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STANDARDIZATION OF CARBON-PHENOLIC COMPOSITE TEST METHODOLOGY

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ABSTRACT

The objective of this study was to evaluate the residual volatiles, filler content, and resin flow test procedures for carbon-phenolic prepreg materials. The residual volatile test procedure was rewritten with tighter procedure control which was then evaluated by round robin testing by four laboratories on the same rolls of prepreg. Results indicated that the residual volatiles test was too operator and equipment dependent to be reliable, and it was recommended that the test be discontinued. The resin flow test procedures were rewritten with tighter procedure control, and it is now considered to be an acceptable test. It was recommended that the filler content determination be made prior to prepregging.

INTRODUCTION

Carbon-carbon and carbon-phenolic composites are the most common nozzle materials utilized in space vehicles. These materials have been developed and placed into service based on empirical information and evaluation. In an attempt to place this critical field on a more technical basis, Marshall Space Flight Center (MSFC) established a program entitled Solid Rocket Motor (SRM) Enhancement and Technology Development Program. The objectives of this program included the following; to implement a carbon-phenolic processing variable study, to expand the design and evaluation data bases, to enhance SRM quality and productivity, to solve current problems in SRM nozzle performance, and to improve SRM technology in general. The accomplishment of these objectives would certainly establish MSFC as the NASA lead center in SRM technology. If the improvements are made in the nozzle materials field, then new test methods and specifications are neeeded to measure the improvements and to define the necessary materials and processing to routinely obtain and keep these improved materials.

Objective

The objective of this study was to look at three test methods and specifications currently in use in SRM technology. The tests were to be evaluated on two basis; first, does the test method yield the desired results, and secondly, do these results give useful information in evaluating the products. The three tests were percent resin flow, percent residual volatiles and percent filler content. These tests were chosen as the first tests to evaluate because at the present time there are 45,000 lbs. of SRM prepreg out of one of these specifications and cannot be used. The value of this prepreg exceeds one million dollars, and in addition, this problem has created a shortage of acceptable prepreg. The problem is not critical at this time because procurement of prepreg followed original scheduling while actual prepreg usage fell below the predicted rate because of delays in nozzle fabrication and shuttle flight launch schedules.

Test Methodology Studies

Filler Content: At the present time, there is no accurate method to measure carbon filler content in carbon-phenolic prepreg material. Two methods currently utilized are the Soxhlet extraction method and the DMF wash method. Both systems remove some of the fabric and do not remove all of the carbon filler. The amount of filler left depends on the type, size, and shape of the carbon filler material. In general, the DMF wash method results in values approximately 2% higher than those obtained by the Soxhlet extraction method, as shown in the data given below:

Percent Filler in C.C. Phenolic Lot C01656*

Roll #1	DMF	Soxhlet	Roll #2	DMF	Soxhlet
Sample 1	16.6	15.2	Sample 1	16.2	14.1
Sample 2	16.8	15.3	Sample 2	15.4	14.1
Sample 3	16.0	15.7	Sample 3	14.8	13.9
Sample 4	17.2	14.5	Sample 4	16.6	14.2
Sample 5	15.8	14.2	Sample 5	15.9	13.9
Sample 6	15.7	14.3	Sample 6	15.6	13.9
Avg. X =	16.5	14.9		15.8	14.0

* MTI data

It should be possible to prepare small batches of accurately measured filler/resin ratio, and add this mix to a accurately weighed cloth and prepare calibration curves for both the DMF wash and Soxhlet extraction methods. However, a better control could be acheived by constant monitoring the filler/resin ratio just prior to its being applied to the carbon cloth. Since the filler content does not change with aging, the initial determination should be sufficient for the life of the prepreg.

Percent Resin Flow: The test procedure for percent resin flow is given in Appendix D. This test is important because it assures that the prepreg can be tape wrapped and properly cured. The percent resin flow not only is a measure of staging of the resin, but of total resin content. The content is a function of the cloth itself in that the amount retained is a function of several characteristics of the cloth and the filler/resin mixture. However, there is a wide variance in the percent resin flow data, especially when tested in different laboratories. The initial explanation for this variance was the delay in closing the press, as step c of appendix D just specifies immediately. Closing time versus percent resin flow was determined for three different rolls of prepreg with the following results:

Precent Resin Flow

Delay in Closure	Roll	1	2	3
0 sec		29.6	18.7	31.5
20 sec		31.1	19.1	30.0
40 sec		30.0	20.1	--
60 sec		29.3	22.1	30.7
120 sec		29.9	19.4	24.8

The closure time with 0 seconds delay was 15 seconds, so the total closure time was delay time plus 15 seconds. It can be seen that total closure times of 75 seconds and less had a negibile effect on the percent resin flow.

<u>Percent Residual Volatiles</u>: The major difficulty with the original residual volatiles test method was the variance in results between the two prepreg suppplier, U.S. Poly and Fiberite, and the user of the prepreg, Thiokol. The problem was compounded when one lab obtained results that were high but still within specs and the other lab obtained results that were too high, i.e., out of specification. During a meeting at MSFC with U.S. Poly, Fiberite, Thiokal and MSFC represented, the original test method (Appendix A) was rewritten to tighten the test procedure. The reason that it was felt that it was necessary to rewrite the test method is shown in Figure 1. Although each laboratory was following the same test procedure, there was significant difference in the actual time-temperature-pressure sequence in the prepartion of test specimen. This would give different amounts of staging and resin flow yielding significant different results. In an attempt to solve this problem, the test procedure was modified to tighten up the test method. The agreed upon new test method is shown graphically in Figure I and written in Appendix B. The four labs then agreed to a round robin testing of the same prepreg rolls to evaulte the precision and the ability of each lab to duplicate each others results. The four labs, U.S. Poly, Thiokal, Fiberate and MSFC then tested the same seven rolls of prepreg utilizing the rewritten test method. The results of the test are given below:

ROUND ROBIN TESTING OF RESIDUAL VOLATILES IN SELECTED MATERIALS

MATERIAL USP -2115-

40	46	56
F-1.21	F-1.35	F-1.52
M-2.23	M-1.85	M-1.89
P-2.47	P-2.08	P-2.21
T-2.50	T-2.14	T-2.63

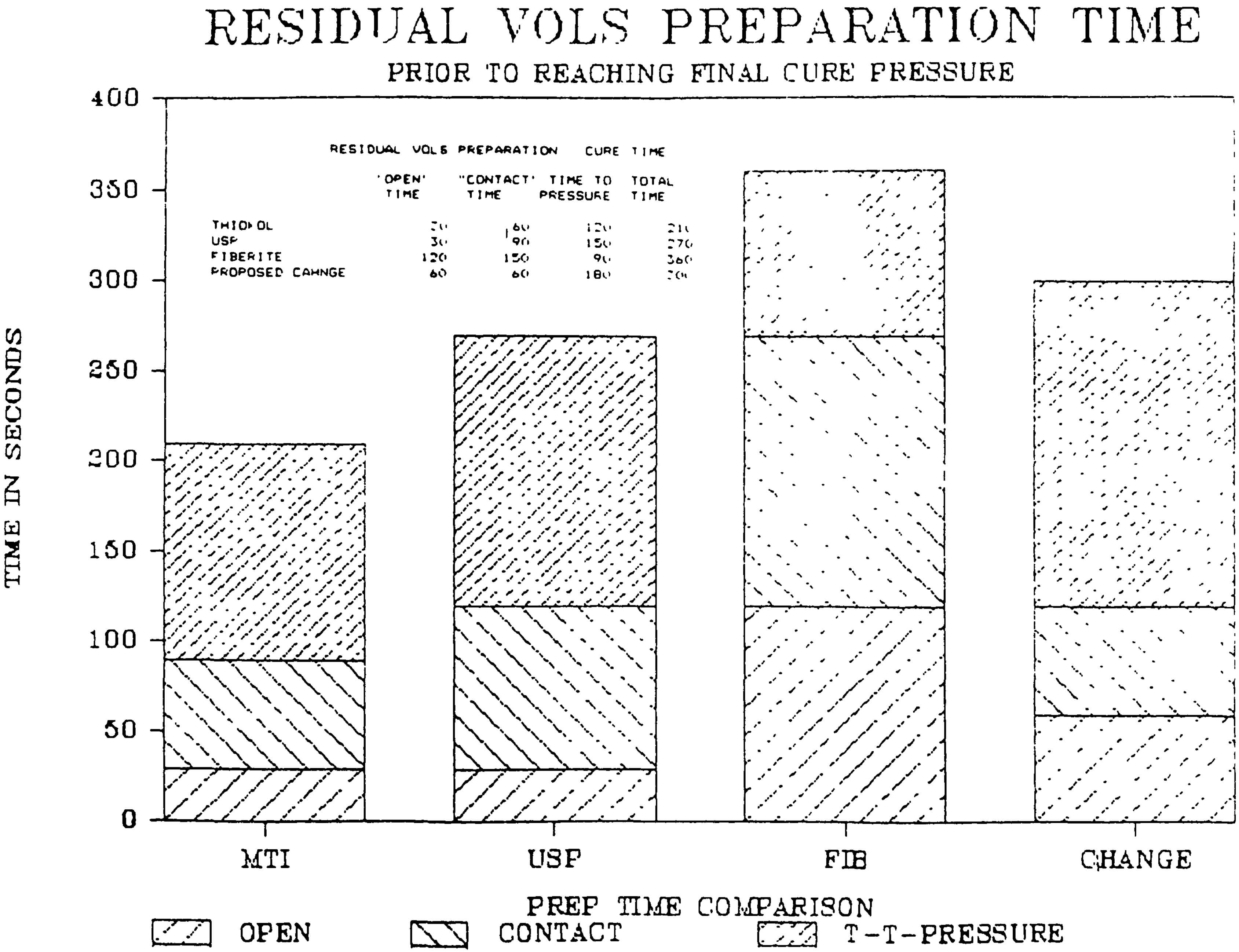
FIBERITE 1029-

4A	19A	22A	26A
F-0.99	F-1.43	F-1.04	F-1.44
M-1.31	T-1.69	M-1.52	M-1.51
T-1.44	M-1.76	P-1.88	T-1.94
P-1.79	P-2.29	T-1.90	P-2.21

LAB KEY, F=FIBERITE. M=MARSHALL. P=USP. T=THIOKOL

Data from MSFC testing is shown in Figure 2, indicating that the precision was excellent, but as shown in the above data , the ability of the labs to reproduce the same results did not improve. It is the opinion of the author that the major reason for this difference in lab agreement is difference in the equipment utilized in the testing. Different presses, drying ovens, and bleeder cloth could result in different amount a resin left in the specimen. In addition, the last time any of the presses and/or ovens were calibrated is also an unknown.

After the round robin test were completed, the general consensus was that it appeared that it was not possible under the current laboratory procedures



RESIDUAL VOLS PREPARATION	'OPEN' TIME	"CONTACT' TIME	CURE TIME TIME TO PRESSURE	TOTAL TIME
THIOKOL	30	60	120	210
USP	30	90	150	270
FIBERITE	120	150	90	360
PROPOSED CAHNGE	60	60	180	300

Figure 1. Preparation Time for Residual Volatiles Test Specimen

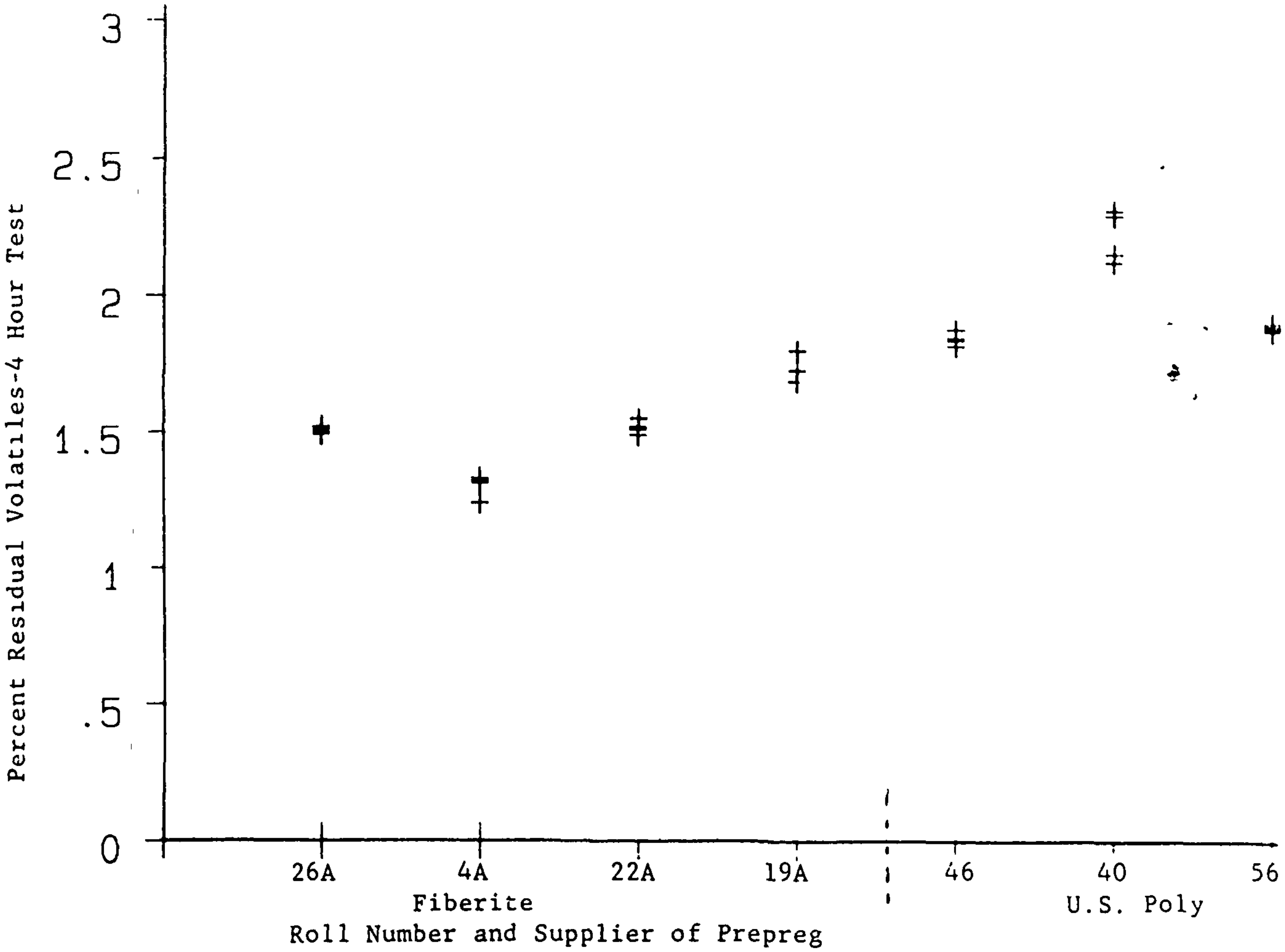


Figure 2. MSFC Residual Volatiles Test Values for Round Robin Test

to obtain reproducible results utilizing the residual volatiles test procedure. Therefore, since the first objective of the basic policy was not met, the second overall objective was not addressed. It is the authors opinion that the second basic policy objective was also not met. The minimum additional information needed to meet the second objective would be to identify and quantify the residual volatiles.

A new volatile content procedure was established to circumvent the above problems, and this test procedure is given in Appendix C. One change in the procedure was to change the phase "place specimen in oven" to "suspend specimen in oven" since laying the specimen on racks at 325 degree F causes sticking and excessive resin loss. A round robin evaluation between the same four labs for one roll of prepreg gave the following results:

Lab	Percent Volatiles (Average of 12 Specimens)	Variance
Fiberite	4.3	0.20
MTI	4.8	0.21
U. S. Poly	4.8	0.41
MSFC	4.9	0.30

The data is also shown graphically in Figure 3. It is noted that Fiberite was the lab with the lowest value as it was with all the rolls evaluated in the percent residual volatiles round robin, eight out of eight rolls tested. This would indicate some constant function such as lower than indicated temperature causing the difference in values between Fiberite and the other labs. The other three labs were extremly close so it does appear that the percent volatiles test can be duplicated in the various labs. It is still considered necessary, for the second objective or the basic policy for this study to be satisfied, to identify and quantify the volatiles coming from the specimen.

It is known that carbon-phenolic composite pick up moisture when exposed to humid conditions. Both cured and uncured (prepreg) samples were exposed to 100 percent relative humidity for 30 days. The weight gain versus exposure time curves for both of these materials are shown in Figure 4 (uncured) and Figure 5 (cured). The uncured curve is interesting in that it seems to indicate a weight gain for the first week followed by a weight loss the second week and then a gradual weight gain. The high value specimen on the 21st day is not the same high value specimen on the 29th day. This curve indicates varying reactivities and could be the area of a mare complete study. The curve for the cured and specimen indicates a gradual increase in weight for the entire exposure time of 30 days. The values remain approximately the same for the 36 day exposure time, so it would appear that a constant weight was achieved at 29-30 days of exposure time to 100 percent humidity conditions. The normal testing for residual volatiles that had picked up extra moisture was to dessicate for a minimum of 24 hours or a minimum of 72 hours on retest. The weight loss versus time in desicator is shown in Figure 6 and indicates an increase in weight loss continuing up to the 72 hours. Therefore, time in desicattor should be specified in a plus or minus frame instead of a minimum value. The weight loss versus exposure time in humidity champer is shown in Figure 7 indicating fairly constant loss of weight in the desiccator regardless of the time in the humidity chamber.

After the 72 hours in the desicator, percent residual volatiles were

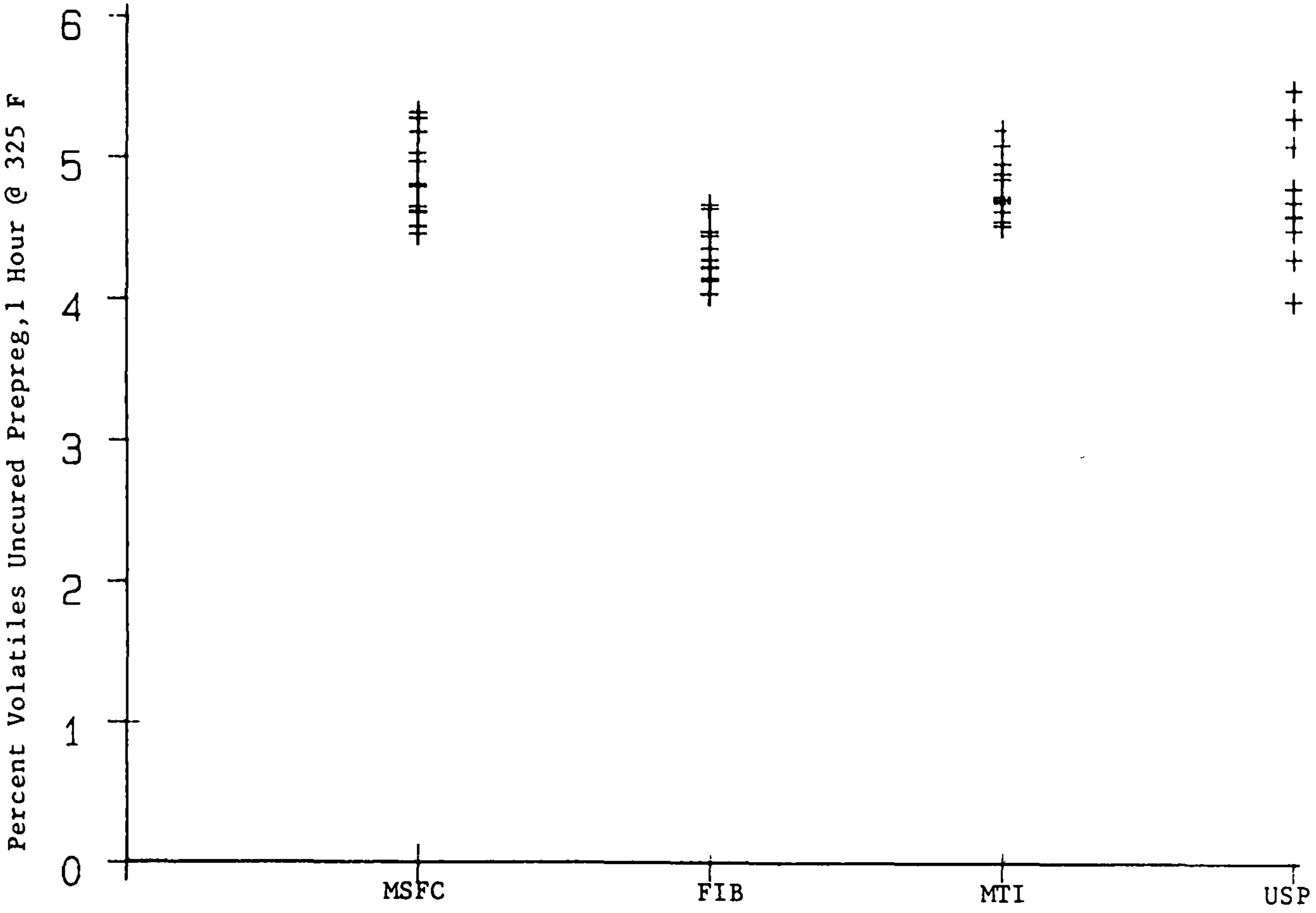


Figure 3. Values for Percent Volatiles from Round Robin Test

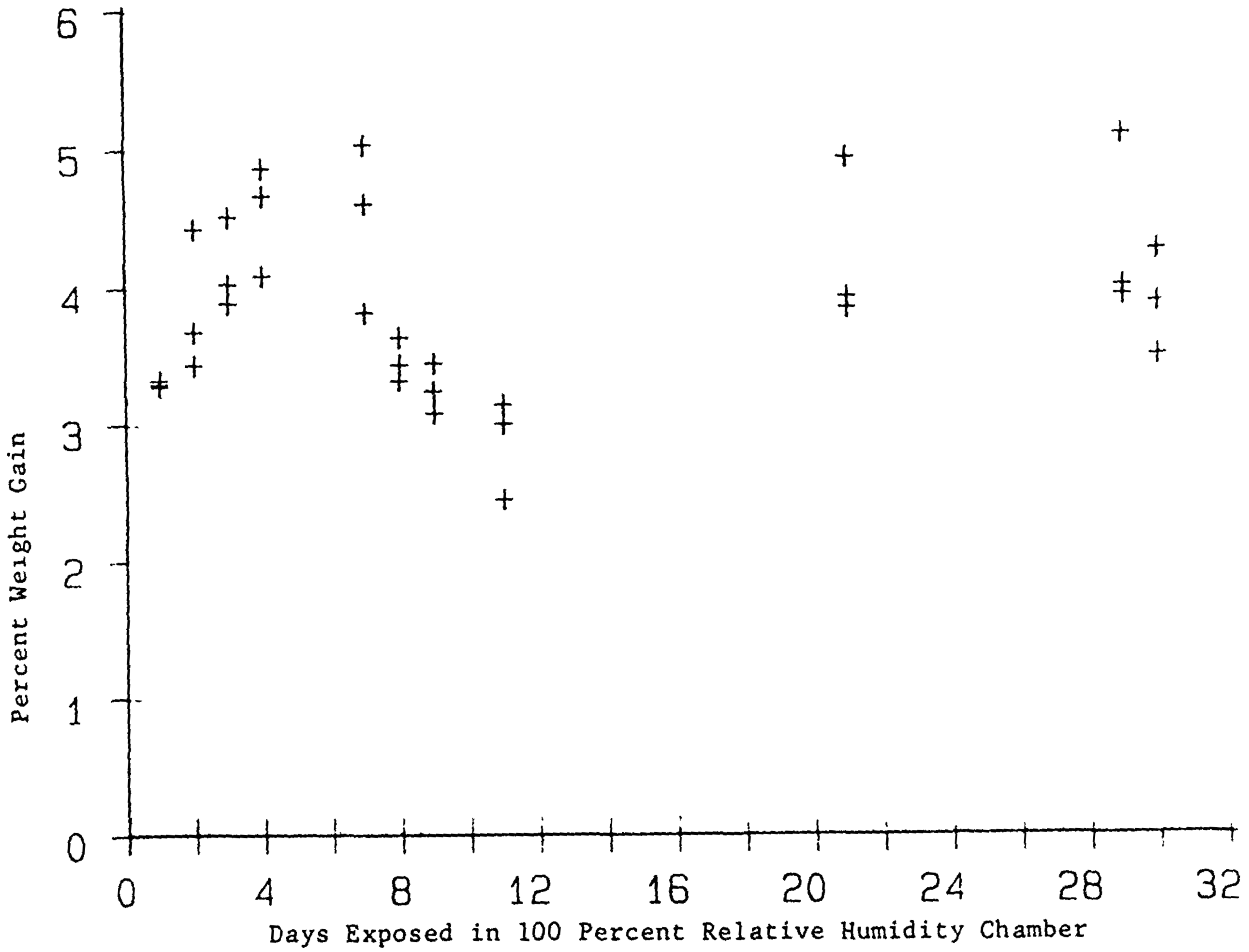


Figure 4. Weight Gain versus Time in Humidity Chamber for Uncured Prepreg

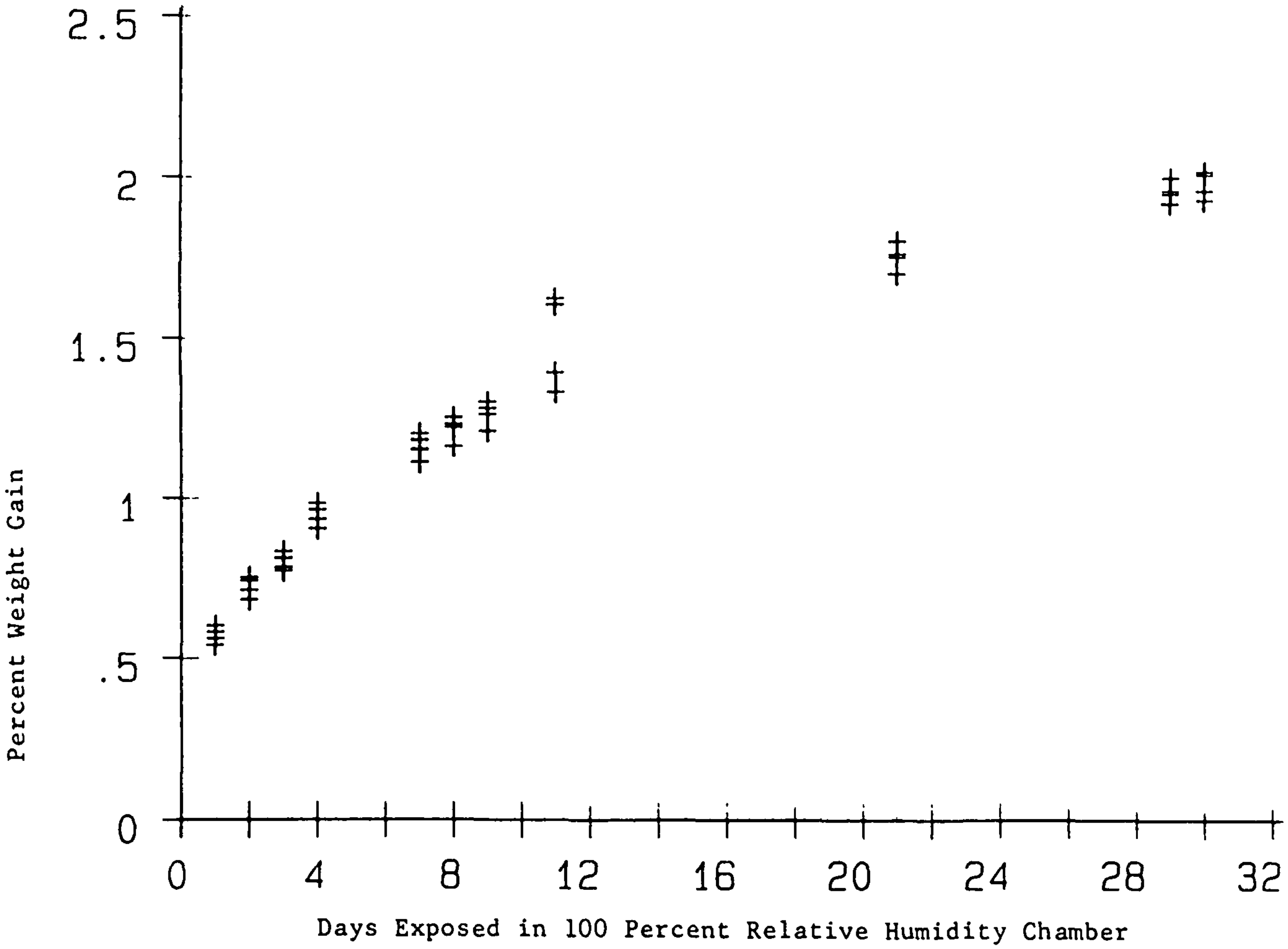


Figure 5. Weight Gain versus Time in Humidity Chamber for Cured Specimen

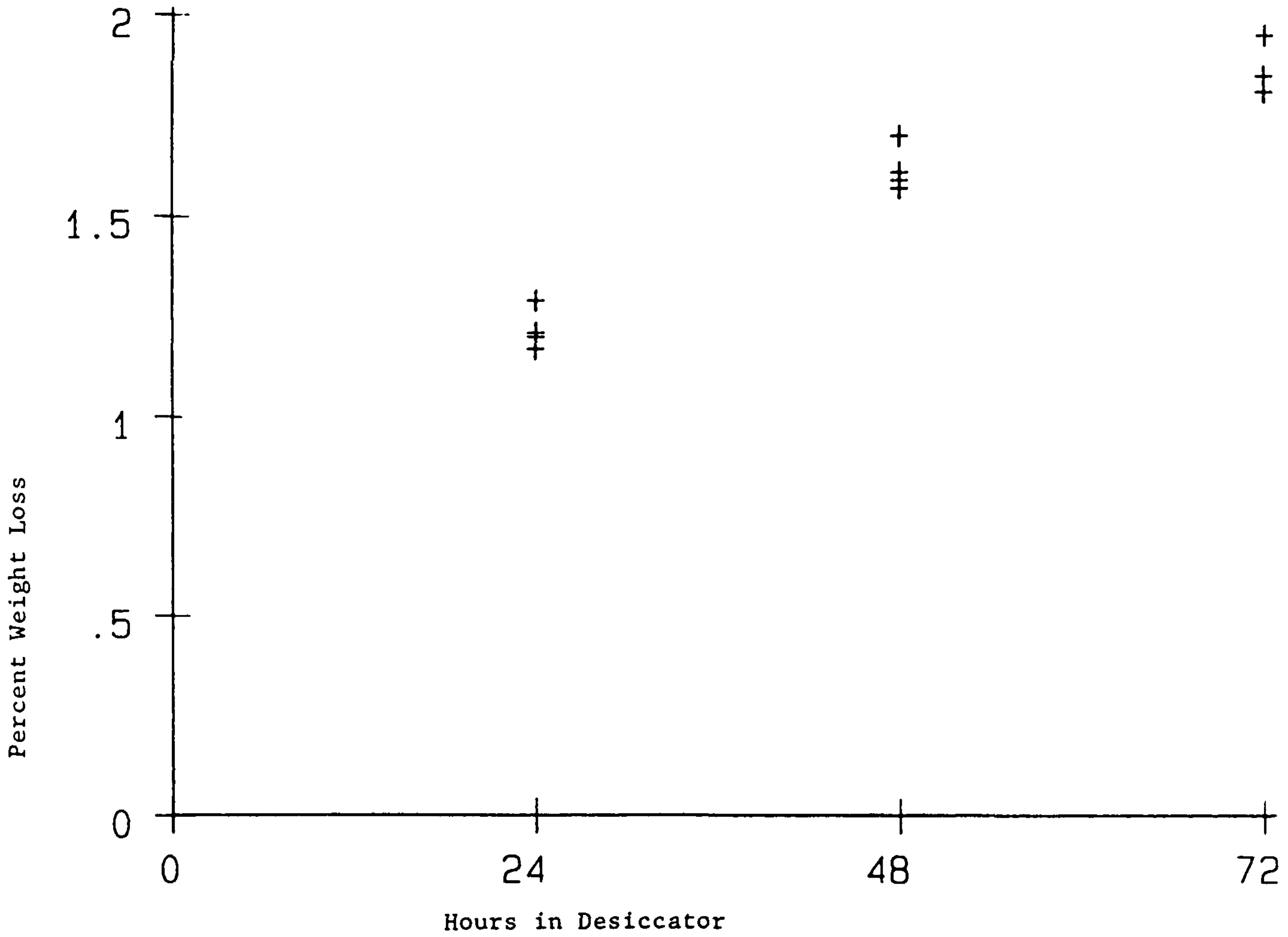


Figure 6. Weight Loss versus Time in Desiccator

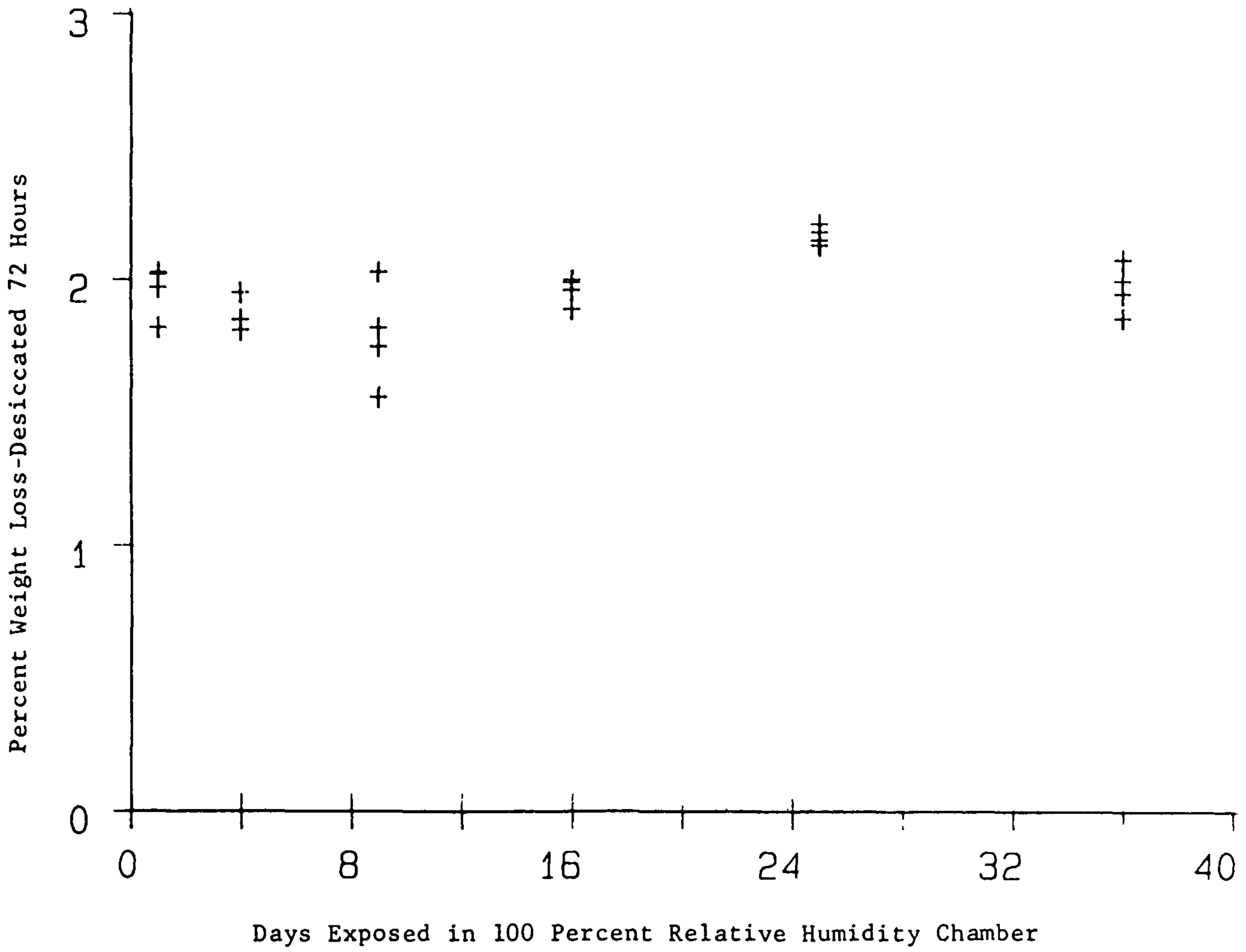


Figure 7. Weight Loss after 72 Hours in Desiccator versus Time in Humidity Chamber

determined for the exposed specimens. The results of this study is shown in Figure 8, indicating a slight increase in percent residual volatiles with an increase in exposure time in the humidity chamber. This was expected since Figure 5 indicates increase in weight versus exposure time while Figure 7 indicates essentially constant weight loss in the desiccator.

The last area studied was percent residual volatiles versus oven curing time. Figure 9 shows the percent residual volatiles for a oven period up to 48 hours, while Figure 10 extends the time to 360 hours. The important points in these two curves are that there is about one percent higher values when tested at 24 hours instead of 4 hours, and that constant values are achieved after 100 hours. It is the authors opinion that the specifications hould require the 24 hours oven time and adjust the percent residual volatiles value as required.

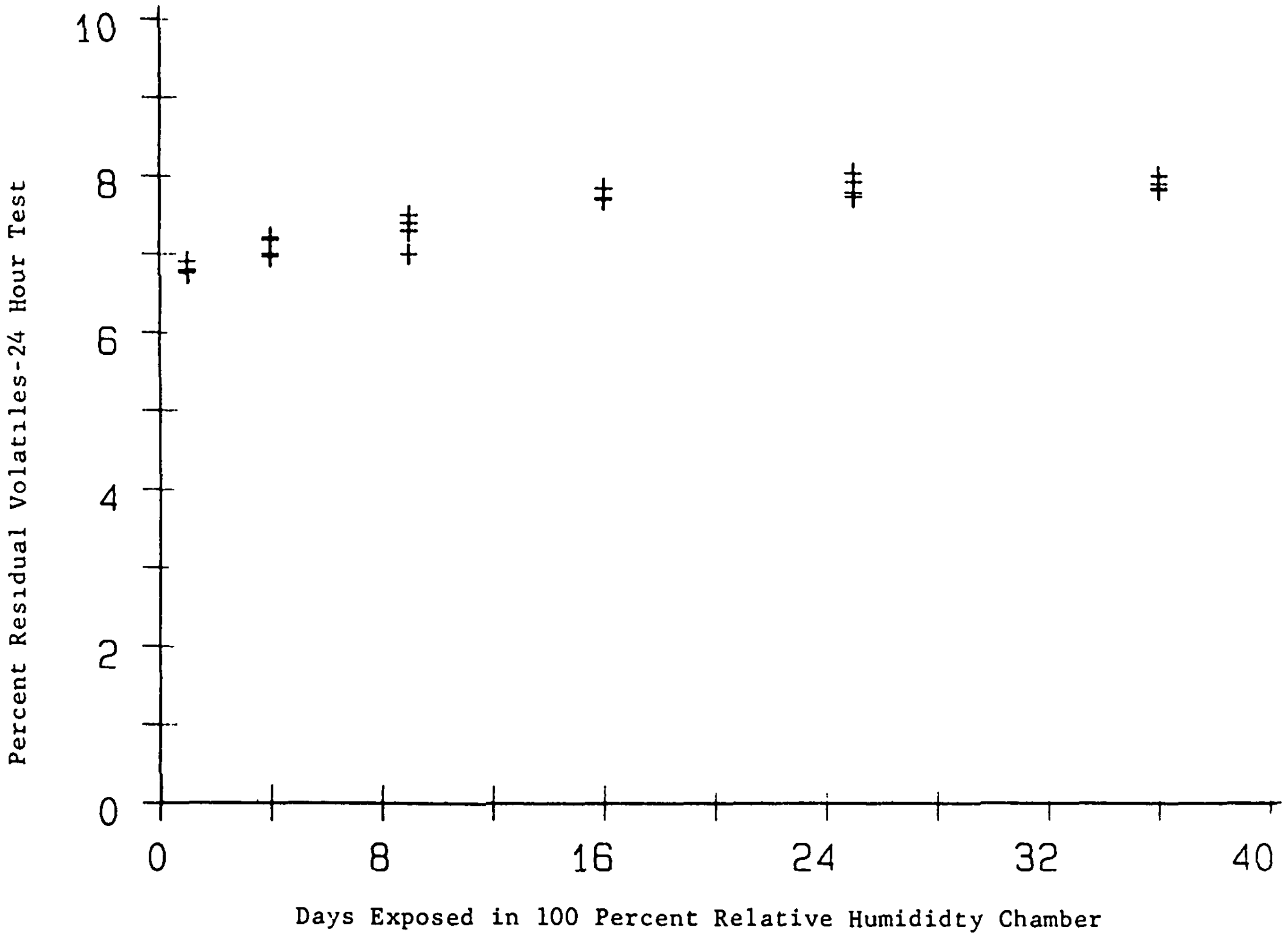


Figure 8. Percent Residual Volatiles versus Time in Humidity Chamber

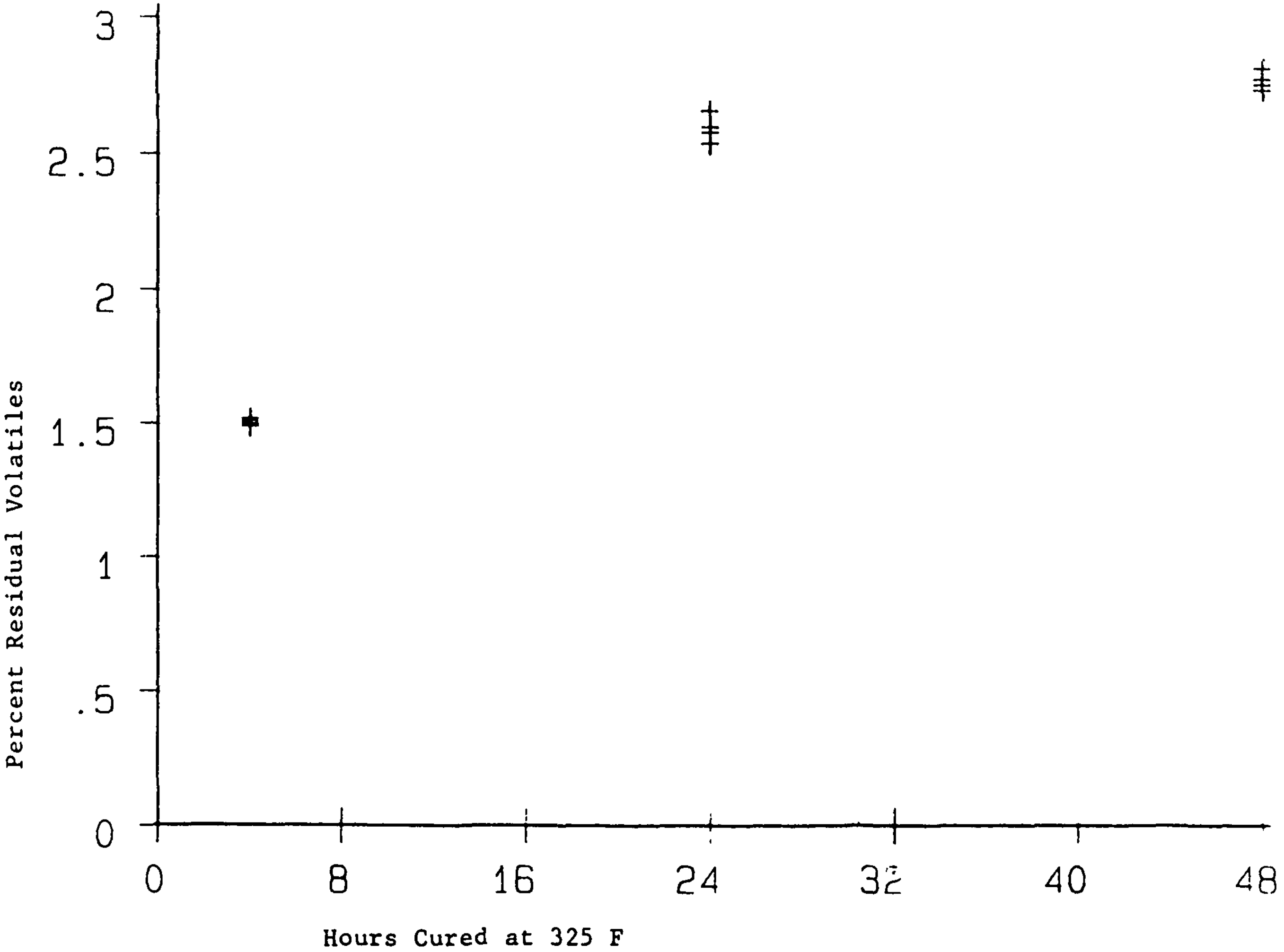


Figure 9. Percent Residual Volatiles versus Hours Cured at 325 F

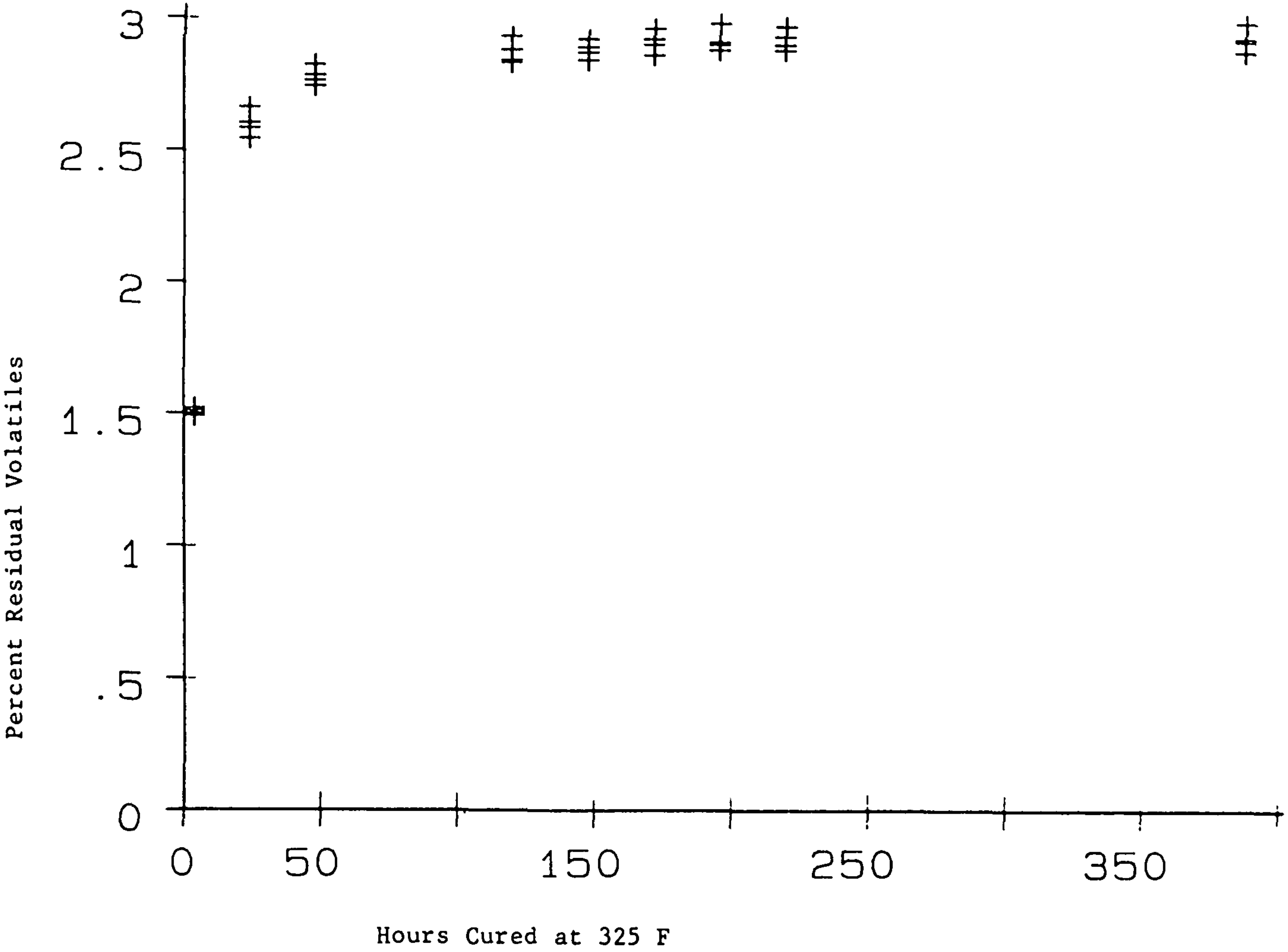


Figure 10. Percent Residual Volatiles versus Hours Cured at 325 F

CONCLUSIONS

Conclusions: Three standard test utilized in the carbon-phenolic composite industry were studied. These three test were percent residual volatiles, percent filler, and percent resin flow. The percent resin flow test was found to be acceptable in the present form, with the addition of one change. The change was to substitute for "apply press load immediately" to the following "apply press load in less than 30 seconds". The percent filler is determined at present by two alternative procedures, both yeilding different and incorrect results. It is recommended that this test be discontinued at the prepreg state and be conducted on the resin-filler mixture prior to prepregging. The percent residual volatiles test was determined to be to dependent on lab procedure for reproducibility and it is recommended this test be dropped and a now test for percent volatiles be utilized.

Appendix A

Orginal Residual Volatiles Test Procedure

Residual Volatile Content: The residual volatile content of the cured material shall be determined in accordance with the following:

a. Cut sufficient plies to produce a test panel 0.250 ± 0.050 thickness by 4 ± 0.125 by 4 ± 0.125 inches. Cure the panel as follows:

1. Place the stack of plies into a press preset at 325 ± 10 degrees F.

2. Apply contact pressure for 30 ± 5 seconds and dump pressure for 2 cycles before slowly applying maximum pressure. (The material shall not be prestaged.)

3. Increase the pressure slowly to 1000 ± 50 psi, allowing the resin to stage (see 6.3.1) to minimize flash at ply edges.

4. Hold the pressure and temperature for 120 ± 15 minutes.

5. Decrease the temperature and pressure to ambient.

The outer 1/2 inch of the test panel shall not be used for preparation of specimens.

b. Cut a specimen 1.000 ± 0.050 inch by 1.000 + 0.050 inch panel thickness from the center 2 inch by 2 inch section of the test panel. Top and bottom molded surfaces shall not be machined. Wipe the specimen clean using MEK and allow to air dry 20 minutes minimum before testing.

c. Place the specimen in a desiccator and desiccate for 18 hours minimum.

d. Weigh the specimen to the nearest 0.01 gram and record as W1.

e. Place the specimen in an air circulating oven, preheated and stabilized at 325 ± 10 degrees F for approximately 30 minutes; condition the specimen at a temperature of 325 + 10 degrees F for 24 hours minimum.

f. Remove the specimen from the oven and cool in the desiccator for approximately 30 minutes or until the specimen reaches room temperature.

g. Reweigh the specimen to the nearest 0.01 gram. Record as W2.

h. Calculate the percent residual volatiles as follows:

$$\text{Percent volatiles} = \frac{W1 - W2}{W1}\ 100$$

Where: W1 = original weight of specimen in grams

W2 = devolatilized weight of specimen in grams

i. Report residual volatiles to the nearest 0.01 percent.

Appendix B

Proposed Residual Volatiles Test Procedure

Residual Volatile Content: The residual volatile content of the cured material shall be determined in accordance with the following:

a. Cut 18 plies to produce a test panel 4 ± 0.125 by 4 ± 0.125 inches. Cure the panel as follows:

a. Cover top and bottom of lay-up with one layer of non-porous release film

b. Place the stack of plies into a press preset at 325 ± 10 degrees F.

c. Insert into the press and immediately close to contact pressure (close time ten seconds or less)

d. Hold for 30 plus or minus 5 seconds (at "contact" pressure)

e. Open the press to 1 - 2 inches and allow to "dwell" for 20 plus or minus 5 seconds

f. Immediately close to contact pressure and hold for 30 plus or minus 5 seconds.

g. Open the press to 1 - 2 inches and allow to dwell for 20 plus or minus 5 seconds.

h. Immediately close to contact pressure and slowly increase the pressure to 1000 - 1200 psi over a period of 180 plus or minus 30 seconds.

i. Total prep time is approx 300 seconds (assuming 10 seconds close times)

j. Cure time will be 120 - 135 minutes

k. Decrease the temperature and pressure to ambient.

l. The outer 1/2 inch of the test panel shall not be used for preparation of specimens.

m. Cut a specimen 1.000 + 0.050 inch by 1.000 + 0.050 inch by panel thickness from the center 2 inch by 2 inch section of the test panel. Top and bottom molded surfaces shall not be machined.

n. Place the specimen in a desiccator and desiccate for hours 18 hours minimum.

o. Weigh the specimen to the nearest 0.01 gram and record as W1.

p. Place the specimen in an air circulating oven, preheated and stabilized at 325 ± 10 degrees F for approximately 30 minutes; condition the specimen at a temperature of 325 ± 10 degrees F for 4 hours minimum.

q. Remove the specimen from the oven and cool in the desiccator for approximately 30 minutes or until the specimen reaches room temperature.

r. Reweigh the specimen to the nearest 0.01 gram. Record as W2.

s. Calculate the percent residual volatiles as follows:

$$\text{Percent volatiles} = \frac{W1 - W2}{W1}\ 100$$

where W1 = original weight of specimen in grams

W2 = devolatilized weight of specimen in grams

t. Report residual volatiles to the nearest 0.01 percent.

Appendix C

Proposed Volatile Content Test

The volatile content of 12 specimens taken randomly from the uncured material shall be determined in accordance with the following:

a. Cut a 16 ± 2 square inch specimen.

b. Weigh the specimen to the nearest 0.01 gram (W1).

c. Place specimen in a recirculating oven preheated and stablized to 325 ± 10 degrees F for 60 ± 1 minutes. Specimen should be placed to get adequate air circulation.

d. Remove specimen and place in a desicator and cool to room temperature.

e. Remove from the desicator and weigh the specimen to the nearest 0.01 gram (W2).

f. Calculate percent volatiles as follows:

$$\text{Percent volatiles} = \frac{W1 - W2}{W1} \times 100$$

Where: W1 = uncured weight of specimen, g
W2 = final weight of specimen, g

g. Report volatile content of specimen to the nearest 0.1 percent.

Appendix D

Percent Resin Flow Test Procedure

Resin Flow: Resin flow of each sample of the uncured material shall be determined in accordance with the following:

a. Cut a 4-inch by 4-inch ± 1/8-inch squares across the width of the fābric. All squares shall be bias cut to eliminate fiber loss in testing. Stack the squares uniformly on each other to make a specimen. Where the width of the tape is less than 4-inches wide, cut the tape in 4-inch lengths and place side by side to fabricate a 4-inch by 4-inch specimen ply. Stack four plies alternately placed 90 degrees to the previous ply roll direction. Place each ply uniformly on each other to make up a specimen.

b. Weigh the specimen of 4 plies to the nearest 0.01 gram and record as W1.

c. Place the specimen between release film. Preheat the press to 325 ± 10 degrees F, position the specimen in the middle of the press plate and apply the press lead of 150 ± 10 psig immediately. Press load the specimen for a minimum of 10 minutes at 325 ± 10 degrees F.

d. Remove the specimen from the press and cool to ambient temperature.

e. Using a knife, scrape off the resin flash to the original size of the specimen. Do not remove any reinforcement from the original dimensions.

Note: Any fibers which may be displaced and scraped off during the process shall be included in the weighed back specimen weight (W2).

f. Reweigh the specimen to the nearest 0.01 gram and record as W2.

g. Calculate the percent resin flow as follows:

$$\text{Percent flow} = \frac{W1 - W2}{W1} \times 100$$

where: W1 = uncured weight of specimen, g

W2 = final weight of specimen, g

h. Report resin flow to the nearest 0.1 percent.