AD-757 763

TAILORING THE INTERFACE IN GRAPHITE-REINFORCED POLYCARBONATE

J. L. Kardos, et al

Monsanto Research Corporation

Prepared for:

Advanced Research Projects Agency

February 1973

**DISTRIBUTED BY:** 



National Technical Information Service U. S. DEPARTMENT OF COMMERCE 5285 Port Royal Road, Springfield Va. 22151 HPC 71-145

3

0

でし

20

~

ITEM A002

# MONSANTO/WASHINGTON UNIVERSITY ONR/ARPA ASSOCIATION

TAILORING THE INTERFACE IN GRAPHITE-REINFORCED POLYCARBONATE

BY

J. L. KARDOS F. S. CHENG T. L. TOLBERT

PROGRAM MANAGER ROLF BUCHDAHL



APPROVED FOR PUBLIC RELEASE. DISTRIBUTION UNLIMITED.

Details of illustrations in this document may be better studied on microfiche

# MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

SOO N. LINDBERGH SOULEVARD

ST. LOUIS, MISSOURI 63166

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U. S. Government.

> Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151

Online function with the sense of the s	(Security classification of this had the	T CONTROL DATA - F	C & D	
Monsanto Research Corp.       Inclassified         Transferred       Inclassified         Tailoring the Interface in Graphite-Reinforced Polycarbonate         October State       Inclassified         Authonis (first mane, model (with), farsame)         J. L. Kardos and F. S. Cheng, Washington University         T. L. Tolbert, Monsanto Co.         Rebruary 1973       Inclassified         Contract on denary two         NO0014-67-C-0218         Proved for public release; distribution unlimited.         Details of fiber distance         Details of fiber distance         Instructure         Office of Naval Research         Washington, D. C.         Indexnet and and the distance and glass fiber/polycarbonate composites         Indexnet and and explained. At 20 volume percent loading         random-in-a-plane, discontinuous fibers, both specimen strength         I modulus in both fiber systems was         from fiber to fiber. Regardless of the type and treatment of a crystalline interface, which aparently transfers the stresses more effective         from fiber to fiber. Regardless of the type of fiber, moling adove 260-265°C, whereas only the graphite system was         from the to fiber. Regardless of the type of fiber, moling at crystalline poly-thonate between the moling and annealing steps takes         imodulus in both fiber systems were found to increase dram	ORIGINATING ACTIVITY (Corporate author)	Indexing annotation must be	entered when I	he overall report is classified)
Approved for public release; distribution unlimited.         Difference         Outset         Outset         Outset         Approved for public release; distribution unlimited.         Difference         Outset         Outset         Outset         Outset         Pebruary 1973         Image: Pebruary 1973      <	Monsanto Research Corp.		Unc] 26. GROUP	assified
Tailoring the Interface in Graphite-Reinforced Polycarbonate  CERCENTIVE worts (Type al report and inclusive dates)  AUTHORISI (First mean. and disc influence dates)  Authorized for public release; distribution unlimited.  Aut	REPORT TITLE			
Determined with the provise of the provise provise provise of the provise provise of the provis	Tailoring the Interface in G	raphite-Reinfo	rced Pol	ycarbonate
Authoms (finite name, middle inflict, Harmane) J. L. Kardos and F. S. Cheng, Washington University T. L. Tolbert, Monsanto Co. February 1973 Pebruary 1973 (outraction chanton N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. N00014-67-C-0218 Project No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No. No.	OESCRIPTIVE NOTES (Type of report and inclusive dates)			
J. L. Kardos and F. S. Cheng, Washington University T. L. Tolbert, Monsanto Co.	AUTHORISI (First name, middle initial, laat name)			
T. L. Tolbert, Monsanto Co.	J. L. Kardos and F. S.	Cheng, Washing	ton Univ	ersity
REPORTATE       Pebruary 1973       It Total No. of PAGES       10. NO OF ACTS         CONTRACT OF CAMENTO       If It Total NO. of PAGES       17         N00014-67-C-0218       If December of PAGES       17         PROJECT NO       If December of PAGES       17         ONTATE OF CAMENTO       If December of PAGES       17         OUTING STATEMENT       If December of PAGES       17         OPERATION       If December of PAGES       17     <	T. L. Tolbert, Monsanto	Co.		
CONTRACT ORMATING       27 35       17         N00014-67-C-0218       HPC 71-145         PROJECT NO.       HPC 71-145         Details of instruction and the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites of aphite fiber/polycarbonate and glass fiber/polycarbonate composites of aphite fiber/polycarbonate and glass fiber/polycarbonate composites was the instruction of the instruction of the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites was the instruction of the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites from fibers, both specimen strength and moduling above 260-265°C, whereas only the graphite system was the interface, which apparently transfers the stresses more effective from fiber to fiber. Regardless of the type of fiber, molding at 5°C (slightly above 260-265°C, the melting point of crystalline polychonate) results in improved properties due to better wetting of the fiber to fiber. Regardless of the type of fiber, molding at 5°C (slightly above 260-265°C, the melting point of crystalline polychonate) results in improved properties due to better wetting of the top of the polychonate of polychonate and strength in the final ded article.	REPORT DATE	74. TOTAL NO.	F PAGES	75. NO. OF REFS
N00014-67-C-0218 PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROJECT NO. PROVED FOR PUBLIC RELEASE; distribution unlimited. PROJECT NO. PROVED FOR PUBLIC RELEASE; distribution unlimited. PROJECT NO. PROVED FOR NUCLEARY ACTIVITY Office of Naval Research Washington, D. C. Pronounced effects of thermal treatment on the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites random-in-a-plane, discontinuous fibers, both specimen strength d modulus in both fiber systems were found to increase dramatically on molding above 260-265°C, whereas only the graphite system was rther improved by subsequent annealing. In the latter case, pro- the interface, which apparently transfers the stresses more effective S°C (slightly above 260-265°C, the melting point of crystalline poly- thomate) results in improved properties due to better wetting of i fibers by the resin. Hot forming of graphite reinforced poly- thonate composites between the molding and annealing steps takes rantage of the higher processability of the unannealed material in ded article. PORM_1473 (PAGE 1)	CONTRACT OF GRANT NO	37.	3.5	17
PROJECT NO  PROJECT NO  PROJECT NO  PROJECT NO  PROJECT NO  PROVED for public release; distribution unlimited.  Proved for public release; distribution unlimited.  Proved for public release; distribution unlimited.  Pronounced effects of thermal treatment on the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites ve been demonstrated and explained. At 20 volume percent loading random-in-a-plane, discontinuous fibers, both specimen strength discontinuous fibers, both specimen strength on molding above 260-265°C, whereas only the graphite system was refound to increase dramatically the improvement is due to generation of a crystalline innerlayer the interface, which apparently transfers the stresses more effective from fiber to fiber. Regardless of the type of fiber, molding at the resin. Hot forming of graphite reinforced poly-chonate composites between the molding and annealing steps takes antage of the higher processability of the unannealed material in lition to providing increased modulus and strength in the final ded article.	N00014-67-C-0218	HPC	5 REPORT NU	ABER(5)
OUTTRIBUTION STATEMENT     Approved for public release; distribution unlimited.     Definite of indextrement     Definite     Definite of indextrement     Definite     Definit     Definite     Definit     Definite     Definite     Definit	PROJECT NO.			
OBTRIBUTION STATEMENT Approved for public release; distribution unlimited. Details of blash-block in this document may be better studied on microfiche Details of blash-block in this document may be better studied on microfiche		95. OTHER REPO	RT NOISI (Ank	
Approved for public release; distribution unlimited.  Details of floctrations in this document may be better studied on microfiche  Teronounced effects of thermal treatment on the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites ve been demonstrated and explained. At 20 volume percent loading random-in-a-plane, discontinuous fibers, both specimen strength dimodulus in both fiber systems were found to increase dramatically on molding above 260-265°C, whereas only the graphite system was rther improved by subsequent annealing. In the latter case, pro- the interface, which apparently transfers the stresses more effective from fiber to fiber. Regardless of the type of fiber, molding at chonate) results in improved properties due to better wetting of the inter processability of the unannealed material in lition to providing increased modulus and strength in the final		this report)		oner numbers that may be assigned
Approved for public release; distribution unlimited. Defails of Mostrations in this document may be better studied on microfiche Terrace Pronounced effects of thermal treatment on the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites ve been demonstrated and explained. At 20 volume percent loading random-in-a-plane, discontinuous fibers, both specimen strength d modulus in both fiber systems were found to increase dramatically on molding above 260-265°C, whereas only the graphite system was rther improved by subsequent annealing. In the latter case, pro- tty improvement is due to generation of a crystalline innerlayer the interface, which apparently transfers the stresses more effective from fiber to fiber. Regardless of the type of fiber, molding at S <sup>o</sup> C (slightly above 260-265°C, the melting point of crystalline poly- thonate) results in improved properties due to better wetting of a fibers by the resin. Hot forming of graphite reinforced poly- chonate composites between the molding and annealing steps takes antage of the higher processability of the unannealed material in lition to providing increased modulus and strength in the final ded article.	OISTRIBUTION STATEMENT			
Studied on microfiche Washington, D. C. Washington, C. C. Washington, D. C. Washingto	Details of instructions in this document may be better	Office of	MILITARY ACT	Research
Pronounced effects of thermal treatment on the properties of aphite fiber/polycarbonate and glass fiber/polycarbonate composites ve been demonstrated and explained. At 20 volume percent loading random-in-a-plane, discontinuous fibers, both specimen strength d modulus in both fiber systems were found to increase dramatically on molding above 260-265°C, whereas only the graphite system was rther improved by subsequent annealing. In the latter case, pro- rty improvement is due to generation of a crystalline innerlayer the interface, which apparently transfers the stresses more effective from fiber to fiber. Regardless of the type of fiber, molding at boom to be the resin. Hot forming of graphite reinforced poly- chonate composites between the molding and annealing steps takes vantage of the higher processability of the unannealed material in lition to providing increased modulus and strength in the final .ded article.	studied on microfiche	Washingt	on, D. (	2.
FORM 1473 (PAGE 1) 1a	Pronounced effects of them			
FORM 1473 (PAGE 1)	Pronounced effects of therm aphite fiber/polycarbonate and we been demonstrated and expla random-in-a-plane, discontinu d modulus in both fiber system on molding above 260-265°C, wh rther improved by subsequent a rty improvement is due to gene the interface, which apparent from fiber to fiber. Regardl 5°C (slightly above 260-265°C, rbonate) results in improved p e fibers by the resin. Hot fo rbonate composites between the vantage of the higher processal lition to providing increased in lded article.	al treatment of glass fiber/p ined. At 20 v ous fibers, bo is were found t ereas only the nnealing. In ration of a cr ly transfers t ess of the typ the melting p roperties due rming of graph molding and a bility of the modulus and st	n the project of the special of the special of the stress of fibroint of the stress of fibroint of the rein nnealing unanneal rength i	coperties of onate composites ercent loading men strength use dramatically e system was er case, pro- e innerlayer ses more effective er, molding at crystalline poly- r wetting of forced poly- steps takes ed material in n the final
1 17	Pronounced effects of therm aphite fiber/polycarbonate and we been demonstrated and expla- random-in-a-plane, discontinu d modulus in both fiber system on molding above 260-265°C, wh rther improved by subsequent a rty improvement is due to gene the interface, which apparent from fiber to fiber. Regardl 5°C (slightly above 260-265°C, rbonate) results in improved p e fibers by the resin. Hot fo rbonate composites between the vantage of the higher processal lition to providing increased in lded article.	al treatment of glass fiber/p ined. At 20 v ous fibers, bo s were found t ereas only the nnealing. In ration of a cr ly transfers t ess of the typ the melting p roperties due rming of graph molding and a bility of the modulus and st	n the prolocarbo olycarbo olume per th specio o increa graphit the latt ystallin he stres e of fib oint of to bette ite rein nnealing unanneal rength i	coperties of onate composites ercent loading men strength ase dramatically te system was ter case, pro- te innerlayer ses more effective er, molding at crystalline poly- r wetting of forced poly- steps takes ed material in n the final

KEY WORDS	LIN	КА	LIN	IK B	LIN	кс
	ROLE	WT	ROLE	WT	ROLE	w
alass fiber						
glass fiber						i
graphite liber						
compositor						
composites						
inperlayer						
interface						
thermal tractment						
hot forming						
molding						
annealing						
Wetting		1				
strength						
modulus						
reinforced thermoplastic						
	1					
					- 1	
				1		
				- 1		
	1 1					
			1			
					(	
1. 1.					1	
	1 1					
				[		
					l l	
			I			
		1				
				ł		
		1				
			[			
FORM & A TO						
1 NOV 55 1473 (BACK)						

### ITEM A002

HPC 71-145

# TAILORING THE INTERFACE IN GRAPHITE-REINFORCED POLYCARBONATE

BY

J. L. KARDOS F. S. CHENG T. L. TOLBERT

### FEBRUARY 1973

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION HIGH PERFORMANCE COMPOSITES PROGRAM SPONSORED BY ONR AND ARPA CONTRACT NO. NOO014-67-C-0218, ARPA ORDER 876 ROLF BUCHDAHL, PROGRAM MANAGER

> MONSANTC RESEARCH CORPORATION 800 NORTH LINDBERGH BOULEVARD ST. LOUIS, MISSOURI 63166

#### FOREWORD

The research herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (phone 314-694-4721).

The contract is funded for \$7,000,000, and expires 30 June 1974.

ΪI.

### TAILORING THE INTERFACE IN GRAPHITE-REINFORCED POLYCARBONATE

J. L. Kardos and F. S. Cheng Washington University St. Louis, Mo. 63130

> T. L. Tolbert Monsanto Co. St. Louis, Mo. 63166

#### ABSTRACT

Pronounced effects of thermal treatment on the properties of graphite fiber/polycarbonate and glass fiber/polycarbonate composites have been demonstrated and explained. At 20 volume percent loading of random-in-a-plane, discontinuous fibers, both specimen strength and modulus in both fiber systems were found to increase dramatically upon molding above 260-265°C, whereas only the graphite system was further improved by subsequent annealing. In the latter case, property improvement is due to generation of a crystalline innerlayer at the interface, which apparently transfers the stresses more effectively from fiber to fiber. Regardless of the type of fiber, molding at 275°C (slightly above 260-265°C, the melting point of crystalline polycarbonate) results in improved properties due to better wetting of the fibers by the resin. Hot forming of graphite reinforced polycarbonate composites between the molding and annealing steps takes advantage of the higher processability of the unannealed material in addition to providing increased modulus and strength in the final molded article.

(Contribution HPC 71-145 from the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research Contract No. N00014-67-C-C218).

ill

### TAILORING THE INTERFACE IN GRAPHITE-REINFORCED POLYCARBONATE

J. L. Kardos and F. S. Cheng Washington University St. Louis, Mo. 63130

> T. L. Tolbert Monsanto Co. St. Louis, Mo. 63166

#### INTRODUCTION

One of the more promising recent discoveries in composites research is that the structural properties of certain composites systems can be markedly changed through incorporation of a resin innerlayer between the matrix resin and the reinforcement. In contrast to the coupling agents often employed to improve the environmental resistance of FRP systems, these innerlayers may be up to several mils in thickness and vary in their effect depending on their own physical properties. Kenyon and Duffy (1) observed, for example, that the ultimate elongation of cast, glass bead filled epoxy composites can be increased simply by altering the nature of resin in the vicinity of the interface with an excess of glycidoxy silane. Kenyon (2) went on to show that the toughness of such systems also can be increased by coating the beads with a thin layer of flexibilized epoxy prior to casting. More recently, Lavengood and co-workers (3) found that the transverse strength and fatigue properties of fiber reinforced composites can be increased through use of a ductile innerlayer; in some cases, the improvement in fatigue life was as much as two orders of magnitude. Benefits were also seen in the axial flexural properties of unidirectionally reinforced continuous and discontinuous fiber composites, but this was attributed more to reduction of stresses at points of environmental corrosion than to any other factor. In all cases, the effects on composite properties were very sensitive to innerlayer thickness.

Little advantage has been taken of innerlayer or interface effects in thermosetting composites because of the difficulty in incorporating them into practical systems. However, several workers have reported that innerlayers of the type required can be readily generated in-situ in certain thermoplastic systems. Baer et al., (4) demonstrated sometime ago that polymers could be epitaxially crystallized from solutions and melts on heterogeneous surfaces to yield a layer of oriented crystallites. In-situ crystallization of polyamides was observed by other workers at about the same time (5,6). Lando and Frayer (7) reported epitaxial crystallization of nylon 6 and 66 monomers on graphite surfaces followed by topotactic reaction to yield layers of epitaxial oligomer. Epitaxial crystallization of polyethylene on single crystals of graphite has been demonstrated by Tuinstra and Baer (8). While none of these workers were directly concerned with composites, they nonetheless demonstrated that oriented crystallites could be generated on heterogeneous substrates. In reinforced thermoplastic systems, this presents the possibility of producing an innerlayer modulus intermediate between that of the substrate and the bulk resin, a prime requirement for good stress transfer.

- 2 -

The so-called "high temperature" engineering thermoplastics' are particularly desireable as composite matrices because of their high toughness, heat stability and processability, in addition to good strength and stiffness characteristics. Many of this family also are amorphous in nature, or are at least very difficult to crystallize under usual processing and use conditions, and remain in the glassy state with little change in properties as long as they are held below Tg and protected from solvents. As indicated, some can be made to crystallize, however, and so have the potential for forming crystallite-rich innerlayers around reinforcing agents embedded in the resin. When crystallization does occur, the physical properties of the resin usually change greatly.

The morphology of a surprising number of these amorphous thermoplastics is strikingly similar. As indicated in Table I, these include polycarbonate, polyethylene terephthalate and polysulfone. In the "non-crystalline" state these materials have been found (9, 10) to consist of tiny ball-like structures of about 75Å in size. When the system is held at temperatures near Tg for long periods or is exposed to certain solvents, morphological changes begin to occur which involve gradual alignment of these structures to form lamellae and, subsequently, spherulites. Similar changes can be induced by strain crystallization. The

- 3 -

mechanisms of crystallization by annealing and straining are not fully understood but appear to be the same for all the systems exhibiting the ball-like morphology.

The key question in our study was whether or not these crystallization techniques could be applied to composite systems. The previously mentioned work of Lando and Frayer and Tuinstra and Baer suggested that graphite such as found in high modulus graphite fibers might be a suitable substrate for crystallization if the system was subjected to the proper conditions, e.g., long term annealing. If this were the case, it seemed likely that advantage could be taken of the property enhancement obtainable with innerlayers and that unusually high levels of composite performance could be achieved.

This paper concerns the application of these crystallization techniques in thermoplastic composite systems. Preliminary work (15) showed that graphite fiber could be used as nucleating sites for polycarbonate resin and that the properties of resulting composites were significantly improved. Completion of the study has verified the early findings and shown that thermal tailoring of the interface in thermoplastic composites is applicable to practical polymer processing.

#### FABRICATION OF COMPOSITES

Pclycarbonate composites were prepared from five different types of reinforcement:

- 4 -

silane-treated glass spheres<sup>1</sup>, carbospheres<sup>2</sup>, heat cleaned 1/4"glass fibers<sup>3</sup>, 1/8" Thornel<sup>4</sup> 40 graphite fiber sized with polyvinyl alcohol and 1/8" HMG<sup>5</sup> graphite fibers sized with Epon 828<sup>6</sup>. Loading was 20% by volume in all cases. The reinforcements were chosen to permit differentiation between simple wetting of the surface by the resin and development of a partially crystallized layer of resin bonded to the surface. In addition, these materials permitted comparison of the degree of reinforcement obtainable with spheres versus short fibers and with fibers of varying stiffness. Fiber properties ranged from a nominal strength and elastic modulus for the glass fiber of  $300 \times 10^3$  psi and  $10.6 \times 10^6$  psi to those of Thornel 40,  $200 \times 10^3$  psi and  $36.5 \times 10^6$ psi, to those of the HMG fiber,  $300 \times 10^3$  psi and  $56 \times 10^6$  psi, respectively.

The sphere-containing composites were prepared by dry blending 40 mesh vacuum dried polycarbonate powder with "cleaned" spheres and then molding under positive pressure. Cleaning of the glass spheres was accomplished by removal of metallic particle contaminates with a magnet, slurrying them in an equal weight of acetone containing 5 w/o A-1100<sup>7</sup> silane and then filtering and drying

- 5 -

Soda-lime glass spheres averaging 40 microns in diameter produced by the Microbeads Division of Cataphote Corp. 2. Hollow, thin-walled carbon spheres, averaging 40 microns in diameter, trade-marked by the General Techniologies Corp. 3. Type CS-250 produced by Johns Manville Fiber Glass Inc.; sizing removed at 600°C. 4. Trademark of Union Carbide Corp. 5. Trademark of Hercules Powder Co., Inc. 6. Trademark of Shell Chemical Co.
 7. Trademark of Union Carbide Corp.

them under vacuum at 110°C. The carbon spheres were simply freed of broken sphere fragments by floatation in methanol and dried under vacuum at 110°C. Apparent density of the latter was determined to be 0.475 g/cc by casting them in epoxy resin, care being taken to exclude voids, measuring composite density with a water pycnometer and determining the sphere weight content in the composite by the method of Haynes and Tolbert (16). Direct measurement of Carbosphere apparent density using a Beckman Model 930 Air Comparison Pycnometer gave a value of 0.5g/cc; this is considered to be slightly in error but to provide a valid upper limit. Molding of the polymer/sphere blends was carried out under the same conditions used to mold unfilled specimens from polycarbonate powder alone. Specimens were prepared by heating the resin mix to molding temperature under low contact pressure, followed by (1) holding at 190°C for 10 minutes under 1000 psi before cooling to room temperature, (2) holding at 275°C for 10 minutes under 100 psi, then cooling to 200°C and increasing the pressure to 1000 psi for the remainder of the cool down period or (3) holding at 275°C for 10 minutes under 50 psi, annealing at 245°C for 10 minutes under 50 psi and then annealing at 245°C for 3 hours before cooling to 200°C and increasing the pressure to 1000 psi for cool down. The pressure cycles were chosen to prevent excessive flashing of the resin and formation of voids and to provide uniform thickness in all specimens. A minimum of four tensile specimens of each material and the unfilled resin were prepared for each molding condition.

- 6 -

The fiber reinforced specimens were prepared by sonically dispersing the appropriate fiber in a 75% methanol/25% water solution along with 60-100 mesh polycarbonate powder. A preform mat of fibers, random in two dimensions and uniformly mixed with resin power, was then prepared from the suspension by draining off the solution through a filter shaped like the final sample  $(5 \times 1/2 \times 1/16$  in. plate) in the bottom of the container. The mat was dried at 110°C for 8 hr. under vacuum and compression molded at 5000 psi using the following temperature cycles. The fiber/resin mixture was heated under pressure to 190°C, held for 10 min. and slowly cooled to room temperature; to 275°C, held for 10 min. and cooled; or to 275°C, held for 10 min. and annealed for 3 hr. at 245°C before cooling. A total of 12 specimens was prepared under each regime and an equal number of unfilled bars of the same geometry and molded under the same conditions were prepared as standards.

The temperature cycles employed for the moldings were chosen to permit differentiation of effects occuring (1) under normal molding conditions (190°C) for the pure resin, (2) when the melting point (265°C) of the resin was exceeded (275°C), (3) when the development of crystallites in a layer of resin at the resin/reinforcement interface was most favored (annealing at 245°C after melting. Selection of 245°C as the annealing temperature was based on earlier observations indicating that this was the point (about 20° below Tm) of most rapid crystal growth.

- 7 -

#### RESULTS AND DISCUSSION

#### Composite Properties

The tensile properties and glass transition temperatures of the various composites which were prepared are shown in Tables II and III. In all cases, there was an observable effect of the thermal treatments on mechanical properties. In the sphere-reinforced systems the effect was largely deleterious, particularly in the case of annealing which caused marked decreases in the already low elongations of the filled materials.

Effects in the fiber-reinforced systems were beneficial, however, and much more dramatic. Increasing the molding temperature of the graphite fiber system to 275°C resulted in a 60% increase in strength and more than a 50% improvement in the modulus. Adding the annealing step caused further increases, nearly doubling both the strength and modulus obtained in the 190°C specimens (changes in the properties of the Thornel composites were of the same order, though slightly smaller, as those shown for the HMG materials). Oddly enough, the properties did not improve significantly until the molding temperature exceeded the 260-265°C range. In the glass fiber system, increasing the molding temperature to 275°C resulted in a 30% increase in strength and nearly doubled the tensile elongation. In contrast to the graphite, annealing of this 275°C material had little effect on the strength or modulus. Thus, there appear to be two distinct effects, one common to both the glass and graphite fibers and the other

characteristic of graphite alone. Though by no means conclusive, the property data imply that on being annealed the graphite fiber composites experienced unique internal changes which enhanced reinforcement efficiency. As indicated earlier, this is precisely the sort of change that would be expected if resin crystallization occurred on or near the fiber surface. This is further supported by the fact that the modulus increases were large, a phenomenon requiring development of oriented structures and/or crystallites within the resin itself.

# Evidence for Crystallinity and Improved Wetting

The existence of a crystalline region generated around the fibers in graphite composites by annealing, as suggested by the changes in mechanical properties, has been verified. The layer is in fact quite readily seen on fibers exposed by fracture of annealed composites. Figures 1 and 2 are scanning electron micrographs of Thornel 40 fiber on the fracture surfaces of composites molded at 190°C and at 275°C with subsequent annealing at 245°C; similar results occur for the HMG system. In Figure 2 the existence of a tightly adhering layer is apparent. The micrograph in Figure 3 shows the angular character of the material on the annealed Thornel fibers more clearly.

- 9 -

That the material on the surface of the graphite fiber from annealed composites is indeed oriented, if not crystalline, polycarbonate was confirmed by transmission electron diffraction measurements on detachment replicas of the fibers on the fracture surfaces of annealed samples. The diffraction pattern shown in Figure 4A exhibits discrete arcs corresponding to polycarbonate unit-cell spacings (see schematic) which are present initially in these measurements. The arcs disappeared rapidly when the very low beam current was increased (see Figure 4B), even when a cold stage was employed, indicating that the polymer melted in the heat of the beam. It is possible, of course, that oriented material could arise from polymer deformation during fracture, as well as crystallization. This seems most unlikely, however, especially in light of the very large increases in the glass transition temperatures (Tg) of the matrix resin in the graphite composites as compared to those of the unfilled resin and of the glass fiber system (see Table III). An increase in Tg of this magnitude, 10-13°C, above those of similar materials molded under the same conditions indicates a considerable effect of the fiber surface on the order of the resin with which it is in contact. Comparison with the composites reinforced with graphite fibers which are completely free of sizing agents indicated that sizing agents are not responsible for the increases in order observed, although the sized fibers employed here do tend to give slightly stronger composites.

- 10 -

The decreased elongation and slightly higher modulus obtained on annealing carbosphere composites also suggest the possibility that some molecular orientation or crystallization may have occurred even though little effect on strength was observed. Figure 5, a scanning electron micrograph of the "socket" from which one of the spheres at the fracture surface has been wrenched, shows that this is the case. The tiny angular particles in the cavity seem to be relatively highly developed polycarbonate dendrites. The glass spheres in analogous composites, on the other hand, bear only occasional fragments of polymer which has wetted and adhered to the surface and leave relatively smooth cavities without any evidence of crystallinity in the resin surface.

This leaves only the property improvements achieved by molding both graphite and glass fiber composites at 275°C to be explained. As indicated by Figures 1 and 6 for the Thornel and by Figures 7 and 8 for glass, which show electron scanning micrographs of fibers at the fracture surfaces of composites processed at 190°C and 275°C respectively, this can be explained simply as a difference in wetting of the fibers by the resin. The fiber from the composite molded above the melting temperature of the resin (265°C) is completely enveloped by the resin, having been pulled out of the matrix during fracture with its coating of resin relatively intact, whereas the fiber from the composite

- 11 -

processed at conventional temperatures was completely denuded in pull-out. Some improvement in wetting of the glass spheres by the higher temperature processing also was observed, as noted above, but the effect was not nearly as great as in the fiber system. No explanation for the difference between the glass spheres and fibers can be offered at this time, other than to suggest that the silane size on the spheres may be involved. While found beneficial to bonding in 190° processing in earlier studies, it is possible that for some reason it impeded wetting by molten polycarbonate at the higher temperature.

The fact that better wetting appears to occur only after a critical molding temperature (260 - 265°C) is reached deserves further comment at this point. This temperature range is about where polycarbonate crystals would melt if they were present. While containing no measurable crystallinity initially, Carr, et al. (9) have shown that "amorphous" polycarbonate is made up of the tiny 75Å balls referred to earlier. It is known that these balls generally possess unidirectional order (10) which may well be destroyed at 260-275°C. With the balls destroyed and the melt more randomized, wetting of the fiber surfaces should be greatly facilitated.

### Hot Forming of Polycarbonate Composites

The facts that conventionally processed graphite-reinforced polycarbonate sheet is relatively ductile and that its properties can be nearly doubled by simple annealing suggest that this

- 12 -

material may be ideal for hot forming operations. Preliminary evaluations in the laboratory have shown that this is indeed the case. Graphite-filled (10 v/o of 1/8" fiber) polycarbonate sheet formed at 190°C was rapidly reheated to 190°C and formed under about 50 pounds of pressure between matched aluminum hand molds into right-angle and semi-circular channel specimens. The molds were then C-clamped and annealed at 235°C in a constant temperature oven for 3 hours.

The specimens were tested in flexure by a method proposed by Lavengood (17) in order to avoid shear coupling effects and obtain an indication of breaking load in the region which had undergone greatest deformation. Cross-sectional "L" and "C" shaped test samples (1/2" wide) were accurately cut from the specimens and loaded at the midpoints in such a way as to cause flattening. Failure occurred near the point of loading.

In hindsight, it is likely that such a long period of annealing is not really necessary and that it can be shortened even more by exposing the clamped specimens briefly to temperatures above Tm, 265°C, prior to annealing. The temperatures used were dictated by limitations of the particular press and oven employed. Nonetheless, the test results clearly show the effectiveness of such an approach. Resistance to flexural load was doubled in each case; see Table IV below. Here again is evidence that thermal tailoring of the polycarbonate in the region of the resin/fiber interface improves the ability of the system to carry load.

- 13 -

#### CONCLUSIONS

Significant improvements in the strength and modulus of fiber reinforced polycarbonate composites can be achieved by increasing molding temperatures to above the melting point of the resin. In glass fiber composites improvement also is seen in the elongation to failure. In graphite fiber reinforced systems strength and modulus can be further enhanced by annealing moldings at temperatures 20-30° below the melting temperature. This results in formation adjacent to the fiber surface of a partially crystalline layer of resin through which stresses on the composite can apparently be more effectively transferred from fiber to fiber. It is analogous to use of innerlayers of intermediate modulus in thermosetting systems to improve performance

No improvement in properties was observed when glass and carbon sphere composites were subjected to similar molding temperatures and to thermal annealing. This seems to have been due in part to the fact that, in contrast to the fiber systems, improvements in wetting were only marginal. It is likely that this could be overcome, especially with the glass spheres, by heat cleaning prior to molding. Resin crystallization did occur in the region immediately surrounding the carbospheres, but had little effect on composite properties, perhaps because of the random dendritic nature of the crystallites with attendant formation of small voids.

- 14 -

The practical implications of these experiments are threefold. Use of higher processing temperatures to improve wetting of the reinforcement by the resin certainly seems desirable for all polycarbonate composites. Addition of an annealing step in a way somewhat analogous to the heat-treating of metals also seems desirable where graphite or other fibrous reinforcing agents able to nucleate crystallization in the resin are employed. So long as crystallinity is restricted to the region immediately surrounding the resin, marked improvements in composite strength are possible. Finally, hot forming of graphite and carbon-reinforced polycarbonate composites between the processing and annealing steps appears to offer particular advantages. It takes advantage of the higher processability of the unannealed material while developing higher strength and stiffness in the molded article.

- 15 -

#### ACKNOWLEDGEMENT

The excellent work of Mr. Trung Chinh Nguyen in preparing, thermally treating and testing the glass bead, carbosphere and glass fiber composites is gratefully acknowledged. Appreciation is also expressed to Mr. John Ruprecht for preparation of the scanning electron micrographs of the carbosphere composite fracture surfaces.

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by the Office of Naval Research under Contract No. N00014-67-C-0218.

## REFERENCES

1.	A. S. Kenyon and H. J. Duffey, Polymer Engineering and Science, 7, 189 (1967).
2.	A. S. Kenyon, Journal of Colloid and Interface Science, 27, [4], 761 (1968).
3.	R. E. Lavengood, et al, to be published.
4.	E. Baer, J. A. Koutsky and A. G. Walton, <u>Polymer Letters</u> , <u>5</u> , 177 (1967), <u>ibid.</u> , <u>5</u> , 185 (1967).
5.	E. W. Fisher and J. Willems, <u>Die Makromoleculare Chemie</u> , <u>99</u> , 85 (1966).
6.	H. Seifert, <u>Journal of Physical Chemistry, Solids</u> , <u>Supplement No. 1, 534 (1967).</u>
7.	J. B. Lando and P. D. Frayer, <u>J. Colloid and Interface</u> Science, <u>31</u> , 145 (1969).
8.	F. Tuinstra and E. Baer, <u>Journal of Polymer Science</u> , <u>B8</u> , 861 (1970).
9.	S. H. Carr, P. H. Geil and E. Baer, <u>Journal of Macro-</u> molecular Science-Physics, <u>32</u> , [1], 13 (1968).
10.	G. S. Y. Yeh and P. H. Geil, Journal of Macromolecular Science-Physics, Bl, 2, 235 (1967); ibid., 2, 251 (1967).
11.	K. Yang and J. L. Kardos, to be published.
12.	S. L. Lambert and G. S. Y. Yeh, <u>Proceedings of the</u> Electron Microscopy Society of America, page 414 (1968).
13.	D. Gesovich, Master of Science Thesis, Case Western Reserve University (1967).
14.	T. G. F. Schoon and D. Teichmann, <u>Kolloid Zeitschrift</u> , <u>197</u> , 35 (1966).
15.	F. S. Cheng, J. L. Kardos and T. L. Tolbert, SPE Journal, 26, [8], 62 (1970).
16.	W. M. Haynes and T. L. Tolbert, <u>Journal of Composite</u> <u>Materials</u> , <u>3</u> , 709 (1969).
17.	R. E. Lavengood, Monsanto Company, St. Louis, Missouri; private communication.

Ł

### TABLE I

### Amorphous Thermoplastics Exhibiting Modular Microstructure

# Thermoplastic

1

### Investigators

Polycarbonate	Carr, Geil and Baer (9)
Polyethylene Terephthalate	Yeh and Geil (10)
Polysulfone	Yang and Kardos (11)
Polystyrene	Lambert and Yeh (12)
Polypropylene (Quenched)	Gesovich (13)
Polymethyl Methacrylate	Schoon and Teichmann (14)

### TABLE II

# EFFECT OF THER AL TREATMENT ON COMPOSITE PROPERTIES

Glass	Sphere	Composites	
		the second s	

(Thermal Treatment)

3	<u>190°C</u>	_275°C	275°/245°C
Tensile Strength, psi x 10 <sup>3</sup>			
Unfilled Filled	9.0	9.0	8.9
Flongation &	5.2	5.4	11.2
Unfilled	5.1	5.5	4.9
Filled	1.7	2.3	1.0
Modulus, psi x 10 Unfilled	3,25	3,30	2 11
Filled	5.05	5.05	5.05
Glass Transition			
Unfilled	145-150	145-150	145 150
Filled	147-148	140-141	141-142
Carbosphere Composites			
Tensile Strength, psi x 10 <sup>3</sup>			
Unfilled	9.0	9.1	8.9
Filled	4.9	5.4	4.3
Elongation, %			
Unfilled	5.05	5.3	4.85
Filled	2.3	1.7	1.2
Modulus, psi x 10 <sup>5</sup>			
Unfilled	3.25	3.30	3.11
Filled	. 3.80	3.82	4.04
Glass Transition Temperature (DTA), °C			
Unfilled	145-150	145-150	145-150
Filled	143-146	143-144	140-144

# TABLE III

# EFFECT OF THERMAL TREATMENT ON COMPOSITE PROPERTIES

Glass Fiber Composites

# (Thermal Treatment)

	_190°C	275°C	275°/245°C
Tensile Strength, psi x $10^3$			
Unfilled Filled	9.0 7.6	9.1 11.1	8.9
Elongation, % Unfilled Filled	5.1	5.3	4.9
Modulus, psi x 10 <sup>5</sup>	1.3	2.0	2.3
Unfilled Filled	3.25 8.19	3.30 8.20	3.11 9.28
Glass Transition Temperature (DTA),°C Unfilled Filled	145-150 147-148	145-150 143-144	145-150 145-146
Graphite Fiber (HMG) Composites			100 140
Tensile Strength, psi x 10 <sup>3</sup> Unfilled Filled	8.3 8.6	8.6 13.7	8.2
Elongation, % Unfilled Filled	5.1 0.8	6.2	2.8*
Modulus, psi x 10 <sup>5</sup> Unfilled Filled	3.1 19.3	3.4	3.3
Glass Transition Temperature (Torsion Pendulum) °C		47 . U	37.8
Unfilled Filled	150 164	150 162	150 164

\*Some crazing observed in this series of specimens.

- 20

# TABLE IV

\_21\_

# FLEXURAL LOADING OF HOT FORMED POLYCARBONATE COMPOSITES

	Flexural Load to Break	(Pounds Force*)
Composites Molded at 190°C	Half Cylinder	90° Channel
Unfilled	30-40	20-30
Filled (10%)	15-30	20-35

Composites Molded at 190°C and Annealed at 235°C

11-6411-1		
Unilled	**	**
Filled (10%)		~ ~
1100 (100)	46-62	54-64

•

\*Range of breaking loads observed

1

**\*\***Excessive creep prevented annealing of unfilled specimens





Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 190°C. Scale bar represents 2 microns.





Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C and then annealed at 245°C for three hours. Note the coating of matrix which almost completely covers the fiber. Scale bar represents 2 microns.



24.



High magnification scanning electron micrograph of a Thornel fiber surface in the annealed sample. The adhering polymer particles appear to have an angular morphology characteristic of polymer crystals. Scale bar indicates 1 micron.









Diffraction patterns from a detachment replica of unsized Hercules/ polycarbonate composite molded at 275°C and then annealed at 245°C for three hours, Pt. shadowed: (A) before electron beam heating, (B) after electron beam heating.

FIGURE 4

#### FIGURE 5



Empty socket left by a smooth carbon sphere on the fracture surface of a 245°C annealed carbon/polycarbonate composite. Polycarbonate dendrites appear to be well developed at the interface. Scale bar represents 2 microns.



Fracture Surface of a Polycarbonate - glass fiber composite molded at 190°C, 1800X.

FIGURE 6

27



FIGURE 7



Scanning electron Laicrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C. Note the increase in adhering matrix on the fiber over that seen in Figure 1. Scale bar represents 2 microns.



Scanning electron micrograph of tensile fracture surface of an E-glass fiber/polycarbonate composite molded at 190°C. Note the void around the fiber caused by poor wetting. Scale bar represents 5 microns.

Fracture surface of a Polycarbonate - glass fiber Composite molded at 275°C, with subsequent annealing at 245°C for 3 hours, 1800X

FIGURE 8