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KEVLAR/EPOXY AND KEVLAR/GRAPHITE/EPOXY COMPOSITES FOR THE C-4 (TRIDENT) CHAMBER PROGRAM

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ABSTRACT

Lawrence Livermore Laboratory, at the request of the U.S. Navy Strategic Systems Project Office, performed research on Kevlar*/epoxy and Kevlar/graphite/epoxy composite materials used in the C-4 (Trident) container program. This research involved assessment of tensile properties, determining effects of moisture during filament winding, determining interlaminar-shear properties and measurement of volumetric shrinkage of epoxy resin systems during cure. Research methods are described and results and conclusions are presented.

INTRODUCTION

As part of its work on the C-4 (Trident) program, the U.S. Navy Strategic Systems Project Office requested the assistance of Lawrence Livermore Laboratory (LLL) on five special tasks related to the use and processing of Kevlar/epoxy and Kevlar/graphite/epoxy composite materials. The need for this research arose when Hercules Incorporated, which was fabricating the C-4 chambers, encountered various problems in processing new materials. Although these tasks are all related to the chamber program, they are not obviously related to one another. Consequently, in this report no attempt will be made to integrate the results of the various tasks. These five tasks are:

1. Assess the tensile properties of Kevlar/epoxy strands.
2. Assess the effect of moisture during filament winding on elongated-ring tensile properties of laminated Kevlar/graphite/epoxy composites.
3. Assess the effect of moisture during filament winding on elongated-ring interlaminar-shear properties of Kevlar/graphite/epoxy composites.
4. Determine the effect of various epoxy resin systems on transverse tensile properties of Kevlar/epoxy composites.
5. Measure the volumentric shrinkage of epoxy resin systems during cure.

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*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

SUMMARY AND CONCLUSIONS

This section summarizes the research activities and the major conclusions reached for each of the five tasks. Greater detail as to methods and procedures for each of the tasks is presented in Appendices A through E.

Tensile Properties of Kevlar/Epoxy Strands

Procedures — Three types of Kevlar 49 strands were studied:

- Four-end 4560-denier roving (768 filaments per 1140-denier end combined to make 4560-denier roving)
- Four-end 4560-denier roving coming from partially used spools which had been roughly handled during use
- Single-end 1140-denier yarn obtained on special order from duPont.

The fibers were impregnated with Hercules 55A epoxy resin to form strands which were then tensile-tested at room temperature at a strain rate of $6.57 \times 10^{-4}/s$. The mean breaking-stress and breaking-strain of 91 samples taken from five carefully handled spools of four-end roving were 2780 MPa (403 ksi) and 2.42% respectively. This compares with mean values of 3180 MPa (461 ksi) and 2.53% strain for 20 samples taken from the single-end 1140-denier spool. Two roughly handled partially used four-end spools gave mean values for 18 samples of 2180 MPa (316 ksi) and 1.98% strain. This work is described in more detail in Appendix A.

Conclusions — It was concluded from these results that the process of making four-end (4560-denier) roving from single-end (1140-denier) yarn lowers the breaking strength. In addition, rough handling further lowers the breaking strength.

Effect of Moisture During Winding on Elongated-Ring Tensile Properties of Laminated Kevlar/Graphite/Epoxy Composites

Procedures — Because of the large size of the C-4 chamber the filament winding cannot be completed in one shift. Consequently, after completion of a layer the chamber is placed in a freezer overnight to prevent the epoxy from setting up. LLL was asked to do moisture studies to determine the effect of this procedure on the quality of the winding.

To perform this study, elongated rings were first wound as follows: one layer of Hercules ASMS graphite impregnated with Fiberite X507 epoxy was wound between two layers of Kevlar 49 four-end roving impregnated with an epoxy system designated by Hercules as HBRF 55A. Specimens were then subjected to four different moisture and gel conditions:

1. No moisture. Control specimens were wound under no-moisture conditions.
2. Light moisture. Specimens were placed in an -18°C (0°F) freezer for about 2 hours between layers. The frost and moisture were lightly wiped off before winding the next layer.

3. Heavy moisture. Specimens were prepared in the same manner as the light-moisture specimens but with the moisture not wiped off before winding the next layer.

4. Heavy moisture with an extended gel time. The gel time for these specimens was nine times longer than for the other heavy-moisture specimens.

Tensile tests of the elongated-ring specimens showed little change in the breaking stress of the five light-moisture specimens (1170 MPa (170 ksi)) as compared to that of the five control specimens (1200 MPa (174 ksi)). The five heavy-moisture specimens, however, showed a decrease in breaking stress to 1080 MPa (156 ksi). The breaking stress decreased yet further to 970 MPa (141 ksi) for the four heavy moisture specimens which had received an extended gel time. This work is described in more detail in Appendix B.

Conclusions – It was concluded that light moisture has little effect on composite strength but that heavy moisture and frost should be wiped off before resumption of winding on parts taken from a freezer.

Effect of Moisture During Winding on Elongated-Ring Interlaminar-Shear Properties of Kevlar/Graphite/Epoxy Composites

Procedures – Elongated rings were wound in the same manner as the ring tensile-specimens. The same four different moisture and gel conditions were studied. The rings were cut into 1.90-cm (0.75 in.)-long specimens and tested in short-beam shear in accordance with ASTM D2344. Like the results for the ring tensile tests, the 20 light-moisture specimens had a shear strength (46.3 MPa (6.71 ksi)) comparable to that for the 20 control specimens. Again, the heavy-moisture specimens showed reduced strength (33.9 MPa (4.91 ksi)). It was found, however, that the 20 heavy-moisture specimens given an extended gel time displayed increased shear strength (41.6 MPa (6.03 ksi)). This work is described in more detail in Appendix C.

Conclusions – It was concluded that small amounts of moisture have little effect on shear strength, but that heavy moisture has a significant effect. Also, shear strength can be improved by wiping off excess moisture and frost prior to the resumption of winding on parts taken from a freezer, or by subjecting the part to an extended gel time.

Effect of Epoxy Resin System on Transverse-Tensile Properties of Kevlar/Epoxy Composites

Procedures – Preliminary pressure-vessel data obtained by Hercules indicated that the EA953 epoxy resin system gave strengths at least 10% higher than those for the next best resin system. Part of the program was designed to determine why the EA953 system should give better performance than other systems. The following six resins were studied:

Epoxy resin (Hercules Inc. designations)	Modulus (MPa)	Modulus (ksi)
EA 953	830	120
HBRF 160	1050	153
9801	1150	167
EA 919	1720	250
HBRF 55A	2760	400
X507	3150	457

It was found that the resins 9801 and EA 919, which have intermediate moduli, gave the highest ultimate strengths (18.3 MPa (2.66 ksi) and 17.6 MPa (2.55 ksi) respectively). These compared with a value of 14.0 MPa (2.03 ksi) for the EA 953 system. The elongation of the EA 953 system was higher (1.95%) than either the 9801 system (0.564%) or the EA 919 system (0.595%), however. In addition, both high strength, 14.3 MPa (2.08 ksi), and high strain to rupture, (2.60%) were obtained for the HBRF 160 system. This work is described in more detail in Appendix D.

Conclusions – It was concluded that the transverse tensile tests give no indication as to why the EA 953 system should give better pressure vessel performance than some of the other resin systems studied.

Volumetric Shrinkage of Epoxy Resin Systems During Cure

In an attempt to understand the superior pressure vessel performance of the EA 953 epoxy systems, we obtained data for volumetric-shrinkage upon curing. We studied the Union Carbide ERL 2256/Uniroyal Tonox 6040 system plus the six epoxy-resin systems previously tested in transverse tension. Volumetric-shrinkage data was expected to give an indication of the residual stresses after cure. The two anhydride-cured systems, HBRF 160 and X507, were found to show less shrinkage (3.7% and 2.5%) than any of the amine-cured systems. Of the amine-cure systems, the EA953 system showed the least shrinkage (4.2%) while the ERL 2256/Tonox 6040 system and the HBRF 55A systems gave the most (5.0%). The shrinkage in the amine-cured systems correlated inversely with epoxide equivalent-weight. This work is described in more detail in Appendix E.

Conclusions – It was concluded that the shrinkage values alone could not give an adequate estimate of residual stresses without additional information on thermal expansion characteristics of the epoxy systems.

ACKNOWLEDGMENTS

Other contributors to this report were E. S. Jessop, L. S. Penn and R. J. Sherry. T. T. Chiao was the LLL Program Manager.

APPENDIX A

TENSILE PROPERTIES OF KEVLAR/EPOXY STRANDS

Preparation

Both partially used and full spools of 4560-denier Kevlar 49 (768 filaments per 1140-denier end) were obtained from Hercules Inc. In addition, one spool of single-end 1140-denier Kevlar 49 was specially obtained from duPont. The spools of Kevlar 49 were dried in a vacuum oven for 16 hours at a temperature of 70°C (158°F) and a pressure of 1.3 Pa (10^{-2} mm of mercury) to remove absorbed water. A minimum of three lengths from each spool were weighed to determine cross-sectional area. The strands were vacuum impregnated with Hercules HBRF 55A resin and wound on frames to cure. The cure cycle was two hours at 54°C (130°F) to gel, with two hours at 93°C (200°F) and four hours at 149°C (300°F) to cure.

Testing

A portion of the approximately 100 strands from each spool was weighed to determine the fiber volume percent. Others were bonded in clamps for tensile tests. The strands were tensile tested with a 25.4-cm (10-in.) gage length at a crosshead speed of 1 cm/min or a strain rate of 6.57×10^{-4}/s. The data were recorded on magnetic tape and computer processed.

Results and Discussion

The test results are given in Table 1. Figure 1 compares representative stress-strain curves. The spool numbers (1 to 3 and 6 to 9) were an arbitrary designation made at LLL. The lower breaking stresses of spools No. 1 and No. 2 (2010 MPa (291 ksi) and 2340 MPa (340 ksi) respectively) as compared to the strands from spool No. 3, a new spool of four-end roving (2750 MPa (399 ksi)), would indicate possible damage in handling. In fact, there was visual evidence of damage to the outer layers of spools No. 1 and No. 2. The later results from the more carefully handled partial spools No. 6 to No. 9 appear to confirm this conclusion. The mean breaking stress and strain for the 18 samples taken from spools No. 1 and No. 2 were 2180 MPa (316 ksi) and 1.98%, while the means of the 91 samples taken from spools No. 3 and No. 6 to No. 9 were 2780 MPa (403 ksi) and 2.42% strain. The higher breaking stress and breaking strain of the single-end 1140 denier strands (3180 MPa (461 ksi) and 2.53%) are to be expected due to the absence of the uneven tension applied during the combining process used in making the four-end roving.

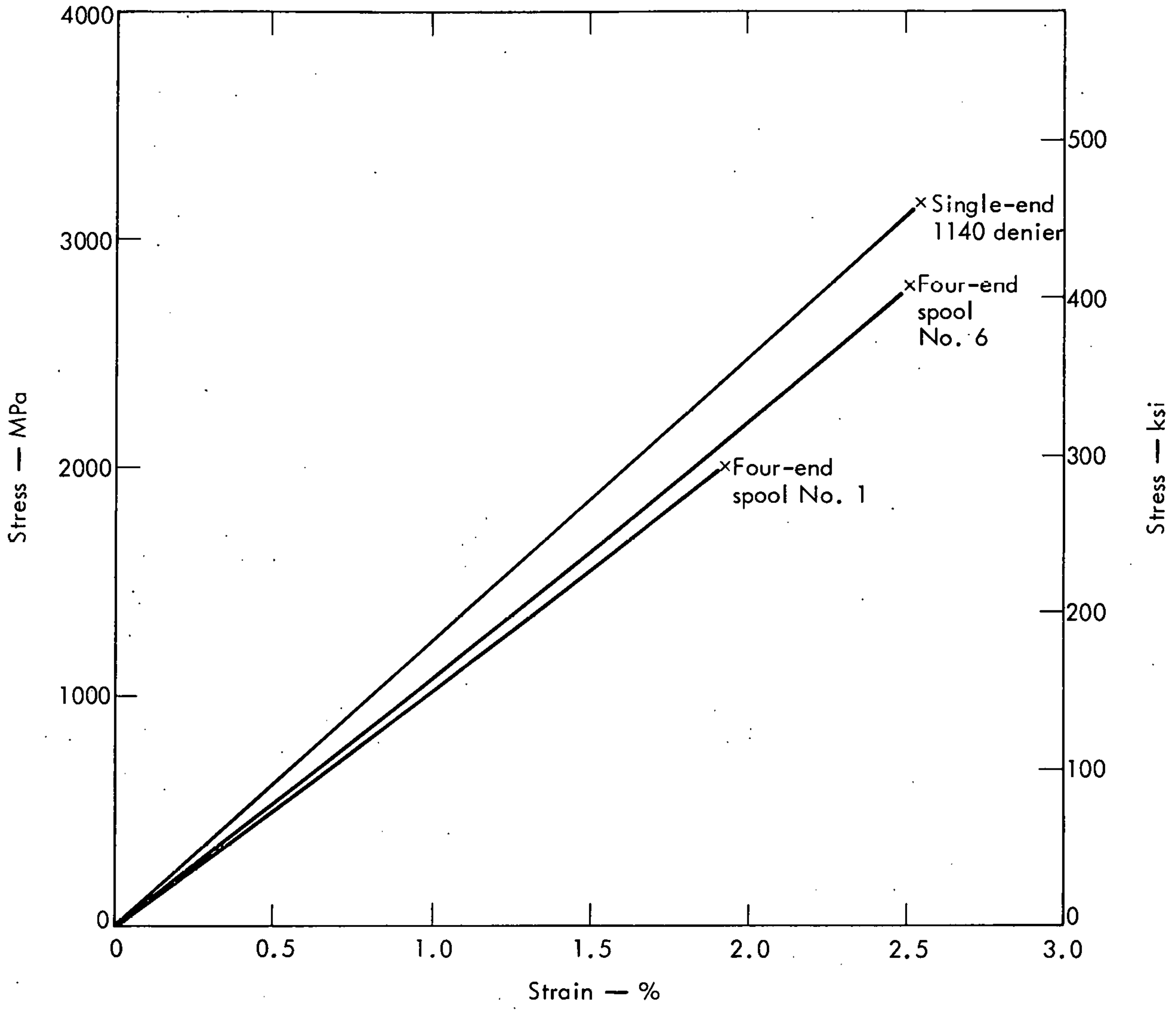

Fig. 1. Representative stress-strain curves of Kevlar 49/epoxy strands.

Table 1. Tensile properties of Kevlar 49/epoxy strands.

Sample	Breaking stress (MPa)	Breaking stress (ksi)	Breaking stress CV (%)	Breaking strain (%)	Breaking strain CV (%)	Fiber vol. (%)	No. of specimens tested
Four-end spool No. 1	2010	291	6.1	1.91	6.4	69.4	9
Four-end spool No. 2	2340	340	5.8	2.06	4.5	68.2	9
Four-end spool No. 3	2750	399	6.4	2.22	6.4	65.5	19
Four-end spool No. 6	2800	406	7.4	2.49	7.4	55.5	18
Four-end spool No. 7	2570	373	11.1	2.20	11.5	62.3	18
Four-end spool No. 8	2870	416	8.8	2.66	9.5	59.2	17
Four-end spool No. 9	2900	420	8.9	2.51	8.0	53.7	19
Single-end 1140 denier (from duPont)	3180	461	5.6	2.53	5.9	66.7	20

Note: 1. Spools No. 1 and 2, and No. 6 to 9 are four-end rovings from spent spools provided by Hercules. Spool No. 3 was a full spool provided by Hercules.

2. CV = Coefficient of Variation.

Conclusions

- Rough handling (as evidenced by dirt and fraying of the spool) lowers roving strength.
- Uneven tension during the combining process lowers the strength of four-end roving.

APPENDIX B

EFFECT OF MOISTURE DURING WINDING ON ELONGATED-RING TENSILE PROPERTIES OF LAMINATED KEVLAR/GRAPHITE/EPOXY COMPOSITES

Preparation

The elongated rings were wound using four different conditions: no moisture (for control specimens), light moisture, heavy moisture, and heavy moisture with an extended gel time. All rings were wound with the same amount of fiber. One layer of Hercules ASMS graphite (four turns) was wound between two layers of Kevlar 49 four-end fiber (4560 denier) from spool No. 3 (six turns each layer). All rings were nominally 0.635 cm (0.25 in.) wide and 0.152 cm (0.060 in.) thick and had a 14.605 cm (5.75 in.) inside radius with a 5.09 cm (2.00 in.) straight section. The control specimens were wound with no moisture. The light-moisture specimens were wound and placed in a -18°C (0°F) freezer for about two hours between layers. The frost and moisture were lightly wiped off before winding the next layer. The heavy-moisture specimens were prepared in the same way except that the frost and moisture were not wiped off. The Kevlar was impregnated with Hercules 55A resin and the graphite was impregnated with Fiberite X507 resin. The cure cycle was two hours at 54°C (130°F) to gel, with two hours at 93°C (200°F) and four hours at 149°C (300°F) to cure. The specimens receiving an extended gel were gelled for 18 hours at 54°C (130°F).

Testing

The rings were tensile tested at a crosshead speed of 0.2 cm/min on split "D" fixtures lubricated with MoS_2 powder. The data were recorded on magnetic tape and computer processed.

Results and Discussions

The results of the elongated-ring tests are given in Table 2. The accumulation of a small amount of moisture between the fiber layers seemed to have very little effect on the tensile properties of the material as evidenced by the composite rupture-stress of the control specimens (1200 MPa (174 ksi)) and the composite rupture-stress of the light-moisture specimens (1170 MPa (170 ksi)). The composite rupture-stress for the heavy-moisture specimens, however, was quite a bit lower (1080 MPa (156 ksi)), and was found to be even lower for heavy-moisture specimens that had an extended gel time (970 MPa (141 ksi)).

Table 2. Ring composite tensile data.

Specimen moisture-exposure	Breaking stress (MPa)	Breaking stress (ksi)	Breaking stress CV (%)	Breaking strain (%)	Breaking strain CV (%)	No. of specimens tested
Control (no moisture)	1200	174	8.8	1.63	5.9	5
Light moisture	1170	170	4.9	1.68	2.5	5
Heavy moisture	1080	156	4.3	1.63	6.0	5
Heavy moisture. Extended gel time (18 hours at 54°C (130°F))	970	141	8.5	1.62	3.0	4

CV = Coefficient of Variation.

Conclusions

- Light moisture between layers has little effect on tensile strength.
- Heavy moisture significantly reduces shear strength.
- Heavy moisture and frost should be wiped off before winding on parts fresh from the freezer (i. e. before resumption of winding).

APPENDIX C

EFFECT OF MOISTURE DURING WINDING ON ELONGATED-RING INTERLAMINAR-SHEAR (ILS) PROPERTIES OF LAMINATED KEVLAR 49/GRAPHITE/EPOXY COMPOSITES

Preparation

Specimens were wound in the same manner as the ring tensile specimens except for an increase in thickness to a nominal 0.318 cm (0.125 in.). The layers of Kevlar 49 had 11 turns and the graphite layers had 8. The specimens were sanded flat before removal from the winding molds and cut to a nominal 1.90 cm (0.75 in.) length with a water-cooled friction cut-off saw. Both curved and straight sections were used. The cured specimens were vacuum dried overnight at a temperature of 49°C (120°F) and a pressure of 1.3 Pa (10^{-2} mm of mercury) to remove water that was absorbed during cutting. The specimens were then conditioned for 24 hours in the test laboratory which is temperature controlled at 24°C (75°F) and 50% relative humidity.

Testing

The specimens were tested with a cross-head speed of 0.1 cm/min and a span of 1.27 cm (0.50 in.) between 0.64 cm (0.25 in.) diameter steel rods (ASTM D2344). The test data were recorded on a strip-chart recorder and the maximum load from each test was used to calculate the shear stress.

Results and Discussion

The results of the ILS specimen tests are given in Table 3. The accumulation of a small amount of moisture seemed to have no effect on the interlaminar-shear stress, judging from the value of 44.7 MPa (6.48 ksi) for the control specimens and 46.3 MPa (6.71 ksi) for the light-moisture specimens. Like the tensile-breaking stress, the shear stress for the heavy-moisture specimens was reduced to 33.9 MPa (4.91 ksi). However, unlike the result for the tensile rings, the shear stress for the heavy-moisture specimens with an extended gel time increased to 41.6 MPa (6.03 ksi).

Conclusions

- Light moisture between layers has little effect on shear strength.
- Heavy moisture significantly reduces shear strength.
- Filament-wound shapes that must be stored in a freezer before winding is complete can be protected against reduced shear strength by wiping off excess moisture before resumption of winding, or by an extended gel cycle that allows evaporation of excess moisture before cure.

Table 3. Interlaminar-shear properties of laminated (Kevlar/graphite/epoxy) composites.

Condition	Shear strength (MPa)	(ksi)	CV (%)	No. of specimens tested
Control (no moisture)	44.7	6.48	7.6	20
Light moisture	46.3	6.71	3.2	20
Heavy moisture	33.9	4.91	7.2	20
Heavy moisture (16 hours extra gel-time at 54°C (130°F))	41.6	6.03	8.8	20

CV = Coefficient of Variation.

APPENDIX D

EFFECT OF EPOXY RESIN SYSTEM ON TRANSVERSE TENSILE PROPERTIES OF KEVLAR/EPOXY COMPOSITES

Preparation

Unidirectional laminates were wound on flat aluminum plates using Kevlar 49 four-end roving, spool No. 3. The fiber was vacuum impregnated with an excess of the epoxy resin and wound with a tension of 8.90 N (2 lbs). The laminates were cured between polished-aluminum plates that were shimmed to 0.203 cm (0.080 in.). The amount of fiber was calculated to give an 8-layer laminate with a fiber content of 65% by volume. The laminates were cured in a press having heated platens. Minimum pressure was used to assure contact and to squeeze out the excess resin. The cure cycle was two hours at 54°C (130°F) to gel, and then two hours at 93°C (200°F) and four hours at 149°C (300°F) to cure. The same cure cycle was used for each of the resin systems except for a slight difference in the time to gel for each system. The test specimens were cut to dimensions of 2.54 cm (1 in.) wide by a nominal 14 cm (5.5 in.) long on a water-cooled friction saw. The specimens were then dried overnight in a vacuum oven at a pressure of about 1.3 Pa (10^{-2} mm of mercury) and a temperature of 60°C (140°F), after which they were left to stabilize in the test area at 24°C (75°F) and 50% relative humidity for several days. Strain gages were bonded to two specimens from each of the resin systems. The gages were bonded on both sides of a specimen transverse to the fiber direction and on one side of the specimen axial to the fiber direction.

Testing

The specimens were tested in tension transverse to the fiber direction in accordance with ASTM D3039-T71, at a crosshead speed of 0.05 cm/min or a strain rate (relative to the 3.81 cm (1.5 in.) gage length between the grips) of 2.17×10^{-4}/s (1.3%/min). The specimens were tested without bonded end-tabs, and any specimens that failed near the grips were not included in the data. Specimens that did not have bonded gages were tested using a clip-on type extensometer.

Data Reduction

All data were recorded on incremental magnetic tape for computer reduction. Data both from samples having bonded gauges and from samples having clip gauges were combined in the calculation of maximum stress and strain-to-rupture. The transverse elastic-modulus (E_{22}) and Poisson's ratio (ν_{21}) data were taken from the bonded strain-gage samples only.

It is interesting to note that the elastic properties of the resins are not totally reflected in the composite materials. The 9801 system appears to produce a composite modulus disproportionately high with respect to that of the 9801 resin modulus itself, which is surprising in light of the system's reduced strain-to-rupture. It is possible, however, that the 9801 system produces a well-bonded composite which, nevertheless, contains quite a number of flaws. The good bonding would produce a high modulus but the flaws might produce a reduction in ultimate properties.

Conclusions

The transverse-tensile results indicate no reason for the outstanding properties of the EA 953 system as a pressure-vessel material. On the contrary, it would appear from this work that the 9801 or EA 919 systems should give the best combination of high maximum stress, moderate strain-to-rupture, and reasonable elastic modulus of any of the systems studied.

Results and Discussion

Table 4 shows the averaged data for the six resin systems studied. The stress-strain curves for the six resins (taken from the bonded-gage samples) are compared in Fig. 2. It may be noted that because of the difficulties intrinsic to the use of clip gages, the bonded-gage data should produce the better representation of the stress-strain curves at low strains, although both sets of data are found to be comparable at higher strains. The coefficient of variation (CV) demonstrates that there is considerable spread in the test data, particularly for maximum stress and for strain-to-rupture. Samples with obvious flaws have been eliminated from this data, so such a data spread apparently represents something more basic than simply the occurrence of defective samples. However, it is important to note that the transverse-tensile test is an extremely severe test, and small variables such as misalignment, minor flaws, voids, edge effects, etc. will tend to significantly alter the ultimate properties of the material.

From the data of Table 4 there seems to be no apparent reason why the EA 953 system should show outstanding performance as a pressure-vessel material. The 9801 system, to which it has been compared for pressure vessel performance, shows a significantly greater maximum stress (18.3 MPa (2.66 ksi)) than that of the EA 953 system (13.9 MPa (2.02 ksi)). Contrary to the base-resin results (where the resins are comparable), the 9801 system ($\epsilon_r = 0.56\%$) shows about one-third the strain-to-rupture of the EA 953 system ($\epsilon_r = 1.95\%$). This factor, however, would not be expected to control failure properties (particularly in light of the higher maximum stress of the 9801 system) since the strain-to-rupture would still appear to be adequate. The HBRF 160 resin system displays a maximum stress (14.3 MPa (2.08 ksi)) comparable to that of the EA 953 system and an even greater strain-to-rupture (2.60%) in addition to a higher modulus. Thus, even if the strain-to-rupture of the EA 953 system is the controlling variable in pressure-vessel performance, the HBRF 160 system would be expected to give even better properties when transverse properties are important.

The data of Table 4 indicate that the resin systems 9801 and EA 919 provide the best combination of properties, since these materials have the highest maximum stresses (18.3 MPa (2.66 ksi) and 17.6 MPa (2.55 ksi) respectively); moderate strain-to-rupture (0.56% and 0.60% respectively); and reasonable elastic-modulus values (4010 MPa (581 ksi) and 3720 MPa (540 ksi) respectively). The higher-modulus HBRF 55A and X507 systems (E = 5050 MPa (732 ksi) and 5430 MPa (787 ksi)) have the poorest maximum stress values (8.69 MPa (1.26 ksi) and 12.5 MPa (1.82 ksi) respectively) due to their reduced strain-to-rupture values of 0.20% and 0.29% respectively. The EA 953 and HBRF 160 systems have lower moduli (2130 MPa (309 ksi) and 2630 MPa (382 ksi) respectively) and lower maximum stresses (14.0 MPa (2.03 ksi) and 14.3 MPa (2.08 ksi) respectively) although they display high strains-to-rupture (1.95% and 2.60%).

Table 4. Transverse-tensile properties of Kevlar 49/epoxy composites.

			Bonded-gage and clip-gage tests						Bonded-gage tests					
Material (Hercules designation)	Resin modulus		Maximum stress			Strain to rupture		No. of specimens tested	Transverse modulus (ϵ = 0.05%)			Poisson's ratio ν_{21} (ϵ = 0.05%)		No. of specimen tested
	(MPa)	(ksi)	(MPa)	(ksi)	CV (%)	(%)	CV (%)		(MPa)	(ksi)	CV (%)		CV (%)	
EA 953	830	120	14.0	2.03	9.8	1.95	44.6	11	2130	309	9.8	0.0177	17.9	2
HBRF 160	1050	153	14.3	2.08	8.5	2.60	31.8	5	2630	382	4.3	0.0158	3.5	2
9801	1150	167	18.3	2.66	14.2	0.564	11.4	9	4010	581	14.2	0.0172	27.8	2
EA 919	1720	250	17.6	2.55	8.7	0.595	13.8	12	3720	540	5.7	0.0226	6.7	2
HBRF 55A	2760	400	8.7	1.26	35.5	0.200	30.6	9	5050	732	1.1	0.0226	11.9	2
X507	3150	457	12.5	1.82	27.3	0.286	20.0	10	5430	787	1.6	0.0262	4.9	2

CV = Coefficient of Variation.

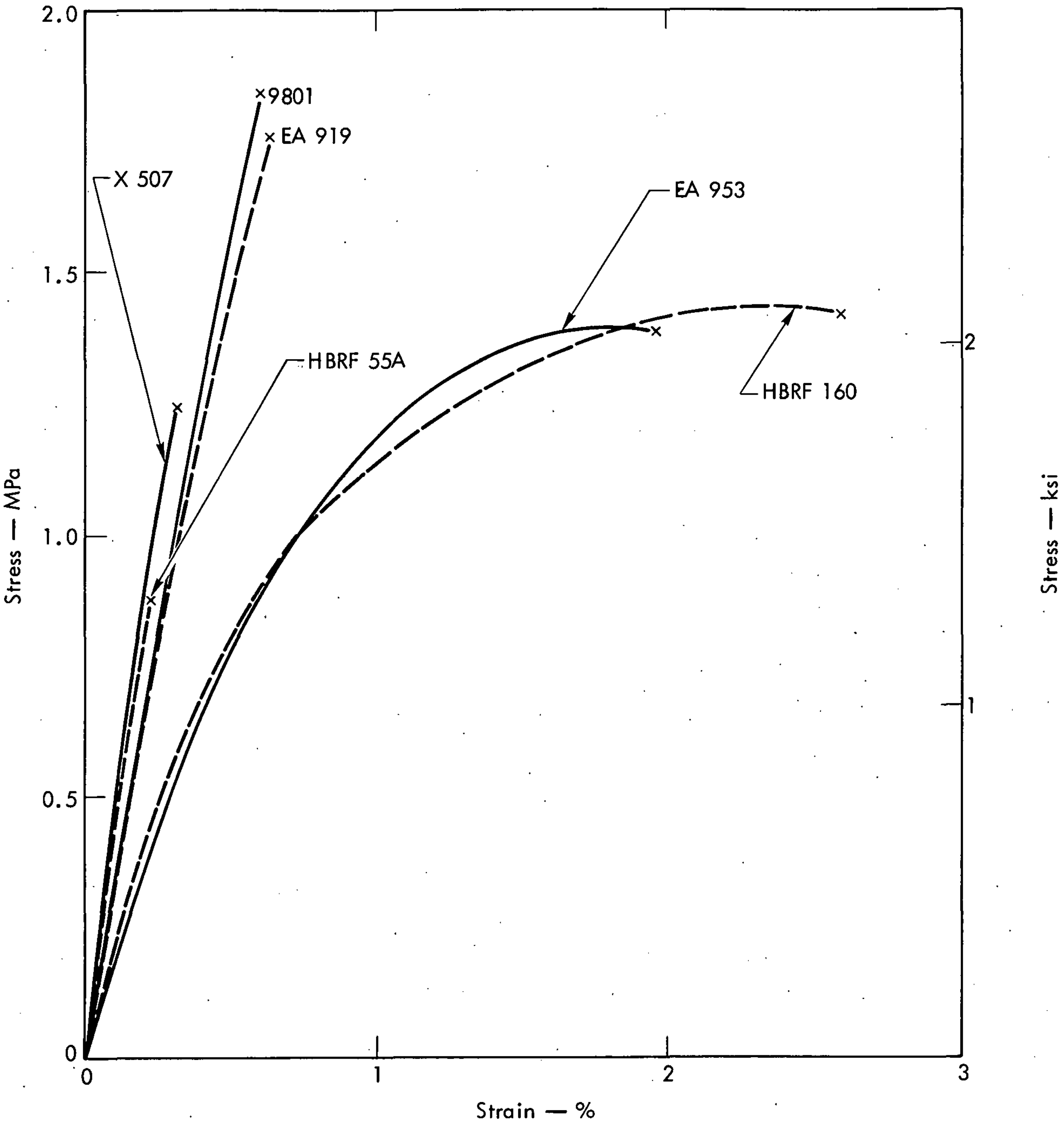

Fig. 2. Comparison of transverse tensile stress-strain curves for six Kevlar 49/epoxy systems.

APPENDIX E

VOLUMETRIC SHRINKAGE OF EPOXY RESIN SYSTEMS DURING CURE

Introduction

Seven different epoxy resin systems were evaluated for volumetric shrinkage as a result of the curing process. The systems were Union Carbide ERL 2256/Uniroyal Tonox 6040, and the following epoxy systems designated by Hercules Incorporated: EA 953, EA 919, X507, HBRF 55A, and HBRF 160.

Preparation

The resins to be tested were mixed for 15 minutes in a Hobart mixer. The mixed resins were then deaereated at a pressure of 666 Pa (5 mm of mercury). Specimens were prepared by pouring 10 g of each liquid resin into 30-ml-Nalgene beakers treated with Garan-225 mold release. The mold release was baked on for 1 hour at 150°C (302°F) prior to filling with resin. The specimens were then placed an oven and run through the various cure cycles listed in Table 5. Specimens were removed from the oven for each test in the cure cycle and cooled to 23°C (73°F).

Testing

Specimens in the liquid state were tested in accordance with ASTM D-1963-61 (pycnometer method). The specific volume of the liquid specimens was determined at 23°C (73°F) ± 0.5°C. The specific volume of solid specimens was determined in accordance with ASTM D 792 (weight in water vs weight in air). The measurements were made at 23°C (73°F) ± 0.5°C.

Results and Discussion

The volume shrinkages shown in Table 5 reflect the relationship, at room temperature, between the resin uncured volume and its volume after the specified portion of the curing cycle. The anhydride-cured systems X507 and HBRF 160 exhibit less shrinkage than the amine-cured systems when cured as indicated in Table 5. It is possible that the cure cycle in the case of the anhydride systems was not sufficient for complete cure. If this were so it would be one possible explanation for the low shrinkage. Shrinkage in the amine-cured systems tested here appears to vary directly with the decreasing epoxide equivalent weight of the epoxy resin. Figure 3 shows this result graphically for the final shrinkage values. To a first approximation, this would seem to indicate that the shrinkage, inversely related to the epoxy equivalent weight, reflects the cross-linking density.

Table 5. Volumetric shrinkage data for several epoxy systems at various stages of cure.

Resin system (Hercules designations except as noted)	Epoxide equivalent weight	Stage 1				Stage 2				Stage 3			
		Time (h)	Temp (°C)	Temp (°F)	Shrinkage (%[a])	Time (h)	Temp (°C)	Temp (°F)	Shrinkage (%)	Time (h)	Temp (°C)	Temp (°F)	Shrinkage (%)
ERL 2256[d]/Tonox 6040[e]	140	–	–	–	–	2	93	200	4.9	3	149	300	5.0
HBRF 55A[b]	136	6	49	120	5.2	2	93	200	5.0	4	149	300	5.0
9801	235	2	66	150	1.4	2	121	250	4.7	1	149	300	4.8
EA 919	261	–	–	–	–	2	121	250	4.3	1	149	300	4.5
EA 953	332	–	–	–	–	2	121	250	4.2	1	149	300	4.2
HBRF 160	332	6	49	120	0.6[c]	2	93	200	2.9	4	149	300	3.7
X507[b]	188	2	66	150	0.6[c]	1.5	93	200	3.0	4	149	300	2.5

Notes:

Two specimens were used for each test-data point. Six to eight specimens were used for each resin-system.

[a] The coefficient of variation is 3.2% or less.

[b] Four specimens were run; 16 specimens were run for each resin system.

[c] Liquid at this stage.

[d] Union Carbide.

[e] Uniroyal.

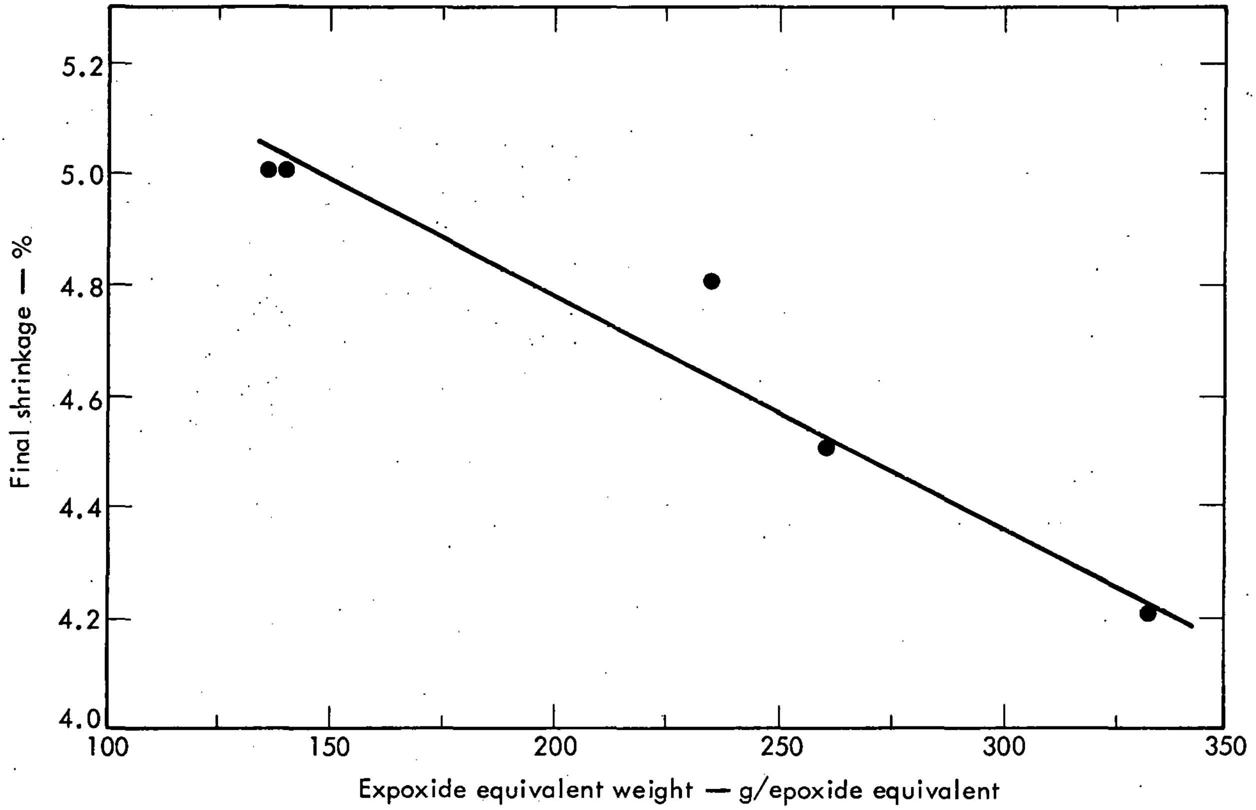

Fig. 3. Final shrinkage vs epoxide equivalent weight for amine-cured systems.

The following points can be made about the seven resin systems of Table 5:

- Anhydride-cured X507 and HBRF 160 exhibit lower shrinkage than the amine-cured systems.
- Of the amine-cured systems, HBRF 55A and ERL 2256/Tonox 6040 shrink more than EA 953, EA 919, or 9801.

It may be observed that in order to predict the level of thermal stress, the thermal expansion characteristics as well as the shrinkage properties must be known. Cure cycles could then be selected to minimize the thermal stresses. Thus, the maximum shrinkage undergone by a resin anywhere in the cure cycle could be known. This could range from some high temperature where thermal expansion may be larger, to room temperature where there is net shrinkage.
there is net shrinkage.

Conclusions

The shrinkage is tabulated for seven epoxy systems at various points in their cure cycles. The shrinkage varied from 2.5% for anhydride-cured systems to 5% for amine-cured systems. For the latter the shrinkage was correlated to epoxide equivalent weight. Further conclusions are not drawn for lack of complete data.

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