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TECHNICAL REPORT

NATICK/TR-77/007

THERMAL DEGRADATION STUDIES OF FIBERS AND COMPOSITE BASE MATERIALS

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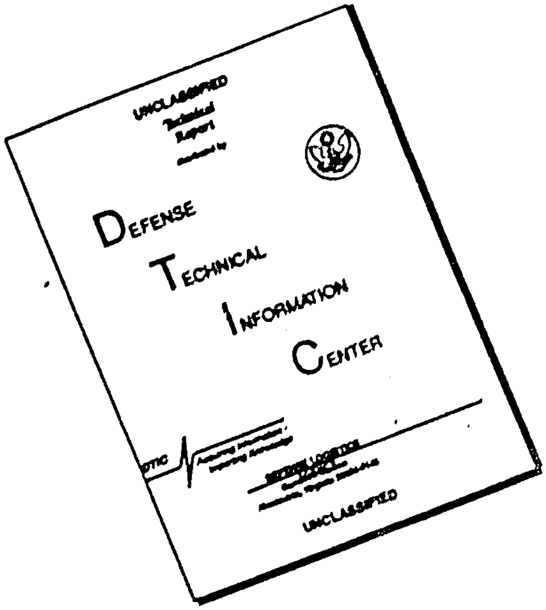
UNITED STATES ARMY
NATICK RESEARCH and DEVELOPMENT COMMAND
NATICK, MASSACHUSETTS 01760

Food Sciences Laboratory



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: NATICK/TR-77/007 ✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): ⑥ THERMAL DEGRADATION STUDIES OF FIBERS and COMPOSITE BASE MATERIALS.

5. TYPE OF REPORT & PERIOD COVERED: Technical Report-Final

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): ⑩ M. L. Bazinet, C. DiPietro & C. Merritt, Jr

8. CONTRACT OR GRANT NUMBER(s): ⑨ Final rept.,

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Analytical Chemistry Group/FSL
USA Research & Development Command ✓
Natick, MA 01760

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Pron.Nos. AW6-RA003-06-AW-BG & AW-T-RA003-01-AW-BG

11. CONTROLLING OFFICE NAME AND ADDRESS:
Army Materials & Mechanics Research Center
Watertown, MA

12. REPORT DATE: ⑪ Nov[redacted]76

13. NUMBER OF PAGES: 25

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): Same as above ⑫ 27p.

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report): Approved for public release; distribution unlimited.

⑭ NARADCOM-TR-77-007

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report): N/A

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APR 1 19
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18. SUPPLEMENTARY NOTES: None

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

THERMAL DEGRADATION
FIBERS
CARBON FIBERS
KEVLAR
SCOTCHPLY 1009-26
GAS CHROMATOGRAPHY
MASS SPECTROMETRY
PYROLYSIS
FIBERS (GLASS)
EPOXY RESINS

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Data are required on the thermal degradation properties of certain polymeric substances being considered for various material applications. This report describes the development and utilization of some specialized analytical techniques and the results obtained in analysis of certain materials. The polymer systems studied included carbon fibers, Kevlar fibers, weathered and unweathered specimens of Scotchply 1009-26 composite systems, modified and unmodified 3M SP 250 glass fiber composites, and Reliabond 7250 glass fiber composites → next page

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The analysis sequence involved the use of a pyrolysis device to form the decomposition products, and gas chromatography for their collection and separation. The volatile decomposition products were identified by mass spectrometry.

PREFACE

Work performed by Analytical Chemistry Group, Physical Sciences Division, FSL, NARADCOM for US Army Materials and Mechanics Research Center, Watertown, Massachusetts per Customer Order request Pron. Nos. AW6-RA003-06-AW-BG and AW-T-RA003-01-AW-BG.

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INTRODUCTION

Many new materials are being considered for structural applications in aircraft, helicopters, ships, ground vehicles, missile cases, rocket motors, helmets, etc. Data on the thermal stability and fire resistance of the new and novel polymeric systems anticipated for material applications has been lacking. Moreover, data are also lacking on the formation of potentially toxic substances from such materials upon heating.

In this project a method has been developed to evaluate thermal stability, fire resistance, and the products of different types of thermal degradation processes. Certain relevant materials as outlined below have been studied and the results of the experiments are presented.

EXPERIMENTAL

A combined pyrolysis/gas chromatography/mass spectrometry analysis system was chosen as the principal means of elucidating the thermal behavior of the substances to be studied. Several excellent reviews of the principles of combined pyrolysis/gas chromatographic/mass spectrometric analysis are available in the literature.[1,2,3].

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[1] R.L. Levy, Chromatogr. Rev. 8, 49-89 (1967).

[2] D.A. Leathard and B.C. Shurlock, "Identification Techniques in Gas Chromatography", John Wiley and Sons, Ltd., London (1970), p. 123.

[3] S.G. Perry in "Advances in Chromatography", Vol. 7., J.C. Giddings and R.A. Keller, eds., Marcel Dekker, Inc., New York (1968) p. 221.

This report, accordingly, will be restricted to a description of the applications of the techniques that have been made to problems relating to studies of polymeric materials of concern to the Army Materials and Mechanics Research Center.

I. Description of apparatus

A schematic diagram of the analytical system employed in this study is seen in Figure 1. Pyrolysis may be accomplished by several means under a variety of conditions. The thermal degradation products from solids pyrolyzers such as resistive type heater wires or ferromagnetic (Curie point) wires may be introduced to the GC/MS analysis system at the points indicated by arrows. The products from a boat pyrolyzer

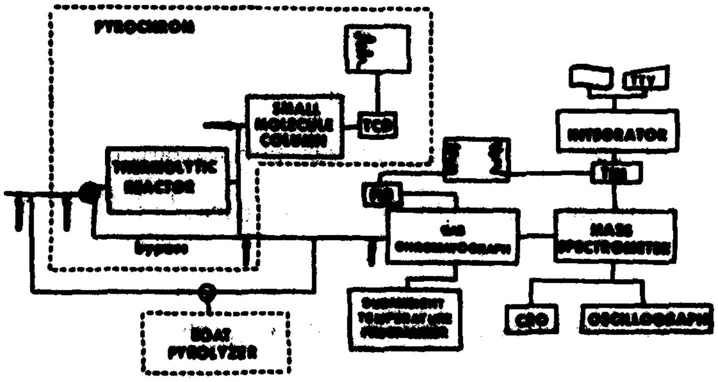

Figure 1. Schematic diagram of the apparatus.

may be similarly introduced. The conditions of temperature and atmosphere may be carefully controlled if desired. A vapor phase pyrolyzer (Pyrochrom) is also incorporated. Pyrolysis products are normally swept into a cold chromatography column with helium carrier gas as they are formed. Upon completion of the pyrolysis, a column temperature program is initiated to separate and elute the components. The eluents are then identified by means of the mass spectrometer (MS).

A photograph of part of the system is seen in Figure 2. The combined vapor phase and solids phase pyrolyzer is seen at the left of the gas chromatograph (GC). The heater furnace for the boat pyrolyzer is attached to one of the GC inlet ports. The time-of-flight mass spectrometer (TOFMS) ion source may be seen at the top right.

Figure 2. Pyrolysis/GC/MS analysis system.

Another system has been configured for TGA/GC/MS analysis. A photograph of this system is shown in Figure 3. The thermogravimetric analyzer (TGA) cell is mounted beside the gas chromatograph at the left. The mass spectrometer is a double focussing magnetic deflection type and utilizes a small (8K) computer system for data acquisition. The direct coupling of the thermogravimetric analyzer (TGA) to the GC/MS system was found to be inefficient for many reasons depending on the type of polymeric sample being tested. This method sometimes led to the loss of components of lower volatility through condensation in the extended conduction line from the TGA to the inlet of the GC. The heating rate of 10^{o}C per minute made the experiment very time consuming, thus involving greater background errors during analysis.

Figure 3. TGA/GC/MS analysis system.

Several descriptions of various analysis systems used at the Natick Research and Development Command laboratories for pyrolysis/GC/MS have been given in the literature.[4,5,6,7]

II. Collection of samples

Various methods for collecting the sample before admitting it to the mass spectrometer were tested and evaluated in an effort to avoid the loss of materials of lower volatility. Percentage of component recovery tests were conducted using solvents such as methylene chloride, benzene, toluene, and some lesser volatile chemicals as synthesized monomer, dimer, and trimer of polymeric compounds to simulate typical decomposition products. Sample collection traps utilized were of stainless steel tubing 20 inches by 0.06 mil I.D. having a four-way stopcock (which allowed flow-through or bypass conditions). These traps were attached to the exit end of the TGA oven, and refrigerated to effect

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[4] C. Merritt, Jr., "Microsimulation Air Pollution Studies by Pyrolysis/GC/MS". 21st Annual Conference on Mass Spectrometry and Allied Topics, pp. 320-324, May 20-25, 1973, San Francisco, CA.

[5] C. Merritt, Jr., C. DiPietro, D.H. Robertson, and E.J. Levy, "Characterization of Amino Acids by Pyrolysis/Gas Chromatography/Mass Spectrometry of Their Phenylthiohydantoin Derivatives". J. of Chromatographic Science, Vol. 12, November 1974, pp. 668-672.

[6] C. Merritt, Jr., R.E. Sacher, and B. Petersen, "Laser Pyrolysis/Gas Chromatographic/Mass Spectrometric Analysis of Polymeric Materials". J. Chromatography, 99 (1974) pp. 301-308.

[7] C. Merritt, Jr., C. DiPietro, C.W. Hand, J.H. Cornell, and D.E. Remy, J. Chromatography, 112 (1975) pp. 301-309.

condensation of volatiles as they emerged from the TGA. At the completion of the TGA temperature program the sample trap stopcock was closed, and the sample trap was detached from the TGA and connected to the gas chromatographic inlet of the Bendix-MA-2-TOFMS. A photograph of the system is seen in Figure 4. The sample trap was heated to 200°C with a heater tape envelope and the contents of the trap then flushed under a helium flow of 60cc per minute onto a cryogenically refrigerated GC column for a period of five minutes to sweep the volatile gases onto the cooled column for condensation. The cooled GC oven was then temperature programmed from -100°C to +250°C, and the eluents were sampled by the TOF mass spectrometer.

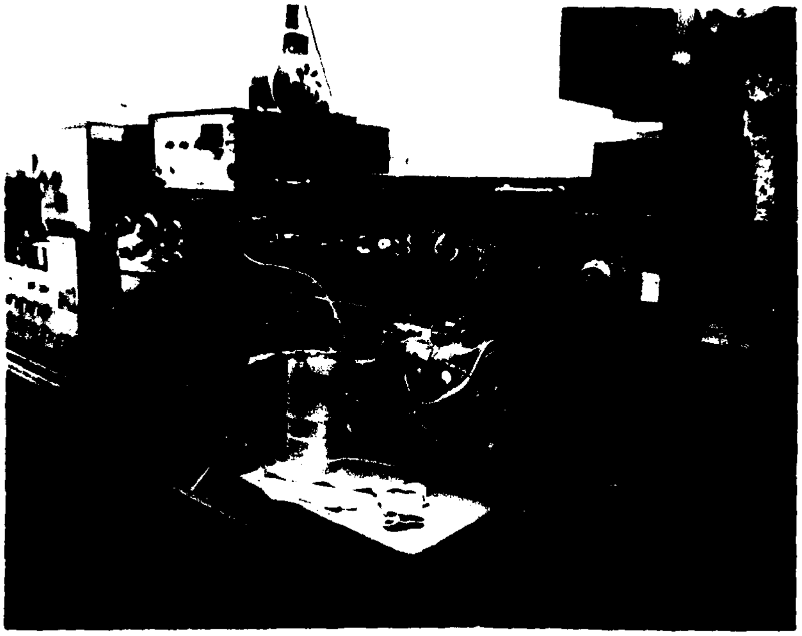

Figure 4. GC/MS analysis system with trap.

In order to avoid secondary reactions of the pyrolysis products it is desirable to provide for a fast temperature rise time, to rapidly sweep out the products and to employ small samples.

In further studies to improve on the decomposition product delivery to the GC column, a small volume pyrolysis oven was attached to the inlet of the GC/MS system.

The specially devised sample probe to achieve these objectives is shown in Figure 5. The sample (1-5 μg) is placed in the small cavity near the end (left), and the probe, after connecting to the heater chamber, is inserted quickly into the hot zone. The temperature employed for most of the analyses of polymers described below was 950°C. Fast pyrolysis tests were tried where the sample was heated at a selected temperature for one minute (the degradation temperature preselected by a separate TGA determination) the degradation products were collected on a -50°C column under a 15cc per minute constant flow of helium. Pyrolyzates were analyzed on the mass spectrometer, and the residual of the pyrolyzed sample was weighed to determine the amount of material decomposed. This method was useful for the identification of the major decomposition products formed.

Figure 5. Pyrolysis sample probe.

A slow pyrolysis procedure differed from the above pyrolysis method only by the slow heating (45 minutes) of the sample to a selected temperature. The results obtained compared favorably with the effects achieved with the directly coupled TGA and were more reproducible.

The essential preliminary tests were made on every polymeric sample. First, a polymer purity determination was made which involved the search for solvent and/or monomer by direct insertion probe analysis on the mass spectrometer. Then a separate TGA analysis of the polymeric material was useful in determining the thermal stability of the sample; that is, the critical temperature and the extent of decomposition involved. This was done by first weighing, then decomposing the sample in the TGA oven chamber, under a constant flow of helium or oxygen atmosphere, at a temperature program rate of 10°C per minute from ambient to the critical temperature where the degradation accelerated. A thermogram was obtained. The curve indicated the weight loss with temperature and the temperature range where the major portion of the thermal degradation occurred.

Chromatographic separations were performed on a 1/8-inch x 4-foot stainless steel column packed with 1% silicone SE-30 on Chromosorb. The column was programmed from -50°C to 250°C at 20° per minute.

RESULTS and DISCUSSION

The pyrolysis/GC/MS system has been used for a wide variety of studies of polymer characterization. These are summarized in the sections below.

I. Carbon Fibers

TGA/GC/MS analyses of 11 carbon fiber, high-temperature polymer samples were characterized at 1000°C. Figure 6 is an example of a typical total ion current chromatogram obtained in an analysis. It shows a broad GC peak for water and sharp, well-defined peaks for carbon dioxide and other components. No water was observed for samples 3, 4, 6, 8, 9, 10 and 11. Samples 2, 5, and 7 had trace amounts of water. A calibration for carbon dioxide was made to enable quantitation of the carbon dioxide evolved as a percentage of the total weight of the sample used in the thermal decomposition.

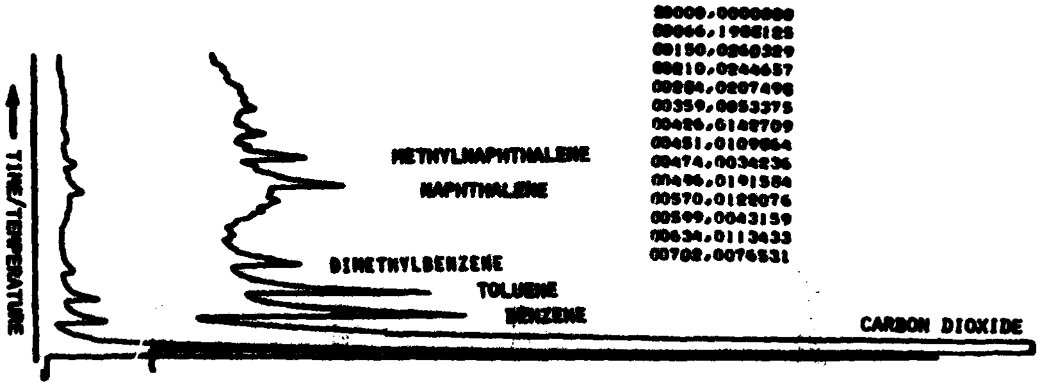

Figure 6. Chromatogram of pyrolysis products from carbon fibers.

Table 1. MS analysis of volatiles (Determined on waterfree basis)

Carbon Fiber Sample	Carbon Dioxide	Methane	Propane	Propene	Benzene	Toluene	Dimethyl-benzene	Naphtha-lene	Methyl-naphtha-lene	Estimated Carbon Dioxide Evolved as % of Sample Weight
1	100									1.58
2	100									1.00
3	100									0.06
4	100									0.05
5	48	23.0	0.5	2.0	9.5	8.3	2.9	2.9	2.8	2.34
6	100									0.07
7	100									0.02
8	32	20.0	19.0	20.0	7.0	2.0				0.35
9	100									0.13
10	100									0.16
11	48	2.0	14.3	15.0	14.4	6.4				0.36

A summary of the composition of components evolved from several different carbon fiber samples is seen in Table 1. Two parameters are seen to be significant in characterizing the fibers; viz, the amount of CO_2 evolved and the occurrence of various aliphatic and aromatic hydrocarbons. These factors may be ultimately related through correlation studies to the structure of the fiber.

II. Kevlar fibers

A series of pyrolysis experiments was conducted on samples of Kevlar polymer. Figure 7 shows the effect of fast pyrolysis as 2.8 mg of Kevlar was introduced into a 650°C furnace. The gas chromatographic

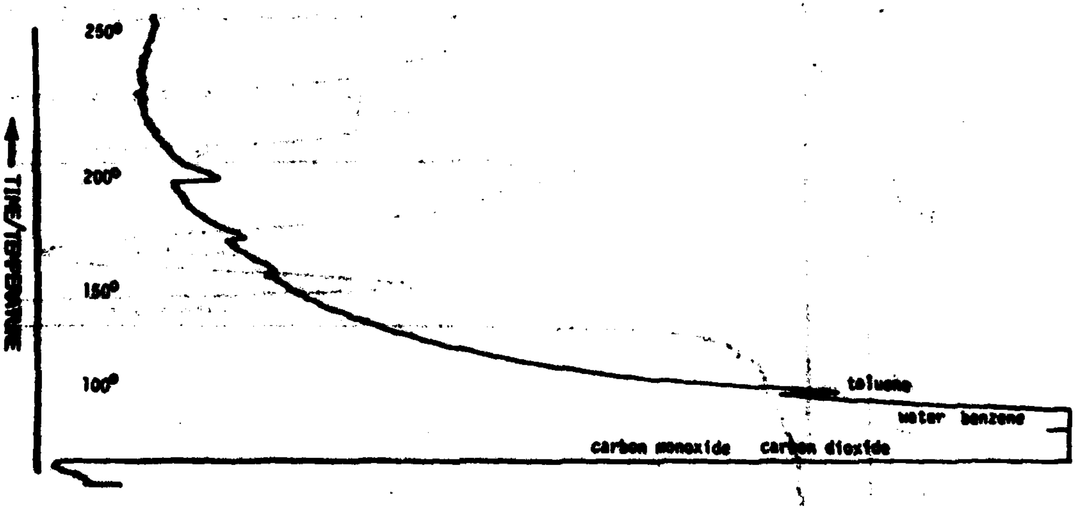

Figure 7. Chromatogram of products obtained from rapid pyrolysis of KEVLAR.

oven was programmed from -50° to +250°C at the rate of 10°C per minute. A 6-foot x 1/8-inch 10% SE 30 column was used with a flow rate of 25cc per minute. Approximately 63% carbon monoxide, 35% benzene, and 2% toluene were observed. The residue after pyrolysis weighed 0.6 mg.

Figure 8 depicts a slow pyrolysis of 3.4 mg sample of Kevlar which was heated to 650°C at 40° per minute for 15 minutes on a sample probe (Figure 5). The GC column was cooled to -100°C prior to sample pyrolysis.

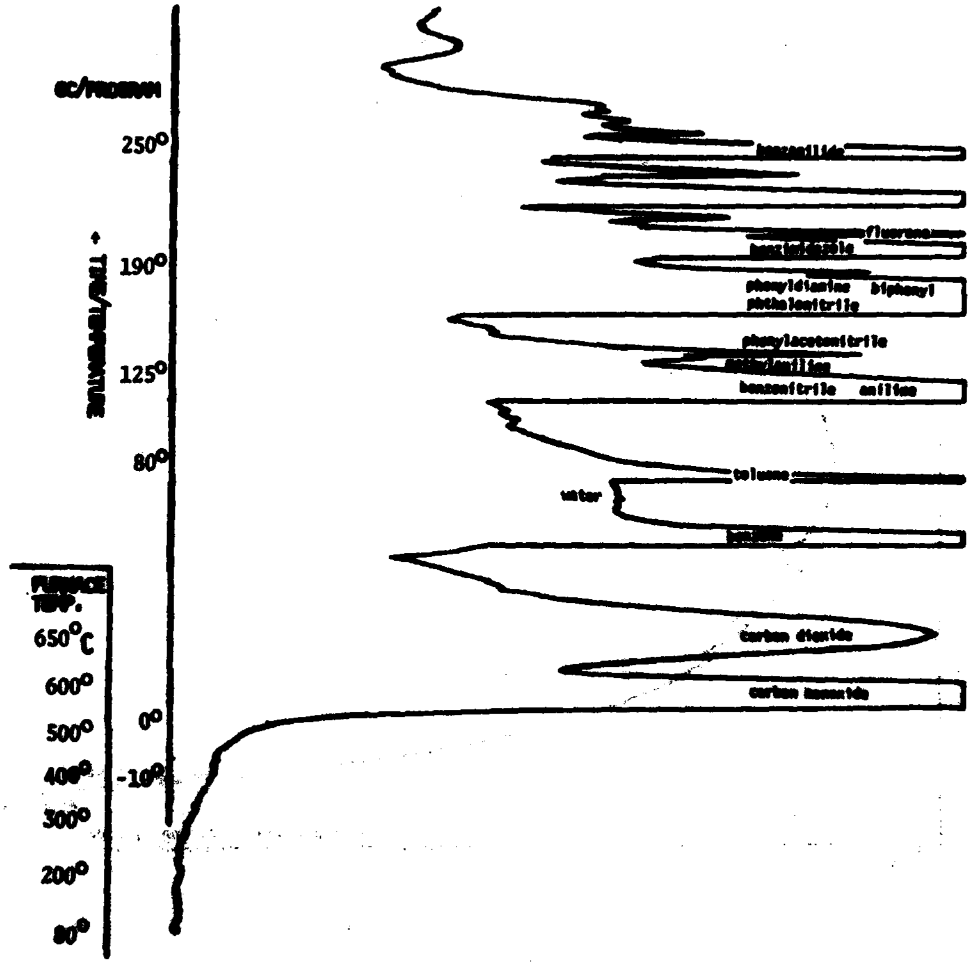

Figure 8. Chromatogram of products obtained from slow pyrolysis of KEVLAR.

After pyrolysis the GC column oven was programmed to 250°C at the rate of 10°C per minute. At least 15 compounds and a series of nitrogen containing cyclic components were determined on the time-of-flight mass spectrometer. No ammonia or hydrogen cyanide was observed. The identification of these compounds is given in Table 2.

Table 2

Compounds identified among the pyrolysis products of KEVLAR

nitrogen
carbon monoxide
carbon dioxide
methane
ethylene
propene
benzene
toluene
benzonitrile
aniline
methylaniline
phenylacetonitrile
phthalonitrile
phenyldiamine
biphenyl
benzimidazole
fluorene
benzanilide

A test was developed to detect the presence of residual hexamethyl phosphoramide in Kevlar. Samples of Kevlar (7 to 10 mg in weight) were analyzed on the Perkin Elmer 3920 GC/duPont 491 MS system by heating slowly to 275°C in an external furnace attached to the GC inlet. The furnace chamber was constantly flushed with a flow of helium carrier gas, and the effluent was collected on a cooled GC column until the collection was completed. The GC column oven was then temperature programmed from 70°C to 250°C. No trace of hexamethyl phosphoramide (HMPA) was observed. Sensitivity level for HMPA is 20 ppm.

Other samples of Kevlar were examined on the duPont 21-110 MS direct insertion probe, at 150° to 175°C. No hexamethyl phosphoramide was observed in these samples. Instrument sensitivity for HMPA in this case is 1 ppm.

III. Scotchply 1009-26 Composite System

A series of samples of exposed and unexposed glass-fiber epoxy resin composites was analyzed to ascertain the effect of environmental deterioration on polymeric materials in an attempt to correlate chemical and mechanical properties. Panels of these materials, Scotchply 1009-26, were exposed at a group of meteorological sites encompassing a great variety of exposures to extremes of sunlight and rainfall (Table 3).

Table 3

Test Sites

		TYPE OF ENVIRONMENT		
Fort Sherman, Sunshine (Atlantic) (Open Site)	**Panama**	Sun	Hot	Humid
Fort Sherman, Jungle (Rain Forest)	**Panama**	Hot	Humid	Microbiological
Maynard, Sunshine	**Mass**	Temperate		
Yuma, Sunshine	**Arizona**	Sun	Hot	Dry

The chemical composition of the 1009-26 system is depicted as follows:

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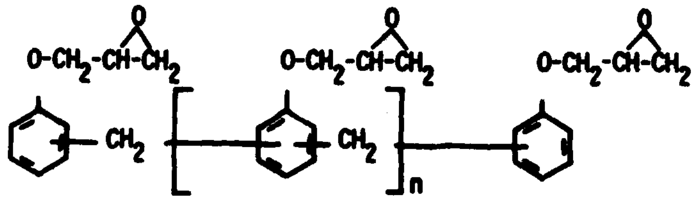
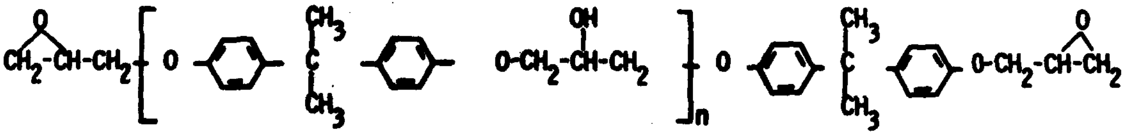


EPON 828



BF_3 • MEA COMPLEX

DOW CORNING 801-E GLASS FIBER

Samples of Scotchply 1009-26 composite panels were exposed for twenty-four months at various experimental sites with extremes in temperature and moisture. Test samples of these panels were pyrolyzed under similar condition, and results may be seen in Figures 9-10. An example of pyrolysis test on an unexposed twenty-four month sample of Scotchply 1009-26 composite is seen in Figure 11. Comparison of Figures 10 and 11 (exposed and control samples) indicate the differences observed are mostly due to the total amount of each decomposition product formed rather than differences in the chemical composition of the product formed. These differences in exposed and unexposed Scotchply 1009-26 composite samples are being compared with the chemical changes detected on the samples by analytical chemical techniques.

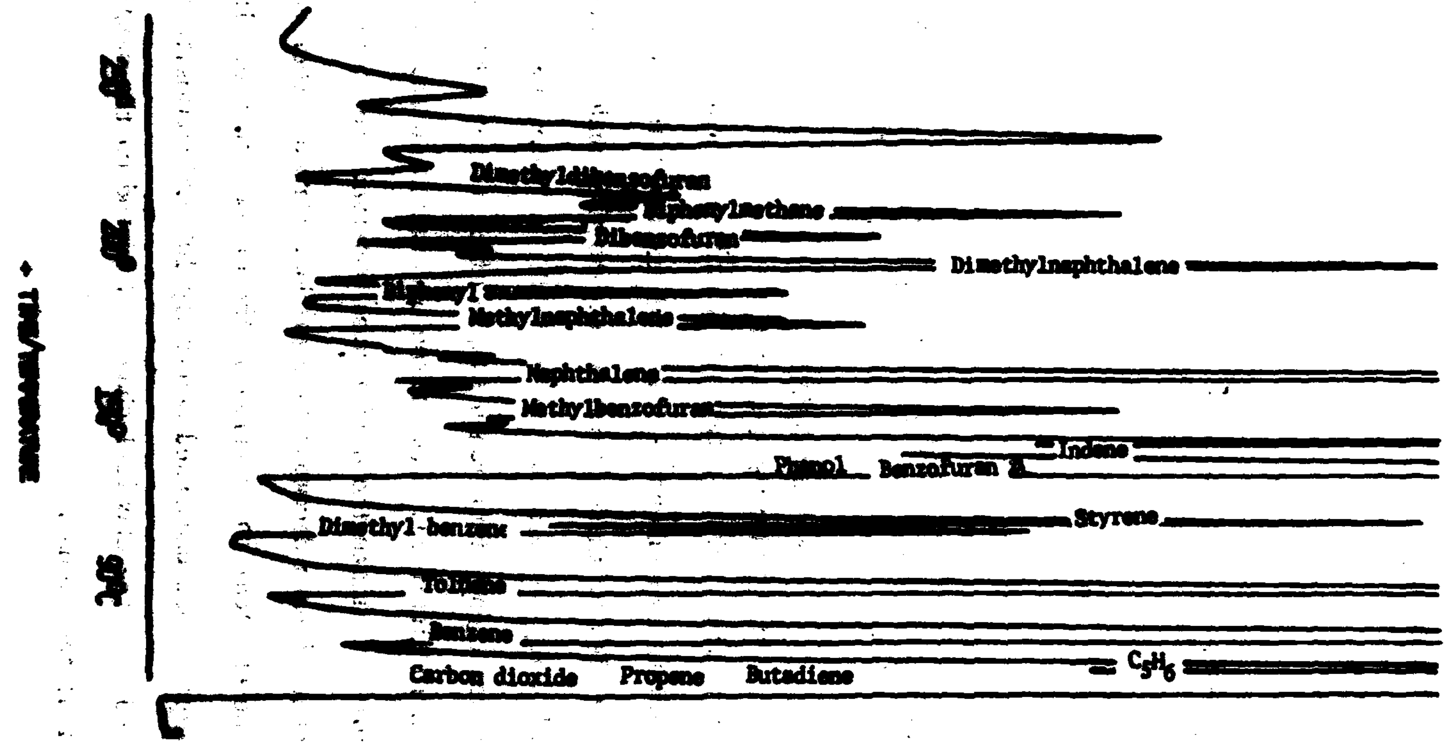


Figure 9. Chromatogram of pyrolysis products from epoxy resin panel exposed at Maynard site for 24 months.

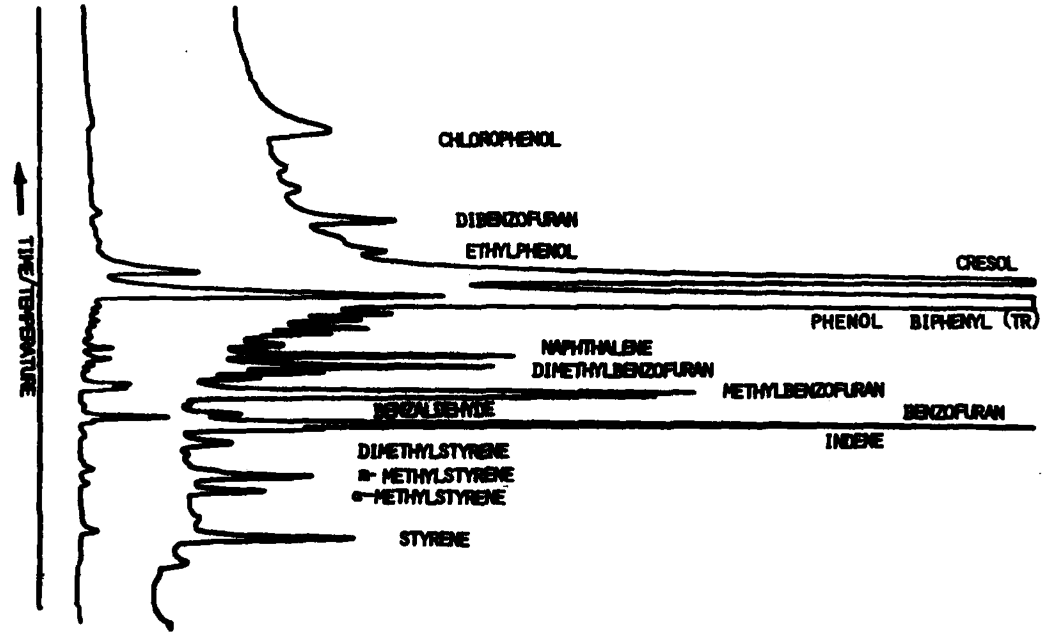


Figure 10. Chromatogram of pyrolysis products from epoxy resin panel exposed at rain forest site for 24 months.

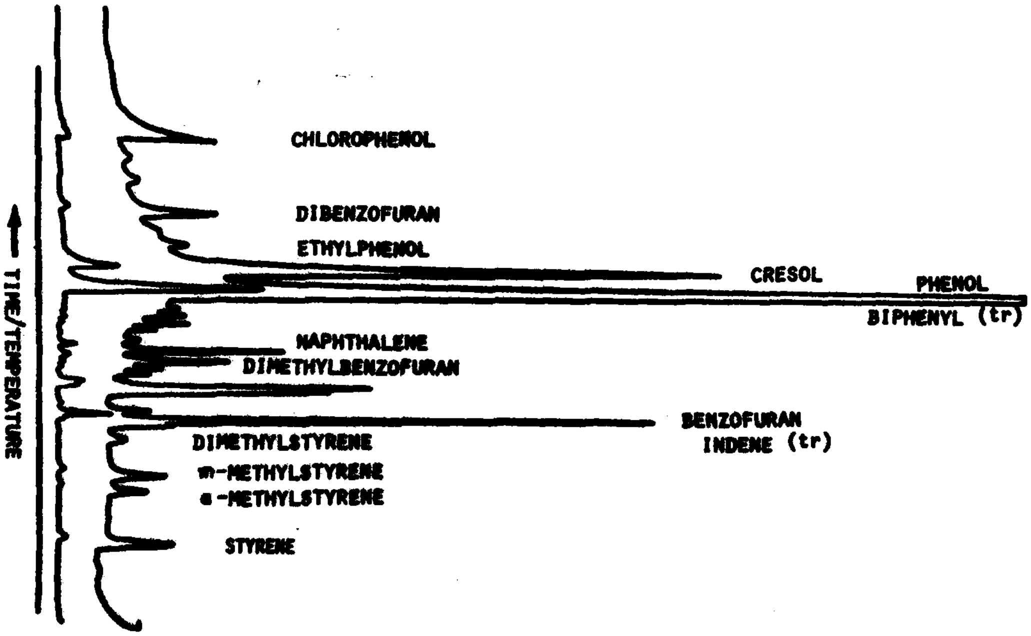


Figure 11. Chromatogram of pyrolysis products from unexposed epoxy resin panel.

IV. Rotor blade composites

A series of epoxy resin-fiberglass composites evaluated for use in helicopter rotor blades were examined by pyrolysis/GC/MS to determine the decomposition products formed in the pyrolysis of the various types of resins and modified composite systems.

The chromatograms may be seen in Figure 12. In this study the type of additive curing agent, and other modifications of EPON 828 resins may be discerned from differences in the pyrolytic decomposition products. Common components are seen in the chromatogram corresponding to sample D-3 (Figure 12). A change in the resin composition in samples D-1 and D-2 is discerned from the occurrence of 1,3-dimethyl-2-ethylbenzene, in their respective pyrograms. A further difference between D-1 and D-2 is indicated by the appearance of acetone in D-1.

The pyrolysis products from other resin systems used for rotor blade application composites is seen in Figures 13-14.

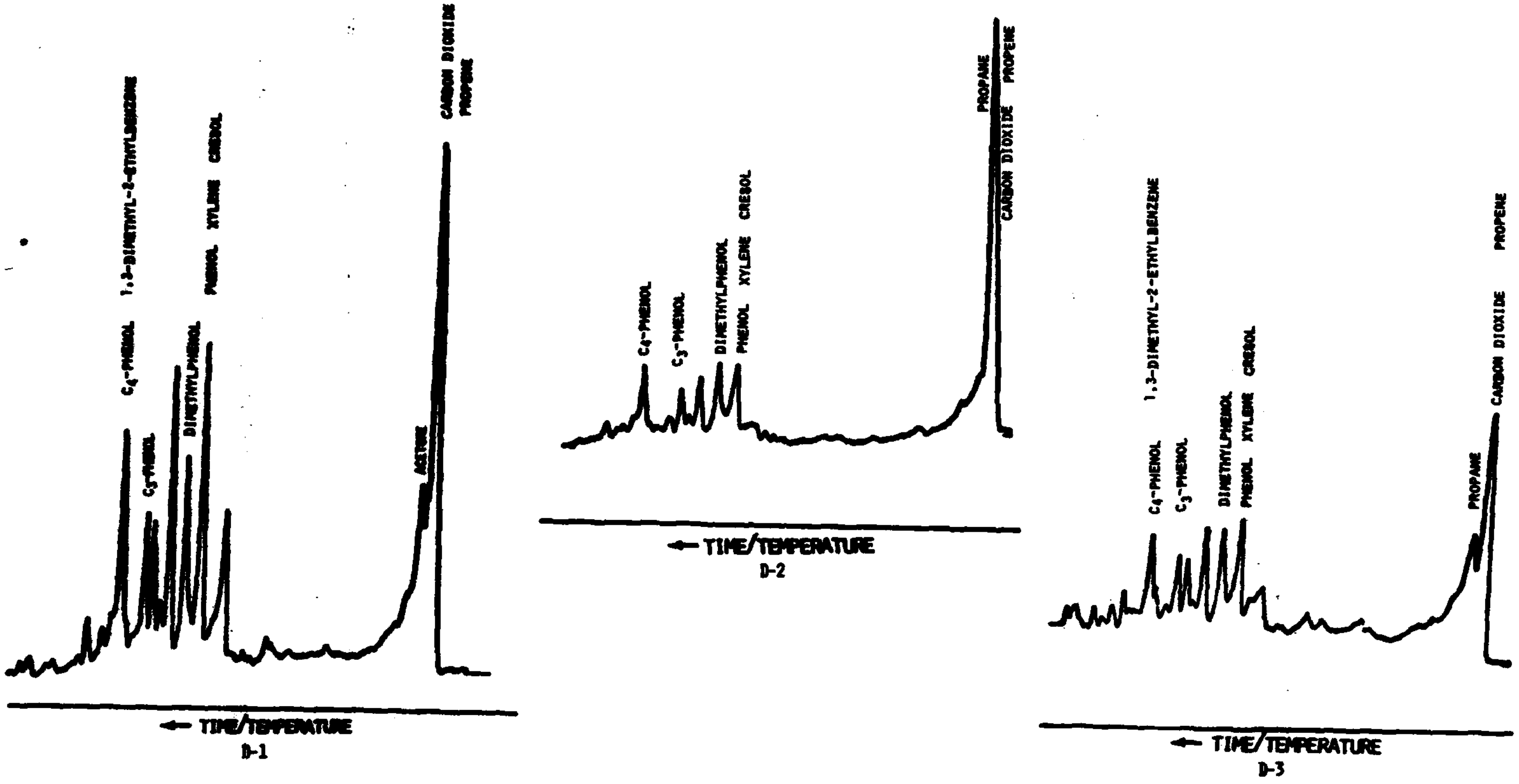


Figure 12. Chromatograms of various epoxy resin-fiberglass composites.

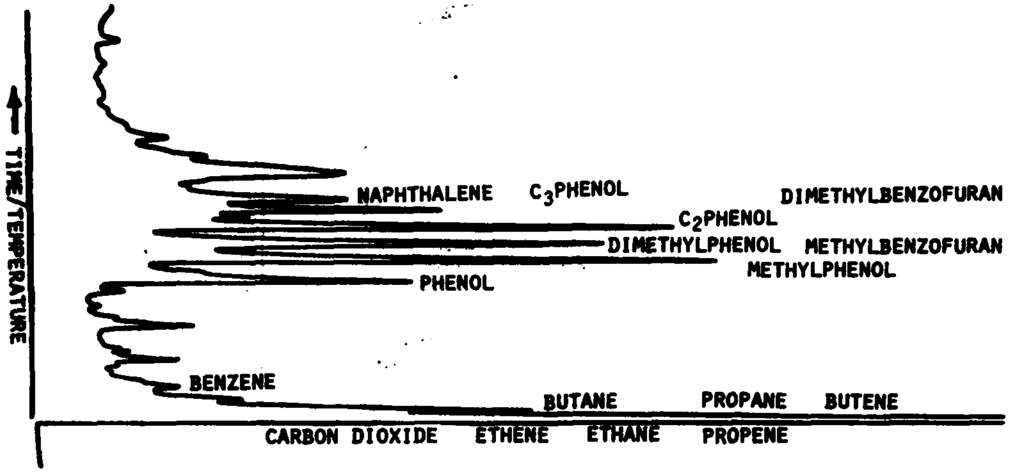


Figure 13. Chromatogram of pyrolysis products from SP 250 resin.

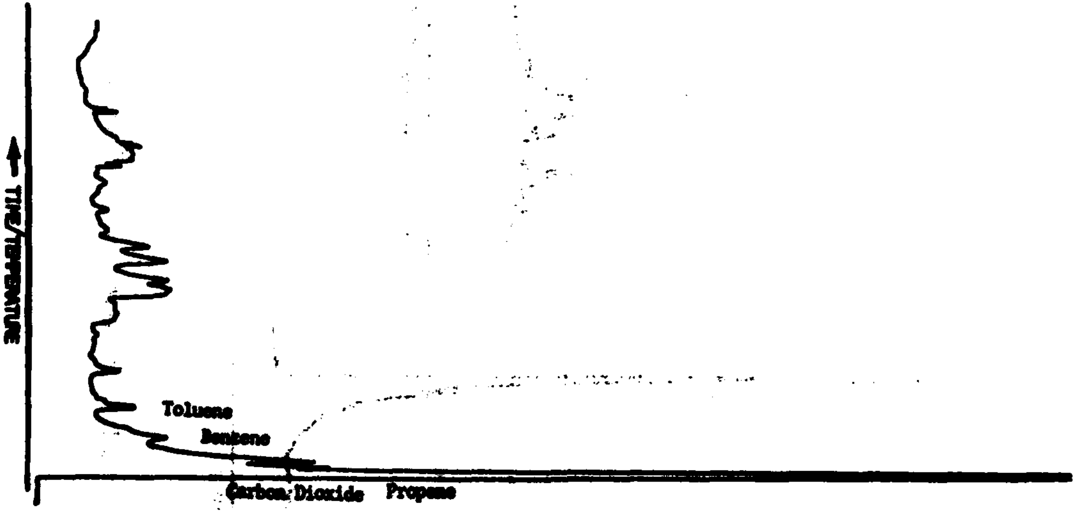


Figure 14. Chromatogram of pyrolysis products from Reliabond 7250 resin.

CONCLUSIONS

A reliable technique has been developed to identify the degradation products of the high temperature interaction of fibers and composite based polymers and evaluate the effects of the different types of thermal degradation processes.

The analysis sequence involves the use of a pyrolysis device for heat stressing the organic based materials to form the decomposition products, gas chromatography for the separation and quantitation of these volatiles, and mass spectrometry for the identification of eluted degradation products.

This technique produces vital information on the thermal stability, fire resistance, and potential toxicity of identified products formed from thermal stressing of pertinent materials used in army applications.