OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 26

Molecular Composites from the Phase Separation at Low Temperatures of Kevlar and Diaminophenylindane Polyimide in Sulfuric Acid

by

Maria A. Alonso and M. T. Shaw

Liquid Crystalline Polymer Research Center
University of Connecticut
Storrs, CT 06268

Pulished

in

Proc. of the ACS Division of Polymeric Materials:
Science and Engineering, 59
Fall Meeting, 1988, Los Angeles, California

September 30, 1988

SECURITY CLASSIFICATION OF THIS PAGE

ADA200505

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS: None
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for Public Release, Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 26	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: University of Connecticut; 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION: Office of Naval Research
6c ADDRESS (City, State, and ZIP Code): Storrs, CT 06268	7b ADDRESS (City, State, and ZIP Code): 800 North Quincy Avenue Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION; 8b OFFICE SYMBOL (If applicable): ONR/DARPA	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-86-K-0772
8c ADDRESS (City, State, and ZIP Code): 800 North Quincy Avenue Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO; PROJECT NO; TASK NO; WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
"Molecular Composites from the Phase Separation at Low Temperatures of Kevlar and Diaminophenylindane Polyimide in Sulfuric Acid" (Unclassified)

12 PERSONAL AUTHOR(S)
M.A. Alonso and M.T. Shaw

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim Technical	FROM _____ TO 09/30/88	1988/09/30	8

16 SUPPLEMENTARY NOTATION
Prepared for presentation at ACS PMSE Symposium in Los Angeles from September 25 - 28, 1988. (LCPRC Publication No. LCPRC88-17)

17 COSATI CODES		
FIELD	GROUP	SUB GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Kevlar
Molecular Composites
Liquid Crystalline Polymers
3-dimensional fibrous material

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

In a molecular composite, a ductile matrix is reinforced with a stiff, strong, rigid-rod polymer molecule. One of the approaches used to make a rigid-rod molecular composite involves the physical mixing by coprecipitation of single-phase solutions of a rigid-rod and a flexible-coil polymer in a common solvent. We and others have reported previously on the preparation of three-dimensional fibrous materials using the phase separation of polymer solutions at low temperature and sublimation or extraction of the solvent. It is conceivable that a molecular composite would give a superior 3D fibrous material by combining the strength of the rigid-rod macromolecules with the better processibility of the random-coil polymer. This prepint describes our attempts to test this hypothesis. "Molecular composites" from Kevlar and diaminophenylindane polyimide were fabricated by quenching sulfuric acid solutions. The structure and properties of the resulting three-dimensional fibrous structures were then determined.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: Dr. Kenneth J. Wynne	22b TELEPHONE (Include Area Code): (202) 696-4410; 22c OFFICE SYMBOL: ONR

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

Molecular Composites from the Phase Separation at Low Temperatures of Kevlar and Diaminophenylindane Polyimide in Sulfuric Acid

M. A. Alonso and M. T. Shaw
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

Introduction

In recent years, a great deal of work has been done in the fabrication of rigid-rod molecular composites. In a molecular composite, a ductile matrix is reinforced with a stiff, strong, rigid-rod polymer molecule. One of the approaches used to make a rigid-rod molecular composite involves the physical mixing by coprecipitation of single-phase solutions of a rigid-rod and a flexible-coil polymer in a common solvent.[1]

We[2,3] and others[4] have reported previously on the preparation of three-dimensional fibrous materials using the phase separation of polymer solutions at low temperature and sublimation or extraction of the solvent. It is conceivable that a molecular composite would give a superior 3D fibrous material by combining the strength of the rigid-rod macromolecules with the better processibility of the random-coil polymer.

This preprint describes our attempts to test this hypothesis. "Molecular composites" from Kevlar and diaminophenylindane polyimide were fabricated by quenching sulfuric acid solutions. The structure and properties of the resulting three-dimensional fibrous structures were then determined.

Experimental

Starting Materials

Kevlar (poly-p-phenyleneterephthalamide)($\bar{M}w$=26,500 g/mole) was obtained from E.I. Dupont. Matrimid 5218 (Diaminophenylindane polyimide) ($\bar{M}w$=40,000 g/mole) was obtained from Ciba Geigy . All solvents were used as received.

Procedure

Solutions were prepared from a 25:75 ratio of Kevlar and Matrimid 5218 in 96% sulfuric acid at different concentrations of polymer (from 1% to 20% by wt). In addition, solutions of the two polymers were prepared at 4% total polymer concentration by weight but with different ratio of the two polymers (from a 19:1 to 1:19 Kevlar:Matrimid in 20 uniform increments). The gel points of the solutions were measured using a low temperature bath programmed at either 2°C/min or 0.2°C/min.

Three dimensional fibrous materials were made by placing the solutions into capped, cylindrical polyethylene molds (1.5 cm x 2.5 cm) and cooling to -80°C at a rate of 2°C/min. The gels, generally transparent, were removed from the mold and extracted overnight using a 50/50 methanol/ water mixture at -45°C . This was followed by overnight extraction with 75/25 water/methanol at -15°C; and, finally, 100% H_2O for one week at 0°C, changing the solvent every day. After this, the three- dimensional materials were freeze dried at 50 millitorr.

The morphology of the reinforcements was studied using a scanning electron microscope (Model Amray 1000A) at 20 kV. Optical microscopy studies of the composites were done with a polarizing microscope (Nikon metaphoto). The embedding media used were: EMI (4-ethyl-2-methyl-imidazole) (2%) in Epon 815 and commercial epoxy penetrant ("wood rot cure").

Composites

A third polymer (epoxy resin) was incorporated into the three dimensional materials. To accomplish this, The 3D material was placed into a polyethylene mold and covered with degassed epoxy. The mold was put under a

vacuum until no more air bubbles were observed (2 hours at 50 millitorr). Then the mold was capped and the epoxy cured at room temperature for 24 hours; or, in the case of the Epon 815/2% EMI, at 90-100°C for 24 hours.

Mechanical Measurements

Because of their small size, the stiffness of the composites was measured using a penetrometer. (The L.S. Starrett Co. cat #4101). Tests were done on a polished surface of the composite and in the adjacent unreinforced matrix. The stylus was a commercial needle from Ogura Jewell Industry, Co., LTD the (radius 10^{-2}mm). Tensile compliance, was calculated according to the method described by Clough, Gillen and Quintana.[5]

Results and Discussion

The structure obtained by SEM showed a rope-like structure with small cells (1-10 microns)(Fig. 1). As the ratio of the polyimide to Kevlar was increased, nodules of polyimide were formed on the Kevlar-rich struts, implying phase separation. The nodules of polyimide found at large concentration of this polymer were found to be related to the solvent. This conclusion is based on a comparison of materials made from the polyimide dissolve in dioxane vs sulfuric acid. The morphologies of materials from this solvent are different from those made using sulfuric acid (Fig. 2). In addition, a comparative study of sublimation vs extraction in the processing of the reinforcements suggest that the mere fact that the acid is extracted (rather than sublimed) is not important.

Preliminary penetration results suggest that the fibrous materials are increasing the modulus of the epoxy by about 20%. If the modulus of the

reinforcement were that of fully aligned Kevlar (~130 GPa), a modulus increase of 11% would be expected, assuming random placement of the fibers. Thus, our results are consistent with an efficient reinforcement of the epoxy matrix by the 3-D fibrous structures.

References

1. Helminiak, T. E., Benner, C. L., Arnold, F. E. and Husman, G. E., U.S. Pat. Appl. 902525, (1978).

2. Jackson, C. L., Samulski, E. T. and Shaw, M. T., "Foams from Rod-like Molecules", ACS PMSE Division Proceeding, Vol. 57, 107 (1987).

3. Alonso, M. A. and Shaw, M. T., "Isotropic Kevlar and PBA (poly 1.4 benzamide) Reinforcements from Composites", ACS PMSE Toronto, Canada meeting; June 1988 (In press).

4. Auburt, J. H. and Clough, R. L., Polymer, 26, 2047 (1985).

5. Clough, R. L., Gillen, K. T. and Quintana, C. A., J. Polym. Sci., Polym. Chem. Ed., Vol. 23, 359-377 (1985).

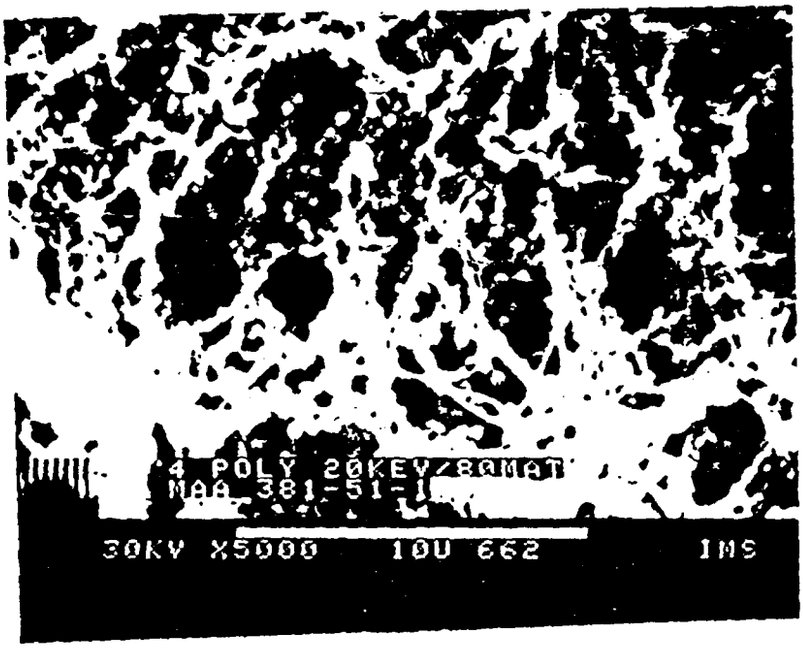

Figure 1. SEM of a three dimensional reinforcement containing 20% Kevlar and 80% matrimid 5218 prepared in 96% sulfuric acid.

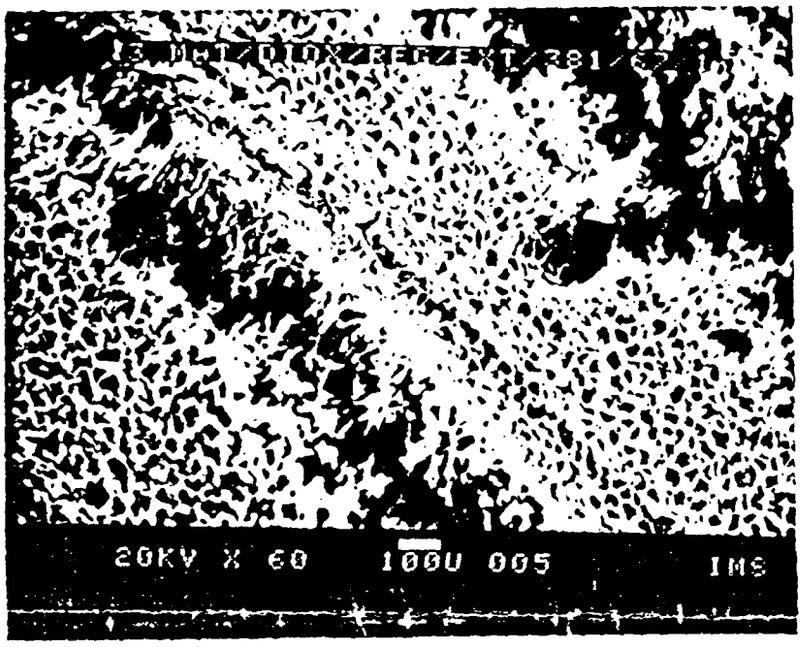

Figure 2. SEM of a 3% Matrimid 5218 reinforcement prepared in Dioxane.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1