

DEGRADATION OF AN ACETYLENE TERMINATED SULFONE (ATS) RESIN

II. Under partially anaerobic conditions

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Using a custom built reactor, we modelled the decomposition of a high performance Acetylene Terminated Sulfone (ATS) resin, more precisely bis[4-(3-ethynyl phenoxy) phenyl] sulfone and its higher oligomers, under partially anaerobic conditions. The residue of thermal degradation was shown to possess a higher oxidative stability than early products of thermal degradation, which "scavanged" oxygen in the reactor to form secondary products such as carbon monoxide, carbon dioxide, and water: thus preventing direct oxidation of the resin. On removal of volatile products of thermal degradation, the carbonaceous char residue of thermal degradation is directly oxidized to carbon monoxide, carbon dioxide, and water.

As part of an ongoing research effort aimed at the development of novel high performance thermosets, the Air Force has developed the Acetylene Terminated or "AT" concept which hinges upon the free radical oligomerization of terminal acetylene groups synthesized onto a thermally stable resin precursor [1]. One such resin, bis[4-(3-ethynyl phenoxy)phenyl] sulfone and its higher oligomers, given the pseudonym Acetylene Terminated Sulfone or "ATS", was selected for scale up work, mainly due to the room temperature "tack and drape" imparted by the bridging sulfones, good solvent compatibility, and the relatively low cost of the feed chemicals required for its synthesis.

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A pilot plant batch of the resin, designated ATS-G, was synthesized by Gulf Chemicals for evaluation by AFOSR [2]. In part I of this series, we focused on processes involved in the degradation of this high temperature material in the absence of oxygen [3]. In this, the second member of the series, we discuss the decomposition of ATS resin in contact with a small, limited supply of oxygen; in other words, under partially anaerobic conditions. In a subsequent communication, we will report on the accelerated high temperature oxidations of ATS resin under a flowing atmosphere of air [4].

Resin of this type is fated to be used as the matrix binder in high performance fiber reinforced composites. In a rapid oxidation, such as would accompany a cabin fire, we would expect available oxygen to be limited, a situation further exacerbated by the low diffusivity of a (normally) thick composite part. This would result in an oxidation process in which the diffusion of oxygen to the active site may be expected to be somewhat limited. It, therefore, becomes apparent that some way must be devised to model the decomposition of ATS resin in this common "real life" situation, to measure stabilities and identify possible toxic products of flash oxidation.

On a more fundamental level, we became intrigued by the ongoing controversy with regards the applicability of accelerated thermal testing under vacuum or inert atmosphere to the corresponding problem of materials stability in air. Only in some instances has any concensus of opinion emerged in the thermal analysis community on the applicability of accelerated inert atmosphere testing to the problem of oxidative stability of materials in a "real" environment. This issue is, of course, of interest in many laboratories due to the reliance upon such tests for the rapid evaluation and "grading" of the stabilities of new polymers and composites as they are synthesized. For example, it is rightly held that such comparisons are invalid at temperatures at which reaction is slow, and where the presence of oxygen completely changes the course of degradation. Good examples of this phenomenon would be long term polyolefin and polydiene oxidation. Most contentious still is the extrapolation of results of accelerated thermal testing under inert atmospheres to grade the resistance of plastics to rapid oxidation or burning. Some contend that volatile products of polymer thermal degradation, through rapid gas phase oxidations (burning), denude the polymer surface of oxygen and encourage thermal degradation as the primary decomposition process, especially of thick parts where oxygen, while others contend that oxygen, even at very low concentrations, is still able to play a significant part in the primary decomposition process. For instance, a simple comparison of weight loss profiles generated by

programmed thermogravimetry of ATS-G resin in air and under argon, to be made in Part III of this series [4] appeared to suggest that rapid oxidations of ATS resin in a ramped heating experiment are delayed to temperatures which correspond to the termination of bulk processes of thermal degradation, after which they volatilize the remainder of the sample.

To evaluate products of oxidation, and resolve, to our satisfaction, the thermal or oxidative nature of the primary decomposition reactions of this class of highly crosslinked thermally stable resin, we devised and built a degradation reactor of novel design for the study of the accelerated oxidation of polymeric materials in the presence of small and carefully metered amounts of oxygen. We have employed this experiment here to a study of the decomposition of ATS-G resin under partially anaerobic conditions, using throughout, as a benchmark for comparison, earlier studies of the thermal degradation of the resin [3].

Materials and methods

(Development and Use of the Oxidation Reactor)

Encouraged by the results of TG experiments, which appeared to suggest that the primary decomposition reaction in these highly stable polymers was thermal in nature [4], we set out to construct a reactor with which to study more closely the high temperature decomposition reactions of ATS and other such resins.

We chose to develop a system operable at reduced pressures for ease of coupling to a glass vacuum manifold, that products of degradation be amenable to subsequent chemical analysis. An added advantage of so doing, is that conditions of restricted oxygen access to the resin, as would be found within a part of some thickness, could be simulated. To our knowledge, such equipment could not be purchased, and so we set out, first of all, to develop the operating requirements for such a reactor, to design and build a reactor meeting those requirements, to test its operation, and finally apply it to a study of the decomposition of ATS-G resin under partially anaerobic conditions. Details of this progression form the basis of this publication.

Description of the reactor

The oxidation reactor, alluded to above, had to be operable at reduced pressures for reasons mentioned earlier. For design purposes we decided

that a closed system oxidation was also preferable in that the polymer could be made to react with precisely measured amounts of oxygen. However, allowance then had to be made to prevent a static build up of unreactive gas at the polymer surface, in other words, a recirculating loop of gas had to be formed to maintain the efficiency of the oxidation process. In tandem, a method had to be developed to condense from the gas stream the volatile products of oxidation for their eventual analysis. Our final reactor design is illustrated in Fig. 1, and its special relationship with other components of

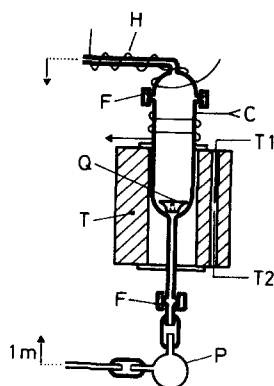


Fig. 1 Oxidation reactor: C - Cooling coils; F - Flange joint with viton "O" ring; H - Electrical heating tape; Q - Quartz sample crucible; T - Tubular muffle furnace; T₁ and T₂ - controller and recorder thermocouples; P - Water cooled magnetic drive pump

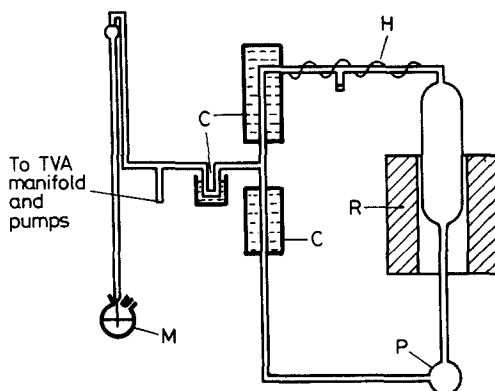


Fig. 2 Complete assembly: C - Cold traps; H - Heating coils; M - Mercury manometer; P - Magnetic drive pump; R - Reactor

the degradation assembly shown in Fig. 2. The reactor is connected to the vacuum pumps through the Thermal Volatilization Analysis (TVA) fractionation grid mentioned in Part 1 of this series [3]. An oxygen cylinder is connected also to the reactor through a gas manipulation assembly then the TVA manifold. Exact procedures for the operation of the experiment are discussed elsewhere.

Description of the experiment

With reference to Figs 1 and 2, we may subsequently "define" the oxidation experiment as performed here. The sample to be oxidized is placed in a quartz crucible with fluted base, so designed to encourage air flow past the sample. The sample "boat" is then lowered into the open ended quartz degradation tube which is enclosed in the muffle furnace, then sealed, at top and bottom "O" ring joints, into the static glassware assembly. The whole assembly is pumped to a hard vacuum, and prepurified oxygen (220 mg) is then admitted to the reactor through the vacuum line. The cold traps, illustrated in Fig. 3, are filled with liquid nitrogen, the heating tape and magnetic drive pump are switched on, and the assembly is warmed to 700° or

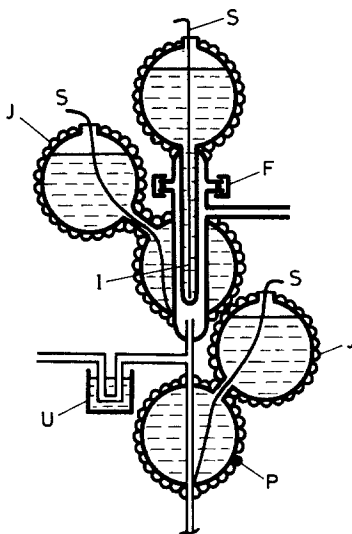


Fig. 3 Cold traps: F - Flange joint with viton "O" ring; I - Internal cold finger; J - Jacketing cold traps; P - Polyurethane insulation; S - Siphon tube; U - "U" trap with Dewar flask

800° at a programmed heating rate of 5 deg/min. The oven is then switched off and lowered below the sample which is allowed to cool to (100-200)°. The condensable, noncondensable, oligomeric, and residual products of oxidation are then subjected to analysis.

Having described the experiment per se, we will next discuss individually, such important experimental details as sample preparation, oven calibration, oxygen purification, and efficiencies of product recovery.

Oven calibration

The heat source used throughout this work was a Marshall 2000°F tubular muffle furnace coupled to a West temperature programmer. All degradations were performed at a nominal heating rate of 5 deg/min. Oven temperatures were recorded as a function of time using a Chromal Alumel thermocouple adjacent to the programmer controller.

The temperature of the polymer sample was always lower than that of the furnace because of the thermal lag between the furnace, the degradation tube, and the crucible. The reactor was temperature calibrated by recording simultaneously the oven temperature and that of a thermocouple fed into the reactor through a vacuum port and arranged to press firmly onto the surface of the sample crucible. Both the oven and the calibration thermocouple were connected to the same recorder, and temperature profiles recorded as corresponding millivolt outputs. Thereafter, sample temperatures at any point in the warm up curve could be deduced from the oven thermocouple trace by simple reference to that calibration curve.

Sample preparation

Samples of ATS-G were deposited as thin films onto the base of quartz crucibles, and cured by programmed heating at 5 deg/min to 334° under high vacuum conditions in the TVA apparatus [3], to produce solvent free polymer films which were stored at room temperature until use. The 50 mg and 100 mg samples used in this work produced films of average thickness 60 and 120 micrometers respectively, both of which are below the limit of 180 microns at which gas diffusion appears to begin to play a major role in the bulk oxidation process [5, 6].

Gas flow in the reactor

Gas, in contact with the degradation tube, expands, becomes less dense, and rises due to simple convection. In contrast, gas in contact with the cold

traps contracts, becomes more dense, and falls. It was hoped that a circuit would be completed by gas flow through the horizontal connecting tubes, to produce a recirculating loop of gas powered by heat exchange from the oven to the cold traps. Unfortunately, the oven and cold traps produced isolated convection currents in the two vertical members of the reactor. We then wrapped the top cross member in electrical heating tape and installed a small water cooled magnetic drive pump into the assembly below the oven. The heating tape was maintained at $(60-80)^{\circ}$ and the pump was operated at a low voltage to produce a gentle flow of gas through the system, which was confirmed by introduction of bromine to the reactor under reduced pressure at the feed through point used in the temperature calibration of the reactor, and by observation of the slow one way movement of the gas to the cold traps.

Reactor volume calibration and oxygen measurement

A volume calibrated storage bulb was attached to the reactor at the upper feed through point, and the volume of the reactor assembly was subsequently determined to be (1229 ± 5) ml by simple gas expansion through application of Boyles law. To simplify matters, all degradation experiments were performed under an oxygen pressure of 1 cm of Mercury. It was shown that 220 mg of oxygen in the reactor produced a pressure corresponding to 1 cm Hg at room temperature. A 4% pressure drop was recorded when the heating tape was switched on and the cold traps were filled with liquid nitrogen. In all experiments, oxygen was introduced with the system at room temperature, in other words, with polymer initially in contact with about 220 mg oxygen.

The pressure in the reactor increased with oven temperature as the degradation experiment progresses. Oxygen is, however, partially converted to condensable materials which are removed from the gas phase by condensation into the cold traps. The two effects tended to cancel with the result that the maximum pressure recorded in any experiment was 2 cm Hg. This is, of course, well below the 15 cm pressure of oxygen gas required for condensation at -196° , and so problems of safety were never encountered. Even so, the mercury manometer, depicted in Fig. 2, was left open to the atmosphere during the course of experiments as a potential pressure release valve.

Oxygen purification

Oxygen was purified in the assembly by making use of a simple gas manipulation manifold attached to the vacuum line. Oxygen gas was flushed into the manifold to exit through a manometer column. A gas storage reservoir was cooled to -196° and approximately 5 ml of liquid oxygen was condensed into the bulb. The system was isolated and a "top cut" of 1-2 ml was flushed to the pumping system (to remove from the system traces of nitrogen gas, which requires for its condensation at -196° a pressure of 1 atmosphere). A middle cut was then expanded from the reservoir held at -196° through an activated 5 A molecular sieve trap held at room temperature, and a cold trap at -196° , to the oxidation reactor (to remove traces of water and carbon dioxide from the gas flux). The molecular sieve trap was then reactivated at 200° under a high vacuum and made ready to receive the non-condensable volatile product fraction of oxidation as mentioned later in this report.

System leakage and gas purity check

To perform properly, the reactor must be supplied with pure oxygen (by methods outlined in the previous section) and remain leak tight throughout the course of the experiment. We, therefore, had to determine the purity of gas introduced to the reactor and the leak rate of that reactor throughout the course of the experiment, as such impurity and leakage can introduce extraneous water and carbon dioxide to the products of degradation. To do so, the following experiment was performed:

The reactor was assembled, pumped to a high vacuum (10^{-4} torr) sealed, and left for 24 hours. The reactor was then opened to a section of evacuated TVA manifold equipped with a Pirani gauge to measure pressure built up in the reactor over that time period. By this experiment it was estimated that leakage into the system occurred at a rate of less than 1 mm Hg/24 h period.

The reactor was assembled, pumped to a high vacuum (10^{-4} torr), and 220 mg of purified oxygen was admitted. A blank run to 800° was performed and condensable volatile "products" were examined by gravimetry in a preweighed gas tight container, by the Sub Ambient Thermal Volatilization (SATVA) experiment [3, 7] as illustrated in Fig. 4, and by quantitative gas phase Infrared spectroscopy [3]. By these means it was shown that about 0.8 mg of carbon dioxide and 0.5 mg of "other material" accumulated in the reactor during the course of a blank run. Background levels of these "other" materials (presumably benzene and phenol, left in the reactor from prior ex-

periments) were subsequently reduced by preevacuation for 48 h prior to each experiment.

Condensable gas trapping efficiency

To properly use the reactor described here it was essential that the condensable gas trapping efficiency in the cold traps be determined. Essentially, all the noncondensable volatile products of degradation are removed from the reactor at the end of the experiment, through a liquid nitrogen cold trap, to the molecular sieve containing trap also held at -196° . A poor trapping efficiency of condensable gas in the reactor and transfer cold traps would result in a fraction of the condensable volatile products reaching the molecular sieve, from which they would not be removed for subsequent examination. To determine the trapping efficiency of condensables in the reactor traps and in the "U" trap, therefore, it was enough to perform a degradation experiment and determine the proportions of probe gas (in this

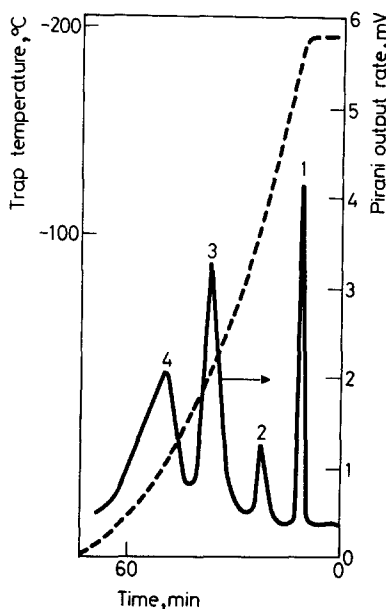


Fig. 4 An SATVA trace of condensable volatiles collected during a blank run to 800°C with purified gas but without a polymer sample. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature). (1) Carbon dioxide, (2) Benzene, (3) Water, (4) Phenol

case carbon dioxide) left in the reactor and in the "U" trap (desired) and transferred to the molecular sieve trap (not desired).

As determined by preliminary experiments, small amounts of carbon dioxide appeared to be irreversibly bound to activated 5 A molecular sieve at room temperature under high vacuum conditions and could not be removed for analysis by simple pumping. To study this effect we condensed measured aliquots of carbon dioxide onto the molecular sieve trap at -196° , then measured the amount or proportion recoverable at room temperature. Our results, summarized in Table 1, indicated that small amounts of carbon dioxide are indeed irreversibly bound onto molecular sieve at room temperature under high vacuum conditions, but that good recovery could be had by subsequent heating of the sieve trap to 200° .

Table 1 Efficiency of recovery of carbon dioxide from 5 A molecular sieve at room temperature

Run	mg CO ₂ onto sieve at -196°C	mg CO ₂ sieve at room temperature as measured by I.R. spectroscopy
1	0.17	<0.1
2	0.56	<0.1
3	0.79	<0.1
4	1.10	<0.1
5	7.80	<0.1*

*8.11 mg recovered by heating trap to 200°C

Having determined that the proportions of carbon dioxide in the receiving traps could be properly determined, we were then in a position to determine the trapping efficiency in our reactor using carbon dioxide as a probe gas. A 50 mg sample of ATS-G was heated in the reactor to 800° under 220 mg oxygen. Condensable volatile products were collected in the liquid nitrogen traps during the course of the experiment, and noncondensable volatiles in the molecular sieve trap at the end of the experiment. The sieve trap was then warmed to room temperature and the noncondensable fraction was flushed to the pumps. The sieve trap was then heated to 200° and adsorbed carbon dioxide transferred to a calibrated gas phase infrared cell for analysis by quantitative gas phase infrared spectroscopy [3]. By this method it was found that less than 0.1 mg of carbon dioxide was transferred to the molecular sieve trap at the end of the experiment. Later experiments showed that a 50 mg sample of polymer, under these conditions, produced an average of 20.2 mg of carbon dioxide in this experiment, as measured by material recovered from the liquid nitrogen traps. The trapping efficiency

for carbon dioxide in this experiment, was, therefore, shown to be greater than 99%.

Product analysis

All four of the product fractions of oxidation, namely the condensable and noncondensable gas fractions, the oligomeric products, and the residue of degradation, could be isolated for subsequent analysis using this experiment. Individual cases are summarized below.

The residue of oxidation

Residues of oxidation were determined by simple gravimetry. The pre-weighed crucible was removed from the degradation tube at the end of the experiment and reweighed to determine residual sample weight. The percent residue was then determined as (Final Sample Weight/Initial Sample Weight)X100.

The oligomeric product fraction of oxidation

The sample crucible was removed from the degradation tube at the end of the experiment. The oligomeric products, which condensed onto the upper part of the tube near the cooling coils, were then rinsed from the reactor with chloroform into a small beaker for subsequent analysis by infrared spectroscopy using a Beckman I.R.-33 grating spectrometer.

The condensable volatile product fraction of oxidation

Noncondensable products of oxidation were removed from the reactor, which was pumped to a high vacuum. Siphon tubes were inserted into the cold traps from which liquid nitrogen was sucked using house vacuum. The condensable volatile products of oxidation were then evaporated into the TVA manifold, collected there, and subsequently analysed by Sub Ambient Thermal Volatilization Analysis (SATVA), gravimetry, quantitative gas phase Infrared, and proton N.M.R. spectroscopy, as outlined in Part 1 of this series [3].

The oxidation process produces large quantities of carbon dioxide which could not be properly analysed in the calibrated Infrared (I.R.) gas cell. For this reason, the gas cell was attached to the vacuum manifold through a calibrated gas expansion bulb. Condensable volatile products of oxidation were first condensed into the cold finger of the gas phase I.R. cell. The

whole assembly was then isolated from the vacuum line, and the products warmed to room temperature. By the ideal gas law (which these materials obey due to the low pressures involved) the gas partitioned between the two containers according to the ratio of their volumes. Knowing this ratio, from the quantity of CO_2 in the gas cell, as measured from band intensities, and by making use of the appropriate calibration curve [3], we could work out the total CO_2 produced in the degradation experiment.

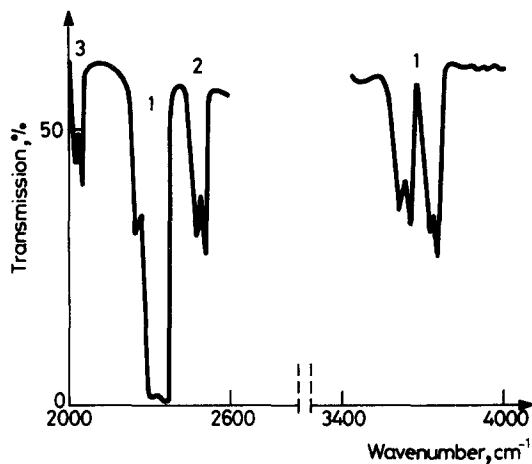


Fig. 5 Gas phase Infrared spectrum of the condensable volatile products of oxidation to 800°C of precured ATS-G resin. (1) Carbon dioxide, (2) Sulfur dioxide, (3) Carbonyl sulfide

A typical gas phase I.R. spectrum of the condensable volatile products of oxidation of ATS-G resin, as reproduced in Figure 5, identifies sulfur dioxide and carbonyl sulfide as components of the product mixture, along with massive amounts of carbon dioxide. All three products are formed in the absence of oxygen [3], and may, therefore, be identified as products of thermal degradation. However, carbon dioxide is shown by this spectrum to be produced in much higher yield in the presence of oxygen (as would be expected). A typical proton N.M.R. spectrum of the same material, shown in Fig. 6, identifies also benzene, phenol, and water as major involatile condensable volatile products of oxidation. All three have also been previously identified as products of thermal degradation of the resin [3], however, water (also as expected) is shown to be produced at enhanced levels in the presence of oxygen.

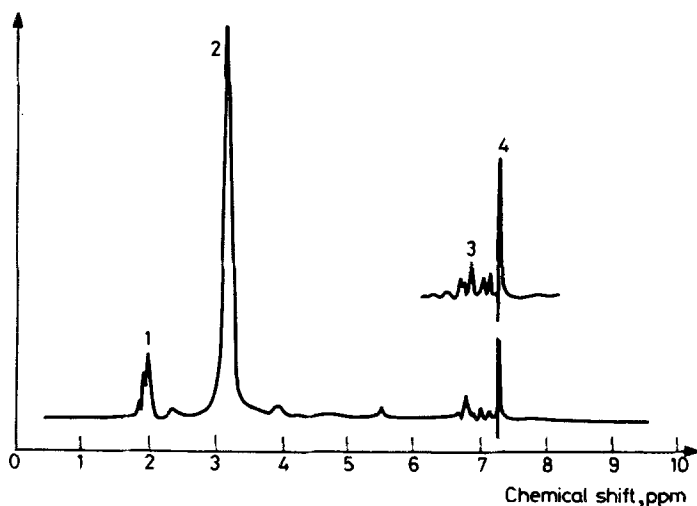


Fig. 6 Proton N.M.R. spectrum of the condensable volatile products of oxidation to 800°C of precured ATS-G. Solvent - deuterated acetone. (1) Solvent, (2) Water, (3) Phenol, (4) Benzene

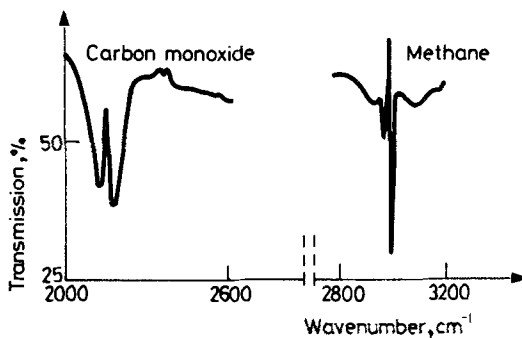


Fig. 7 Gas phase Infrared spectrum of an "aliquot" of noncondensable volatiles produced by oxidation of ATS-G resin to an end temperature of 800°C

The noncondensable volatile product fraction of oxidation

At the end of the experiment, noncondensable material was pumped into a 5 A molecular sieve trap held for that purpose at -196° . The trap was warmed to room temperature, and evolved gas was transferred in 4 aliquotes to a gas phase Infrared cell with molecular sieve, which had been previously calibrated for carbon monoxide and methane [3]. A typical gas phase I.R.

spectrum of one of these aliquots, shown in Fig. 7, identifies carbon monoxide and methane as products of oxidation. Although both gases are produced also in the absence of oxygen [3] the first is shown here to be produced in much larger quantity in the presence of oxygen.

It should be obvious from this and previous discussions, that the addition of small amounts of oxygen to the polymer at elevated temperatures does not result in the formation of new products, but does influence the proportions of those products formed also in the absence of oxygen.

Results and discussion

(Oxidation of ATS-G Resin Under Closed System Conditions)

Using the techniques developed in previous sections, we were able to identify and measure quantitatively, products of oxidation of ATS resins under partially anaerobic conditions, and by so doing, shed some light on the nature of the primary oxidation step under those conditions, and by inference, also within articles of macroscopic dimensions exposed to similar accelerated oxidations in the presence of a limited supply of oxygen.

We, first of all, recount a short list of simple analyses which were performed for this purpose on the four product fractions of oxidation of ATS-G resin. We next explore the nature of the bulk oxidation reaction which commences upon completion of processes of thermal degradation, using pre-degraded resin, and finish with some simple arithmetic which appears to support the contention that the primary reaction of these thermally stable resins under conditions of accelerated decomposition in a limited supply of oxygen is thermal in nature.

SATVA of the condensable volatile products of oxidation to 800°

Samples of pre-cured ATS-G (50 mg and 100 mg) were heated to 800° at a rate of 5 deg/min under 220 mg oxygen in the oxidation reactor. The condensable volatile products of oxidation were then trapped in the vacuum line and separated for analysis by SATVA. SATVA separations of products from 50 mg and 100 mg samples of resin are reproduced in Figures 8 and 9, from which it can be seen that the condensable volatile product distribution of anaerobic degradation, as reproduced in Fig. 10, is somewhat, but not completely, altered by the presence of a limited supply of oxygen. (Although the anaerobic experiment was performed to an end temperature of 1020°, we

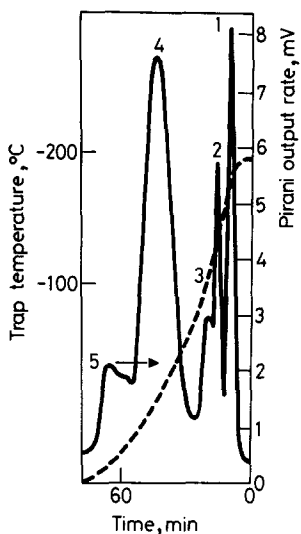


Fig. 8 An SATVA trace of the condensable volatile product fraction of oxidation to 800°C of a 50 mg sample of precured ATS-G resin. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature). (1) Carbon dioxide and carbonyl sulfide, (2) Sulfur dioxide, (3) Benzene, (4) Water (5) Phenol

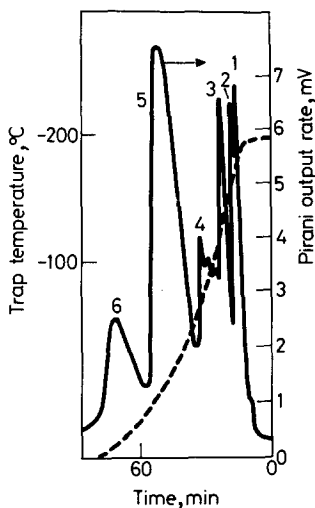


Fig. 9 An SATVA trace of the condensable volatile product fraction of oxidation to 800°C of a 100 mg sample of precured ATS-G resin. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature). (1) Carbon dioxide (2) Carbonyl sulfide, (3) Sulfur dioxide, (4) Benzene, (5) Water (6) Phenol

can compare the two because condensable volatiles are produced only below 800° under high vacuum conditions.)

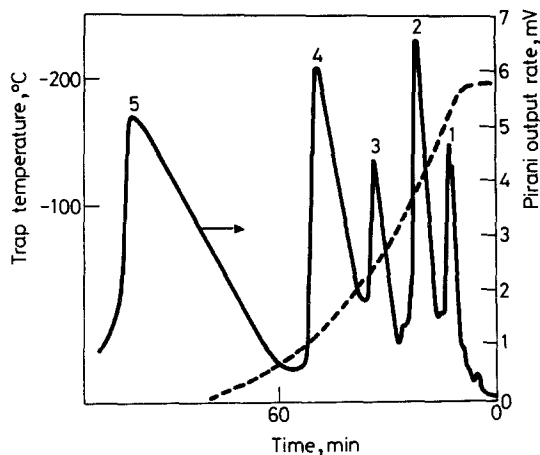


Fig. 10 An SATVA trace of the condensable volatile product fraction of thermal degradation to 1020°C of a 104 mg sample of precured ATS-G resin. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature). (1) Carbon dioxide and carbonyl sulfide, (2) Sulfur dioxide, (3) Benzene, (4) Water (5) Phenol

If we directly compare SATVA traces from 100 mg samples degraded under vacuum and in the presence of a small amount of oxygen, as illustrated in Figures 9 and 10, we can see that the yields of sulfur dioxide are similar, but that the yields of benzene and phenol are reduced, and that the yields of carbon dioxide and water are increased in the presence of oxygen. The obvious, and quite probably true, explanation for this effect, is that benzene and phenol are oxidized after formation to carbon dioxide and water. If we compare the SATVA traces from 50 mg and 100 mg samples of polymer which had been oxidized in the reactor, it can be seen that a proportionately larger fraction of benzene and phenol are converted to carbon dioxide and water in the product distribution from the 50 mg sample than in the corresponding distribution from the 100 mg sample. From this comparison, it becomes obvious that the oxidation reaction proceeds more efficiently as the mass ratio of oxygen to polymer in the reactor increases.

Gravimetric analysis of the residues of oxidation to 800°

The percentage residues of degradation of ATS-G to 800° in air, under helium, and in a high vacuum, were measured, in most cases, simply by comparing "before and after" weights as (After/Before)X100. The sole exceptions were results from the TG experiments performed under Helium and in air, which were simply read from the dynamic weight loss curves. Residues of degradation are quoted in Table 2.

Table 2 Residues of thermal and oxidative degradation of ATS-G to 800°C at 5 deg/min

Experiment	Residue ar wt.% of the cured polymer
TVA (high vacuum)	55.2
TG under Helium	57.6
50 mg in oxidation reactor	58.5
100 mg in oxidation reactor	59.4
TG in air	0.0

Similarities between sample residues measured in weight loss experiments performed under helium and under vacuum were expected from previous work [3]. A discrepancy between those results and that from the TG experiment performed in air was also expected, due to the operation of the high temperature "bulk" oxidation reaction which quantitatively volatilizes the remainder of the sample after completion of the major volatile producing processes of thermal degradation. More surprising, was the good agreement between weight loss experiments performed under inert conditions and in the oxidation reactor, from which it can be deduced that the bulk oxidation reaction is heavily suppressed under conditions where oxygen is present in small quantities only. Presumably, under these conditions, oxygen, at the temperatures at which the bulk oxidation reaction is operative, has been reduced below a level at which it can quantitatively react with the sample, perhaps by reaction with volatile products of thermal degradation, as is suggested by the results of the SATVA experiments.

Oligomer product analysis

A small quantity of oligomer was recovered from experiments in which 100 mg samples of ATS-G were degraded to 800° in the oxidation reactor. Material collected from several experiments was combined to obtain the Infrared spectrum shown in Fig. 11, which appears similar to that produced by the oligomeric product fraction of thermal degradation of the resin [3], ex-

cept for the appearance of absorption bands which suggest the presence of more saturated material and some carbonyls in the oxidized material. It was interesting to note that no oligomeric products were recovered from 50 mg samples which were oxidized under the same conditions.

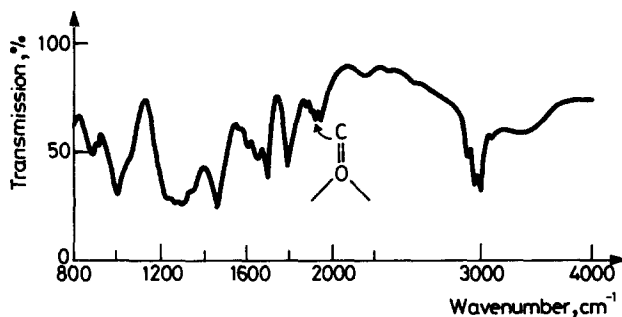


Fig. 11 Infrared spectrum of the oligomeric product fraction of oxidation to 800°C of precured ATS-G resin as a thin film on a NaCl salt plate

Oligomeric products of the thermal degradation of ATS-G, formed predominantly in the temperature range (400-600)°, must, therefore, be completely oxidized in the gas phase to lower molecular weight products when oxygen is more freely available for reaction with the polymer, as is encountered with smaller samples in contact with the same amount of gas.

Quantitative volatile product distributions of oxidation to 800°

The volatile products of oxidation to 800° of ATS-G were analysed quantitatively by methods outlined earlier in this discussion. Average product distributions from 50 mg and 100 mg samples are illustrated in Tables 3 and 4 respectively.

Degradation experiments performed in the presence of oxygen differ from those performed in the absence of oxygen in that the combined weight of volatile products plus residue is not equal to the initial sample weight, because of reactions of the polymer and its degradation products with oxygen. For this reason, the volatile products of oxidation were monitored by total mass and carbon content (Tables 3 and 4), for comparison with the products of thermal degradation of the resin (Tables 5 and 6).

Table 3 Product distribution of closed system oxidation to 800° of 50 mg ATS-G

Product	Product weight,	Weight volatilized carbon/50 mg
	mg	cured polymer
H ₂	Negligible	0.0
CH ₄	0.5	0.4
CO	11.5	4.7
CO ₂	20.2	5.5
SO ₂	5.1	0.0
Benzene	Negligible	0.0
H ₂ O	11.8	0.0
Phenol	Negligible	0.0
COS	0.6	0.1
Total	49.2	10.7

Table 4 Product distribution of closed system oxidation to 800° of 100 mg ATS-G

Product	Product weight,	Weight volatilized carbon/50 mg
	mg	cured polymer
H ₂	Negligible	0.0
CH ₄	4.6	3.5
CO	20.1	8.6
CO ₂	11.6	3.2
SO ₂	12.6	0.0
Benzene	1.3	1.2
H ₂ O	18.3	0.0
Phenol	2.4	1.9
COS	1.3	0.3
Total	72.2	18.7

Similarities between the volatile product yields expressed in terms of carbon content appear rather compelling evidence in support of the contention that such products of accelerated oxidations of the polymer under conditions of limited oxygen availability, arise, in the main, from secondary gas phase oxidations of corresponding products of thermal degradation. The relatively lower yield of carbon from a 100 mg sample of the resin upon degradation in the reactor, is probably a direct result of inefficient oxidations of the oligomeric product fraction of thermal degradation. (Remember that carbon in the oligomeric product fraction of thermal degradation was counted in that product distribution, that no oligomeric products were detected in the product distribution of oxidation of a 50 mg sample of polymer in the reactor, and that some oligomeric products of oxidation were

detected in the oxidative product distribution from a 100 mg sample in the reactor, but those products could not be quantified for addition to the total carbon count.)

Table 5 Weight % carbon volatilized from ATS-G degraded under high vacuum conditions

Product	wt.% volatilized carbon
Phenol	9.1
SO ₂	0.0
Oligomeric material	5.1
CO	2.7
H ₂ O	0.0
CH ₄	2.2
Benzene	2.0
CO ₂	0.3
H ₂ S	0.0
COS	~0.1
H ₂	0.0
Total	21.5

Table 6 Weight % carbon volatilized from ATS-G degraded under high vacuum and in oxygen

Conditions of experiment	wt.% total volatiles	wt.% volatilized carbon
TVA (Vacuum)	47.9	21.7
50 mg in reactor	98.4	21.4
100 mg in reactor	72.2	18.7

This situation is concisely illustrated by comparing the carbon dioxide to carbon monoxide product ratios of oxidation of 50 mg and 100 mg samples of resin in the reactor. The results, illustrated in Table 7, show clearly that the carbon dioxide to carbon monoxide ratio, which may be thought of as an index to the efficiency of the gas phase oxidation reaction, supports the contention that volatiles from 50 mg samples are more efficiently oxidized than those from 100 mg samples.

Table 7 Carbon dioxide/carbon monoxide product ratios of oxidation to 800°C of ATS-G

Sample size, mg	Mole ratio CO ₂ /CO (Efficiency of oxidation)
100	0.4
50	1.2

Oxidation of thermally degraded ATS-G, the "bulk" oxidation reaction

Due to the fact that oxygen is efficiently consumed by reaction with the volatile products of thermal degradation of ATS-G in the reactor, it is not possible to obtain a product distribution from the high temperature bulk oxidation reaction by directly oxidizing the base resin. However, this process may be conveniently studied in isolation by oxidizing pre-degraded ATS-G. In brief, a sample (54.2 mg) of pre-cured ATS-G was heated to 700° under vacuum in the TVA oven assembly to drive off products of thermal degradation. The residue of degradation (28.3 mg of almost pure carbon), was reheated to 700° at 5 deg/min in the presence of 220 mg oxygen in the usual fashion, to leave a residue of oxidation (21.4 mg). The volatile products of the bulk oxidation reaction were collected and analysed by quantitative gas phase Infrared spectroscopy and by SATVA, which yielded the trace shown in Fig. 12. If we consider that the Pirani gauge output is decidedly non linear and much compressed towards higher pressures [7], it can be seen from the SATVA trace, that, as expected, carbon dioxide and water constitute the bulk of the product distribution of oxidation of this material. A quantitative product distribution for this process is shown in Table 8, from which it can be seen that 6.7 mg of volatile carbon is produced in a process which removes 6.9 mg of material from the sample. The discrepancy between the two may have been produced by errors in the experiment, or may give some indication of the quantity of hydrogen in the residue which reacts with oxygen to form water. Oxygen is, therefore, shown to volatilize the residue of vacuum (or thermal) degradation of ATS-G, by removing carbon as carbon monoxide and carbon dioxide, and possibly hydrogen as water through direct reaction with the resin, in quantities which are presumably dictated by the availability of oxygen to the polymer.

Table 8 A product distribution for the high temperature bulk oxidation reaction of ATS-G

Product	wt. product	wt. carbon in the product, mg
CO	4.4	1.9
CO ₂	17.7	4.8
Benzene	Negligible	Negligible
Total	22.1	6.7

Translation to a composite environment

ATS-G is under evaluation primarily as a resin adhesive for the formulation of high performance composites for use in the aerospace industry. As such, most resin, by virtue of the low surface to volume ratio of a composite piece of finite size, if subjected to flash thermolysis in air, would do so under conditions of restricted oxygen access, such as is encountered with the oxidation reactor. Of course, low temperature, long term oxidations of the resin will be fed by diffusion of oxygen through the resin matrix, and, in the time frame of the experiment, be relatively free of diffusion controls. In contrast, higher temperature flash oxidations of the bulk resin in an intact composite piece, must be powered by immediately available oxygen, presumably contained in adjacent voids or other structural irregularities. For background information on this rather contentious subject the reader should consult reference 8.

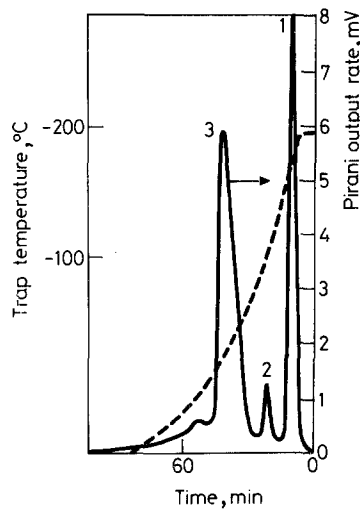


Fig. 12 An SATVA trace of the condensable volatile product fraction of oxidation to 700°C of ATS-G resin which had been predegraded under vacuum to 700°C. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature)/(1) Carbon dioxide, (2) Benzene, (3) Water

We have shown in this series of experiments that the high temperature bulk oxidation reaction of a 60 micron thick, 50 mg sample of ATS-G resin, in contact with 220 mg oxygen, is effectively suppressed under closed system conditions in the oxidation reactor. Using this fact it becomes possible to es-

timate a relative (gas containing) void/resin volume ratio which approximates the purely artificial conditions within the reactor. We will subsequently assume that the bulk oxidation reaction is effectively suppressed at void/polymer ratios below this value. Of course we do not possess any information which would suggest behaviour at such ratios in excess of this value.

We will, first of all, state some facts. For example, the average thickness of a composite article will be significantly greater than the 60 micron samples used here. Problems of gas diffusion to the active site (the degrading polymer) will, therefore slow down the process of oxidation with respect to samples examined in the reactor. In a similar vein, nitrogen, from air in the composite, and the volatile products of gas phase oxidations such as carbon monoxide, carbon dioxide, and water, will not be efficiently removed from that composite, and will hamper the inward diffusion of fresh oxygen, to further slow down the process of oxidation.

We will next make some assumptions. First of all, we will assume that any voids within the composite contain unmodified air with about 20% oxygen content, initially at 1 atmosphere pressure at room temperature. We next assume that air is not lost from the composite by gas expansion through the void system as the composite is heated quickly to degradation temperatures. Finally, we assume that the density of ATS-G resin is approximately 1 g/ml, although a figure of about 1.4g/ml would probably be more correct.

The "Calculation"

(1). Volume of 220 mg O₂ at STP

$0.220 \text{ g O}_2 = 6.9 \cdot 10^{-3} \text{ M O}_2 = 3.44 \cdot 10^{-2} \text{ M of Air}$
Volume at STP from the ideal gas law $\approx 840 \text{ ml}$

(2). Volume of 50 mg ATS-G at STP

50 mg resin at a density of about 1 g/ml $\approx 0.05 \text{ ml}$

(3). Void (Gas Volume)/Polymer Ratio at STP

Ratio $\approx 16800/1$ (an impossible figure for a structural composite)

The volume ratio calculated above (16800/1) suggests that the primary processes of flash degradation within an article of any size and composed of ATS-G must be thermal in nature, thus validating the use of programmed TG under inert atmosphere as a tool for the rapid evaluation of the stability of these materials. We are now also in a position to examine a worst case

scenario — for example, if we instead, postulated that the composite contained pure oxygen at a pressure of 10 atmospheres carried through from autoclave manufacture (an unlikely situation), the calculated void to polymer ratio to match the conditions met in the oxidation reactor would still exceed 300/1 — a figure more applicable to a blown polyurethane foam than to a structural composite. The high temperature flash oxidation reaction of ATS-G resin is, therefore, probably efficiently suppressed while that composite retains its structural integrity.

Conclusions

A reactor was designed and built to subject polymeric materials to accelerated high temperature oxidative degradation under partially anaerobic conditions. Analytical protocols for the subsequent isolation of all four product fractions of oxidation were then developed and tested in operation. Using this experiment, it was shown that volatiles produced in the first stage of thermal degradation of a 50 mg sample of pre-cured ATS-G resin in contact with 220 mg of oxygen, are efficiently oxidized in the gas phase to carbon monoxide, carbon dioxide, and water, in a process which lowers the oxygen level in the reactor below that which can efficiently support the higher temperature bulk oxidation reaction. When isolated, by oxidizing pre-degraded ATS-G in the reactor, the higher temperature bulk oxidation reaction was shown to volatilize the residue of almost pure carbon, with some hydrogen, to carbon monoxide, carbon dioxide, and water, in proportions which are determined by the availability of oxygen in the reactor.

With reference to the previous conclusion, some simple calculations were used to confirm, first of all, that the initial mechanisms of decomposition of most resins of this type, in a part of finite size, and subjected to flash pyrolysis in air, must be thermal in nature, thus validating the use of programmed TG under inert gas as a tool for the rapid evaluation of the stability of such resins, *and* secondly, that oxidative as opposed to thermal degradation of bulk ATS-G resin under accelerated conditions is unlikely while the part retains structural integrity.

* * *

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Zusammenfassung — Unter Anwendung eines spezialangefertigten Reaktors modellierten wir die Zersetzung eines acetylenendständigen Sulfonhochleistungsharzes (ATS), genauer gesagt von bis[4-(3-ethinylphenoxy)phenyl]sulfon und seiner höheren Oligomere, unter partiellen anaeroben Bedingungen. Die im Endergebnis des thermischen Abbaues erhaltene Substanz verfügt über eine höhere oxidative Stabilität als die während des thermischen Abbaues vorher erhaltenen Produkte, die im Reaktor mit Sauerstoff sekundäre Produkte wie Kohlenmonoxid, Kohlendioxid und Wasser bilden; somit wird einer direkten Oxidation des Harzes vorgebeugt. Bei Entfernung der flüchtigen Produkte des thermischen Abbaues wird der kohlenstoffreiche Halbkoksrest des thermischen Abbaues direkt zu Kohlenmonoxid, Kohlendioxid und Wasser oxidiert.