



CoA Memo. No. 114

October, 1966

THE COLLEGE OF AERONAUTICS

DEPARTMENT OF MATERIALS

The Thermal Degradation of Epoxy Resins

- by -

D.P. Bishop, Ph.D., A.M.C.T.



The Thermal Degradation of Epoxy Resins

Progress Report: A summary of work carried out between 1st April and 1st September, 1966.

Introduction

The work in this period has been devoted to (i) an extensive literature survey, part of which has been written up as a critical review with a view to publication, and (ii) preliminary experimental work.

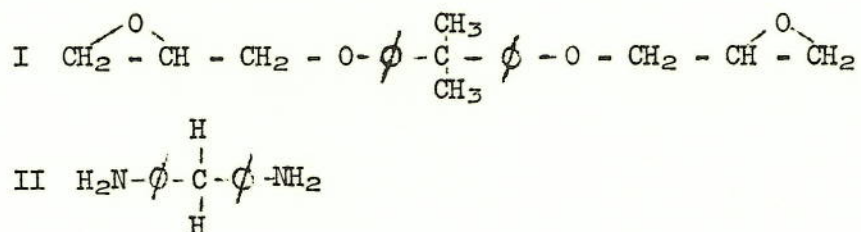
(i) Literature Survey

A copy of the review which it is hoped to publish is enclosed with this report.

(ii) Preliminary Experimental Work

Materials. It was suggested in the concluding remarks of the review that future work in this field should be carried out with carefully characterised epoxides and hardeners to eliminate effects of unknown additives to commercial products.

For the experimental work conducted so far, cured resins have been prepared from a purified sample of the diglycidyl ether of bisphenol A, (m.p. 42°C) I, and a pure sample of pp' diamino diphenyl methane, (m.p. 91°C) II.



The resin and hardener were mixed together at 100°C in the ratio 100/27, W/W, that is, 1/1, $\text{CH}_2\text{OCH}_2/\text{N-H}$. When a homogeneous mixture had been obtained it was cooled to room temperature and placed under vacuum for a period of 3 hours to remove entrapped air. The material was then poured into a mould and cured in a thermostated oven for:

- 16 hours at 55°C
- 2 hours at 125°C
- 2 hours at 175°C

Thermal Degradation

To date, the thermal degradation of the resin has been studied on the equipment described by Stuart and Smith (1); a 'hot wire pyrolysis' technique followed by separation of the volatile degradation products by gas chromatography.

Although this work was really intended to provide the author with some experience of gas chromatography techniques, it proved possible to identify some of the degradation products by their retention times.

The identification of compounds by their retention times would be more satisfactory if the separated products were collected on emerging from the column and identified by independent means. In order to collect suitable quantities of the products without carrying out a large number of identical 'burnings', the gas chromatograph has been modified to take semi-preparative sized columns, and a larger electrically heated filament.

It is possible that the 'hot-wire' catalyses degradation reactions occurring at the surface of the resin and it is intended to compare the results obtained with filaments of different materials. The author also considers that the results obtained by 'hot-wire pyrolysis' should be compared with those of 'pyrolysis in vacuo'.

Results

The preliminary gas chromatography work has shown that one of the principle volatile degradation products from this particular resin in water. The only other volatile products which have been positively identified are benzene and toluene.

Some 'pyrolysis in vacuo' work carried out on the same resin in these laboratories (2) shows that phenol and N-substituted anilines are present amongst the less volatile degradation products. The presence of N-substituted anilines is of particular interest because although no other workers in the field have identified products of the rupture of the 'cure-link', it suggests that this may well be one of the principle degradation mechanisms.

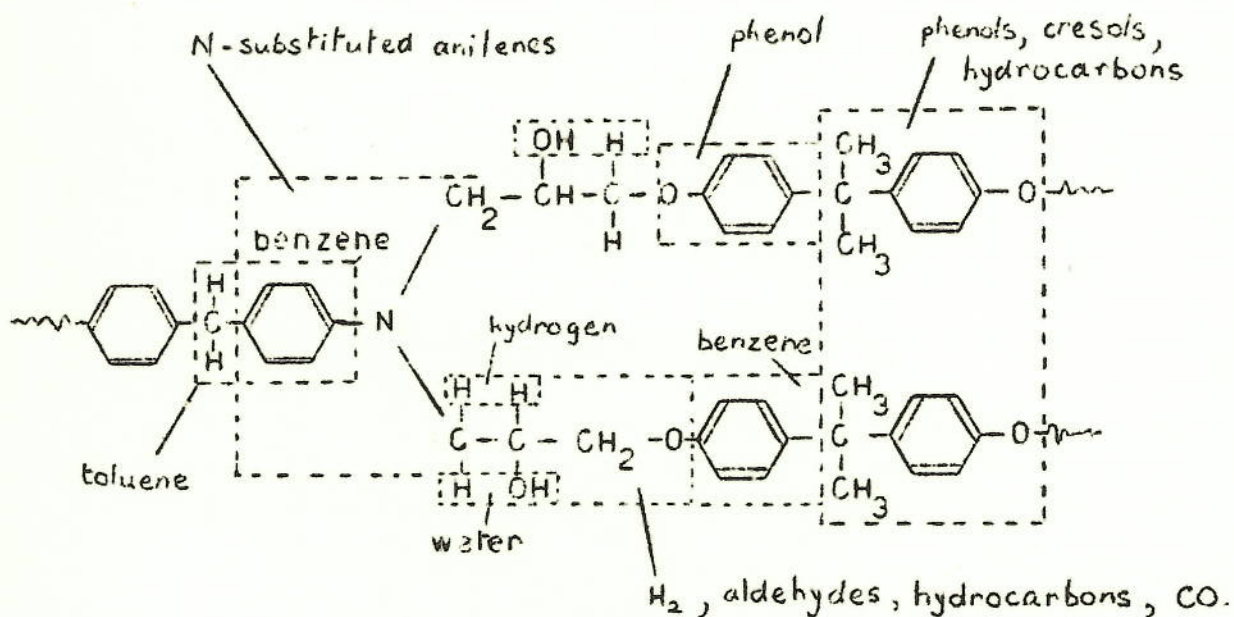
Discussion

It is possible to postulate a number of degradation mechanisms from the evidence which has been accumulated so far (Fig. 1), but in order to obtain positive evidence it is proposed to make use of radioactive tracer techniques. It should be possible to prepare a number of similar resin samples which are C^{14} labelled in different positions. After degradation and separation of volatile products by gas chromatography, the gas stream from the chromatograph may be passed directly through a glass scintillator flow cell. The presence of C^{14} labelled material amongst the degradation products would indicate the breakdown of the particular labelled portions of the resin. A trace of counts/min. vs. time would pinpoint active

peaks on the chromatograms, and once these have been identified, complete degradation mechanisms may be deduced. This technique could prove to be a powerful tool in elucidating the degradation mechanisms of a wide variety of resins and polymers.

Figure 1

Principle resin structure and possible degradation products



Future Work

(a) Before embarking on the radioactive tracer work it will be necessary to prepare a variety of labelled epoxides and hardeners from C^{14} labelled compounds available from the Radiochemical Centre. Some of the reactions involved (these will first be attempted on inactive materials) may prove to be impracticable in the laboratory. Should this be the case it may be possible to obtain outside assistance. In the immediate future, therefore, attempts will be made to prepare the diglycidyl ether of bisphenol A and *pp'* diamino diphenyl methane in the laboratory.

(b) Preliminary work will be started on the resin formed by cross-linking the diglycidyl ether of bisphenol A with maleic anhydride. This anhydride is available C^{14} labelled in the C-1,4 or C-2,3 positions, so no preparative problems arise with this compound.

References

1. Stuart, J.M., and Smith, D.A. J. Appl. Polymer Sci., 9, 3195, (1965).
2. C. Pattison-Jones Unpublished work.