. Ingraham in 1962(3) has listed a large number of polymers having low temperature peaks and measured their room temperature impact strength.

Despite the appealing simplicity of this correlation, it has become increasingly evident to us that the full story is quite complex. Thus, for example, there are polymers, such as poly(vinyl chloride), which have a low temperature peak and yet are not particularly impact resistant. As Ingraham(3) has indicated some of these polymers are strongly rate dependent - that is they are brittle at high rates of loading and tough at low rates. Also, with the advent of very low temperature measurements loss peaks have been found in polystyrene at about 40°K(4) and in PMMA at 4°K.(5) Since these peaks are apparently ineffective in impact behavior it is plausible that the temperature position of the peak must be of some importance.

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Furthermore, it seems clear that the type of transition involved must have a strong influence on the mechanical properties. There are, for instance, loss peaks due to crystal-crystal phase transformations. An example is the transition in Teflon at room temperature. It is probable that these transitions are of much less importance (if any at all) than the transitions we have mentioned.

Finally, the position of the chemical group involved must be important. A methylene chain always gives a characteristic peak at -125°, but it is far more effective in impact as part of the polymer main chain than as a side group.

Impact Strength in Inorganic Materials:

There is, of course, no reason why these considerations should necessarily apply to inorganic materials. For one thing the "polymeric" nature of inorganic compounds is usually quite different from the common organic polymers, involving such things as ionic bonds and sheet and layer structures. Nevertheless, it is instructive to see if the analogy can be made. For example, we have measured the mechanical loss of corundum (a very hard form of aluminum oxide) - see Fig. 2. There is a total absence of loss peaks of any kind; in fact the line shown probably represents more the "background loss" of the torsion pendulum than the material itself. At least in a negative way this correlates with the brittle behavior of this compound. It is more important, however, to make a positive correlation, that is, to find a low temperature peak in a material which is impact resistant. But so far, at least, (excepting metals) we are not aware of any really "tough" inorganic substances.

Transitions in Inorganic and Organic Compounds:

If we expand our viewpoint beyond polymeric compounds, it is a natural step here to consider generally all the various types of transitions which occur in known compounds. As examples we may cite 1) first order phase transitions, such as solid-liquid and solid-solid between different crystal forms, 2) rotational or lambda transitions, characteristic of spherical molecules which undergo free rotation in the crystal and 3) ferromagnetic transitions, which involve cooperation movement of dipoles or magnetic moments.

Traditionally in this field workers have used experimental methods such as X-ray diffraction, specific volume, and dielectric loss. It occurred to us that the mechanical loss technique might be able to shed some new light on these transitions, particularly in view of the fact that the time of measurement can be readily varied and hence, transitions with characteristic relaxation times can be noted. (For a general review of thermal transitions in solids see Ref. 6).

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Experimental Details: Measurement of Transitions by Mechanical Loss

Our first investigation was the well-known rotational transition in ammonium chloride crystals at -30°C. The first problem we had was in trying to get the sample in suitable form for the torsion pendulum apparatus. For plastics one typically uses a thin strip about 1 inch long, 1/4 inch wide and 20 to 50 mils thick. It is possible to press out a sample of pure ammonium chloride in this shape, but it is so brittle that it breaks apart as soon (or before) it is mounted in the torsion pendulum. One way out of this dilemma might be to grow a big single crystal and cut it to the right size, but as a general technique for all types of compounds this would be prohibitively difficult. We therefore decided to work on embedding the salt in a suitable matrix, hoping that the transition could then be detected. Two such attempts are shown in Fig. 3, where loss is plotted on a logarithmic scale to magnify the effect. In one the salt was mixed with powdered poly-acrylic acid and then molded. In the other a cellulose blotter strip was dipped into a concentrated salt solution and then dried. There appears to be a definite small peak at about -30 in both cases, which is not present in the pure matrix material. However, the loss is so small that this technique can not be called very successful.

After some further experimental work we hit upon a matrix which was much better - namely Dow Corning's encapsulating resin which has the trade name of "Sylgard". This material is a silicone which is cured at room temperature and becomes a transparent rubber. It has a main glass transition of about -100°C and a secondary peak at about -50°. (See loss curve in Fig. 4). With ammonium chloride mixed in (before curing) the system shows a large loss peak at about -30 to -35 which must be attributed to the salt (Fig. 5). A consideration of the physical properties of the encapsulating resin explains what our experimental problem was. The torsion pendulum measures largely the most rigid component in a matrix. In the case of poly(acrylic acid), the matrix itself was too rigid. At -30° the Sylgard is a soft flexible rubber and contributes very little resistance; hence, the loss due to the salt is easily detected.

It is not yet known whether all of the types of transitions listed above can be detected in this way. One might well have doubts about measuring a ferromagnetic transition by purely mechanical means; nevertheless, we plan to try some experiments in this direction. It is clear, however, that mechanical loss can be used for rotational transitions. In addition to NH_4Cl we have done NH_4Br, camphor and benzophenone, and in each case have succeeded in detecting the rotational transition.

Impact Modification of Inorganic Materials: Asbestos Board

Although this work on transitions is of great interest in itself as a sort of new direction in the field of thermal transformations, nevertheless continual study of this kind clearly will not fulfull the main objective of the project. We were first drawn to the problems of inorganic polymers by discussions with Mr. H. Reichard of the Nuclear Division. His group has been working for sometime on making rigid board and pipe from asbestos. The first product, called P-38, is an asbestos board made by mixing phosphoric acid with fine asbestos. The acid reacts with the free hydroxyls of the mineral and on vigorous mixing produces a polymeric paste which after extruding is cured at 150°C to give a rigid, but rather brittle material that can be used for construction. (The loss curve of this substance is shown in Fig. 6 - note again the absence of low temperature peaks). The relatively mild chemical and thermal conditions employed here gave us hope that an organic polymer might be somehow added to this process and become incorporated in the material. If so, one ought to be able to markedly improve the brittle character of the board. The most logical polymer additives are, of course, those which are themselves very tough.

So far our experimental results have been quite limited, due in part to lack of equipment. Recently we have obtained a mechanical mixer to make up the paste, but, lacking an extruder, we are unable to suitably press out the asbestos paste, and our finished board is thus somewhat inferior to that made at the Nuclear Division. However, we expect that an extruder and suitable die-head will be available to us shortly, so this situation should be soon remedied. We have tried adding both a polyhydroxether and a polycarbonate to the asbestos paste, but in neither case was any change in properties observed. It is possible that these are not the right materials to add or, more likely, that they are not being successfully incorporated in the inorganic structure. There are a number of directions to take: use of latexes, polymers with more active functional groups, or even the possible use of inorganic substances to mention a few. In succeeding months we plan to pursue these avenues intensively in an attempt to demonstrate that inorganic materials can, in fact, be impact modified.

Acknowledgement

Those familiar with any aspects of this project will readily recognize that the basic ideas here on impact strength stem largely from Dr. F. P. Reding and the work of his Physical Studies group several years ago. It was also his interest and incentive which first drew our attention to the asbestos derivatives of the Nuclear Division.

Dr. C. N. Merriam and Mr. G. Ingraham of the Plastics Division have helped notably in filling out the experimental correlation between low temperature loss and impact strength.

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5. K. M. Sinnott, J. Polymer Sci. 35, 273 (1959).

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J. A. Faucher

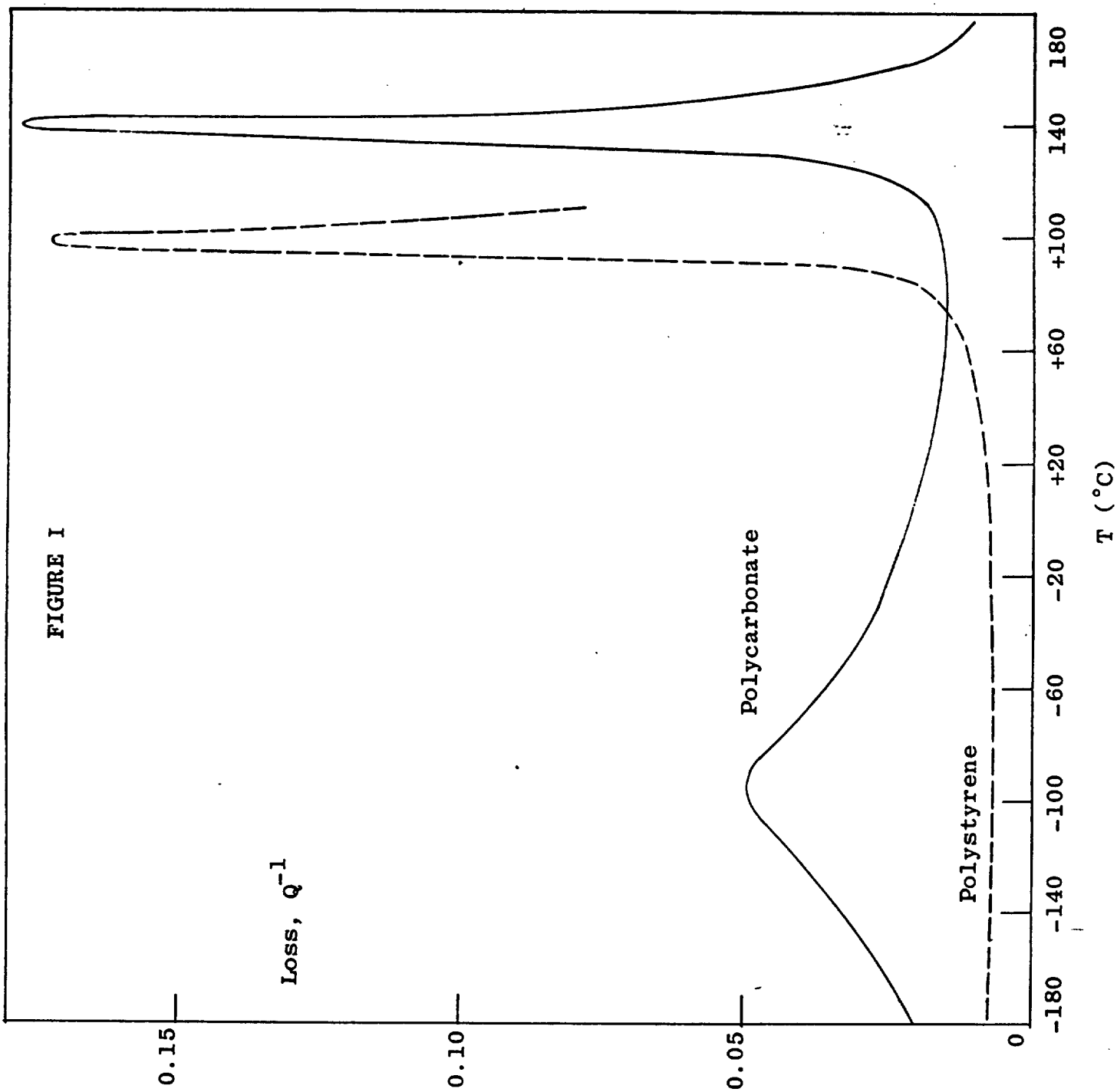
ATTACHMENTS: Appendix
7 Figures

APPENDIX

MEASUREMENT OF MECHANICAL LOSS WITH THE TORSION PENDULUM

The low frequency recording torsion pendulum operates at a frequency of about 1 cycle per second. The sample to be tested is cut to dimensions of a strip about 1 inch long, 1/4 inch wide and 10 to 50 mils thick. The strip is placed in the jaws and a suspended moment of inertia wheel set in motion. The sample then damps out the free vibrations of the inertia wheel. From the damping the mechanical loss, Q^{-1}, can be calculated as shown in Fig. 7. The apparatus is run at different temperatures and the loss plotted vs. temperature. When transitions occur (of any kind) one typically gets a peak or maximum in the loss curve.

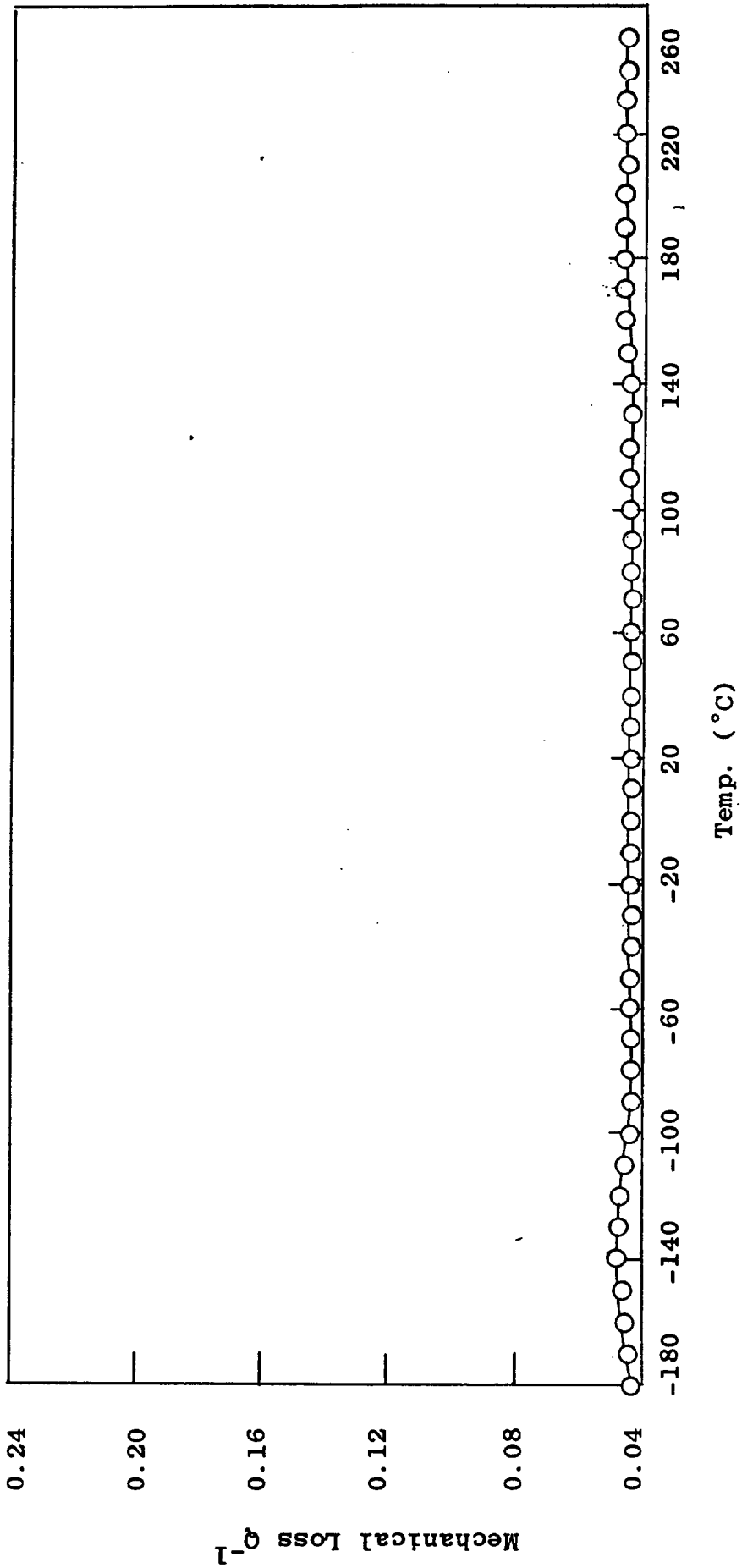
From this apparatus one can also measure the real and imaginary parts of the complex modulus (G' and G"). To calculate these quantities one must know the sample dimensions and frequency of vibration. Loss measurements, however, are relatively independent of these parameters and hence particularly simple to make.



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FIGURE II

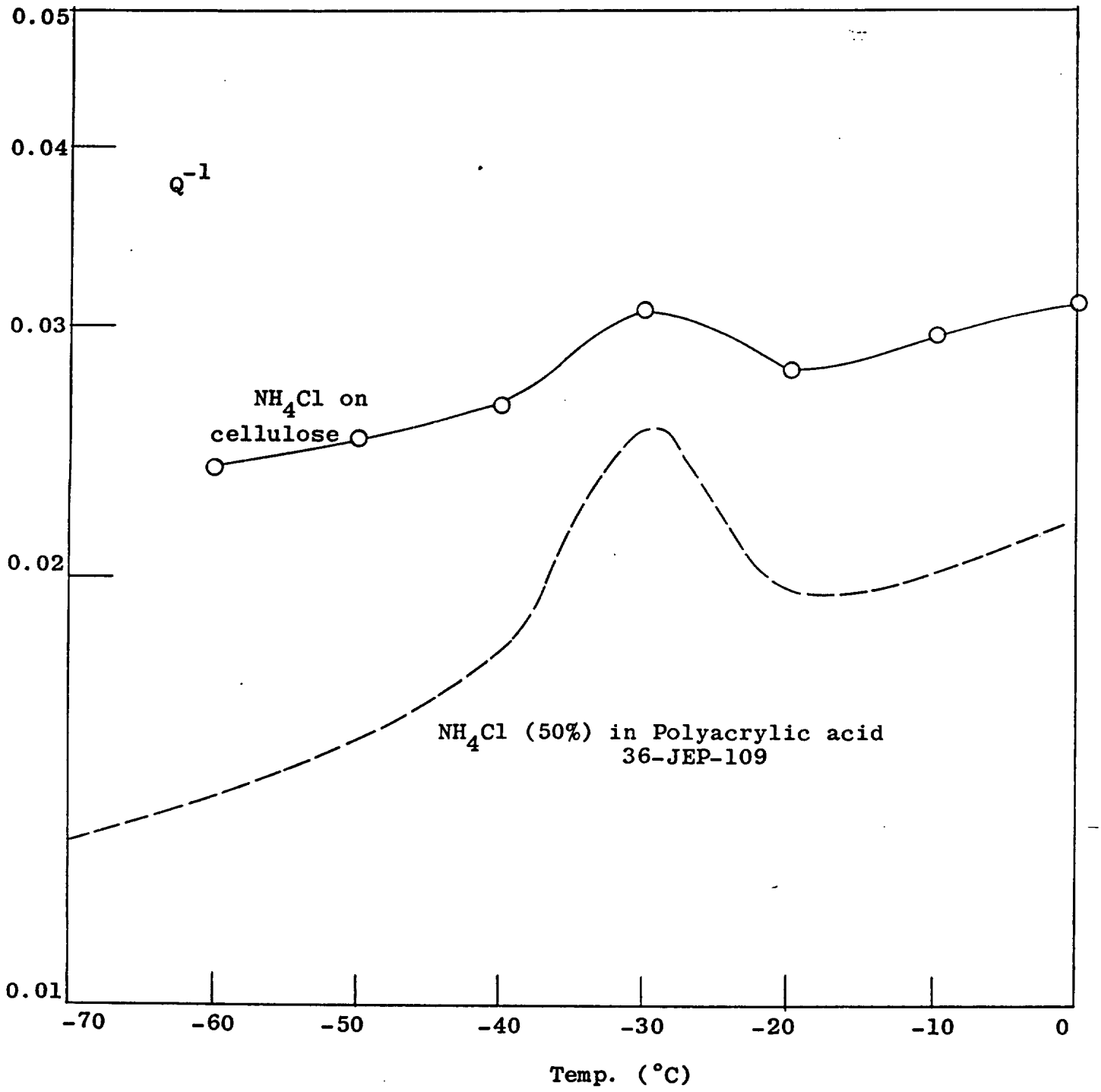
SAXONBURG ALUMINA S-696 39JEP-14



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FIGURE III

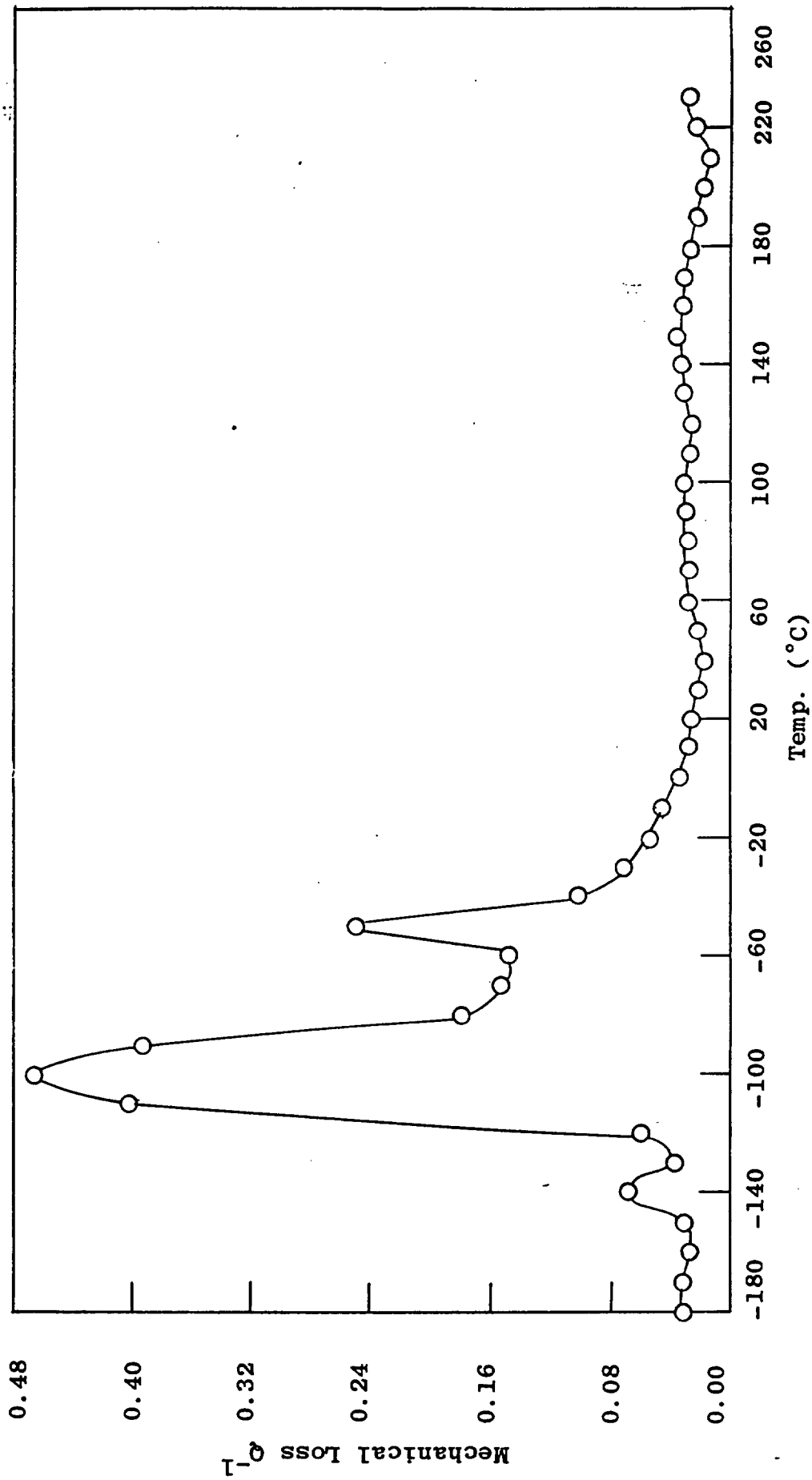
AMMONIUM CHLORIDE LOSS PEAKS



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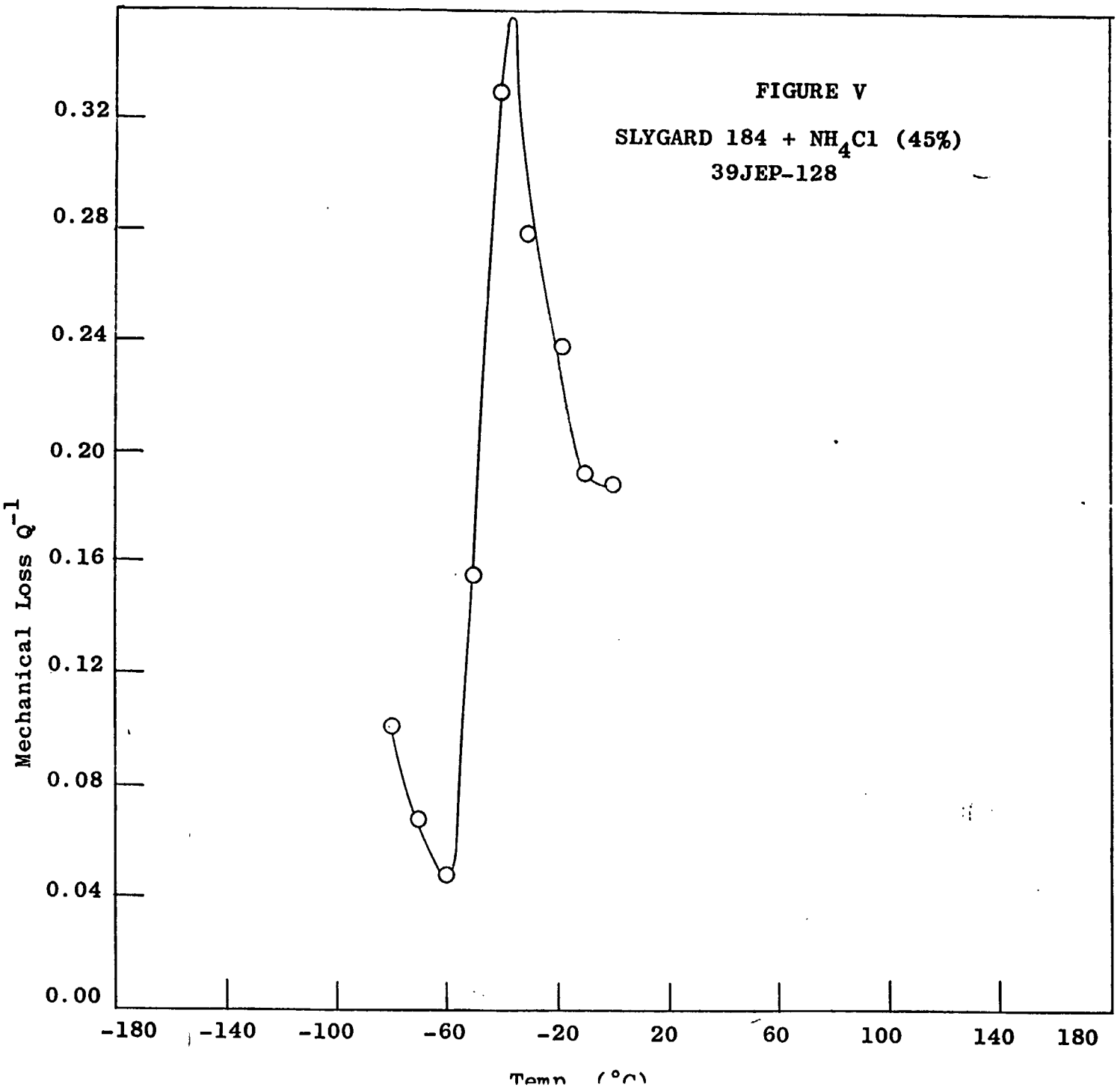
FIGURE IV

SLYGARD 184 39JEP-117



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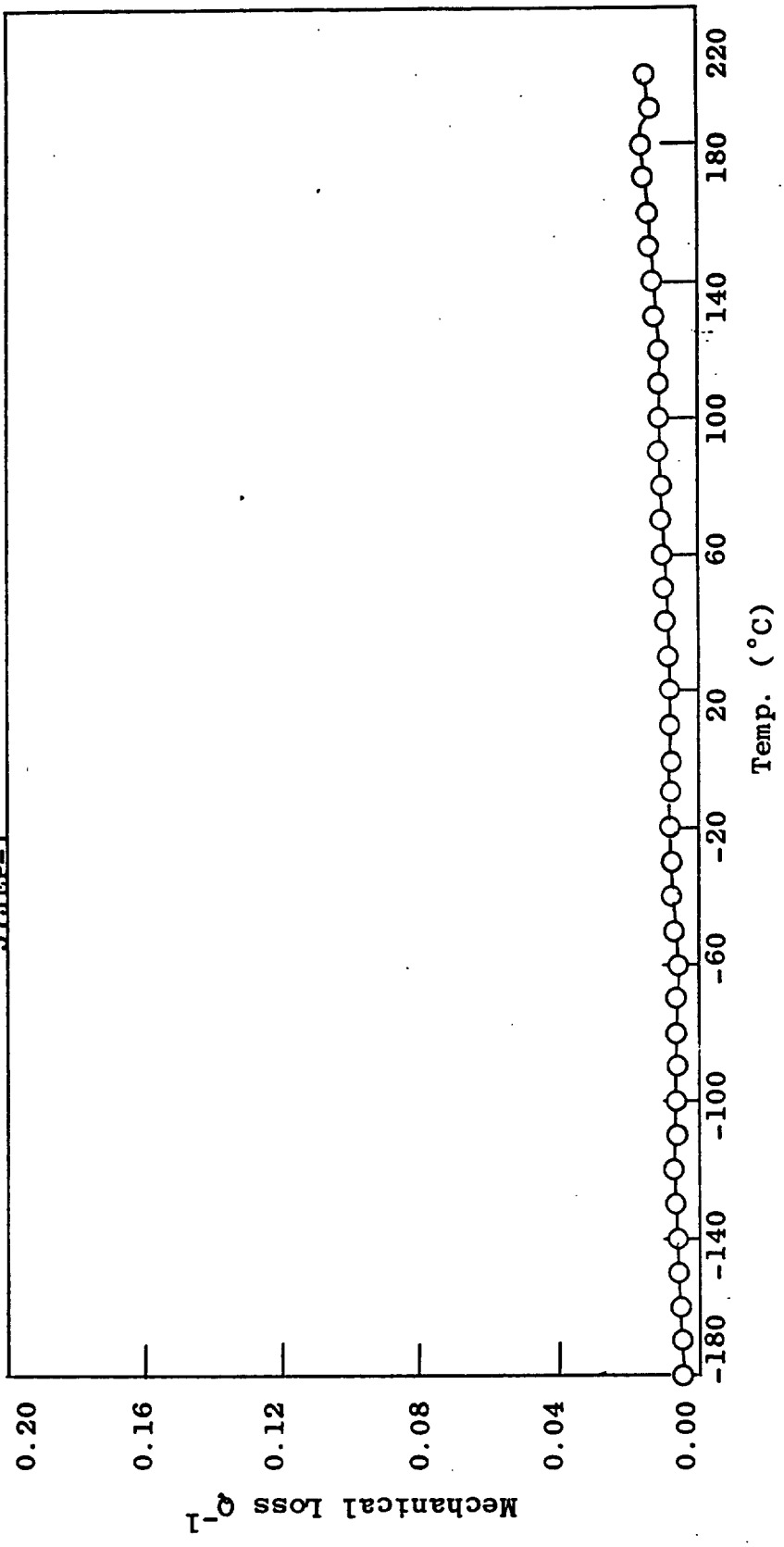


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FIGURE VI

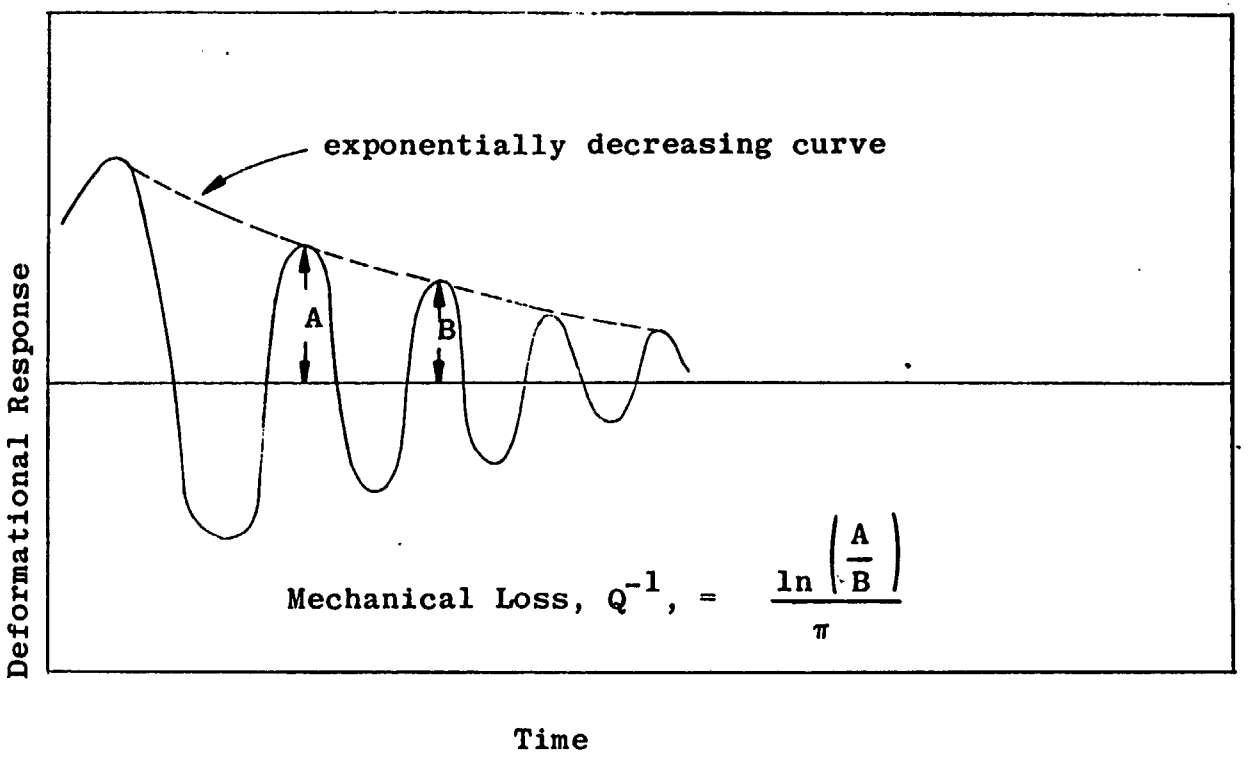
ASBESTOS BOARD

(NUCLEAR COMPANY DESIGNATION P-38)
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FIGURE VII



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STATUS REPORT

NEW ENTERPRISES
CHEMICAL REACTIONS OF ASBESTOS

Authors: C. W. McGary
G. W. Rausch

Date: November 2, 1964

Project No.: 162D21

File No.: 3180

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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Chemicals Division
Union Carbide Corporation

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.)

CMS Coalinga Chrysotile

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

Reference: 3GWR130 July 27, 1964

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(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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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		
									25	14.1		
3GWR96-2						2			1	20.5		
									15	16.4		
									18	15.5		
									25	14.6		
3GWR96-3						3			1	20.6		
									7	18.0		
									11	16.3		
									15	16.2		
									18	15.1		
									25	13.7		
3GWR96-4						6			3	22.2		
									14	20.0		
									17	18.2		
									24	17.0		
3GWR96-5						10			3	22.8		
									10	20.1		
									14	19.0		
									17	19.0		
3GWR96-6						16			1	28.3		
									2	27.5		
									6	24.6		
									10	23.8		
									13	24.0		
									21	21.4		
3GWR96-7						24			1	29.2		
									2	28.3		
									6	25.8		
									10	24.9		
									13	24.9		
									21	24.0	50	
3GWR104-1	107	268.5	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						18			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	12.6		
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	8525	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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INORGANIC POLYMERS:

IMPACT MODIFICATION OF ASBESTOS-

PHOSPHORIC ACID COMPOSITION BOARD

Authors: G. D. Jacobs
J. A. Faucher

Date: July 6, 1964

Project No.: 191G31

File No.: 2777

SUMMARY: The work on this project has been concerned mainly with the inorganic mineral chrysotile, a form of asbestos currently being mined by the Nuclear Division at Coalinga, California. Attempts have been made to impact modify an asbestos-phosphoric acid-water composition board (code designation P-38) originally produced by the Nuclear Division. Previous experience here had shown that impact strength correlated well with low temperature "transitions" in the mechanical loss spectrum of organic polymers, and it was felt that the incorporation of one of these organic polymers in the asbestos board might lead to the desired product. To date, however, the addition of a rather large number of organic polymers in various percentages has not improved the strength of the board to any great extent. It is now felt that some material will be necessary that is capable of chemically reacting with the hydroxyls of either the asbestos or the phosphoric acid. Very little is known about the chemical reaction between the asbestos and phosphoric acid. In fact, the physical characteristics of the asbestos fibers are still open to controversy and a great deal of basic research is currently being carried out on this material. A brief sampling of some of this work is given in this report.

Present work on this project to modify the P-38 composition is concerned with the possibility of adding fibrous organic polymers to the mixture. This phase of the work is a direct result of the work carried out by the U.S. Army on the addition of nylon fibers to cement in which they were able to improve the impact strength of cement by a factor of twenty-seven. Preliminary work with asbestos shows an increase in impact strength, although not nearly as large as in the case of cement. Projected work includes the use of polycarbonate and polyhydroxyether fibers as additives.

INTRODUCTION: Asbestos is the generic name given to a number of mineral silicates varying quite widely in chemical composition. These silicates are divided into two mineral classes; serpentine and amphibole. A list of the more common types is presented in Table I along with their chemical formulae.

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By far the most important single type of asbestos is chrysotile, accounting for nearly 90% of world production. Certain ones of the amphibole group, noteably crocidolite (blue asbestos), amosite, and anthophylite, do find use in specialized plastics applications[1,2].

The major portion of this report is concerned with a chrysotile variety being mined by the Nuclear Division at Coalinga, California. Table II is a comparison of the physical properties of a general chrysotile asbestos with the high-purity grade UCC Coalinga fiber.* The unique properties of the Coalinga fiber are attributed to its greater specific surface area and adsorption properties as shown in the table.

Chemically, chrysotile has been described as a hydrated basic silicate of magnesia. Normally, some magnesium carbonate and hydroxide are associated with the fibers in the form of dolomite and brucite. Table III gives the chemical and mineralogical compositions of a general chrysotile fiber as compared to the Coalinga fiber.

Until a few years ago the formula for chrysotile was written as $3MgO \cdot 2SiO_2 \cdot 2H_2O$, implying a di-hydrate. As a result of recent research efforts[3,4], it is now felt that a better representation of the "molecule" is given by the formula $Mg_3Si_2O_5(OH)_4$, where the previous water molecules are now present in the form of hydroxyl groups. The individual fibers are pictured as layers of silicon-oxygen tetrahedra ($Si_4O_{10}^{-4}$) condensed onto magnesium hydroxide layers. Each of the silicon-oxygen/magnesium hydroxide layers is superimposed upon layers of similar composition, but no chemical bonding is thought to occur between the layers. A schematic drawing of a portion of the curved wall layer of a chrysotile fiber is shown in Figure 1[5]. Another view is shown as Figure 2.

A controversy has also arisen over the physical structure of the individual fibrils. Pictures taken with the electron microscope seem to indicate that the fibers are in the form of "hollow tubes"[6]. Recent evidence from X-ray diffraction measurements[5] and density determinations[7] has thrown doubt on this theory and the present proposed picture is that the central portion of the tubes is filled with amorphous or partially oriented material. As pointed out by Dr. E. J. W. Whittaker this filling of the tubes with amorphous material would lead to an appearance of emptiness under the electron microscope due to the contrasting effect between the walls of the fiber and the filling material. A recent study using ultrasonics[8] also provides evidence that the material filling the voids between fibers is amorphous.

Chemical reactions of chrysotile are also now being investigated. X-ray methods serve as the principal tool for studying these hydrothermal reactions, which are found to be predominantly topotactic. Being topotactic implies that the normal reaction involves the migration of cations, including silicon, while having little effect upon the oxygen framework[9,10].

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* Three product grades of asbestos are currently available from the Nuclear Division: Standard Grade, High Purity Grade, and Colloid

The preceding paragraphs should serve as a general introduction to the nature of the mineral asbestos and give some idea of the research being done on this material. Further specific information may be found in the references cited as well as in the four books listed in the bibliography.

Due primarily to the large supply available and to the unique characteristics of Coalinga fiber, the Nuclear Division initiated work on finding saleable products which utilized their asbestos. One of the materials produced was an asbestos-phosphoric acid-water composition board (code designation P-38),[11]. This material suffered, however, from a lack of impact strength as well as poor weatherability. The Nuclear Division also developed an asbestos-phenolic composition (code designation F-100) which showed both improved strength and weatherability[12]. Efforts at Tuxedo have since been directed primarily at improving and marketing the F-100 composition in the form of pipe.

Since previous experience was available on impact strength of organic polymers, as evidenced by studies on the low temperature loss peaks in the mechanical loss spectrum, it was decided to look again at the P-38 compositon with the thought of adding an impact modifying filler to the composition.

Experimental

The Coalinga asbestos used throughout these investigations was the high-purity grade - i.e. the material has been defilibrated and the magnetite removed. Early experiments were concerned with finding the best ratio of asbestos-phosphoric acid-water for easy mixing and extrusion. After several trials using various ratios,it was found that the following proportions were most satisfactory:

70 parts asbestos
35 parts water
30 parts 85% phosphoric acid

The dry, powdery asbestos is loaded into a Cincinnati Mix-Muller* and the phosphoric acid-water solution added through a funnel provided with the mix-muller. The time taken for addition of the phosphoric acid-water solution is rather critical in that water is apparently lost from the mixture for both short times of addition (causes heating of the mix) and also by evaporation if excessive time is involved. We have found, in agreement with the Nuclear Division, that a fifteen-twenty minute period for addition of ingredients is best. Additional ingredients were normally added after the phosphoric acid-water solution and in certain cases (liquid fillers) a proportionately smaller amount of water was necessary in order to acquire an extrudable product. The final product, ready for extrusion, is of a putty-like consistency.

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*Cincinnati Muller Co., Cincinnati, Ohio; Previous experiments had shown that a Hobart blender did not give adequate mixing on this scale (2 lbs asbestos).

The first experiments (before acquisition of an extruder) with the P-38 composition consisted of pressing the material into disc-shapes at 10,000 psi. Tests on these discs showed, however, that in order to obtain material with any strength whatever it would be necessary to extrude the composition. Previous work by the Nuclear Division (see reference 11) had shown that a ram-type extruder was best suited for the P-38 composition.

The ram extruder now in use was designed by Mr. Gene LeRoy of the Research and Development Department Special Projects Division, Machine Design. An Ener Pac* hydraulic, power-operated, pump and cylinder are incorporated in the design. The exit die is of a rectangular shape with dimensions 3" x $^1/_4$".

The P-38 composition is loaded into the extruder and then the ram moved forward to seal-off the chamber. The chamber is evacuated for several minutes before the extrusion is started. Starting with two pounds of asbestos, an extruded "board" approximately four feet in length is obtained (3" in width, $^1/_4$" in thickness). Normal extrusion pressure is 2000-3000 psi.

The "board" is cut into six and twelve inch lengths. The six inch lengths are rolled out (transverse to direction of extrusion) into pieces $^1/_8$" in thickness, using several passes through a large roll mill. All the pieces are then subjected to a room temperature cure followed by a cure at either 110°C or 150°C depending on the type of filler used. It is necessary during the cure-cycle to sandwich the asbestos strips between expanded-metal sheets in order to prevent warping.

After curing, the boards are removed from between the metal sheets and cut into small pieces for testing. The $^1/_8$" thick samples are given flexural strength and flexural modulus tests (ASTM D790-61) while the $^1/_4$" specimans are subjected to the Izod impact test (ASTM D256-56). The Gardner impact test proved unsatisfactory for testing these specimans. All samples are tested in both the parallel and transverse directions (designated P and T respectively in the tables).

DISCUSSION: The first experiments with the P-38 blend were concerned with finding the best ratio of ingredients and optimum mixing time, as pointed out in the experimental section of this report. A short study was also conducted to determine the function of room temperature curing time on the strength of the final board. Previous studies by the Nuclear Division had shown that both a room temperature cure and a final curing at an elevated temperature were necessary for a high-strength board. The results of our room temperature cure-time study are given in Table IV and shown plotted in Figure 3. From these results, it was concluded that a room temperature cure of at least sixteen hours was required. The three points shown plotted for a sixteen hour cure were taken as an indication of the deviation which can be expected from one batch to the next. Several runs were also made using different curing temperatures as well as different amounts of time at this elevated temperature but

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* Blackhawk Industrial Products Co., Butler, Wisconsin.

all seemed to indicate that 16+ hours at room temperature followed by 4 hours at 150°C gave the best results.

The next step in the project was to investigate the effect which various additives would have on the strength of the P-38 composition. The rest of the discussion section will be sub-divided into sections dealing with the various additives thus far investigated.

DQDA 3269 (72/28 ethylene/vinyl acetate copolymer)

An informal report by Dr. G. H. Potter (Project No. 399M20; dated 16 December, 1963) reported the possibility of cross-linking or reaction of some type between asbestos and ester-containing polymers, after mixing on a hot roll-mill. Unfortunately this method coats the asbestos fibers so that they are no longer available for attack by the phosphoric acid-water solution used in the P-38 composition. Even prolonged extraction with toluene did not remove enough of the excess polymer so that the fibers could undergo further chemical reaction. An attempt was also made by first reacting approximately one-half of the phosphoric acid-water solution with the asbestos and then placing the material on the mill with DQDA. However, the DQDA would not react in this case and was present in the extruded board as an inert filler. Adding pulverized DQDA to the mixture in the mix-muller was also unsuccessful.

One further step was taken with this type polymer. Granulated AYAT was added to the dry asbestos in the mix-muller followed by the phosphoric acid-water solution. The AYAT appeared to be present as an inert filler also.

Hercules "Aquapel" (364 and 380)

The next material tried was "Aquapel", an alkylketene dimer manufactured by Hercules Powder Company. The dimer was added both in the form of dry flakes and as an emulsion in water. As can be seen from Table V, no significant increase in the strength of the P-38 composition was obtained.

Cationic Wet-Strength Resin

A cationic wet-strength resin consisting of poly β-asparagine polyamine partially crosslinked with epichlorohydrin (14.2 % total solids) was obtained from Dr. P. M. Westfall and added to the standard P-38 mixture. The material before curing is very difficult to break apart but as shown in Table V, after curing it shows no great improvement in strength or impact.

Gantrez AN-139 Copolymer

As a result of reading U. S. Patent 3,113,064 entitled, "Asbestos paper containing vinyl alkyl ether-maleic anhydride copolymer and method of forming same", we decided to try adding one of these copolymers to the P-38 mixture. The one chosen was Gantrez AN-139, a copolymer of methyl vinyl ether and maleic anhydride manufactured by General Aniline and Film Corporation (gaf). The copolymer was

added both in the dry state and in the form of a water dispersion. There was some improvement in the strength of the cured P-38 board but not a significant amount. (see Table V).

Polyox - Carbopol 940

Carbopol 940 is a water-soluble, high molecular weight poly (acrylic acid) manufactured by the B. F. Goodrich Chemical Company. The Polyox and Carbopol were added to the asbestos in the mix-muller both in the dry state and as a mixture in water. A combination of Polyox and Carbopol was also tried but did not give any great improvement in strength as seen in Table V.

Latexes

Since the best way to obtain good dispersion of the filler material and at the same time enhance the possibility for any reaction between the filler and the asbestos is to add the filler as a water solution, the use of latexes becomes a logical possibility.

After a few batches were prepared, it became apparent that a new study of strength as a function of curing time and temperature was needed. A series of mixtures were prepared using as a filler 10.4% of a 60/40 styrene/butadiene latex containing 48% total solids. The variables included room temperature cure times of from 0 to 36 hours and high temperature cures (110°C) of 4,8,16, and 32 hours. The results are tabulated in Table VI and shown plotted in Figure 4. As a result of this study, the remainder of the runs using latex fillers involved room temperature cure times of 30+ hours followed by 24 hours at 110°C.

As can be seen from Table VII, various types and percentages of latexes were studied, including styrene/butadiene, polyethylene/acrylic acid, phenoxy A, and a carboxylic modified butadiene/acrylonitrile copolymer (a product of the Chemical Division of The Goodyear Tire and Rubber Company, known commercially as Chemigum Latex 550). Again, however, no really outstanding improvement in strength was obtained for any of the latexes used as fillers.

Di-(2-ethylhexyl) phosphoric acid

In place of a portion of the phosphoric acid used in the P-38 composition, di-(2-ethylhexyl) phosphoric acid was substituted. It was hoped that some cross-linking could be promoted by using this material but in all the mixes prepared, the cured board was extremely weak. The use of superphosphoric acid was also investigated but it proved unsuccessful. No testing of these samples was attempted.

Fibrous fillers

The use of fibrous fillers has proved to be the best choice to date. As shown in Table VIII, crocidolite (Cape blue asbestos), glass, and nylon fibers have been tested and they all seem to increase impact strength, especially the nylon. The work on nylon stems from

a report by the U. S. Army[13] on the addition of nylon fibers to cement. The impact strength of cement is reported to be increased by a factor of twenty-seven.

Further work is being planned along these same lines using as fillers, nylon (different denier), polycarbonate, and polyhydroxy-ether fibers.

F-100 Composition

For comparison purposes, a batch of the F-100 composition was prepared and tested. The ingredients were as follows: 60 parts asbestos, 15 parts water, and 25 parts BRL 1100 (water soluble phenolic predominating in dimerized trimethylol phenol with some residual monomer; 64-68% solids content). The test results are listed in Table VIII.

Gerald D. Jordan

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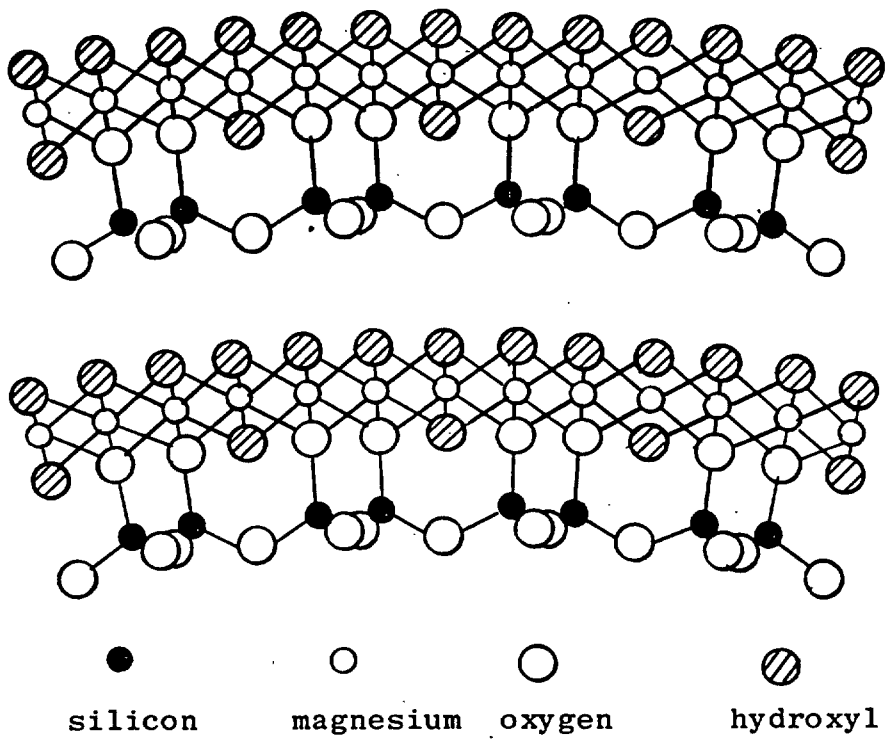
(1) Asbestos, From Rock to Fabric, The Textile Institute, Manchester, 1956.

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(4) Asbestos Fundamentals, H. Berger, Chemical Publishing Co.

Figure 1*

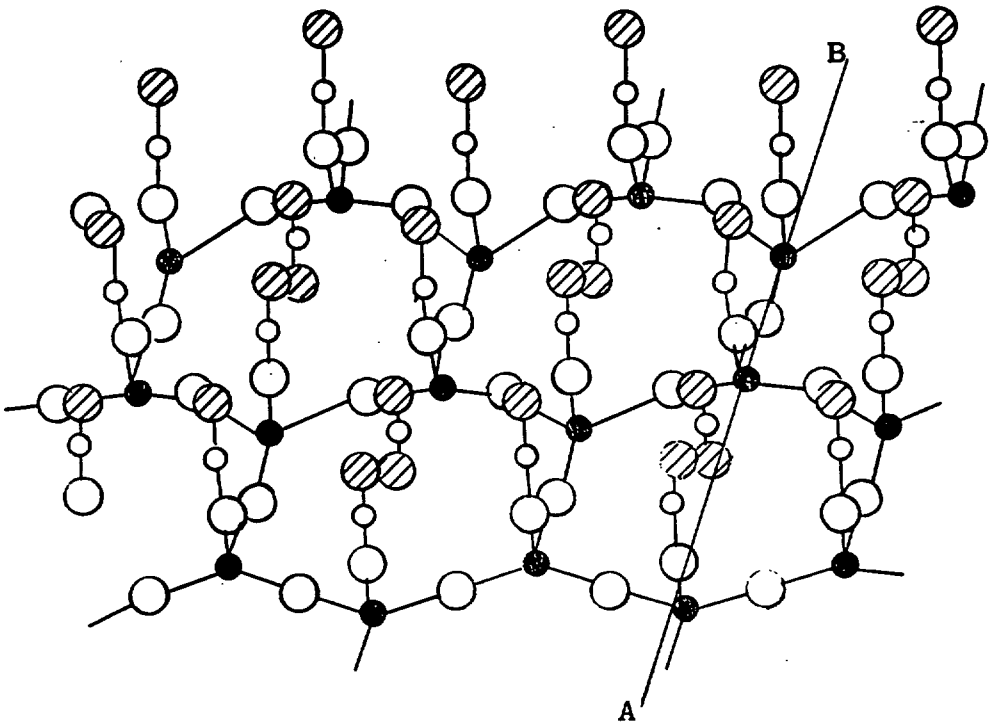


* Chem. and Eng. News. p. 35, 30 Sept. 1963

This drawing represents a portion of the curved wall layer of a fiber of chrysotile asbestos. The fiber walls are composed of 12 to 20 such layers; each layer being about 7.3 Å thick.

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Figure 2



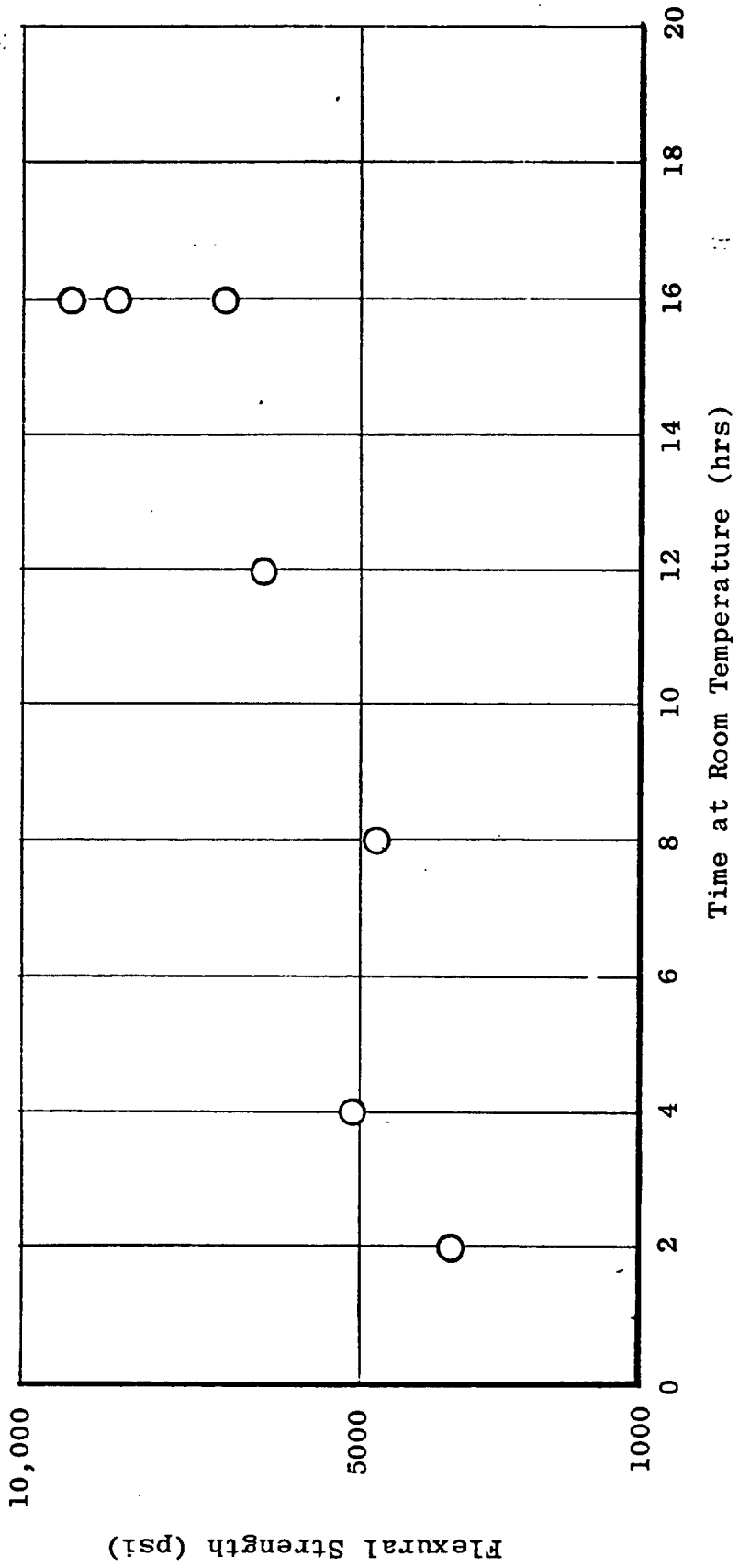
- silicon
- magnesium
- oxygen
- hydroxyl

The line $\overline{AB}$ parallels one of the layers shown in Figure 1.

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Figure 3

Strength as a Function of Curing Time

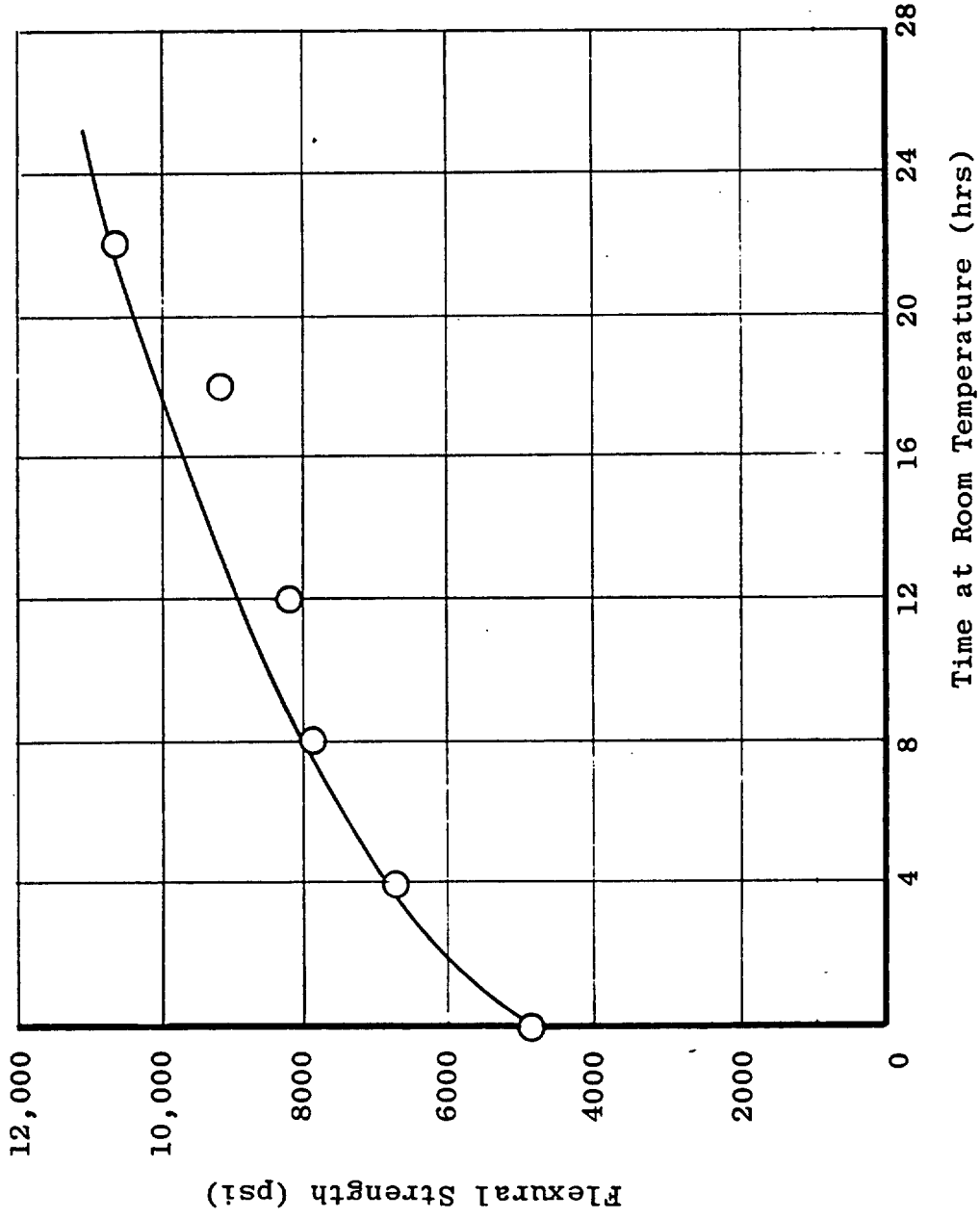


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Figure 4

Flexural Strength vs Time at Room Temperature

(all samples received later cure of 16 hrs at 110°C)



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TABLE I

Classification	Common Name	Formula
Serpentine	Chrysotile*	$Mg_3Si_2O_5(OH)_4$
Amphibole**	Crocidolite	$Na_2Fe_5Si_8O_{22}(OH)_2$
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	Actinolite	$Ca(MgFe)_5Si_8O_{22}(OH)_2$
	Anthophyllite	$(MgFe)_7Si_8O_{22}(OH)_2$
	Amosite	$(MgFe)_6Si_8O_{22}(OH)_2$

---

* chrysotile exists in at least three modifications depending upon the form of the crystal lattice. The following four papers are recommended for the interested reader.

1. E. J. W. Whittaker, Acta Cryst. 6, 747 (1953)
2. E. J. W. Whittaker, Acta Cryst. 9, 855 (1956)
3. E. J. W. Whittaker, Acta Cryst. 9, 862 (1956)
4. E. J. W. Whittaker, Acta Cryst. 9, 865 (1956)

** for more information on the crystal chemistry of amphiboles see:

5. E. J. W. Whittaker, Acta Cryst. 13, 291 (1960)

TABLE II*

Property	General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
Density, g/cc	2.25-2.75	
Hardness	2.5-4.0	
Specific Surface m^2/g	10-50	60-70
Oil Adsorption g/10g	4-5	14-16
Water Retention g/20g	32-34	
Bulk Density		
Wet cc/5g		175+
Dry lb/ft^3	10-15	3-5
Refractive Index	1.50-1.55	
Luster	silky	
Color	green-gray	white
Brightness (% of MgO)		75-80
Electrical Charge	positive	
Acid Resistance	poor	
Alkali Resistance	good	
Specific Heat BTU/lb-°F	0.266	
Tensile Strength lb/in^2	80,000-100,000	
Temp. of Max. Loss	800°C	
Temp. of Struct. Loss	600°C	

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* Table taken from letter of W. H. Dresher, Nuclear Division

TABLE III*

CHEMICAL COMPOSITION

Compound		General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
MgO		36-44%	42
SiO_2		35-44	42
Fe_3O_4		0.5-5.0	<1.0
Fe_2O_3		0-6.0	--
FeO		0-6.0	0.3-1.6
H_2O	Total	12-15	16.0
	Combined	--	13.5

MINERALOGICAL COMPOSITION

Mineral	General Chrysotile Asbestos	UCC Coalinga Asbestos (high-purity grade)
chrysotile	major	major
brucite	moderate	minor
magnetite	0.5-5.0%	<1.0%
hydrotalcite	--	minor

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* Table taken from letter of W. H. Dresher, Nuclear Division

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TABLE IV

Study of Strength as a Function of Curing Time

Notebook Reference 5808-	Curing Time (hours)		Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
			P*	T*	P	T	P	T	
	25°C	150°C							
27-1	2	4	3692	3729	1.61	1.34	0.15	0.12	1.36
27-2	4	4	5171	3981	2.57	1.76	0.16	0.31	1.44
28-1	8	4	4808	3919	2.44	2.05	0.14	0.13	1.48
28-2	12	4	6488	4630	2.89	2.39	0.14	0.17	1.63
25-1	16	4	7059	5562	3.46	2.11	0.13	0.14	1.57
25-2	16	4	8662	6250	3.20	2.64	0.16	0.14	1.57
45-2	16	4	9306	8484	2.86	2.49	0.28	0.20	1.53

Ingredients: 70 parts asbestos; 35 parts water; 30 parts phosphoric acid (85%)

*P - parallel direction, T - transverse direction

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TABLE V

P-38 Composition Plus Additives

Notebook Reference 5808-	Additive*	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
38-1	4.7% Aquapel (emulsion)	4431	4280	1.27	1.18	0.17	0.11	1.44
37-1	4.7% Aquapel (dry flakes)	5076	3759	2.36	1.57	0.17	0.14	1.43
41-2	14.4% Cationic wet-strength resin	7680	7563	1.80	1.75	0.16	0.14	1.55
41-1	28.7% Cationic wet-strength resin	7317	7078	1.76	1.73	0.15	0.14	1.55
62-1	0.3% Gantrez AN-139 (dispersion)	8501	5922	2.66	2.08	0.24	0.18	1.60
62-2	1.3% Gantrez AN-139 (dispersion)	8118	9795	2.61	2.58	0.22	0.17	1.57
63-1	1.3% Gantrez AN-139 (dry)	8295	7716	2.66	2.38	0.27	0.22	1.52
34-1	1% Polyox (coagulant grade)	8083	6553	1.89	1.63	0.17	0.19	1.55
69-1	0.3% Carbopol 940	8329	6733	3.09	2.66	0.28	0.19	1.62
69-2	0.6% Carbopol 940	9589	6964	2.94	2.70	0.24	0.19	1.58
70-1	1.3% Carbopol 940	8076	6019	3.01	2.45	0.25	0.18	1.63
72-1	0.3% Carbopol + 0.3% Polyox	5927	3908	2.29	1.83	0.43	0.14	1.51
72-2	0.6% Carbopol + 0.6% Polyox	4525	4652	2.07	1.83	0.29	0.16	1.52

---

* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VI

P-38 Composition Plus Additives

Notebook Reference 5808-	Additive* 10.4% of a 60/40 styrene/butadiene latex; 48% total solids		Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
			P	T	P	T	P	T	
	Curing Times								
	room.temp.	110°C							
48-4	0 hrs.	8 hrs.	4787	4447	2.45	1.83	0.20	0.17	1.44
48-3	0	16	4861	4520	2.21	1.97	0.21	0.15	1.45
47-2	2	8	5671	5123	2.09	2.01	0.22	0.30	1.47
48-2	4	8	6682	6025	2.27	2.14	0.24	0.23	1.49
48-1	4	16	6726	5872	2.57	2.13	0.21	0.24	1.54
49-4	8	8	7303	6948	2.23	2.04	0.23	0.20	1.51
49-3	8	16	7934	6662	2.29	2.06	0.23	0.34	1.51
47-1	12	4	7197	6417	2.12	2.14	0.27	0.21	1.55
49-2	12	8	9014	7906	2.52	2.26	0.25	0.18	1.55
49-1	12	16	8211	8183	2.96	2.43	0.28	0.32	1.60
49-8	16	8	8753	7790	2.70	2.27	0.23	0.18	1.58
49-7	18	16	9233	8251	2.47	2.34	0.24	0.18	1.57
49-6	20	8	9722	9416	2.56	2.49	0.25	0.20	1.57
49-5	22	16	10,695	8843	3.00	2.61	0.24	0.20	1.57

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* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VII

P-38 Composition Plus Additives

Notebook Reference 5808-	Additives* (latexes)	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
42-1	2.6% 60/40 S/B (48% total solids)	8600	7360	2.73	2.28	0.22	0.17	1.61
42-2	10.4% 60/40 S/B (48% total solids)	8361	7535	2.35	2.14	0.23	0.17	1.58
45-1	20.7% 60/40 S/B (48% total solids)	5833	5062	1.72	1.48	0.26	0.36	1.47
53-1	9.9% 60/40 S/B; 4.7% ZnO	5629	4908	2.22	2.27	0.18	0.16	1.54
53-2	10.2% 60/40 S/B; 2.5% Sulfur	6954	6835	2.36	2.40	0.20	0.17	1.59
44-1	2.6% 50/50 S/B (51.5% total solids)	8156	7850	2.73	2.40	0.20	0.17	1.55
44-2	10.4% 50/50 S/B (51.5% total solids)	7427	6827	2.34	2.20	0.22	0.19	1.56
44-3	20.7% 50/50 S/B (51.5% total solids)	4682	4824	1.46	1.38	0.43	0.21	1.43
67-2	2.6% 45/55 S/B (50% total solids)	9444	8434	2.76	2.54	0.22	0.20	1.63
52-1	10.4% 45/55 S/B	7746	6812	2.34	1.89	0.21	0.17	1.54
46-1	2.6 % polyethylene-acrylic acid latex (7% acrylic; 47.4% total solids)	9415	7842	3.21	3.10	0.25	0.26	1.56
46-2	10.4% " " "	8874	8524	2.50	2.34	0.27	0.28	1.54
55-1	2.6% PE-AA, (15% acrylic; 40% total solids)	8535	7409	2.79	2.54	0.25	0.16	1.59
58-1	10.4% PE-AA, (6% acrylic; 48% total solids)	6977	6507	2.40	2.15	0.17	0.13	1.42
71-1	2.6% phenoxy latex (38% total solids)	4721	3908	1.91	1.78	0.20	0.15	1.49
71-2	5.2% phenoxy latex (38% total solids)	4607	3677	1.83	1.71	0.22	0.17	1.49
71-3	10.4% phenoxy latex (38% total solids)	4580	4101	1.50	1.58	0.18	0.14	1.43
73-2	2.6% Chemigum 550 (38.1% total solids)	5035	3579	2.34	1.77	0.17	0.17	1.54
76-1	5.2% Chemigum 550 (38.1% total solids)	5606	4824	2.41	1.99	0.21	0.17	1.51
76-3	10.4% Chemigum 550 (38.1% total solids)	6608	5760	2.18	1.94	0.24	0.21	0.92
76-4	9.85% Chemigum + 4.92% ZnO	5031	4807	1.45	1.42	0.17	0.15	1.47

* percentages are based on initial charge of ingredients (i.e. before curing)

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TABLE VIII

P-38 Compositon Plus Additives

Notebook Reference 5808-	Additive	Flexural Strength (psi)		Flexural Modulus (psi x 10^6)		Izod (ft. lbs.)		Density (g/cc)
		P	T	P	T	P	T	
26-1	2.8% crocidolite (blue asbestos)	5716	5064	2.64	2.19	0.36	0.25	1.47
26-2	2.8% 1/4" glass fibers	5892	3464	2.77	1.88	0.24	0.14	1.48
30-1	2.8% 1" glass fibers	4587	2691	1.09	0.73	0.32	0.13	1.30
68-1	0.5% 1"-3" nylon fibers (140 denier)	6834	6709	2.66	2.64	0.42	0.17	1.61
68-2	0.3% 1"-3" nylon fibers (140 denier)	8834	6966	2.93	2.24	0.42	0.52	1.62
79-1	F-100 composition	13,912	12,562	2.33	1.91	0.27	0.22	1.59

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STATUS REPORT

INORGANIC POLYMERS: IMPACT MODIFICATION OF ASBESTOS-PHOSPHORIC ACID COMPOSITION BOARD

Authors: J. A. Faucher
G. D. Jacobs

Date: August 20, 1964

Project No.: 191G31

File No.: 2973

SUMMARY Experiments have been continued on the impact modification of the asbestos-phosphoric acid-water composition board originally produced by the Nuclear Division. Earlier work had shown no major modification of impact properties using a rather large assortment of fillers. Work has continued along similar lines using nylon, polyhydroxyether, and polycarbonate fibers as fillers, but again with little success. Unblown Styrofoam beads were also incoporated into the mix but gave little increase in impact strength. A final experiment was carried out using NIAX RO-350 in place of some of the phosphoric acid but this failed to produce a board of any strength.

Work on this project is being terminated.

INTRODUCTION Chyrsotile asbestos, one of several varieties of asbestos, is the type used throughout these experiments. It is presently being mined by the Nuclear Division at Coalinga, California and is available in three product grades: standard grade, colloid grade, and high purity grade; the last of which was used for this project.

The Nuclear Division initiated work several years ago on an asbestos-phosphoric acid-water composition board (code designation P-38) but encountered problems with regard to impact strength and weatherability. They have since been engaged in work on an asbestos-phenolic composition (code designation F-100) which shows both improved strength and weatherability.

Prior experience on impact strength of organic polymers, as evidenced by studies on the low temperature loss peaks in the mechanical loss spectrum, prompted us to reconsider the P-38 blend with the thought of adding an impact modifying filler to the composition.

Details of the experimental procedure and equipment used in these studies may be found in a previous report.(1)

Research and Development Department
Chemicals Division
Union Carbide Corporation

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DISCUSSION The use of many different fillers of a particle nature failed to increase the impact strength of the P-38 composition, as previously reported.(1) Attention was next turned to incorporating fibers into the composition, following a U. S. Army release(2) which reported that the strength of concrete was increased some twenty-seven times upon addition of nylon fibers. Table I lists some of the earlier work on blue asbestos, glass fibers, and nylon yarn as well as entries for the straight P-38 and F-100 blends.

Table I also lists the results for the more recent trials with nylon, polyhydroxyether, and polycarbonate fibers. The 56 mils diameter nylon, polyhydroxyether, and polycarbonate fibers were made by extrusion through a capillary die and unfortunately contained many air bubbles. It was quite difficult to extrude a smooth asbestos board containing these fibers due to their large diameter. There was also a tendency for the fibers to curl during the final curing cycle.

In order to avoid some of the above problems nylon monofilament fishing line was purchased and used for the remaining trials. The fishing line was much easier to blend into the P-38 mix but as shown in Table I no significant increase in impact strength was achieved.

Following a suggestion by Dr. F. P. Reding, unblown Styrofoam beads were added to the P-38 composition. During the curing cycle the beads on the surface of the board appeared to "pop" and then melt while those in the interior region apparently did not "pop". The test results are shown in Table II.

As a final experiment NIAX Polyol RO-350(3) was added in place of some and finally all the phosphoric acid used in the mix. As shown in Table II only the case of total replacement showed any improvement in the Izod impact test. However, for this case the board was extremely soft and very weak as shown by the flexural test results.

REFERENCES

(1) Jacobs, G. D. and Faucher, J. A., "Impact Modification of Asbestos-Phosphoric Acid Composition Board", Status Report, July 6, 1964, File No: 2777.

(2) Technical Report 1757-TR, "Plastic Fibrous Reinforcement for Portland Cement", prepared by S. Goldfein, U. S. Army Research and Development Laboratories, Ft. Belvoir, Virginia.

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(3) Proops, W. R. and Beisner, R. W., "NIAX Polyol RO-350 Hydrolysis Study", Status Report, April 15, 1964, File No: 2301.

ATTACHMENTS: 2 Tables

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TABLE I

Notebook Reference 5808-	Additive	Flexural Strength (psi) P	Flexural Strength (psi) T	Flexural Modulus (psi x 10) P	Flexural Modulus (psi x 10) T	Q	Izod (ft. lbs.) P	Izod (ft. lbs.) T	Density (g/cc)
45-2	P-38	9306	8484	2.86	2.49		0.28	0.20	1.53
79-1	F-100	13912	12562	2.33	1.91		0.27	0.22	1.59
26-1	2.8% crocidolite (blue asbestos)	5716	5064	2.64	2.19		0.36	0.25	1.47
26-2	2.8% 1/4" glass fibers	5892	3464	2.77	1.88		0.24	0.14	1.48
30-1	2.8% 1" glass fibers	4587	2691	1.09	0.73		0.32	0.13	1.30
68-1	0.5% 1"-3" nylon yarn (140 denier)	6834	6709	2.66	2.64		0.42	0.17	1.61
68-2	0.3% 1"-3" nylon yarn (140 denier)	8834	6966	2.93	2.24		0.42	0.52	1.62
82-1	0.5% 1"-3" nylon fiber (56 mils dia.)	5939	5095	1.00	0.87		0.23	0.18	1.52
83-1	0.3% 1"-3" nylon fiber (15 mils dia.)	4777	3577	1.01	0.73		0.27	0.16	1.59
83-2	0.5% 1"-3" nylon fiber (15 mils dia.)	4577	3102	0.93	0.72		0.28	0.22	1.61
84-1	0.3% 1" nylon fiber (294 denier)	4712	3605	0.86	0.75		0.32	0.35	1.49
84-2	0.3% 1" nylon fiber (445 denier)	3662	2740	0.84	0.65		0.27	0.35	1.47
84-3	0.3% 1" nylon fiber (698 denier)	4574	2570	0.81	0.57		0.33	0.26	1.50
82-2	0.5% 1"-3" polycarbonate fiber (56 mils dia.)	5658	4530	0.96	0.91		0.34	0.22	1.55
82-3	0.5% 1"-3" polyhydroxyether fiber (56 mils dia.)	6347	5472	1.08	0.94		0.46	0.21	1.63

TABLE II

Notebook Reference 5808-	Additive	Flexural Strength (psi) P	Flexural Strength (psi) T	Flexural Modulus (psi x 10^6) P	Flexural Modulus (psi x 10^6) T	Izod (ft. lbs.) P	Izod (ft. lbs.) T	Density (g/cc)
88-1	1% Styrofoam beads					0.31	0.18	1.60
88-2	2% Styrofoam beads					0.26	0.48	1.53
85-2	NIAX RO-350 in place of H_3PO_4 (150° cure)	919	945	0.13	0.12	0.52	0.51	1.52
85-3	50:50 NIAX RO-350 : H_3PO_4 (110° cure)	882	881	0.17	0.15	0.25	0.38	1.42
86-1	67:33 NIAX RO-350 : H_3PO_4 (110° cure)	399	338	0.76	0.52	0.20	0.22	1.40
86-2	NIAX RO-350 in place of H_3PO_4 (110° cure)	349	426	0.25	0.25	1.17	1.17	1.68

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WV-0001 #16

STATUS REPORT

NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

Authors: C. W. McGary
G. W. Rausch

Date: July 28, 1964

Project No.: 162D21

File No.: 2853

SUMMARY Attempts to add asbestos to the double bond of activated vinyl compounds were unsuccessful; apparently, the necessary silanol groups are not present.

A 2 per cent addition of organic material to asbestos was achieved by heating a toluene solution of divinylspirobi-(m-dioxane) with asbestos. Sodium hydroxide catalysis, however, resulted in an 8.6 per cent organic loading which was identified as acrylate ion. The acrylate-modified asbestos is a light grey powder which is more easily obtained by direct reaction of asbestos and acrylic acid.

Uncatalyzed mesityl oxide and acrylonitrile do not react with asbestos at 100°. When a sodium hydroxide catalyzed cyanoethylation of asbestos was attempted, vinyl polymerization of acrylonitrile and adsorption of the polymer by asbestos took place. Mesityl oxide underwent an aldol condensation reaction exclusively on sodium hydroxide catalysis. The aldol polymer was physically adsorbed on asbestos.

The products of polymer adsorption on asbestos were colored, organophillic, hydrophobic solids which could be used as compatible resin fillers but which would result in discolored products.

INTRODUCTION The addition of chrysotile asbestos to activated vinyl compounds has been discussed previously in a report surveying the possible reactions of asbestos.(1)

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Union Carbide Corporation

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The formation of stable adducts from asbestos and vinyl compounds is dependent on the existence of weakly acidic silanol groups on asbestos:

$$\geqslant SiOH + CH_2{=}CHX \longrightarrow \geqslant Si\text{-}O\text{-}CH_2CH_2X$$

where X = -CN, $-CO_2R$, $-\overset{O}{\overset{\|}{C}}R$, $-\overset{O}{\overset{\|}{S}}R$, etc.

The theoretical structure of chrysotile currently favored does not contain silanol groups.

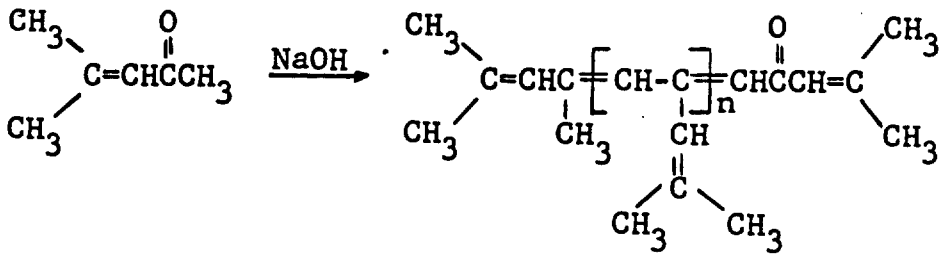
DISCUSSION Chrysotile asbestos, a weak base comparable in strength to magnesium hydroxide, should be sufficiently basic to catalyze the addition of silanol groups to activated carbon-carbon double bonds. Three compounds with activated vinyl groups were studied: mesityl oxide, acrylonitrile, and divinylspirobi(m-dioxane).

Without catalysis divinylspirobi(m-dioxane) in toluene reacted with asbestos to add less than 2 per cent organic material to asbestos. The product was not analyzed since a 2 per cent organic loading is insignificant. When 5 per cent powdered sodium hydroxide based on the divinylspirobi(m-dioxane) concentration was added, an 8.6 per cent organic loading was achieved. The product was identified as an asbestos acrylate salt by infrared analysis. A carbon-carbon double bond was indicated by an absorption band at 6.1μ, and a carboxylate salt by absorption bands at 6.22μ and 6.85μ. Some addition of asbestos to the activated double bond may have taken place but the principal reaction was salt formation:

$$CH_2{=}CHCH(O^-)(O^-) + \geqslant SiOMgOH \xrightarrow{NaOH} CH_2{=}CHCO_2^-\,{}^+MgOSi\leqslant$$

The reaction probably takes place by a base-catalyzed disproportionation similar to a Cannizzaro reaction but could also occur by air oxidation of the dioxolane as has been proposed for the formation of acrylate esters in air drying films from polymeric α-β-unsaturated dioxolanes(3) No attempt was made to isolate by-products.

Although uncatalyzed mesityl oxide failed to undergo any noticeable reaction with raw asbestos, the addition of powdered sodium hydroxide caused a vigorous exothermic reaction resulting in asbestos containing over 13 per cent red organic material. The base catalyzed aldol polymerization of mesityl oxide in water has been reported,(4) and the solid organic material extracted from the treated asbestos was easily identified at a higher aldol condensate by its color and infrared spectrum:

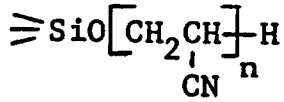


The existence of a conjugated double bond system was supported by the red color of the condensate (indicating a shift in absorption from ultraviolet to visible red light), by a conjugated carbonyl absorption band at 6.0μ and by an intense conjugated carbon-carbon double bond absorption band at 6.32μ. These bands compare with a carbonyl absorption band at 5.9μ and a carbon-carbon unsaturation band at 6.14μ for mesityl oxide.

Exhaustive reflux extraction of the product using different solvents (water, acetone, cyclohexanone) resulted in different organic loadings. The polymeric aldol condensates are probably low in molecular weight, C_{36}-C_{48}.(4)

Reproducible results were not obtained in the polyaldol condensation due to the heterogeneous catalyst.

Cyanoethylation of asbestos by heating an acetonitrile solution of acrylonitrile for 20 hours at 82° was unsuccessful. When the same procedure was repeated with a catalytic amount of powdered sodium hydroxide, polymerization took place. The product could be either a polymer grafted to asbestos:



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or a polymer which is strongly adsorbed by asbestos because of the electron-accepting nitrile groups. A difference in organic loading (3GWR48) on asbestos samples exhaustively extracted with acetonitrile and dimethyl formamide indicates the organic polymer was physically adsorbed since the better solvent removed more material.

When the reaction was run with asbestos pre-fired at 1000° to remove hydroxyl groups, organic material was again added; this is further evidence of a physical adsorption of organic material. In this case (3GWR74), direct boiling in DMF was more effective in removing polyacrylonitrile than was Soxhlet extraction with DMF.

The DMF extractable portions of the organic material were a brown solid residue (polyacrylonitrile) which exhibited a nitrile band at 4.5μ.

CONCLUSIONS If silanol groups are present on chrysotile asbestos, they either exist in very small number or are unreactive toward cyanoethylation-type reactions.

Acrylate ion can be placed on the asbestos surface by a base catalyzed reaction of divinylspirobi(m-dioxane) and probably other acrolein acetals.

Asbestos modified by physically adsorbed polymers of mesityl oxide or acrylonitrile may exhibit increased compatibility[2] with organic resins, but no great increase in strength properties is to be expected over conventional filled resins.

No further work in the area of vinyl additions to asbestos is planned.

EXPERIMENTAL The asbestos, catalyst, and solvent were stirred as a thick slurry with ice water or brine cooling in a jacketed flash while the reagent was added at a rate such that the temperature was easily controlled. After any exotherm had subsided, the slurry was heated to the desired temperature and samples were pulled at the stated intervals. Reaction time was based on time at high temperature during both exotherm and external heating.

The solid product was filtered from the solvent and exhaustively extracted by the Soxhlet technique. After drying at 105° for 16 hours, the samples were ashed at 1000°C. and the weight loss was compared with the weight loss found with fired raw chrysotile asbestos (15.2 per cent).

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1. C. W. McGary and G. W. Rausch, "New Enterprises: Chemical Reactions of Asbestos," Formal Status Report, July 7, 1964, File No. 2746.

2. "Asbestos Data Book," page 12, Union Carbide Nuclear Division.

3. Carol K. Ikeda, U. S. 3,010,923, November 28, 1961.

4. Sumner H. McAllister and Vernon E. Haury, U. S. 2,309,650, February 2, 1943.

ATTACHMENTS: One table

Gerald Rausch

jm

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eference	Reactant	Solvent	Wt. Reactant (1)	Wt. Asbestos (1)	Catalyst	Cat. Wt. (1)	Temp. (2)	Time (3)	Ext. Solvent	% Org. (4)
GWR28	Divinylspirobi-(m-dioxane)	250 ml. Toluene	290	60	--	--	100°	4	Toluene	1.6
								8		1.9
								12		1.9
GWR58	Divinylspirobi-(m-dioxane)	250 ml. Toluene	290	60	NaOH	14.5	100°	18	Toluene	8.1
GWR30	Mesityl oxide	Neat	400	60	--	--	120°	3	Acetone	0.6
								6		0.4
								9		0.4
								12		--
								15		1.0
								18		1.2
GWR62	Mesityl oxide	Neat	400	60	NaOH	20.0	100°	2.5	Acetone	13.5
									Water	13.5
GWR64	Mesityl oxide	Neat	400	60	NaOH	20.0	100°	0.5	Acetone	6.8
								3		6.6
								6		7.5
								10		9.3
								13		7.4
								13	Cyclohexanone	14.5
GWR80	Mesityl oxide	Neat	400	30	NaOH	20.0	100°	18	Acetone	5.2
GWR82	Mesityl oxide	Neat	400	15	NaOH	20.0	100°	18	Acetone	6.8
GWR84	Mesityl oxide	Neat	400	60	NaOH	40.0	110°	18	Acetone	3.9
GWR86	Mesityl oxide	Neat	400	60	NaOH	80.0	110°	18	Acetone	7.7
GWR88(5)	Mesityl oxide	Neat	400	60	NaOH	20.0	110°	18	Acetone	7.0
									Heptane	7.3
GWR44	Acrylonitrile	500 ml. Acetonitrile	33.2	60	--	--	82°	20	Acetonitrile	0.0
GWR48	Acrylonitrile	1000 ml. Acetonitrile	70.4	120	NaOH	3.5	82°	0	Acetonitrile	4.0
								4		5.9
								8		6.4
								12		6.6
								16		6.9
								20		7.1
								24		7.5
									DMF	2.6
GWR74	Acrylonitrile	500 ml. Acetonitrile	31.8	46(6)	NaOH	1.6	82°	24	Acetonitrile	4.6
									DMF	1.7
									DMF(7)	1.2

1. Wt. in grams
2. °C.
3. Time in hours
4. % Organic material ±0.3%
5. Inverse addition of catalyst to reactants
6. Asbestos pre-fired at 1000°C.
7. Boiled in DMF.

Union Carbide trial exhibit UC-805: Union Carbide Research and Development Status Reports on Asbestos-Reinf...
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UC-0001 #15

STATUS REPORT

NEW ENTERPRISES
CHEMICAL REACTIONS OF ASBESTOS

Authors: C. W. McGary
G. W. Rausch

Date: July 16, 1964

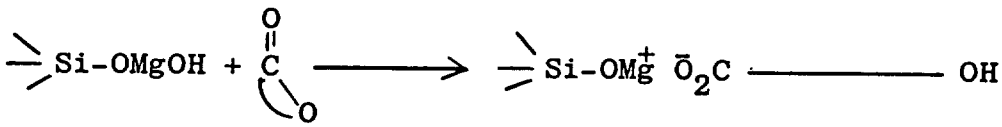
Project No.: 162D21

File No.: 2819

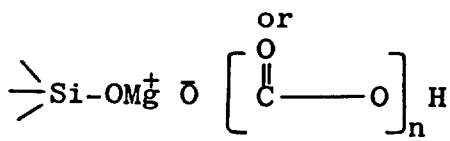
SUMMARY ϵ-Caprolactone has been added to chrysotile asbestos. As high as 8.6 per cent organic material was chemically combined with asbestos by heating asbestos in an aqueous solution of ϵ-caprolactone. Under anhydrous conditions caprolactone also adds but to a lesser degree (4.5 per cent). The products are light tan colored powders resembling the asbestos starting material but showing increased organophillicity and are easily hydrolyzed to asbestos and polycaprolactone. Under both aqueous and non-aqueous conditions, polymerization of caprolactone is several times faster than the chemical addition of caprolactone to asbestos. The product is polycaprolactone grafted to asbestos as a carboxylate salt.

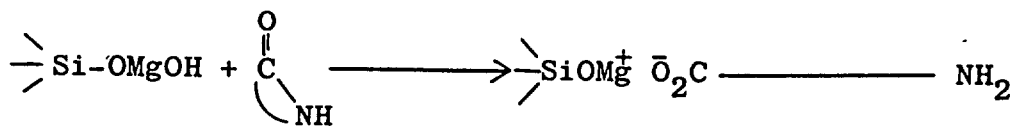
Attempts to add ϵ-caprolactam to asbestos under similar conditions met with failure. No attempt was made to add catalyzed ϵ-caprolactam to asbestos.

DISCUSSION Cyclic esters and amides could be expected to react with pendant -MgOH groups on asbestos to provide a reactive organic surface:

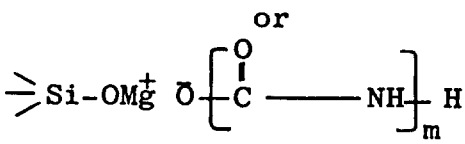


or





or



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Chrysotile asbestos is composed of magnesium hydroxide coordinated with silica as a sheet polymer. The currently favored theoretical structure is 6-10 layers of the sheet polymer forming hollow fibers with OH groups on the outer surface. The crystal structure of a single layer is shown in Figure I. The surface OH groups are at least partially ionic. If an organic acid molecule adds to asbestos by carboxylate salt formation some of the hydroxide ions will be replaced by carboxylate ions. The product should be hydrolytically unstable since slightly acidic magnesium salts are easily hydrolyzed to less soluble magnesium hydroxide and the free acid.

Figure II shows the effect of time on the amount of caprolactone addition to asbestos in hot aqueous solution. The minima were obtained when a sample was pulled after 12-16 hours downtime whereas maxima were obtained by immediate workup of the hot reaction slurry. The rapid readdition of organic material after downtime indicates uptake of polycaprolactone or its magnesium salt rather than monomer.

Under anhydrous conditions (Figure III) the plot of caprolactone addition describes a smooth curve because water was unavailable for hydrolysis of the product salt. On standing in water at ambient temperatures for 24 hours the asbestos-polycaprolactone adducts are hydrolyzed to asbestos and polycaprolactone. Exhaustive extraction of the products with warm acetone, in which polycaprolactone is soluble, leaves a residue of non-extractable organic material on asbestos. The material that was dissolved by acetone was high molecular weight polyester.

The molecular weight of the polycaprolactone on the asbestos has not been determined. By comparing the per cent ash residue after firing the reaction product with the residue from unreacted asbestos, total organic addition was determined. This combined with organic hydroxyl equivalent might be used to calculate the average molecular weight of the polycaprolactone grafts by end group analysis. Unfortunately, conventional hydroxyl analyses are unreliable when performed on a basic solid like the modified asbestos.

No measurable extraction of magnesium was observed in the aqueous reaction and caprolactone (or hydroxycaproic acid) concentration was conveniently followed by titration of samples of the supernatant reaction solution with standard base.

In the non-aqueous reaction samples were analyzed for magnesium gravimetrically with 8-hydroxyquinoline. Total sodium hydroxide consumption in titration of the supernatant reaction solution accounted for both caprolactone concentration and the precipitation of magnesium hydroxide. The caprolactone concentration was then estimated by difference. Figures IV and V illustrate the change in caprolactone concentration with time and the loss of caprolactone by reaction with asbestos in the aqueous and non-aqueous reactions respectively. The data prove uptake of polycaprolactone in the non-aqueous reaction since most of the monomer disappears early in the reaction and thereafter monomer concentration remains constant. Uptake of polymer is probably true of the aqueous reaction as well. Some of the monomer disappearance is due to adsorption on the asbestos surface without reaction but no method was devised for its measurement.

ϵ-Caprolactam, being less subject to polymerization than ϵ-caprolactone, should add monomerically or in short chains. In water at 100° and in diethyl carbitol at 160° no caprolactam addition to asbestos was detected. Polymeric caprolactam might be added by catalysis of the monomer in the presence of asbestos by means of a strong base such as triton B or sodium hydroxide.

CONCLUSIONS ϵ-Caprolactone adds chemically to chrysotile asbestos at a rate slower than polymerization. The product is a magnesium carboxylate silicate salt or asbestos containing adsorbed magnesium dicarboxylate.

The hydrolytic instability of the modified asbestos limits its utility and no effort was made to investigate possible end uses. Other lactones could be employed to produce similar products but no further work on lactone-modified asbestos is anticipated.

EXPERIMENTAL

Reaction of Aqueous Caprolactone With Astestos

To a one liter stirred flask was charged 60 g. of CMS grade chrysotile asbestos*, 148 g. (1.30 mole) of ϵ-caprolactone and 300 g. of distilled water. A sample (109) was removed immediately and the reaction mixture was heated to 100°C. Samples were taken at 3 hour intervals until total reaction time was 18 hours.

Ref. 3GWR18

March 5, 1964

Reaction of Caprolactone With Asbestos in Diethyl Carbitol

A charge of 60 g. CMS grade chrysotile asbestos, 148 g. (1.30 mole) of ϵ-caprolactone, and 300 g. of diethyl carbitol was thoroughly stirred at room temperature and a sample (5-10 g.) was pulled. The slurry was then heated to 180°C. and the temperature maintained for 18 hours. Samples were pulled after 4, 12, and 18 hours of reaction time.

Ref. 3GWR22 March 5, 1964

Attempted Reaction of Caprolactam With Asbestos

Under conditions identical to those above, 60 g. of chrysotile asbestos was treated with 73.5 g. of caprolactam in 300 g. of solvent. Workup of the 18 hour sample in both aqueous and organic slurries resulted in recovery of unreacted asbestos.

Ref. 3GWR32 April 1, 1964
3GWR36 April 1, 1964

Sample Workup and Determination of Ash

The individual samples were filtered and the filter cake was washed 4-6 times with warm acetone (45°C.) until unreacted caprolactone and polycaprolactone were removed. (No residue on solvent evaporation) The solid was dried at 105° and a sample fired at 900°C.

Caprolactone Determination

Aqueous Samples

A portion of the sample filtrate was weighed, treated with 50 ml. of 0.5001 N sodium hydroxide and allowed to stand for 10 minutes. A back titration with 0.5006 N hydrochloric acid to a phenolphthalein end-point was made to determine base consumption.

Magnesium Analysis

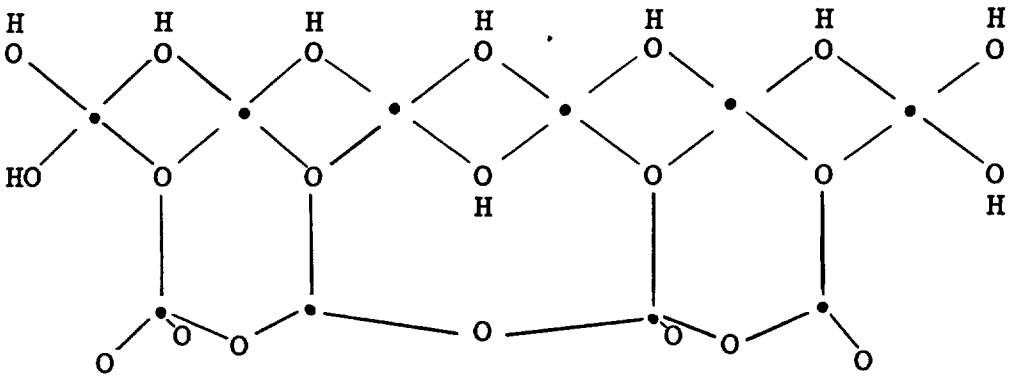
A 4-5 g. sample of supernatant liquid was weighed to the nearest milligram and diluted to 35 ml. with distilled water. One gram of ammonium chloride and 10 ml. of con. ammonium hydroxide were added and the solution was heated to near boiling. An excess of 8-hydroxyquinoline solution (2 g. of reagent in 6 ml. of glacial acetic acid and 95 ml. of water) was added with stirring and the solution was heated for 15 minutes on a steam bath. The yellow precipitate was filtered onto a medium porosity glass crucible, washed twice with 100 ml. hot 1:99 amminium hydroxide, and dried at 105° to constant weight.

Ref. 3GWR43 April 15, 1964

ATTACHMENTS: 5 Figures

FIGURE 1

$Mg_6(OH)_8\ Si_4O_{10}$



6 OH

6 Mg

40, 2OH

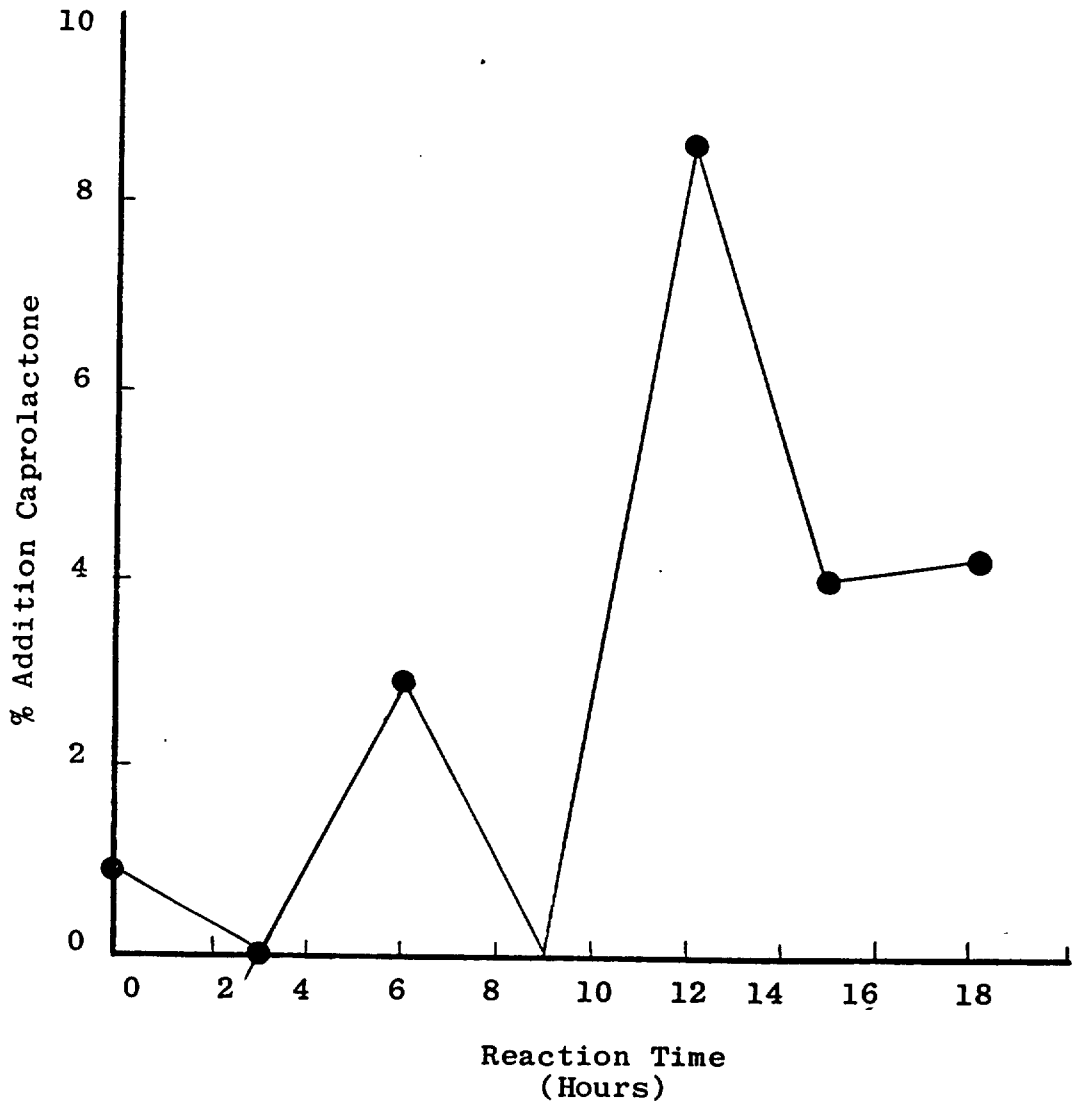
4 Si

6 O

Layer Thickness 7.3 Å

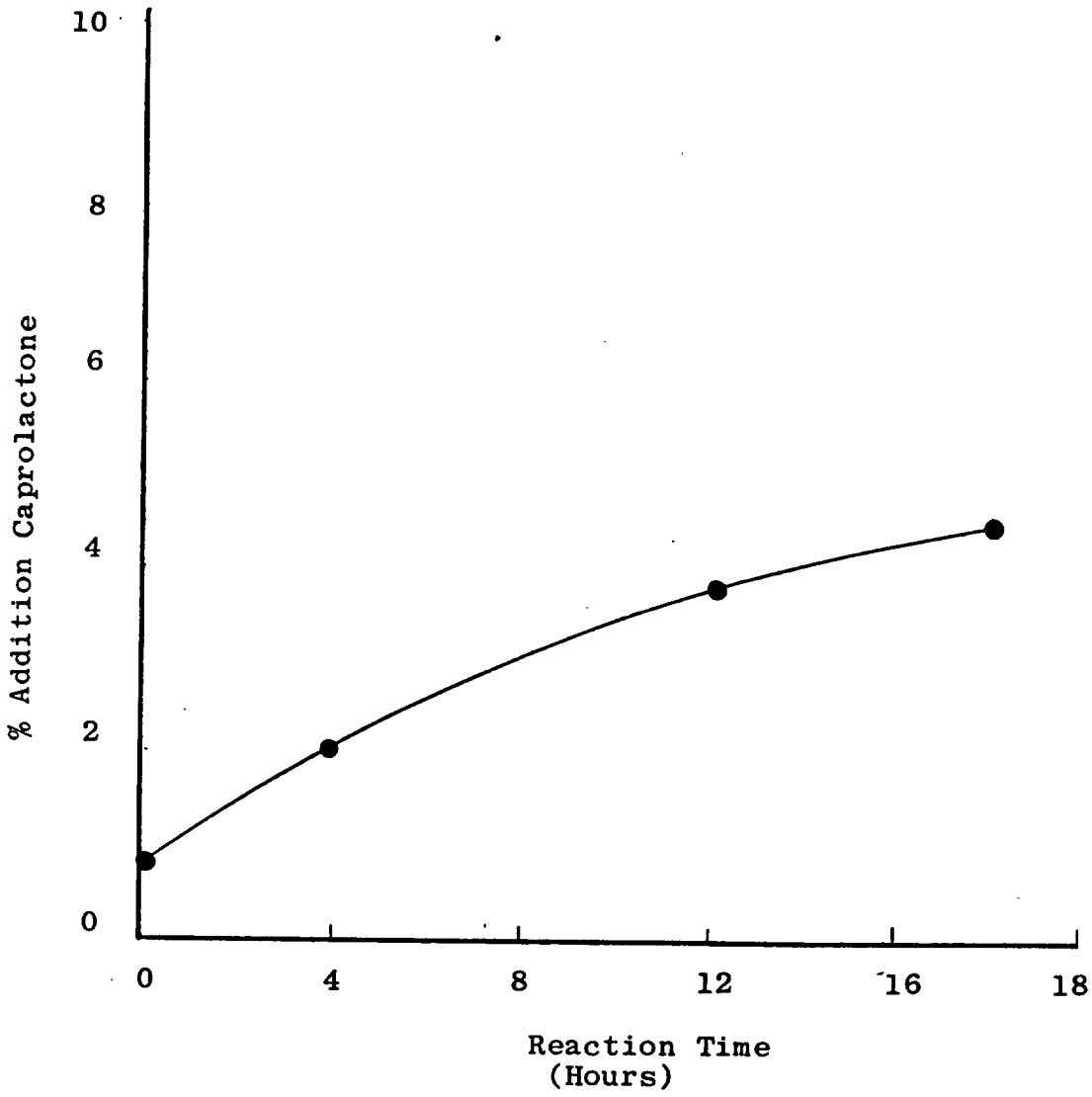
Layers per fiber 6-10

FIGURE II
(Aqueous Reaction)



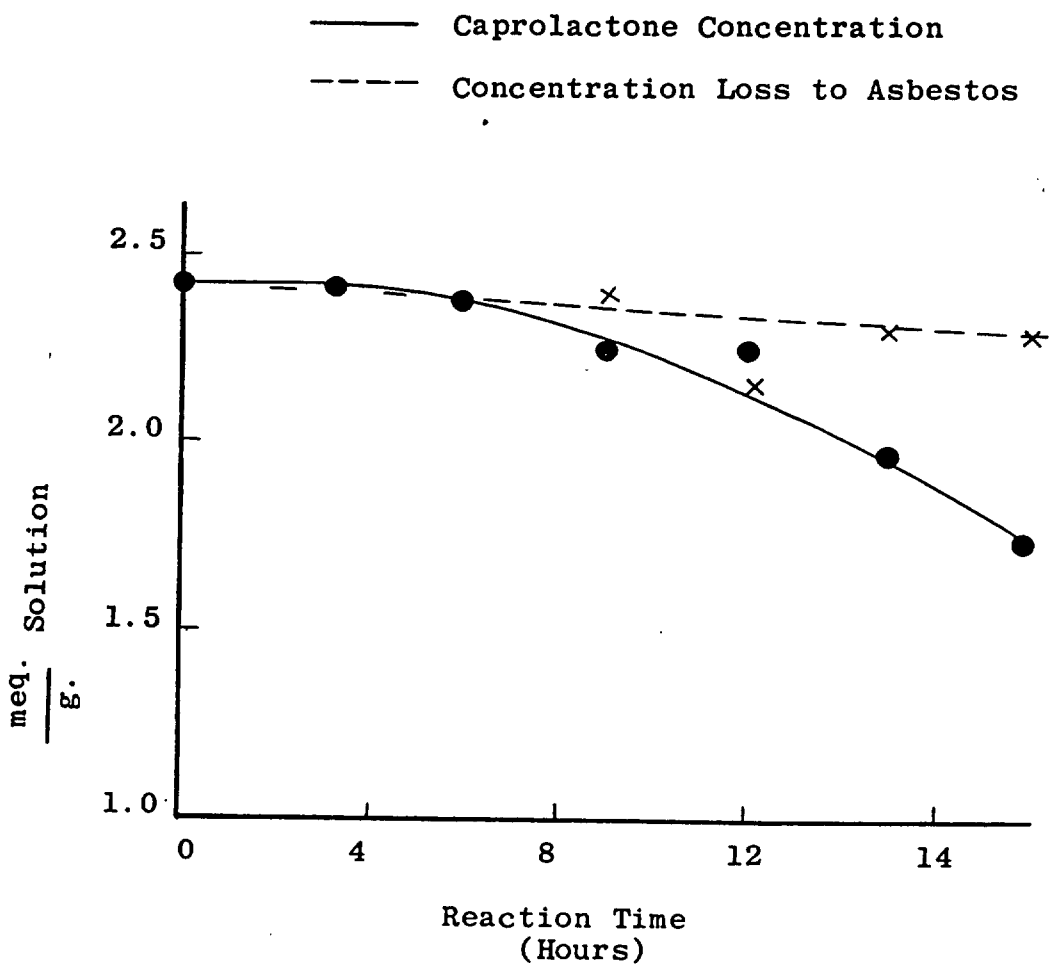
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FIGURE III
(Non-aqueous Reaction)



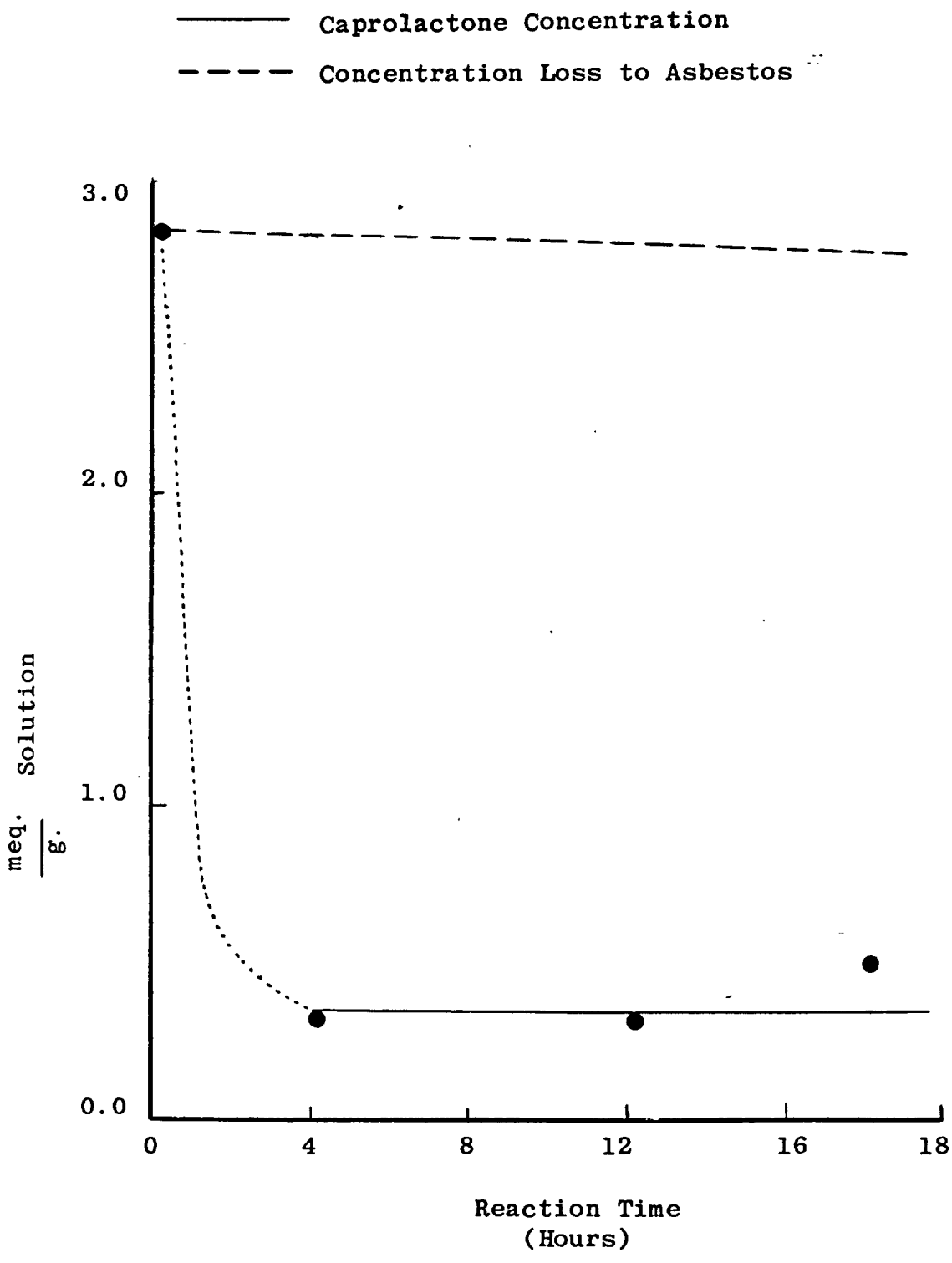
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FIGURE IV
(Aqueous Reaction)



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FIGURE V
(Non-aqueous Reaction)



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UN-0001 #14

STATUS REPORT

NEW ENTERPRISES

CHEMICAL REACTIONS OF ASBESTOS

Authors: C. W. McGary
G. W. Rausch

Date: July 10, 1964

Project No.: 162D21

File No.: 2747

SUMMARY In a survey of chemical reactions of asbestos with organic compounds, a brief study was made of the reactivity of asbestos toward alcohols and phenols.

Under both aqueous and non-aqueous conditions the chemical addition of phenol to asbestos failed to occur. In the presence of anhydrous pyridine only a trace of organic material was detected on asbestos by ashing.

Prolonged heating of 2,6,8-trimethyl-4-nonanol at 200° with asbestos caused dehydration of the alcohol without addition to asbestos.

These data indicate that reactions of either -O-Mg-OH or -SiOH groups on asbestos with phenolic or methylene OH groups of phenol-formaldehyde resins are highly unlikely. No further work is planned in this area.

DISCUSSION Asbestos is usually treated as an inert filler in filled phenol-formaldehyde resin systems. If chemical cross-linking between resin and filler occurs in asbestos filled phenolic resins, a study of the reactive groups and stoichiometry could theoretically lead to filled resins of improved physical properties or the use of small amounts of reactive organic material to cross-link the asbestos itself. The acidic phenolic OH group held promise as a likely point of attachment to -MgOH groups pendant from the asbestos polymer backbone.

It was hoped that the curing conditions for phenol-formaldehyde resins would be approximated by reactions of monofunctional compounds on weakly basic asbestos. Although

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anhydrous materials were sometimes employed, true anhydrous conditions did not exist since asbestos loses water continuously from 100-700°C.

The treated asbestos was washed with an appropriate solvent (ether or absolute ethanol) until no reagent could be detected in the wash solutions and was then dried at 105° prior to firing at 900°. Uptake of organic material was indicated by increased weight loss on ashing.

2,6,8-Trimethyl-4-Nonanol

Heating of a 20/1 mole ratio of 2,6,8-trimethyl-4-nonanol with asbestos at 200° resulted in dehydration of the alcohol with no addition to asbestos. This secondary alcohol was chosen for its high boiling point and availability although a primary alcohol would have undergone less dehydration.

Aqueous Phenol

Both 1.4 per cent and 83 per cent aqueous phenol solutions failed to add to asbestos after 4.5 hours reflux time.

"Anhydrous Phenol"

A 60/1 mixture of anhydrous phenol with chrysotile asbestos was heated at 100° for 4.5 hours with no reaction. To achieve optimum temperature and concentration a 10/1 mixture of phenol and asbestos were heated to 200° for 18 hours under 360 psi of nitrogen. No reaction ensued.

Phenol in Pyridine

A solution of 256 g. of anhydrous pyridine in 300 g. anhydrous phenol was added to 60 g. of chrysotile asbestos and heated to 100° for seven hours. Ashing of the ether washed product revealed no uptake of organic material.

Gerald Rausch

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