International Journal of Adhesion & Adhesives 23 (2003) 261–267

International Journal of Adhesion & Adhesives

www.elsevier.com/locate/ijadhadh

Migration of cross-linking agents to the surface during ageing of a structural epoxy adhesive

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Accepted 3 March 2003

Abstract

During the thermal degradation of a modified structural epoxy adhesive, based on TGDDM and cured with DDA and DDS, there is migration of nitrogen- and sulphur-containing molecules from the bulk towards the surface, as demonstrated by X-ray analysis. In this paper, it is shown that the thermal behaviour of these molecules is similar to that of the cross-linking agents themselves. The hypothesis of a surface layer consisting of DDA and DDS only in a 1/1 molar ratio is consistent with the observed concentrations. Results strongly suggest that the molecules which migrate at the surface are indeed the cross-linking agents.

Keywords: A. Epoxides; B. Interphases; D. Ageing; Degradation

1. Introduction

Epoxy resins are widely used in many industries, (e.g. aeronautic and automotive) either as the matrix in composite materials, or as adhesives. One of the major concerns about these polymers is their long-term behaviour. Much work has been done on the humid ageing of such materials [e.g. 1,2], but new modified epoxy resins are being developed for working at elevated temperatures. Unless very confined conditions of use are envisaged, effects of water should be negligible much above 100°C, but gaseous environments, particularly oxygen, will normally be present, leading potentially to other modes of strength loss. Several studies have been effected in order to explain thermal degradation mechanisms and weight loss [3–10], and also reduction of strength [11–13]. The most commonly reported type of chemical degradation reaction of epoxy resins is intramolecular dehydration [14,15]. Van Krevelen reported that cross-links can be the weakest part of a polymeric network, which means that during thermal degradation, chain depolymerisation can occur and the return to the (partially) uncross-linked material may ensue [16]. In order to contribute to a better understanding of the phenomena of thermal degradation, we have recently undertaken an investigation of the behaviour, at elevated temperatures, of a modified epoxy adhesive. This study has been accomplished by a combination of local methods (SEM, X-ray analysis) and global methods (gravimetry, mechanical properties). In a previous paper [17], we illustrated the complexity of thermodegradation mechanisms and suggested a process occurring in two-stages (each stage involving several phenomena):

- During the first stage of degradation, chain scission occurs by thermolysis. This stage is similar whether oxygen is present or not (some oxidation can occur at the surface of the resin in air). During this stage, there is formation of a thermally more stable compound by molecular rearrangements. Without oxygen, this compound is relatively stable at high temperatures. The segments liberated by chain scission contain sulphur and nitrogen (as shown by X-ray analysis) and migrate towards the surface. Thereafter, either they leave the sample immediately, if they are already sufficiently volatile (in vacuum or at high

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0143-7496/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0143-7496(03)00028-9

temperature), or they are thermo-oxidised to gaseous by-products in the presence of oxygen.

- The second stage of degradation occurs only in the presence of oxygen and leads to the total disappearance of the organic material by thermo-oxidation.

In this article, we shall look in more detail at the processes occurring at the surface during the first stage of degradation and determine the influence of the oxygen on these processes. We shall also focus on the determination of the chemical nature of the molecules migrating to the surface. For this purpose, a study of the thermal behaviour of the cross-linking agents DDA and DDS will be reported.

2. Experimental

2.1. Materials and preparation

The material studied is a structural epoxy adhesive based on N,N,N′,N′-TetraGlycidyl-4-4’-DiaminoDiphenylMethane (TGDDM) cured with a combination of two cross-linking agents : DicyanDiAmide, or DDA, and 4-4’-DiaminoDiphenylSulfone, or DDS. Fig. 1 represents the chemical formulae of the organic compounds constituting the resin. It is of interest to notice that DDS is the only (known) compound of the formulation containing sulphur. The weight composition of the adhesive is 57% of polymeric resin and 43% of inorganic fillers. For commercial reasons, further details of the chemical formulation of the adhesive are not available. Samples of the adhesive in the form of rectangular blocks of dimensions $70 \times 70 \times 2\,\mathrm{mm}^3$ were made by the compression of superimposed films of adhesive in a PTFE lined steel mould and curing at 177°C for 90 min under a pressure of 2 bar with both temperature increase and decrease between ambient and the cure temperature at 3°C/min. It was shown in our preparatory work using DSC that this curing regime leads to complete exhaustion of cross-linking agents (no residual enthalpy peak). DDA and DDS, as separate compounds, were obtained commercially, respectively from Vantico Limited and Sigma-Aldrich Chemical Co., and were used without further purification.

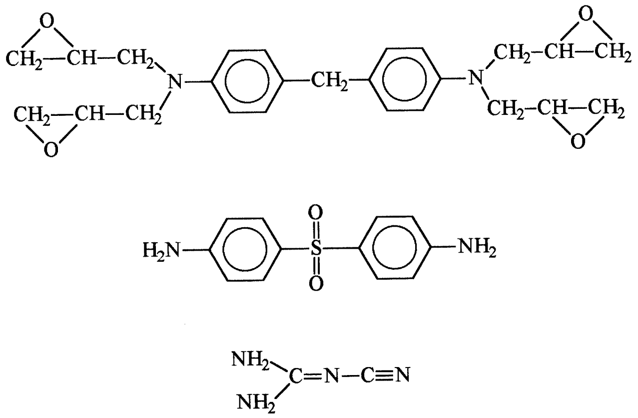

Fig. 1. Chemical formulae of TGDDM, DDS and DDA.

2.2. Methods

The cured adhesive and the cross-linking agents were aged without applied stress at temperatures in the range of 230–300°C for up to 11,000 h. Thermal ageing 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).

Techniques of X-ray analysis and elemental identification were used to obtain depth profiles of concentrations in oxygen, sulphur, 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 surface finish of 0.25 μm. The acceleration voltage used was 15 kV and a current of 30 mA was employed. Depth profiling was effected up to the first 100 μm in depth (every 3 μm). The cartography was effected at a magnification of 400 and represents an area of $256 \times 256\,\mu\mathrm{m}^2$. Quantitative reproducibility was ca. 0.1%. Scanning electron micrographs were also taken with the microprobe.

Gravimetric studies were undertaken corresponding to simple periodic weighing of samples of adhesive and cross-linking agents after various ageing 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 2×10^{-5} g. After weighing, samples were returned to their ageing environment. Results given are the mean of two samples. Reproducibility was good with variation being less than 2% between samples.

Gas formed during the thermal ageing, such as HCN, NH_3, or SO_2, has been detected and identified by detector tubes (Gastec Corporation, Kanagawa, Japan).

3. Results and interpretation

3.1. Effects at the surface during ageing

Fig. 2 represents a scanning electron micrograph and the cartographies of O, S and N in the same area of a sample of adhesive aged for 310 h at 250°C in air. As described previously [18], there is enrichment of O, N and S at the surface or near the surface of the sample.

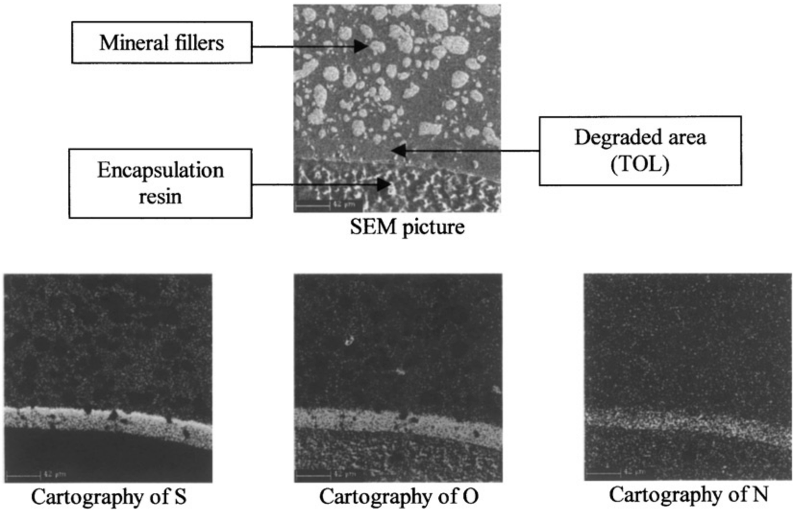

Fig. 2. SEM picture and cartographies in S, O and N of the same area of the adhesive aged for 310 h at 250°C in air.

The cartographies (not represented) of unaged samples present no maxima. We concluded that this enrichment, observed near the surface, is the consequence of thermal ageing. These observations are new, to our knowledge, and distinct from the migration observed *during cure* by some other authors, as, e.g., De Vries et al. who observed the migration of the cross-linking agent DDA towards the adhesive/substrate and adhesive/air interfaces during the curing at elevated temperature of a PVC modified epoxy resin [19]. We shall endeavour to explain the enrichment observed at the surface for each element.

3.1.1. *Oxygen*

We explain, at least partially, the enrichment in oxygen in the surface region by air diffusion from the environment and oxidation, which leads to the formation of a thin oxidized layer (TOL) [20–23]. During thermal ageing, the depth of this layer increases up to a maximum of ca. 50 μm at 250°C. This enrichment in oxygen at the surface may also possibly be due to migration of oxygen-containing molecules from the bulk to the surface. It is of interest to note that during thermal ageing, there is a decrease of the oxygen weight concentration in the bulk, from ca. 23% initially to ca. 10% after 500 h at 250°C. This phenomenon could be explained, either by the migration mentioned above, and/or by dehydration reactions and departure of water formed as a volatile.

3.1.2. *Sulphur*

Potential sources of contamination have been checked and eliminated and thus we conclude that there must be migration of sulphur-containing entities from the bulk to the superficial region due, presumably, to thermodynamic segregation. We previously suggested [18] that the maximum in sulphur corresponds to the superposition of two phenomena: the diffusion of sulphur-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 by thermo-oxidation by air. This would explain the existence of a maximum *near* and not *at* the surface in some conditions. We believe that in the presence of a high oxygen concentration, the diffusion of sulphur-containing molecules to the surface is somewhat slower than the rate of oxidation, and subsequent liberation of sulphur dioxide. This could explain an observed shift of the maximum of sulphur concentration away from the polymer surface when the environment has a higher oxygen content. After ageing under low oxygen partial pressure, there is also diffusion from the bulk of sulphur-containing molecules but no conversion of these molecules into volatiles : they accumulate at the surface. This would explain not only the high value of the concentration in sulphur at the surface after ageing under low oxygen partial pressure (13%, to be compared with the initial value of 2%, or with 5% obtained after ageing under air), but also the fact that the maximum is *at* the surface. Ageing in a primary vacuum led to no observed maximum in sulphur concentration. We explain this observation by the fact that the liberated segments are volatiles under primary vacuum so they leave the polymer during ageing.

3.1.3. *Nitrogen*

Although the evidence is less convincing, we suggest that similar mechanisms exist for nitrogen since we also observe enrichment near the surface of the sample (Fig. 2). Samples aged in air led to a weight percentage maximum of ca. 8% of nitrogen compared to an initial value of 2% and to ca. 24% after ageing under the same conditions but in a low partial pressure of oxygen. The main difference when compared to the observation made with sulphur is that there is no displacement of the peak towards the bulk. The possible explanations of this observation will be discussed later. As in the case of sulphur, no peak was obtained after ageing in primary vacuum.

3.1.4. *Gas production during the thermal degradation*

At the time of writing of Ref. [18], we tried, in vain, to detect nitrogen oxide(s) as degradation products by thermo-oxidation of the nitrogen-containing segments. In fact, it is generally admitted that the degradation of nitrogen-containing molecules produces hydrocyanic acid and/or ammonia, but rarely nitrogen oxide which is the ultimate stage of degradation. The degradation of sulphur-containing molecules leads to the formation of SO_2. During the thermal ageing of the adhesive in air, we detected, by using gas detector tubes, SO_2, NH_3 and HCN, which confirms our hypotheses of thermo-oxidation by air into volatile species of the segments which migrate to the surface. In separate experiments, we noted that during the thermal degradation in air of the cross-linking agents DDA and DDS alone, there was also production of ammonia and sulphur dioxide in large quantities. These observations not only confirm the process of degradation into volatiles by thermo-oxidation of the nitrogen and sulphur containing molecules, but also strongly suggest that these segments are indeed DDA and DDS themselves.

3.1.5. *Effects of oxygen*

During the thermolysis stage of degradation, oxygen plays two roles, (a) the formation of the superficial degraded layer (TOL), and (b) the thermo-oxidation into volatiles of the nitrogen- and sulphur-containing molecules. Fig. 3 represents a SEM picture and the corresponding cartographies of O, S and N of a sample aged for 230 h at 250°C under low oxygen partial pressure. We observe that there is consumption of the sulphur-containing segments (as indicated by the shift away of the maximum from the surface) but only a low enrichment in oxygen at the surface. We can thus infer that the oxygen degrades preferentially the segments at the surface by thermo-oxidation instead of forming the TOL. The degraded layer at the surface can also be observed directly by SEM.

3.2. *Thermal ageing of cross-linking agents*

The above discussion suggests that the nitrogen- and sulphur-containing segments following chain scission are volatiles at 250°C under primary vacuum, but that they need subsequent thermo-oxidative degradation to become volatiles at atmospheric pressure. In order to gain supporting evidence concerning our hypothesis that the segments at the surface are in fact DDA and DDS themselves, we studied the thermal behaviour of these cross-linking agents alone in various gaseous environments.

The first observation we can report is that these molecules, both DDA and DDS, are volatiles at 250°C under primary vacuum. Figs. 4 and 5 show respectively the evolution of the residual mass of DDS and DDA as a function of ageing time in air at various temperatures. We can conclude not only that these molecules are not directly volatiles under these conditions of temperature and pressure, but also that they are slowly degraded. We can also notice that, at a given temperature, the degradation of DDS is more consequential than that of DDA. The temperature and pressure-dependent behaviour observed is very similar to that of the segments at the surface of the resin after thermal ageing. These conclusions seem to confirm our hypothesis about the chemical nature of the nitrogen- and sulphur-containing molecules.

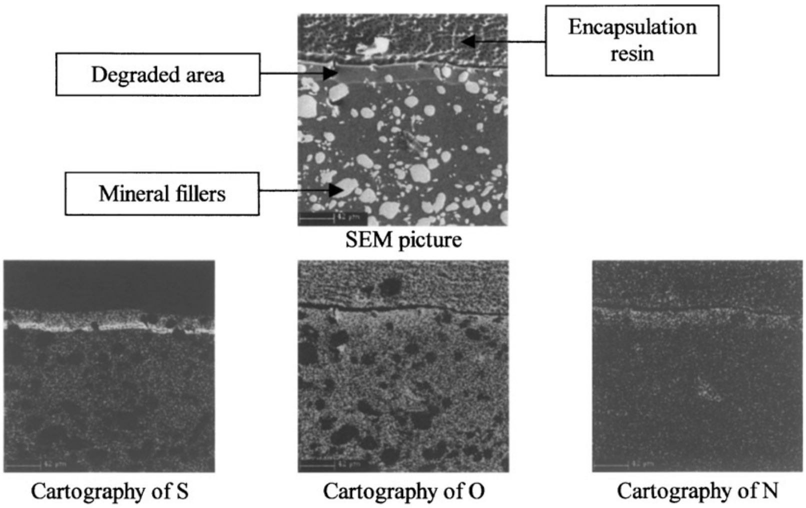

Fig. 3. SEM picture and cartographies in S, O and N of the same area of the adhesive aged for 230 h at 250°C under low oxygen partial pressure.

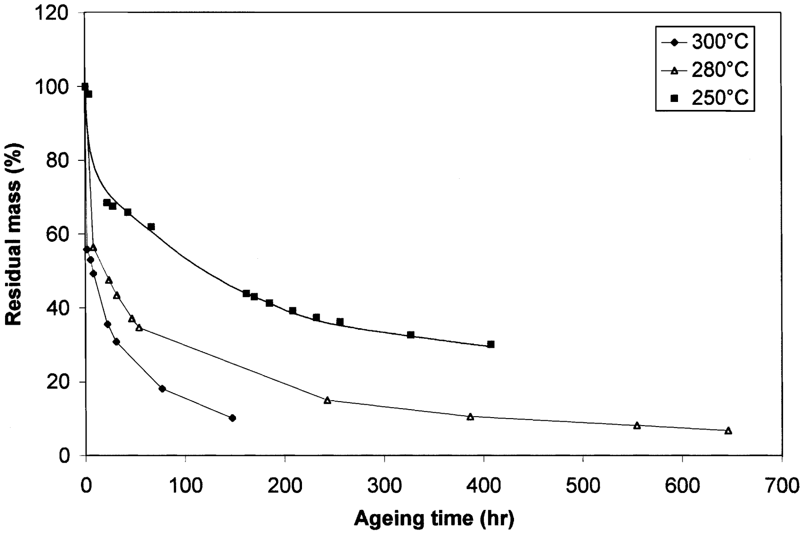

Fig. 4. Residual mass, M, of DDS vs. ageing time, t, in air at various ageing temperatures: (■) 250°C, (△) 280°C and (◆) 300°C.

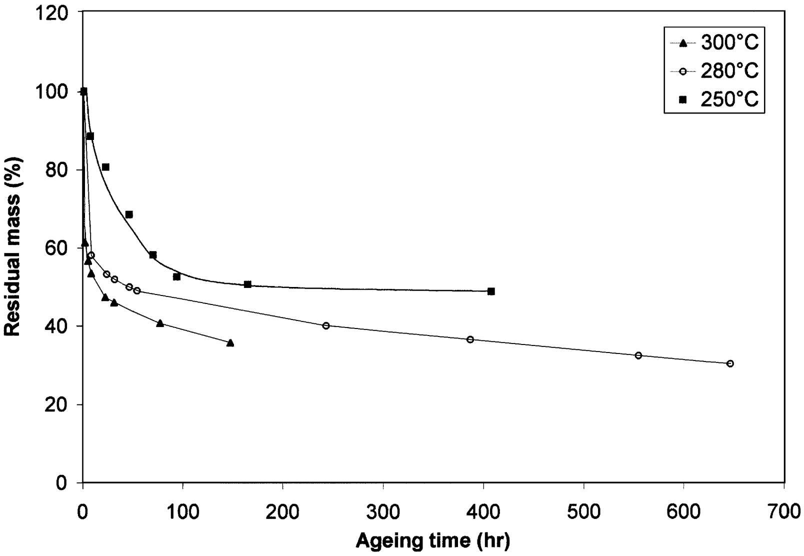

Fig. 5. Residual mass, M, of DDA vs. ageing time, t, in air at various ageing temperatures: (■) 250°C, (△) 280°C and (◆) 300°C.

3.2.1. Determination of kinetic parameters

In order to determine the activation energies of the thermal degradation processes of both cross-linking agents in air at atmospheric pressure, we analysed the results of mass loss at different temperatures as shown in Figs. 4 and 5. The rate of a reaction can generally be expressed by means of the general law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha), \tag{1}$$

where t is time, α the state of conversion or degree of advancement of the reaction, $k(T)$ the rate constant and $f(\alpha)$ the conversion dependence function. An integrated form of Eq. (1) often appears as

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha'}{f(\alpha')} = k(T)t, \tag{2}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function. The temperature dependence of the rate constant, $k(T)$, may be described by the Arrhenius expression:

$$k(T) = A\,\exp\frac{-E}{RT}, \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is (absolute) temperature. Eqs. (2) and (3) may be combined and arranged as

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E}{RT}. \tag{4}$$

According to this expression, the activation energy can be obtained from the gradient of the $\ln t$ vs. $1/T$ plot at a constant conversion level, α, without any specific

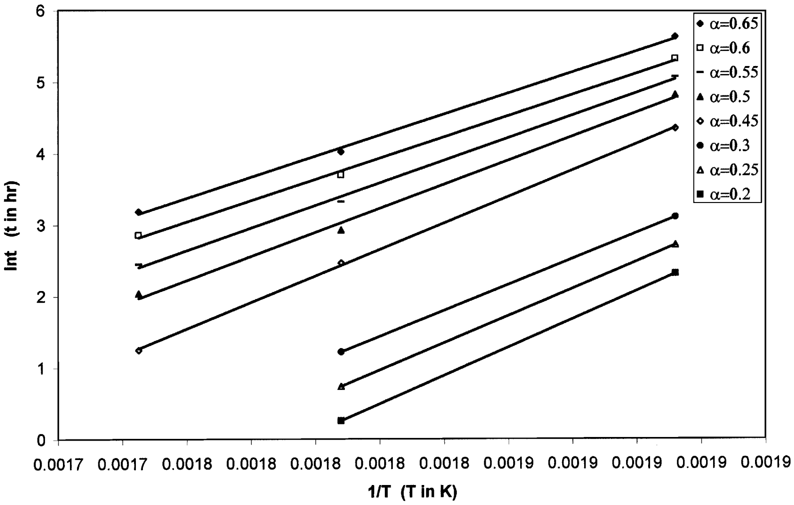

Fig. 6. Results of In t vs. T^{-1} for different values of degree of conversion, α, corresponding to ageing of DDS.

assumption concerning the conversion dependence function. This plot is shown in Fig. 6 for the case of DDS. The gradients are quite similar whatever the value of α which means that the same mechanism(s) is (are) probably occurring during the entire process of thermal degradation. The average value obtained for the activation energy of degradation of the DDS under air is $E = 142 \pm 15$ kJ/mole. By the same method (results not shown), we determined an activation energy of 140 ± 15 kJ/mole for the DDA. These values are quite close to the one calculated for the adhesive (130 ± 4 kJ/mole) [17].

3.3. Concentrations of cross-linking agents at the surface

If we hypothesize that the migrating segments are the cross-linking agents DDA and DDS themselves, and that after ageing in a low oxygen partial pressure, the surface (first ca. 30 μm) is made of these molecules only, it is possible to determine the molar ratio of these molecules at the surface. We can express the elemental concentrations at the surface by Eq. (5).

$$XA_i + (1 - X)B_i = S_i, \tag{5}$$

where X is the weight fraction of DDA at the surface and $(1-X)$, that of DDS. A_i and B_i are the weight concentrations of element i (= N or S), respectively for DDA and DDS, and S_i is the value of the weight concentration in i at the surface. The values of A_i and B_i have been calculated and are: $A_N = 67\%$, $B_N = 11\%$, $A_S = 0\%$ and $B_S = 13\%$. By using Eq. (5) with $S_N = 24\%$ (measured value by X-ray analysis), we determined $X = 23\%$. By using this previously determined value of $X = 23\%$ in Eq. (5) with $i = S$, we obtain a value of weight concentration in sulphur at the surface of about 10% which is very similar to the measured value of 13%. This result emphasizes our hypothesis about the chemical nature of the migrating segments. The weight concentrations of 23% in DDA and 77% in DDS correspond to a molar concentration of 50% of each cross-linking agent.

4. Discussion and conclusions

We have shown that the thermal degradation of a modified structural epoxy adhesive based on TGDDM cured with DDA and DDS is a two-stage process : the first stage is a mechanism of chain scission by thermolysis. During this stage, there is liberation of nitrogen- and sulphur-containing molecules which would seem to migrate towards the surface. These segments accumulate at the surface at atmospheric pressure and are volatiles under primary vacuum. Another explanation for the observed enrichment in nitrogen and sulphur could be that during thermal degradation, there is erosion of the polymer surface and disappearance of the organic compounds with the exception of the cross-linking agents. This hypothesis would suppose good thermal stability of DDA and DDS which is contrary to what we found experimentally. In addition, this could not explain the shift away from the surface of the maximum in sulphur after ageing in air, or the emission of gaseous by-products such as SO_2, NH_3 and HCN which are due to the thermal degradation of the cross-linking agents. We determined that oxygen has two effects during this stage, (a) the formation of a thin oxidised layer (TOL) by oxidation of the polymer surface, and (b) the thermo-oxidation of the liberated segments into volatile species (SO_2, NH_3, HCN). During ageing under low partial pressure in oxygen at 250°C, we observed that there is partial consumption of the liberated segments near the surface but apparently no oxidation of the sample surface. We can then conclude that, under these conditions, the oxygen reacts preferentially to degrade the liberated segments instead of oxidizing the surface. As we noted earlier from Fig. 2, the main difference for the observed maxima in sulphur and in nitrogen is the location of these maxima. Contrary to the observation made for the concentration in sulphur after ageing in air, there is no shift away from the surface of the maximum in nitrogen under the same conditions. The position of these maxima is due to the difference between rate of diffusion of the segments towards the surface and the rate of degradation of these segments. As we saw in Fig. 4, the rate of mass loss of DDS seems to be higher than that of DDA. We may infer that the sulphur-containing segments at the surface will be degraded faster than those containing nitrogen. This could well explain why the maximum in sulphur is shifted away from the surface. If we consider that the migrating segments are DDA and DDS themselves, we can imagine that due to their respective sizes (cf. Fig. 1), the rate of migration of DDA molecules will be higher than that of DDS [24]. We believe that both these considerations contribute to the observed locations of the maxima.

In order to show that the segments liberated by thermolysis which migrate towards the surface are the cross-linking agents DDA and DDS themselves, we studied their thermal behaviour. We found that the cross-linking agents DDA and DDS themselves show thermal behaviour similar to that of the liberated segments which migrate to the surface : at temperatures above 150°C, they are volatiles under primary vacuum but not under atmospheric pressure. Under air at atmospheric pressure, the cross-linking agents are slowly degraded by thermo-oxidation up to their complete disappearance. By gravimetric analysis of the thermal degradation of the cross-linking agents, we have determined that the values of activation energies of degradation are 142 ± 15 kJ/mole for DDS and 140 ± 15 kJ/mole for DDA. These values are quite close to that of 130 ± 4 kJ/mole determined for the adhesive. It then seems reasonable that the process of mass loss of the adhesive is governed by the degradation of the cross-linking agents which migrate to the surface after chain scission.

We have also seen, by using the hypothesis that after ageing under an inert atmosphere, the surface of the sample consists of the two cross-linking agents only, that we could determine the chemical composition and the nature of the surface. In these conditions of ageing under an inert atmosphere, we have shown that the surface would consist of 77% by weight of DDS and 23% of DDA, which means a molar ratio of 1/1 in each cross-linking agent. All these conclusions seem to confirm our hypothesis that the segments migrating at the surface, during the thermal degradation of a modified epoxy resin, are the cross-linking agents DDA and DDS themselves.

Acknowledgements

The authors thank G. Frot for this aid with X-ray analysis, the Direction Générale de l'Armement (DGA) and the Société Hispano Suiza Aérostructures for their material and financial support.

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