

CHROM. 7687

LASER PYROLYSIS-GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF POLYMERIC MATERIALS

CHARLES MERRITT, Jr.

Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Mass. 01760 (U.S.A.)

and

ROBERT E. SACHER and BRUCE A. PETERSEN*

U.S. Army Materials and Mechanics Research Center, Watertown, Mass. 02172 (U.S.A.)

SUMMARY

A technique has been developed employing laser pyrolysis coupled with gas chromatography and mass spectrometry to assess the degree of deterioration produced by weathering of fiber glass-epoxy resin type composite systems. The amount of volatile product obtained may be equated to time of exposure and appears to provide better criteria for evaluation than conventional physical testing methods. Some aspects of the mechanisms involved in photooxidation may be postulated from the qualitative nature of the components obtained on pyrolysis, but more data are required to permit definitive evaluation of various environmental effects.

INTRODUCTION

The effects of oxidation and other surface phenomena related to weathering of polymeric substances have been extremely difficult to evaluate, particularly when the substances involved are highly intractable. Pyrolysis techniques have been used for some time with considerable success for the characterization of conventional polymers¹, but more recently the advantages of laser pyrolysis have attracted attention.

The techniques investigated include both that of pulsed lasers for the rapid heating and cooling of samples, thus minimizing secondary reactions with resulting simpler pyrograms than conventional pyrolysis methods²⁻⁴, and low-power, continuous-wave lasers which allow thermal degradation studies to be conducted for temperature-dependent fragmentation⁵.

Extremely effective methods for the analysis of fragmentation patterns of samples by lasing on-line to a gas chromatograph have been reported^{2,6-8}. Most of the experiments using pulsed lasers for the pyrolysis of polymers involve degradation of the entire area of the laser beam. Under these conditions characteristic fragmentation products of the polymer are dependent upon total power or degree of thermal

* Present address: Department of Chemistry, Northeastern Univ., Boston, Mass., U.S.A.

flux of the laser beam. This type of laser pyrolysis employs a highly focused beam in which the basic energy is concentrated on a minute area. Using this method of focusing, the thermal flux of the laser radiation must pass through the sample and the plume. Because of the extreme heat generated by the lasing event (1200–8000 °K) a gradient is produced through the sample which will effect the degradation. If the sample is transparent to the laser radiation, powdered carbon or a non-absorbing medium may be added to either aid in heat transfer or absorption of the laser energy^{5,7,9}. Control of the temperature gradient throughout the sample is paramount. In order to avoid crater formation, Vanderborgh and Ristau have proposed lasing thin sections of sample so that the energy will drill a hole completely through the sample¹⁰. Guran *et al.*⁶ have shown that by defocusing the laser beam, larger-molecular-weight fragments can be obtained. By using defocused beams, larger fragments are obtained because of the lower energy per unit area with correspondingly less bond breakage.

It was the idea of control of the pyrolysis conditions that stimulated the interest in laser pyrolysis for the surface characterization of composites. The fact that the beam can be precisely focused has permitted a method to be developed that utilizes a pulsed laser beam to "strip" the surface of the photoinduced surface oxidation products without disturbing the unoxidized material below. The degradation products may be readily characterized by gas chromatographic (GC) and mass spectrometric (MS) analysis of the pyrolysates.

A glass fiber-reinforced epoxy system, 3M 1009-26 Scotch ply-composite material, was chosen for this laser pyrolysis study.

The technique involves defocusing a ruby-rod laser to incorporate a larger area and to provide a more evenly dispersed thermal flux across the surface. It was found that by using the laser at relatively low power to keep pyrolysis at a minimum, surface stripping of the oxidized material was obtained. That is, under the conditions of defocusing and low power, the products obtained were not characteristic of pyrolysis, but rather were representative of the fragmentation occurring at the weaker oxidized sites within the polymer chain.

EXPERIMENTAL

Material

The fiber glass-epoxy resin system 3M 1009-26 is a seven crossply laminate containing 27% resin. The glass is Dow Corning 801-E with 0.8% aminosilane coupling agent covering the surface. The epoxy system contains two parts DEN 438 resin, a novoloc system, to one part EPON 828, a bisphenol-A epoxy cured with a BF₃ monoethylamine complex. The structure of the resins may be depicted as follows:

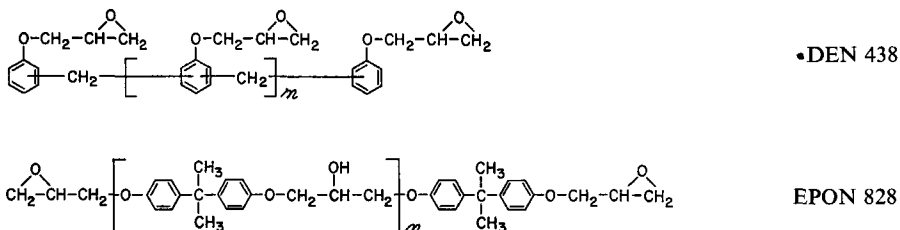


TABLE I
TEST SITES*

<i>Site</i>	<i>Type of environment</i>
Ft. Sherman, Panama, open field	Sun, hot, humid
Ft. Sherman, rain forest	Hot, humid, microbiological
Ft. Sherman, breakwater	Sun, hot, humid, salt content
Chiva Chiva, Panama	Sun, hot, humid
Maynard, Mass.	Temperate

* Samples placed on exposure test, July, 1972.

The composites were exposed to different outside environments for time periods of 6, 12 and 18 months (Table I). The surfaces of these composites began to deteriorate by photooxidation of the resin, primarily within the first 50 Å. This caused erosion of the polymer cross-linking and degradation of their critical mechanical properties as discussed below.

Apparatus

The laser used in this investigation was an Applied Lasers (Stoneham, Mass., U.S.A.) Model 1010C. It employed a ruby rod with an output capacity of 25 J at 6943 Å. The laser was operated in the normal pulse-mode with a pulse width of 2.7 msec. The energy impinging the sample was *ca.* 4 J per pulse. The sample cell (Fig. 1) consisted of a stainless-steel chamber with a quartz window for admitting the laser beam. A switching valve was incorporated in the cell assembly to allow a helium stream to flow through the cell or to bypass it. The cell was also equipped with heaters that were operated at 250 °C. The pyrolysis products were swept by helium carrier gas onto the chromatographic column through heated transfer lines. A photograph of the laser and cell assembly is shown in Fig. 2.

A Barber-Coleman Series 5000 gas chromatograph equipped with a flame

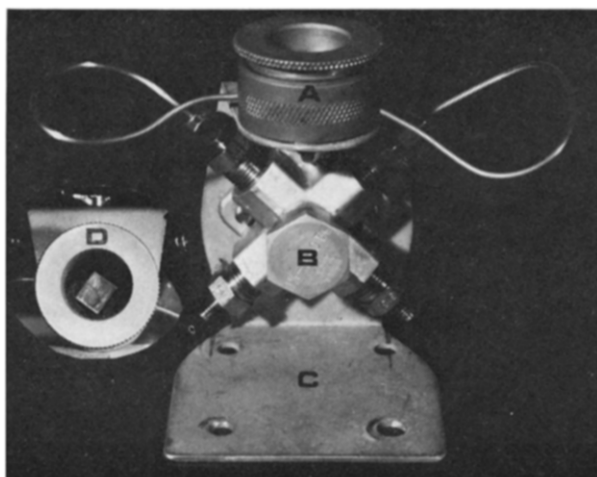


Fig. 1. Photograph of pyrolysis cell. A = Cell chamber; B = bypass valve; C = mounting stand; D = top view.

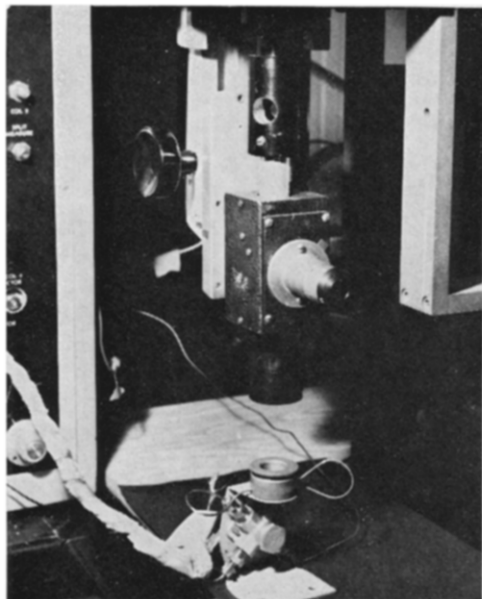


Fig. 2. Photograph of laser and cell assembly.

ionisation detector (FID) and a subambient linear temperature programmer was used to separate and detect the pyrolysis products. The separation column was a 50-ft. \times 0.20-in. support-coated open-tubular column with 3% SE-30. This column provided excellent resolution and efficiency when using subambient as the stationary phase temperature programming. The retention behavior of the lighter hydrocarbon gases using SE-30 as a stationary phase has been shown to be linear as a function of temperature from -180°C to 80°C (ref. 11).

Upon elution from the chromatographic column, the effluent stream was split, one going to the FID and the other to a quadrupole mass spectrometer. No molecular separator was used, but a restrictor was placed to control the pressure drop from the GC line to the spectrometer inlet¹². The mass spectrometer was an EAI Quad 300 capable of measuring masses from 1–500 a.m.u., and operated at 2.45 MHz over a mass range of 10–250 a.m.u. Spectra were obtained using a 70-eV ion source. The pressure range of the mass spectrometer inlet while operating in the dynamic mode was 4×10^{-6} – 2×10^{-5} torr.

Procedure

The composite to be analyzed was placed in the sample cell and sealed, the valve was switched from bypass to sample and helium was allowed to purge the cell of air. After sufficient time to rid the cell of air, the heaters were turned on and allowed to come up to temperature. The laser was first focused by means of the auxiliary ocular viewing lens (see Fig. 2) and then defocused a predetermined degree in order to achieve the largest area that will yield the maximum thermal density across the surface of the composite. The capacitors were charged to 1200 V and fired. The resulting pyrolysis products were then transferred on-line to the chromatographic

column at a flow-rate of 9 ml/min. Prior to pyrolysis the column was maintained at -180°C , and upon lasing, the following temperature program was initiated: starting temperature, -180°C for 5 min; heating rate, $12^{\circ}\text{C}/\text{min}$; final temperature, 200°C for 20 min.

As the components were eluted from the column, a chromatogram was obtained on a strip-chart recorder and the corresponding mass spectra were recorded on an oscillograph. An oscilloscope was used to monitor elution and to aid in selecting the time to scan the mass spectrum. Successive repetitive mass spectral scans were obtained during elution of a chromatographic peak to allow for deconvolution of unresolved components when required. The identification of components was achieved by means of comparison of the mass spectra with those of knowns listed in reference catalogs of spectra^{13,14}, but the spectra obtained from the quadrupole mass spectrometer were normalized to correspond to reference spectra acquired on magnetic deflection mass spectrometers using the relativity method of Karasek¹⁵.

RESULTS AND DISCUSSION

The objective of the laser pyrolysis analysis was to develop a means of evaluating the extent of weathering of the composite materials and, if possible, from the chemical composition of the pyrolysis products gain some insight into the mechanism of deterioration.

Panels of the composite exposed at the five test sites showed severe visual deterioration, especially after twelve and eighteen months' exposure periods (see Fig. 3). Fiber blooming had occurred on the aged specimens and 3–9% of the resin had volatilized (determined by thermogravimetric analysis).

Following conventional procedures for appraising deterioration, the critical mechanical properties were evaluated for the unexposed and exposed materials.

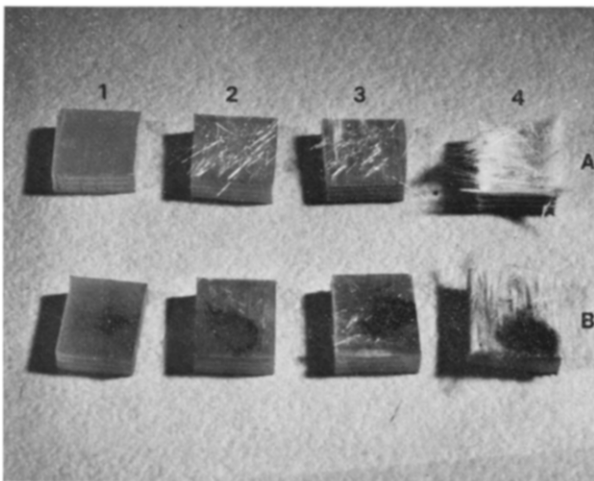


Fig. 3. Photograph of weathered composite samples before (A) and after (B) laser pyrolysis. 1 = Unexposed; 2 = 6 months; 3 = 12 months; 4 = 18 months.

TABLE II
COMPARISON OF TENSILE STRENGTHS FOR THE VARIOUS TEST SITES*

Test sites	6 months		12 months	
	Change	CV**	Change	CV**
Open field	-6.1	3.5	0.3	5.2
Chiva Chiva	-1.1	2.5	-13.8	5.3
Breakwater	-7.1	2.6	-6.0	9.5
Maynard	4.9	7.5	-22.0	4.4
Rain forest	-2.2	7.4	-6.0	9.5

* As % change —unexposed initial control = 735×10^{-2} p.s.i.

** Coefficient of variation, %.

TABLE III
COMPARISON OF FLEXURE STRENGTHS*

Test sites	6 months		12 months		18 months	
	Change	CV**	Change	CV**	Change	CV**
Open field	-21.5	10.5	-19.8	18.0	-13.0	3.7
Chiva Chiva	-15.7	3.7	-1.0	4.3	-13.8	6.5
Breakwater	-27.2	9.3	-4.2	2.3	-16.9	6.7
Maynard	-14.3	2.7	6.6	14.6	-9.7	6.4
Rain forest	-14.5	3.0	-17.0	15.7	-19.2	9.1

* As % change —unexposed initial control = 144×10^{-3} p.s.i.

** Coefficient of variation, %.

These results are tabulated in Tables II and III. Although the mechanical measurements seem to be reliable for the coefficients of variation within the experimental limitation for given exposure sites and times, the measurements at various locations are very inconsistent and do not provide a true measure of the sample deterioration¹⁶. The susceptibility of the resin to thermal decomposition and correspondingly the amount of volatile compounds released from the surface as a result of pyrolysis appears to be a function of the extent of deterioration. The degree of char produced by the laser beam is illustrated in Fig. 3. The unexposed sample yields only carbon dioxide and water as volatile products of laser pyrolysis. Several additional compounds, however, are formed by pyrolysis of the exposed samples. These are summarized in Table IV. The amounts of individual components vary with the type and duration of exposure,

TABLE IV
LIST OF COMPOUNDS IDENTIFIED AMONG THE VOLATILE PRODUCTS OF LASER COMBUSTION OF EXPOSED EPOXY RESIN-FIBER GLASS COMPOSITE

Methane	Methanol
Ethane	Ethanol
Benzene	Acetone
Toluene	Phenol
Ethylbenzene	Acetophenone
2-Phenylpropane	Phenyl ethyl ether

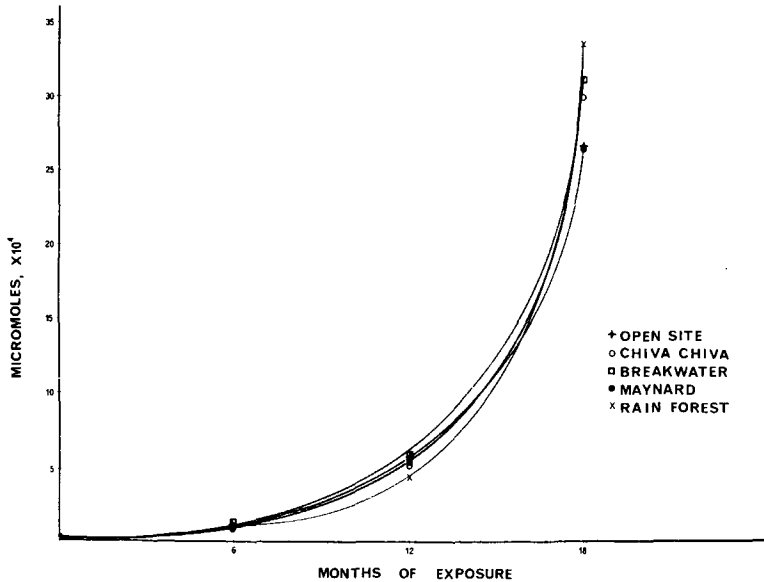


Fig. 4. Graph of total gas evolution from laser event as a function of exposure time.

but in general, the total amount of gas evolution is found to be nearly the same function of exposure time. This is seen in Fig. 4. The variation of certain individual components at two given test sites is illustrated in Figs. 5 and 6.

Environmental deterioration is primarily a surface phenomenon. For the Scotch ply-composite material studied here photooxidation of the epoxy resin system is expected to be the primary mechanism of degradation. In general, the effect upon the resin is predominantly to cleave ether linkages and/or carbon bonds with a resulting

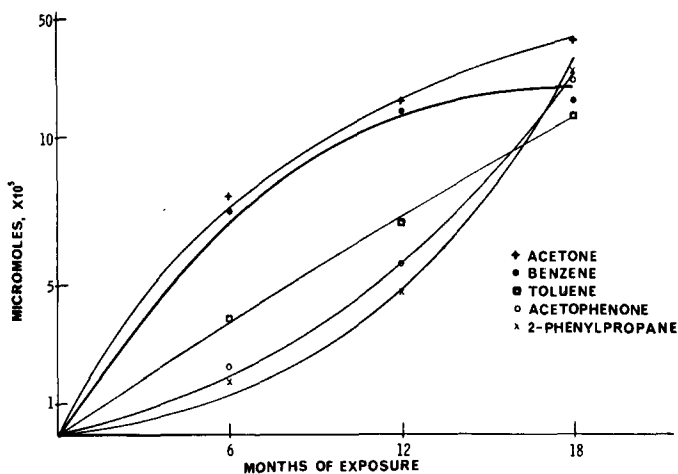


Fig. 5. Graph of amount of volatile component produced by laser pyrolysis as a function of duration of exposure at test site "breakwater".

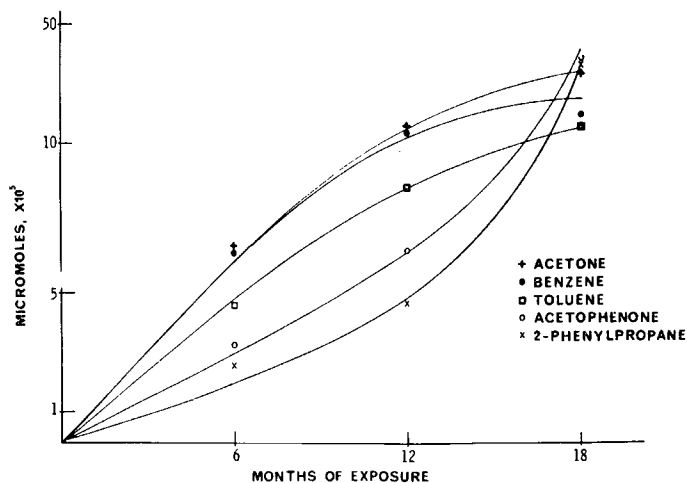


Fig. 6. Graph of amount of volatile component produced by laser pyrolysis as a function of duration of exposure at test site Chiva Chiva.

decrease in polymer chain-length. Correspondingly, the number of terminal groups is increased. The volatile products produced by thermal degradation are probably the result of cleavage of these terminal groups. Accordingly, as photooxidation increases, the susceptibility to thermal degradation likewise increases. Although the pyrolysis products are formed mainly by a mechanism that is related to a photooxidation process on the resin surface, moisture may also be an important secondary force. Further studies of ageing in isolated environments employing humidity and simulation of solar energy will provide new insights into the type of environmental factor causing the various pyrolysis products.

REFERENCES

- 1 R. L. Levy, *Chromatogr. Rev.*, 8 (1967) 49.
- 2 W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, 43 (1971) 702.
- 3 R. J. Levy, C. J. Wolf and J. Oro, *J. Chromatogr. Sci.*, 8 (1970) 524.
- 4 K. A. Lincoln, *Proc. Int. Symp. High Temp. Technol., 3rd, Asilomar, Calif.*, IUPAC, Butterworths, Washington, D.C., 1967, p. 323.
- 5 S. G. Coloff and N. E. Vanderborgh, *Anal. Chem.*, 45 (1973) 1507.
- 6 B. T. Guran, R. J. O'Brien and D. H. Anderson, *Anal. Chem.*, 42 (1970) 115.
- 7 O. F. Folmer and L. U. Azarraga, in A. Zlatkis (Editor), *Advances in Chromatography 1969*, Preston Technical Abstracts Co., Evanston, Ill., 1969, p. 216.
- 8 W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, 42 (1970) 1848.
- 9 W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, 44 (1972) 359.
- 10 N. E. Vanderborgh and W. T. Ristau, *J. Chromatogr. Sci.*, 11 (1973) 535.
- 11 A. G. Altenau, R. E. Kramer, D. J. McAdoo and C. Merritt, Jr., *J. Gas Chromatogr.*, 4 (1966) 96.
- 12 C. Merritt, Jr., *Appl. Spectrosc. Rev.*, 3, No. 2 (1970) 312.
- 13 E. Stenhagen, S. Abrahamsson and F. W. McLafferty (Editors), *Atlas of Mass Spectral Data*, Vols. I-III, Wiley-Interscience, New York, 1969.
- 14 *Eight Peak Index of Mass Spectra*, Imperial Chemical Industries Ltd., Dyestuffs Division, V. I., Mass Spectrometry Data Centre, Aldermaston, Great Britain, 1970.
- 15 F. W. Karasek, *Res. Develop.*, 21, November (1970) 55.
- 16 R. E. Sacher and E. J. Abramo, *Polym. Eng. Sci.*, submitted for publication.