

Influence of the Gaseous Environment on the Thermal Degradation of a Structural Epoxy Adhesive

X. BUCH,¹ M. E. R. SHANAHAN^{1,2}

¹ Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux P.M. Fourt, B.P. 87, 91003 Evry Cédex, France

² Université d'Evry Val d'Essonne, Boulevard François Mitterrand, 91025 Evry, France

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ABSTRACT: A structural epoxy-based adhesive cured with dicyandiamide (DDA) and 4,4' diaminodiphenylsulphone (DDS) has been aged at elevated temperatures under various gaseous environments. Weight loss was accompanied by enrichment of oxygen, sulfur, and nitrogen, near the polymeric surface, after aging in oxygen containing atmospheres, as shown by X-ray analysis. Sulfur dioxide was detected in the aging environment. Results strongly suggest chain scission by thermolysis combined with thermo-oxidative degradation occurring near the exposed surface. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 987–992, 2000

Key words: aging; chain scission; degradation; elevated temperature; epoxy resin; oxidation; sulfur; thermal aging

INTRODUCTION

Cross-linking, or thermoset, polymers play an important role in structural applications both as adhesives and as matrices for fiber-reinforced composite materials. They are becoming widespread in many industries, including use in aerospace, automotive, and marine equipment. As far as thermoset resin-based adhesives are concerned, considerable advantages are manifest compared with more conventional methods of assembly such as bolting and riveting: reduction of weight and stress concentrations (around holes) are but two examples. Notwithstanding, a structural adhesive must often withstand deleterious conditions over long periods during its service life (constant or cyclic loads, changes in temperature, aggressive environments such as water or kerosene, etc.) and these may lead to marked degra-

dation and reduction of mechanical properties. Over a considerable period, effects of water, or atmospheric humidity, constituted the primary goal of studies on adhesive aging due to the ubiquity of moisture.^{1–4} Modern structural adhesives, however, tend not only to present higher resistance to effects of humidity, but are also often conceived for use at temperatures well in excess of 100°C where, under usual (exposed) conditions, the presence of moisture may generally be neglected. Other deleterious factors may nevertheless intervene. Contrary to intuition, cross-linked adhesives may creep under constant load,^{5,6} and adhesives destined to withstand elevated service temperatures (ca. 200°C), such as polyimides, bismaleimides, and modified epoxies, are clearly more exposed to the potential consequences of time-dependent strain due to increased thermal molecular motion.⁷

Another factor related to higher service temperatures is the enhanced rate of (potential) chemical reactions occurring between an adhesive and its (gaseous) environment—oxygen clearly representing the primary threat leading to poly-

Correspondence to: M. E. R. Shanahan, at the Ecole Nationale Supérieure des Mines de Paris.

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meric degradation. Several studies have been effected in order to explain thermal degradation mechanisms and weight loss,⁸⁻¹² and also reduction of strength.¹³⁻¹⁵ Recent studies in this group have demonstrated how a *bulk* thermoset resin (epoxy), when exposed to a water environment at elevated temperatures, may initially absorb water leading to mass gain but, at a later stage, lose mass due to hydrolysis and leaching of macromolecular chain segments severed by water molecules.¹⁶ Mass changes subsequent to exposure to air at elevated temperature may be expected to be somewhat analogous to those observed due to water exposure at more moderate temperatures. In this context, we have recently undertaken an investigation of the behavior, at elevated temperatures, of a modified epoxy resin.

EXPERIMENTAL

The material studied is a modified epoxy resin cured with a combination of two cross-linking agents: dicyandiamide (DDA), and 4,4' diaminodiphenylsulphone (DDS). For commercial reasons, further details of the chemical formulation of the adhesive are unavailable.

Samples of the adhesive in the form of rectangular blocks of dimensions $70 \times 10 \times 2 \text{ mm}^3$ were made by the compression of superimposed films of adhesive in a polytetrafluoroethylene (PTFE)-lined steel mold and curing at 177°C for 90 min under a pressure of two bars with both temperature increase and decrease between ambient and the cure temperature at 3°C per min. It was shown in our preparatory work using differential scanning calorimetry (DSC) that this curing regime leads to complete exhaustion of cross-linking agents (no residual enthalpy peaks). For this cross-linking cycle, the resultant glass transition temperature, T_g , before aging is 225°C . The cured adhesive was aged without applied stress at temperatures in the range of $180\text{--}250^\circ\text{C}$ for up to 5000 h. This thermal aging was effected in environments of air (in an oven at atmospheric pressure), primary vacuum (0.5 mbar in an oven coupled to a vacuum pump), and low oxygen partial pressure (total pressure equal to atmospheric).

Gravimetric studies were undertaken (and, in fact, are still in progress in order to study long-term behavior), corresponding to simple periodic weighing of adhesive samples after various aging times at several temperatures. Samples were allowed to cool to room temperature in a desiccator

before weighing on a Mettler AT250 (Mettler Instrumente A.G., Greifensee, Switzerland) balance with a precision of $2 \times 10^{-5} \text{ g}$. After weighing, samples were returned to their aging environments. Results given are the mean of three samples. Reproducibility was good with variations being less than 2% between samples. As will be seen below, mass loss accompanies exposure to elevated temperatures.

Techniques of X-ray analysis and elemental identification were used to obtain depth profiles of the concentrations in oxygen, sulfur, and nitrogen near the (exposed) adhesive surface. The apparatus used was a CAMECA SX 50 microprobe (Cameca S.A., Courbevoie, France), a wavelength dispersion spectrometer (WDS). Before analysis, adhesive samples were encapsulated and polished to a finish of $0.25 \mu\text{m}$. The acceleration voltage used was 15 kV and a current of 30 mA was employed. Depth profiling was effected up to the first $100 \mu\text{m}$ in depth (every $3 \mu\text{m}$). Quantitative reproducibility was of the order of 0.1%.

As described below, results showed clear effects of weight loss and molecular migration. We therefore attempted to detect the presence of gaseous sulfur and nitrogen oxides in the surrounding environment after aging of the adhesive, believing such by-products to be possibly released from the polymeric surface during the degradation process. This was accomplished by using gas detector tubes obtained from Gastec Corporation, Kanagawa, Japan

RESULTS AND DISCUSSION

After thermal aging in air, color changes appeared in the resin of the samples. The initial gray coloration changed successively to green, then brown, and finally black. This observation, previously reported by others,^{14,15} is indicative of chemical modification occurring in the resin due to thermo-oxidation (aging in vacuum leads to no color change). It is also of interest to note that the initial T_g of the adhesive, of 225°C , decreased very rapidly in initial stages of aging in air, suggesting strongly a rapid process of molecular chain scission. (This aspect will be discussed at a later date.)

Gravimetry

Examples of mass loss in air and in primary vacuum, as a function of the square root of the expo-

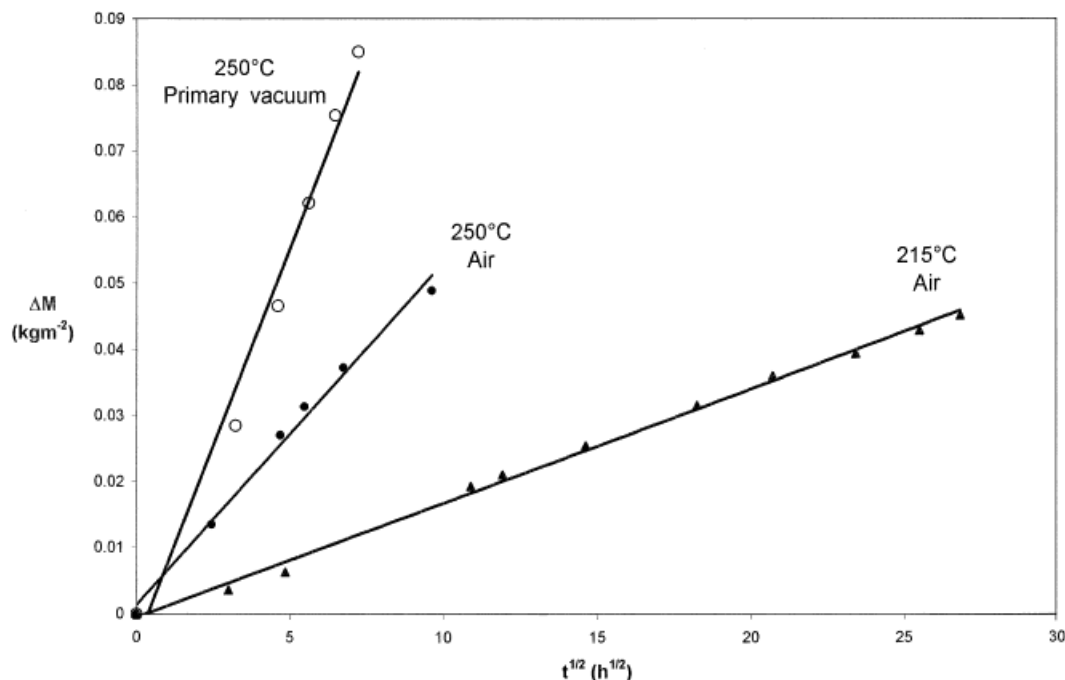


Figure 1 Mass loss per unit of surface, ΔM , vs square root of time, $t^{1/2}$, for adhesive exposed to air at 215°C and 250°C, and in a primary vacuum at 250°C.

sure time, at two test temperatures, are shown in Figure 1 with regression lines. Degradation is evident. The results suggest Fickian behavior.¹⁷ In the ranges of time so far studied, mass loss, ΔM , is a linear function of the square root of aging time, t , for the various atmospheres and temperatures. However, mass loss is clearly more rapid in a primary vacuum, the inference being that the presence of oxygen inhibits dynamic (net) mass loss. We suggest that this effect is a result of oxygen reacting with the polymer, combining with it chemically, and thus causing a partial mass *increase*, which at least to some extent offsets global mass loss during the early stages of aging.^{14,18,19} From the observed behavior in an oxygen-containing atmosphere, it may be considered either that degradation rate is determined by diffusion of oxygen from the surface into the bulk polymer, in an apparently Fickian manner, or alternatively, that diffusion of degradation by-products leaving the adhesive constitutes the rate determining step. However, because mass loss during initial aging in a primary vacuum is also linear with the square root of time, this would suggest some form of thermolysis and clearly in this case, (apparently) Fickian behavior corresponds to the departure of degradation products.

Figure 1 also shows clearly how the rate of mass loss is a thermally activated process, as may be expected.^{20,21}

Elemental Analysis and Gas Detection

Figure 2 presents typical results of depth profiles of concentration by weight of oxygen, sulfur, and nitrogen with the origin of the abscissa corresponding to the surface of the adhesive. Results shown indicate the profiles for the unaged adhesive (dotted lines), the adhesive aged for 115 h at 250°C in air (solid lines), and in vacuum (dashes and dots).

These distributions are of considerable interest. The depth profile for oxygen (Fig. 2a) is not particularly surprising: due to air diffusion and oxidation, we would expect a superficial layer rich in oxygen (thick oxidized layer, or TOL^{18,19,22,23}) with a decreasing concentration towards the bulk material. During thermal aging, the depth of this layer increases up to a maximum of ca. 50 μm at 250°C. (Definition of the depth at which the transition between TOL and unmodified adhesive occurs is, of course, a little arbitrary. We took the estimated value of the onset of the unmodified plateau as a criterion.) Growth in the thickness, δ ,

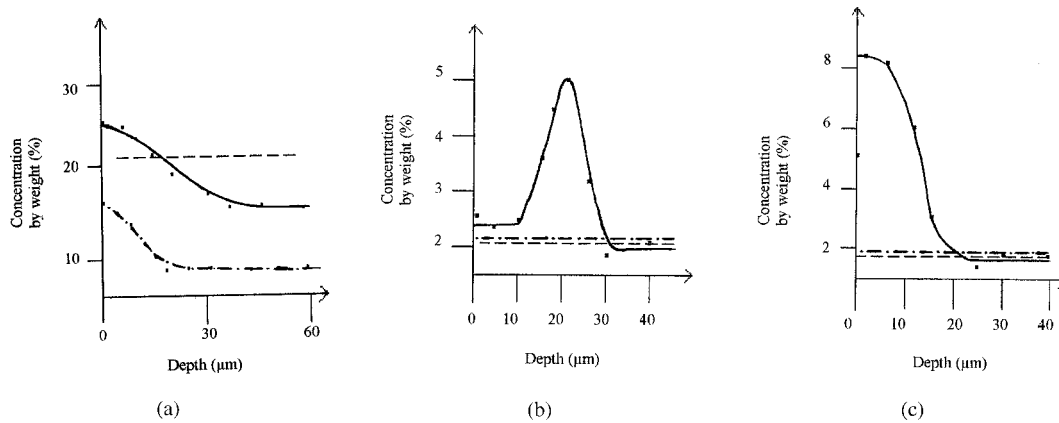


Figure 2 Depth profiles of concentration by weight of (a) oxygen, (b) sulfur, and (c) nitrogen from adhesive surface (on left). --- = unaged adhesive; — = adhesive aged for 115 h at 250°C (in air); and - · - · = (in vacuum).

of the TOL as a function of aging time is shown in Figure 3, corresponding to aging in air at 250°C. As may be expected, the behavior is (apparently) asymptotic.

Perhaps somewhat surprising is the fact that the oxygen concentration towards the bulk of the adhesive becomes diminished after aging in air or in vacuum, when compared with the results obtained with the unaged polymer. These results are quite reproducible. (It is of interest

to note that our measurements were continued to a depth of 100 μm, yet no return to a value of oxygen concentration corresponding to the unaged polymer was observed.) This would tend to suggest that at least some of the degradation products leaving the bulk contain oxygen intrinsically present in the adhesive formulation before aging. It may be envisaged that the oxygen maximum observed near the sample surface is due not only to air oxidation but also to mi-

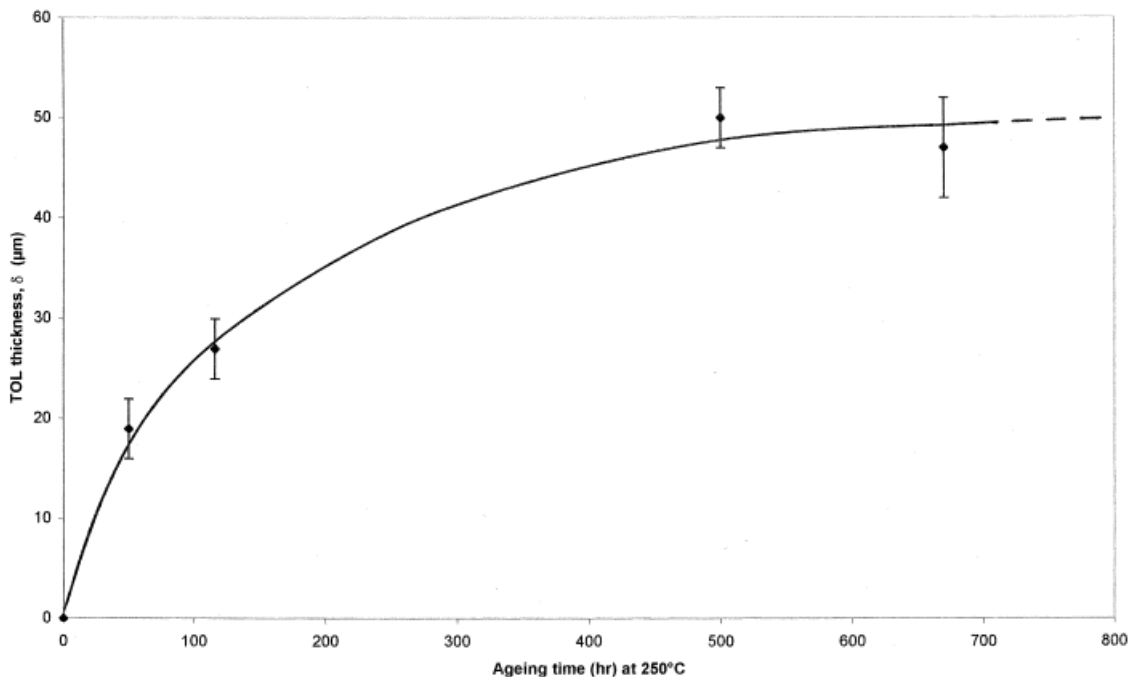


Figure 3 Thickness, δ , of thick oxidized layer (TOL) as a function of aging time in air at 250°C.

gration of oxygen containing products from the bulk.

If the oxygen distribution reasonably seems clear, what about sulfur and nitrogen? In particular, the depth profile for sulfur seems strange (Fig. 2b). This, together with the detection of sulfur dioxide in the aging environment, described below, is the central result of this article. Firstly, why do we obtain an increase in sulfur concentration near the surface? Potential sources of contamination have been checked and eliminated and thus we must conclude that there is some sort of migration of sulfur-containing entities from the bulk to the superficial region due, presumably, to thermodynamic segregation, although the mechanism is unclear. The source of sulfur will be the hardener DDS, but whether DDS itself or some cross-linking or aging by-product(s) (after molecular scission) migrate(s) is unknown. Secondly, the enrichment in sulfur does not continue right up to the adhesive surface. We therefore hypothesize that sulfur in the immediate vicinity of the surface, after migration, becomes oxidized in air at elevated temperature, and then leaves the polymer in the form of (a) gaseous sulfur oxide(s), thus reducing concentration locally. By using gas detector tubes (Gastec Corporation), it was possible to detect sulfur dioxide in the aging environment. This result would seem to confirm our hypothesis. As a result, the shape of the curve in Figure 2b corresponds to the superposition of two phenomena: the diffusion of sulfur-containing entities from the bulk of the adhesive towards the surface exposed to air and the subsequent (and partially concomitant) consumption and transformation of these molecules into volatiles. We believe that in the presence of a high oxygen concentration, the diffusion of sulfur-containing molecules to the surface is slower than the rate of oxidation, and subsequent liberation of sulfur dioxide. This could explain an observed shift of the maximum of sulfur concentration away from the polymer surface with higher oxygen content in the environment. Samples aged under low oxygen partial pressure exhibited a relatively high sulfur concentration (ca. 13% by weight, compared with ca. 5% after aging in air under identical time and temperature conditions). This lends supporting evidence in favor of the hypothesis of oxidative consumption of sulfur-containing entities. Our hypothesis is similar to that proposed by Tsotsis.¹⁴ Using gaseous chromatography coupled with mass spectrometry (GC/MS) to try to identify thermal degradation by-products, Tsotsis ob-

served *only* CO₂ and H₂O following aging of an epoxy resin in air or oxygen, whereas numerous other by-products were detected after aging in nitrogen. Tsotsis believed that volatile by-products produced after aging in nitrogen were oxidized in the presence of oxygen in order to give CO₂ and H₂O, and other small molecules too difficult to be detected.

Aging in a primary vacuum led to no observed maximum in sulfur concentration. We hypothesize, in this case, the scission of macromolecular chains by thermolysis (without the intervention of oxygen) and the subsequent migration of sulfur-containing species from the bulk towards the surface, as is observed for aging in air. At the surface, these degradation products may then be already sufficiently volatile to leave the polymer without further degradation because the local atmosphere is at much reduced pressure (primary vacuum). Under these conditions, further degradation into lower molecular weight species would (by hypothesis) be unnecessary before leaving the polymer. The volatile nature of the degradation products could explain why no maxima in the concentration profiles are observed near the surface after thermal aging in a primary vacuum. Equivalently, this hypothesis is capable of explaining mass loss under these conditions (see Fig. 1).

Although the evidence is less convincing, we suggest that (a) similar mechanism(s) exist(s) for nitrogen (Fig. 2c). Samples aged in air led to a weight percentage maximum of ca. 8% of nitrogen compared with ca. 24% after aging under the same conditions but in a low partial pressure of oxygen. However, no displacement of the peak towards the bulk was observed. This may be due to a higher diffusion rate of nitrogen containing molecules towards the surface. As in the case of sulfur, no peak was obtained after aging in primary vacuum. As yet, nitrogen oxides have not been detected in the aging environment, but this may be due to masking in the presence of sulfur dioxide reacting with the gas detector. Despite the less marked evidence in the case of nitrogen, we believe that molecular scission is occurring and is also due to thermolysis (as opposed to thermo-oxidation).

CONCLUSION

We have undertaken a study of the thermal degradation of a modified epoxy resin cured with a

combination of DDA and DDS as cross-linking agents. Using various environments and aging temperatures in the range 180–250°C, we have observed reproducible mass loss of the adhesive, which is more rapid in a low-oxygen-content environment. Gravimetric results suggest Fickian behavior. A parallel study of elemental concentration depth profiles, both before and after aging, indicated that oxygen, sulfur, and nitrogen concentrations become increased near the surface after aging in air. Although results for oxygen are not surprising, the fact that the maximum for sulfur was observed *near* but not *at* the surface appears strange initially. We hypothesize that low molecular weight sulfur-containing compounds, originating from the cross-linking agent DDS, migrate towards the surface after thermolytic degradation and that the absence of a maximum in sulfur *at* the surface is due to the disappearance of volatile sulfur-containing gases after further oxidation. This, combined with the detection of sulfur dioxide in the aging environment—a fact tending to confirm the validity of our hypothesis—constitutes the central result of this investigation. (No other sources of sulfur are available in the vicinity.)

Similar reasoning has been applied to nitrogen-based compounds and, although the evidence is less clear cut, the hypothesis is consistent with our observations.

Finally we suggest that during the thermal aging *under air* of this epoxy material, degradation occurs essentially by three steps:

1. initially, the presence of oxygen (air) leads to the formation of a surface oxidized layer (TOL)^{18,19,22,23};
2. subsequently (and to some extent concomitantly), there is diffusion of sulfur- and nitrogen-containing molecules towards the surface, following chain scission occurring by thermolysis, (as inferred from the decrease in T_g);
3. finally, oxidation of these species occurs and they are transformed into sulfur (and probably nitrogen) oxides that leave the polymer as volatiles.

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