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COUPLING AGENTS - HME RESIN SYSTEM

L. G. Adams and R. E. Hoffman

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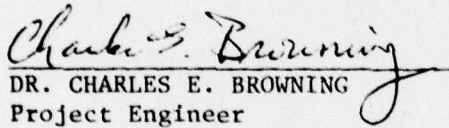
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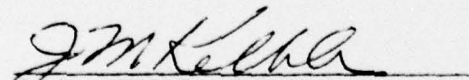
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This Technical Report has been reviewed and is approved.


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Second, attempts were made to reinforce the HME resin with three finely divided fillers: Vulcan 9A32 carbon black, HiSil 233 hydrated silica, and HR-600 polyimide resin. However, these fillers severely degraded composite strengths.

Low profile modifiers, developed to reduce cure shrinkage in polyester resins, were evaluated for this purpose in the HME resin system but were found to be incompatible.

It is unlikely that all of the many approaches to form primary chemical bonds between the HME matrix and graphite fiber failed, yet no significant improvement in SBS was achieved over untreated fiber during this program. The possibility that a low cohesive strength in the HME matrix was the problem was briefly explored using fillers, also without success. Formulary variations (under Contract No. F33615-760C-5169), coupling agents, and fillers all failed to affect SBS strength which indicates that the HME/graphite laminate properties cannot be easily improved.

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FOREWORD

This report documents a 4-month study authorized by Contract F33615-77-C-5124. The work was accomplished at Hercules Incorporated, Bacchus Works, Magna, Utah.

Preparation of this report is authorized under data item 002, Sequence No. 3 of the data requirements list in the contract. The contract was issued to Hercules by the Air Force Material Laboratory, Air Force Systems Command, Aeronautical Systems Division, United States Air Force, Wright Patterson AFB, Ohio. The Air Force Project officer for this work was Dr. C. E. Browning.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
I	OBJECTIVE	1
II	SUMMARY AND CONCLUSIONS	1
III	INTRODUCTION	2
IV	RESULTS AND DISCUSSION	3
	1. Fiber Treatment and Composite Evaluation	3
	2. End Capped PB Sizing	3
	3. Direct Reaction of Epoxides	6
	4. Titanate Coupling Agents	6
	5. Reinforcing Fillers	9
	6. Low Profile-Shrink Reducing Additives	9
V	CONCLUSIONS	10
	BIBLIOGRAPHY	11

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SECTION I

OBJECTIVE

The overall objective of this program was to develop a system of coupling agents to improve the matrix-to-fiber bond between Hystyl Modified Epoxy (HME) resin systems and graphite AS fiber. The goal of the program was to increase short beam shear (SBS) strengths of graphite laminates to 15 ksi and 90° strain values to 0.5 percent with the HME matrix.

SECTION II

SUMMARY AND CONCLUSIONS

Two approaches were taken to improve the SBS strength of HME/AS composites. First, attempts were made to react a number of organo-titanates, epoxides, and modified polybutadiene (PB) epoxides with reactive sites on the graphite fiber surface and then to react, or couple, with the matrix HME resin. Epon 834 (a bisphenol A type epoxy resin), allylglycidyl ether, and a reaction product of C-1000 PB and ERE-1359 epoxy resin produced very slight increases in SBS strengths of HME composites when used as AS fiber sizing. Second, attempts were made to reinforce the HME resin with three finely divided fillers: Vulcan 9A32 carbon black, HiSil 233 hydrated silica, and HR-600 polyimide resin. However, these fillers severely degraded composite strengths.

Low profile modifiers, developed to reduce cure shrinkage in polyester resins, were evaluated for this purpose in the HME resin system but were found to be incompatible.

It is unlikely that all of the many approaches to form primary chemical bonds between the HME matrix and graphite fiber failed, yet no significant improvement in SBS was achieved over untreated fiber during this program. Formulary variations, coupling agents, and fillers all failed to affect SBS strength which indicates that the HME/graphite laminate properties cannot be easily improved.

SECTION III

INTRODUCTION

The Man-Tech division of Wright Patterson Air Force Base contracted with Hercules Incorporated and Northrop Corporation for: (1) The conversion of HME resin system from a solvent-based to a hot-melt system and (2) the development of a graphite prepreg system based on HME resins.

The new HME resin system has several advantages over current epoxy systems: (1) Very low cost, (2) extended tack life, (3) low density, and (4) low-flow low-pressure cure capabilities. One disadvantage of the HME resin became evident when laminates were tested. The HME- or PB-based resin system does not bond to graphite fibers as well as epoxy resin systems. This is evidenced by considerably lower mechanical properties in laminates such as SBS strengths (9 to 10 ksi for HME (PB) systems versus 15 to 18 ksi for epoxy systems) and in scanning electron microscope (SEM) photographs which show practically no adhesion between resin and fiber in failed laminates.

In order to develop the full potential of the HME resin systems, the interfacial bond between resin and fiber must be improved. The bond appears to be mostly mechanical locking. Adhesive bonding may not develop because of insufficient reaction functionality between fiber surface and matrix resin. Adhesive bond, on the other hand, may develop, but debonding may occur from resin matrix cure shrinkage or from very dissimilar thermal expansion characteristics between fiber and matrix. Attempts were made to overcome these deficiencies by developing a chemical bonding interface at the fiber surface and to reduce matrix shrinkage by the use of fillers in the resin.

SECTION IV

RESULTS AND DISCUSSION

The technical approach of this program was primarily to improve the matrix/fiber bond between HME resin and AS graphite fiber by sizing the fiber with compounds which would chemically react with fiber through its surface carboxyl or phenolic hydroxyl groups, and with the matrix through terminal epoxy or chain vinyl groups acting as a coupling agent.

Secondary approaches were made as work progressed. The first approach was to reinforce the PB with fillers, as is done with vulcanized butadiene rubber products, such as carbon black and silica flour. The second was to reduce cure shrinkage of the HME system with "low profile" additives of vinyl esters or acrylate resins, as are used in polyester resins for this purpose. These modifications were made in consideration for the high cure shrinkage that occurs in the HME resin system and which could be a prime cause of no bond or, more precisely, bond destruction between fiber and matrix.

1. FIBER TREATMENT AND COMPOSITE EVALUATION

Hercules graphite AS-1 fiber from Lot 78-1 was selected for the bulk of this work. Lot 78-1 was as typical standard product. The final evaluation of coupling agents, or HME resin modification, was 1-1/2 inch wide prepreg tape converted to graphite/HME composite panels. Tape manufacturing required nine fiber tows so that each surface treatment, or sizing, was done on nine tows simultaneously.

The general procedure for sizing evaluation is described. The selected sizing material was dissolved in an appropriate solvent, usually methylene chloride or alcohol/methylethyl ketone. Sizing pick-up was approximately the same level as solution concentration. Fiber tow was passed through an impregnator containing the sizing solution then over a heated drum at 300° F, to flash off the solvent, and then to a respooling takeup. The spooled tow was further treated, if required for the particular sizing, such as being placed in a 120° F hot room or 250° F oven, or stored at ambient room temperature. The treated fiber was then impregnated with HME 5803-53 resin at approximately 28 percent by weight resin on the 3-inch hot-melt tape line and the HME resin prepreg staged at 120° F for 16 to 24 hours. The prepreg was then laminated and vacuum cured to produce 1-1/2 inch by 10 inch test panels. Specimens from each panel were cut and tested in SBS and in flexure. The HME 5803-53 resin system formulations are shown in Table 1.

2. END CAPPED PB SIZING

Hystyl C-1000 carboxy terminated PB should be the most compatible coupling agent for the HME resin system. The HME resin is normally carboxy terminated so that it would not react with the fiber surface. The Hystyl

C-1000 resin was reacted with stoichiometric amounts of diepoxides, with suitable catalyst, to yield completely epoxy terminated adducts. In the presence of the epoxy/carboxy catalyst, AMC-2 chrome complex, the adduct was expected to be reacted with the fiber surface.

TABLE 1. HME RESIN SYSTEMS

A. <u>5803-50 Adduct</u>	<u>Parts by Weight</u>
C-1000 PB	100
CY-179 Epoxy	25.64
AMC-2 Catalyst	0.15
B. <u>5803-53 Final Composition</u>	
5803-50 Adduct	100
C-1000 PB	48.15
Lupersol 101 Peroxide	6.50
C. <u>5803-53 Non-Adducted</u>	
C-1000 PB	100
CY-179 Epoxy	15.97
AMC-2 Catalyst	0.09
Lupersol 101 Peroxide	5.09

Adducts were used to size AS fiber in two formulations. (Refer to Table 1 for HME 5803-50 resin.) Peroxide initiator was added in the one formulation so that during matrix curing, the matrix/sizing interface would not be deficient in initiator. The second formulation omitted the peroxide with the expectation of leaving a "soft" (flexible) and partially unreacted boundary layer.

Adducts containing the peroxide were heated only enough to remove solvent during fiber sizing so that peroxide curing was not initiated at this point. The soft size formulation was treated similarly and portions

of the sized fiber were also oven heated with the intent of forcing adduct epoxy to complete reaction with fiber carboxy. Sizing composition and test results of the sized fiber impregnated with HME 5803-53 resin and laminated are shown in Table 2. The slightly improved SBS strength of formulation 25-3 over baseline control values is not significant.

TABLE 2. SIZING COMPOSITION AND TEST RESULTS
END CAPPED POLYBUTADIENE SIZING

Components Wt. %	Formulation Number					Control
	23-6	23-7	23-8	25-2	25-3	
C-1000	70.58	70.58	69.60	50.09	75.14	
ERE-1359	21.23	21.23	20.93	15.07	22.56	
AGE	--	--	--	33.33	--	None
AMC-2	0.71	0.71	2.09	1.51	2.26	
Lupersol 101	7.48	7.48	7.38	--	--	
A-Adduct			A	A	A	N/A
B-Mixed	B	B				N/A
Solution, %	0.5	2.0	0.5	2.25	1.2	--
Extractable Wt, %	0.89	2.24	0.68	1.36	1.48	--
Reaction Time Hours	64	64	1	1	1	--
Temperature, °C	55	55	55	125	125	--
SBS, ksi	9.99	9.60	8.96	9.51	11.40	9.91
Flexural Strength ksi	215	205	204	184	189	206

3. DIRECT REACTION OF EPOXIDES

Alternatives to HME end capped sizings were certain monoepoxides and low molecular weight diepoxy resins. Allyl glycidyl ether (AGE) was selected as the monoepoxide because, in addition to its small molecular size, it possessed an unsaturated carbon-carbon bond which was amenable to cross-linking with HME resin. Epon 834 and CY-179 epoxy, the latter being an HME resin component, were selected for diepoxides. Reaction of all the epoxies with fiber carboxy was catalyzed with AMC-2. The diepoxides might be expected to yield a minimal coupling to the HME resin through the few carboxy terminations in the resin. Primarily, these epoxies would produce a "soft" or lubricating size with mechanical entanglement in the HME resin along with some chemical bonding. Elevated temperatures were used to improve the size coupling to the graphite fiber.

The results of direct epoxy reaction with AS fiber is shown in Table 3. Again, laminates fabricated with the sized fiber and HME 5803-53 resin show little improvement over control laminates. The reaction between the epoxies and fiber surface evidently requires elevated temperature to proceed even in the presence of an epoxy/carboxy reaction catalyst. Formulation 26-2, AGE/AMC-2 reacted at 50° C, showed no improvement in SBS strength over controls while 26-1, the same AGE/AMC-2 run but reacted at 125° C, showed a slight improvement. A mixture of Epon 834/AMC-2 reacted at 50° C showed an equivalent improvement to AGE at 125° C.

4. TITANATE COUPLING AGENTS

Organo-titanate coupling agents evaluated were of two types. Kenrich Petrochemical TTAC-139BS and GTDM-133S (Figure 1) were expected to react with carboxyl or hydroxyl groups of the graphite fiber surface through the isopropoxy and oxyacetate ends, respectively, and then to couple with the HME resin through the unsaturated triacrylate and dimethacrylate ends. DuPont Tyzor AA and Tyzor TPT, structurally depicted in Figure 1, are both tetrafunctional in reaction with carboxy and hydroxy groups on the fiber surface or with carboxy end groups on the HME matrix.

Titanium (titanate) analyses were made on treated fiber by washing a known amount of fiber with 1:1 dilute hydrochloric acid, precipitating the titanium with Cupferron and filtering the precipitate. The titanium level in the weighed precipitate was then compared to known standards by X-ray fluorescence.

The reaction of the titanates with the fiber surface appeared to proceed rapidly from methylene chloride solution but very slowly from alcohol/methyl-ethyl ketone solution. The extent of the titanates reaction with the fiber surfaces was uncertain.

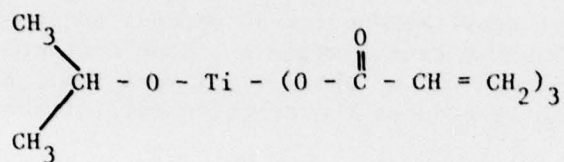
Titanium pick-up on AS fiber, analyzed as described above, was determined after the fiber had been immersed in a 0.02 percent solution of Tyzor AA in methylene chloride for 30 seconds and then immediately washed

in methylene chloride to remove unreacted titanate. Titanium level was 0.016 percent by weight. Fiber treated in a 0.05 percent solution of Tyzor AA in ethyl alcohol/methyl ethyl ketone for 30 seconds and then solvent-washed yielded only 1.5 ppm titanium while a 1 hour contact time yielded 49.6 ppm (about 0.005 percent by weight), still very low. Ethyl alcohol/methyl ethyl ketone greatly reduces the reaction rate of the titanates.

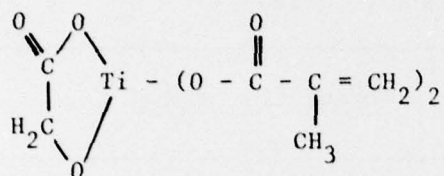
TABLE 3. SIZING COMPOSITION AND TEST RESULTS
DIRECT EPOXY/FIBER COUPLING

Components, Wt. %	Formulation Number				
	26-1	26-2	26-3	27-1	28-4
AGE	90.91	90.91	--	45.45	--
CY-179	--	--	90.91	--	--
Epon 834	--	--	--	45.45	90.91
AMC-2	9.09	9.09	9.09	9.09	9.09
Solution, %	0.25	0.25	0.30	0.30	0.33
Extractable Wt. %	0.04	--	0.11	0.19	0.35
Reaction Time, Hours	1	16	1	>72	3
SBS, ksi	10.20	8.60	8.90	9.51	10.20
Flexural Strength, ksi	207	203	189	190	197

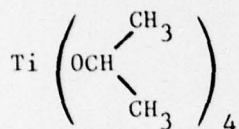
Fiber surfaces treated from titanate solutions but not followed by a washing step showed much higher levels of titanium as would be expected. Titanates which were allowed to air dry were no longer solvent soluble probably due to hydrolysis to TiO_2 or to polymeric titanates. These high titanium levels were not effective as surface treatments.



Titanium isopropoxy triacrylate TTAC-39S

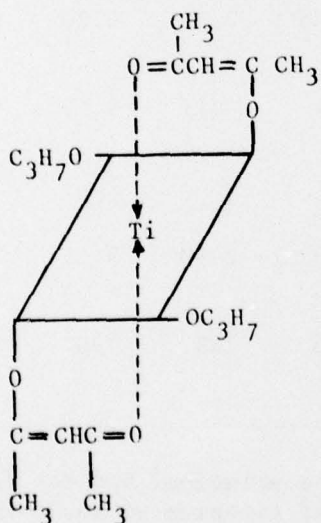


Titanium dimethacrylate oxyacetate GTDM-133S



Tetraisopropyl titanate

Tyzor[®] TPT



Titanium acetyl acetonate Tyzor[®] AA

Figure 1. Titanium Coupling Agents

There appeared to be very little difference in titanium, or titanate, pick-up between the Kenrich and DuPont titanates if a wash bath immediately followed sizing. Tyzor TPT yielded higher titanium levels on the fiber from the same solution level, (0.009 percent by weight titanium with Tyzor AA versus 0.021 percent by weight with Tyzor TPT) but showed no improvements in SBS strengths in final laminates. None of the titanates, or titanate levels, showed any improvement in SBS over untreated fiber.

5. REINFORCING FILLERS

One of the detrimental properties of the HME resin system is its high cure shrinkage. This could cause matrix/fiber debonding if an initial bond was present. Another property is the inherent brittleness of a highly crosslinked matrix. Since the PB resins are similar to vulcanizable rubber polymers, it was expected that they might also be reinforced and shrinkage reduced by addition of reinforcing fillers, such as carbon black and silica flour. Cabot Vulcan 9A32 carbon black and PPG HiSil 233 hydrated silica were selected as fillers to be evaluated. In addition, a finely divided, insoluble polyimide resin, HR-600, was also evaluated. This latter resin has terminal carbon-carbon unsaturation in the molecular structure, which could possibly react with the HME matrix through the surface unsaturated sites.

The fillers were milled into a resin mix formulated to the same component ratios as HME 5803-53. (Refer to Table 1.) Multiple passes on a three roll paint mill gave very good dispersion of the fillers. Prepreg tape was then manufactured and the resin staged at 50° C.

Characteristics of resin filled with carbon black and silica were such that the filler content had to be reduced from an initial 25 percent by weight to 15 percent by weight to prepreg properly. The HR-600 resin was used at 25 percent by weight loading. There was some tendency for the HR-600 resin to be filtered out by the graphite fiber but not with the carbon black and silica filled resins.

Laminates prepared from the prepregs were of very poor quality. The carbon black-filled resin appeared to be only partially cured. Very probably the peroxide curing agent was either absorbed or deactivated by the carbon black. The silica and HR-600 containing systems cured well, but the laminates were high in voids and the resin showed very poor flow. Fillers were calculated to be a part of the total resin content, and thus the laminates may have been too low in liquid resin.

Laminate SBS strengths were less than half that of controls. Strength loss could probably be attributed largely to poor quality laminates.

6. LOW PROFILE-SHRINK REDUCING ADDITIVES

A number of resinous additives have been developed for polyester chemistry to reduce or eliminate the high cure shrinkage inherent in the

free radical-induced crosslink cures. As this shrinkage is also a characteristic of the HME resin system, attempts were made to improve performance by using these same additives.

The additives available were diluted with styrene, as would be proper for polyester work. When the C-1000 PB and the Rohm and Haas Paraplex P-713, an acrylic polymer, or Union Carbide LP 40A, a vinyl acetate polymer, were mixed, a gelatinous mass immediately formed around the stirring bar or blade leaving a separate liquid phase. The two phases could not be mixed. The C-1000 PB itself was readily miscible with styrene. No attempt was made to determine phase compositions. It is assumed that the PB extracted styrene from the additives to the extent that they became gelatinous.

Styrene-diluted polyester resins behaved much the same way with PB resin. The low profile additives mixed readily with CY-179 epoxy resin, but the mixture also turned gelatinous when C-1000 PB was added.

Manufacturers of the low profile additives recommended mixtures of 60 percent polyester resin and 40 percent additive for zero shrinkage formulations. Additive levels in the 10 to 40 percent range investigated in the PB were not compatible.

SECTION V

CONCLUSIONS

Several approaches were made to form primary chemical bonding between AS graphite fiber and HME matrix resin. No significant improvement was achieved over untreated fiber as measured by short beam shear strength. Reinforcing fillers were tested to evaluate the possibility that the HME matrix was highly stressed internally or of low cohesive strength, again without improvement in SBS. Formulation variations in the basic resin composition (under Contract No. F33615-76-C-5169), coupling agents, and fillers all failed to affect the SBS of AS/HME composites. It is concluded that the HME/graphite composite properties cannot be easily improved.

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