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Thermal and thermo-oxidative ageing of an epoxy adhesive

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Abstract

The thermal and thermo-oxidative degradation of a structural epoxy adhesive based on TGDDM and cured with DDA and DDS has been studied using thermogravimetric techniques. Both dynamic, or non-isothermal, and isothermal heating modes have been used and ageing has been undertaken in air at atmospheric pressure, primary vacuum and low pressure nitrogen. Degradation and weight loss of the material occur in two principal stages. In the first stage, weight loss occurs independently of the environment used. In addition, the activation energies calculated by three methods are very close for ageing in the various media. We conclude that this stage corresponds to thermolysis. The second stage exists only in the presence of oxygen, the material remaining relatively stable in nitrogen. This thermo-oxidative process leads to virtually total disappearance of the material with time, leaving only fillers behind. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Degradation; Epoxy; Thermogravimetry; Thermal ageing; Thermo-oxidation

1. Introduction

Crosslinking, or thermoset, polymers play an important role in structural applications both as adhesives and as matrices for fibre-reinforced composite materials. They are becoming widespread in many industries, including aerospace, automotive and marine equipment. As far as thermoset resin based adhesives are concerned, considerable advantages are manifest compared to more conventional methods of assembly such as bolting and riveting: reduction of weight and stress concentrations (around holes) being 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 degradation and reduction of mechanical properties.

Modern structural adhesives are often conceived for use at high temperatures. Contrary to intuition, crosslinked adhesives may creep under load [1], 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 [2]. Research in thermal degradation of epoxy systems is of great interest because this is an outstanding problem in the application of these systems in different types of environments and for the wide usage of these materials. It appears that a 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 polymeric degradation.

Several studies have been effected in order to explain thermal degradation mechanisms and weight loss [3–10], and also reduction of strength [11–13]. In this context, we have recently undertaken an investigation of the behaviour, at elevated temperatures, of a modified epoxy resin. In a previous paper [14], we illustrated the complexity of thermodegradation mechanisms and suggested a process occurring in three stages. Initially, due to high temperature, some chain scission occurs in the sample by thermolysis. The liberated segments containing sulphur and nitrogen atoms (as shown by X-ray analysis) migrate towards the surface of the sample. At the same time, the presence of oxygen (for ageing under air) leads to the formation of a surface oxidized layer (thick oxidized layer, TOL [15–18]). Then, near the surface, there is degradation of the liberated segments by thermo-oxidation into volatiles, which leave the polymer.

In polymer science, thermal methods of analysis have found important applications, among them the

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determination of kinetics parameters (e.g. Ref. [10]). For this purpose, thermogravimetric techniques (TG) are widely used because of their relative simplicity. In TG, the mass as a function of time and temperature is used to assess the thermal stability and degradation of polymers, which include the generation of kinetic data such as activation energies. The aim of this paper is to contribute to a better comprehension of the degradation mechanisms by a comparison of the behaviour under isothermal and dynamic [non-isothermal, dynamical thermal analysis (DTA)] conditions under various gaseous environments.

2. Experimental

2.1. Materials and preparation

The material studied is based on *N*,*N*,*N*′,*N*′-tetraglycidyl-4-4′-diaminodiphenylmethane (TGDDM) cured with a combination of two crosslinking agents: dicyandiamide, or DDA, and 4-4′-diaminodiphenylsulfone, or DDS. 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 $70\times70\times2$ 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 bars with both temperature increase and decrease between ambient and the cure temperature at 3°C per min. For isothermal experiments (see below), samples of dimensions $70\times10\times2$ mm^3 were cut. In the case of dynamic experiments, sample dimensions were $8\times3.5\times2$ mm^3. It was shown in our preparatory work using DSC that this curing regime leads to complete exhaustion of crosslinking agents (no residual enthalpy peak).

2.2. Methods

The isothermal ageing was undertaken, corresponding to simple periodic weighing of adhesive samples after various ageing times at temperatures in the range of 180°C to 250°C for up to 11000 h in an oven, without applied stress. This thermal ageing was effected in environments of air (in an oven at atmospheric pressure) and primary vacuum (0.4 mbar in an oven coupled to a vacuum pump and 4 mbar in the same conditions with a slow nitrogen flow to avoid the presence of oxygen). Samples were allowed to cool to room temperature in a desiccator before weighing on a Mettler AT250 balance with a precision of 2×10^{-5} g. After weighing, samples were returned to their ageing 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.

The dynamic (non-isothermal) DTA experiments were conducted on a Setaram microbalance with a heating rate between 2 and 10°C per minute. Each experiment was accomplished under a light flow of gas, either synthetic air or nitrogen (Air Liquide U grade). Very good reproducibility was obtained for these experiments.

3. Results

After thermal ageing in air, colour changes appeared in the samples. The initial grey colouration changed successively to green, then brown and finally black. This observation, previously reported by others [12,13], is indicative of chemical modification occurring at the surface of the resin due to thermo-oxidation (ageing in vacuum leads to no colour change). It is also of interest to note that the initial glass transition temperature, T_g, of the adhesive, of 225°C, decreased very rapidly in the initial stages of ageing in air, suggesting strongly a rapid process of molecular chain scission.

3.1. Non-isothermal results

3.1.1. Results under air

Fig. 1 shows an example of the typical evolution of the residual weight, M (%), as a function of temperature and its derivative with respect to temperature, (dM/dT), for a DTA experiment under air with a heating rate of 9°C per min. We can decompose this evolution into two stages, a first rapid degradation starting from 340°C and ended by a pseudo-plateau (considerably lower gradient). At this stage, the residual weight is ca. 60% of the initial weight. Allowing for the fact that the inorganic fillers are still present, we determined that only ca. 30% of the organic material is still present after this first stage. The second stage leads to complete degradation of the polymeric part of the adhesive. At 700°C, the sample is only constituted of the inorganic fillers. The temperature derivate of the weight evolution allows us to determine the temperature (T_m) for which the rate of mass loss is maximum during the first stage of degradation, for this example, T_m is 380°C.

3.1.2. Influence of heating rate

We realized the DTA experiments at different heating rates (2,4,7,9,10°C/min). Fig. 2 shows the evolution of the residual weight vs. temperature at different heating rates (4, 7 and 10°C/min) under air. We observe that the higher the heating rate, the higher the temperature at which (significant) degradation commences. A hysteresis effect is apparent. However, the pseudo-plateaux are similar, irrespective of temperature. This suggests that the heating rate modifies the kinetics of the process, as expected, but not the nature of the compound formed after the first stage of degradation.

3.1.3. *Influence of oxygen*

Fig, 3 shows two DTA curves obtained at the same heating rate (9°C/min), one under air and the other under nitrogen. It appears that under nitrogen only the first step of degradation occurs. The same observation was also made at the other heating rates. We can conclude from these experiments that the second stage of degradation needs oxygen to occur. It seems that the oxygen has little influence on the first stage of degradation. The residual weight at the pseudo-plateau is ca. 60% of the initial value which is the same value as that obtained under air.

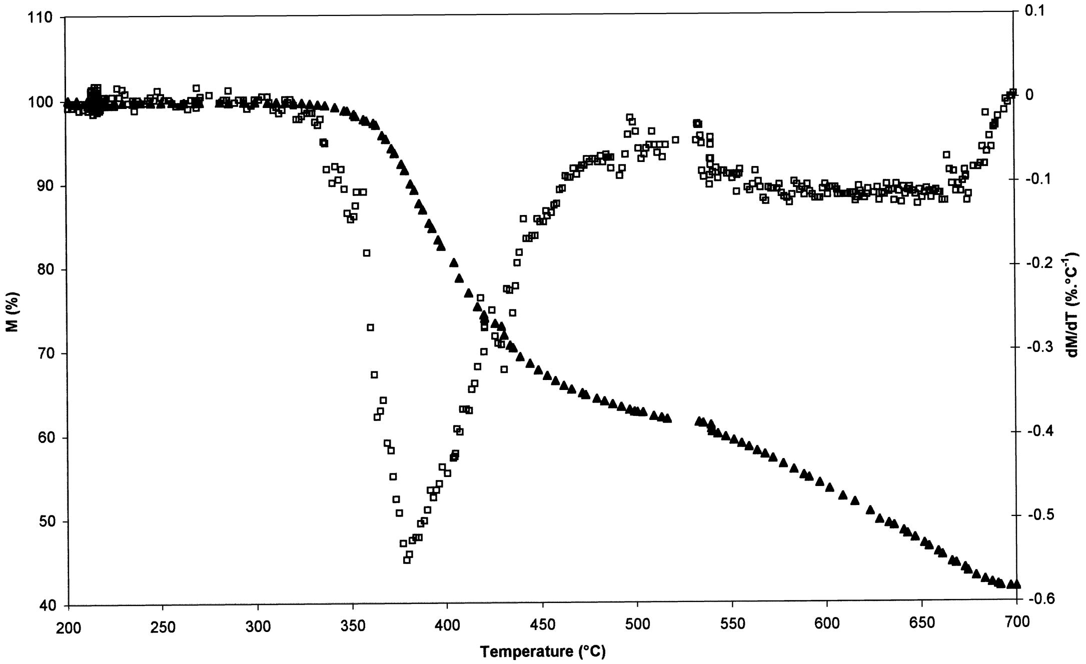

Fig. 1. Residual mass, M, of material (▲) and derivative, dM/dT (□), during non-isothermal heating in air at 9°C min^{-1} vs. temperature.

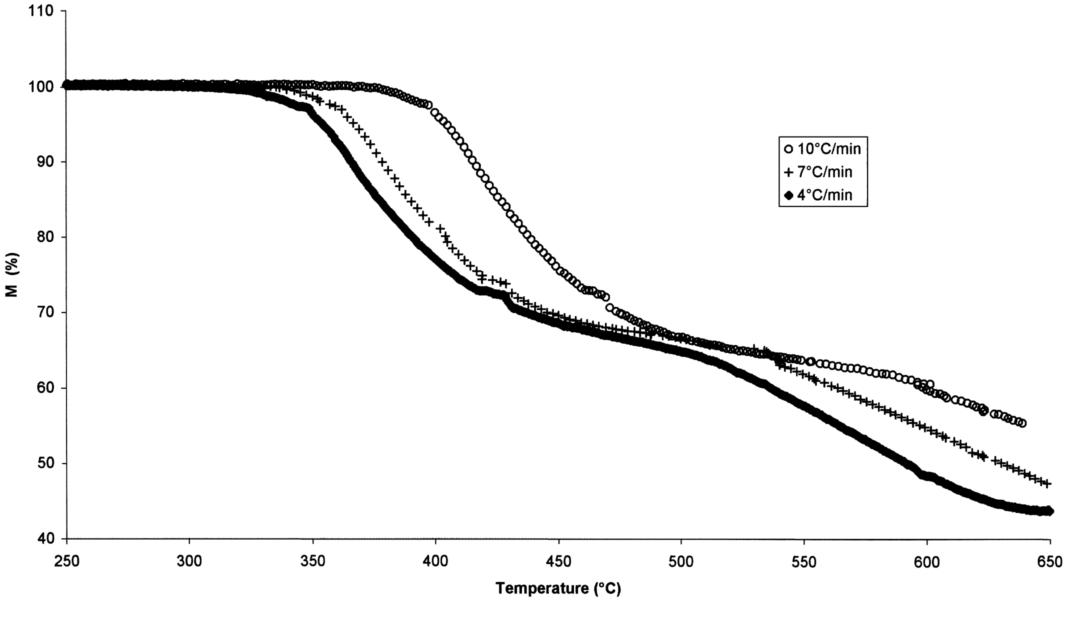

Fig. 2. Residual mass, M, of material during non-isothermal heating in air vs. temperature. Heating rates: (◆) 4°C min^{-1}, (+) 7°C min^{-1} and (○) 10°C min^{-1}.

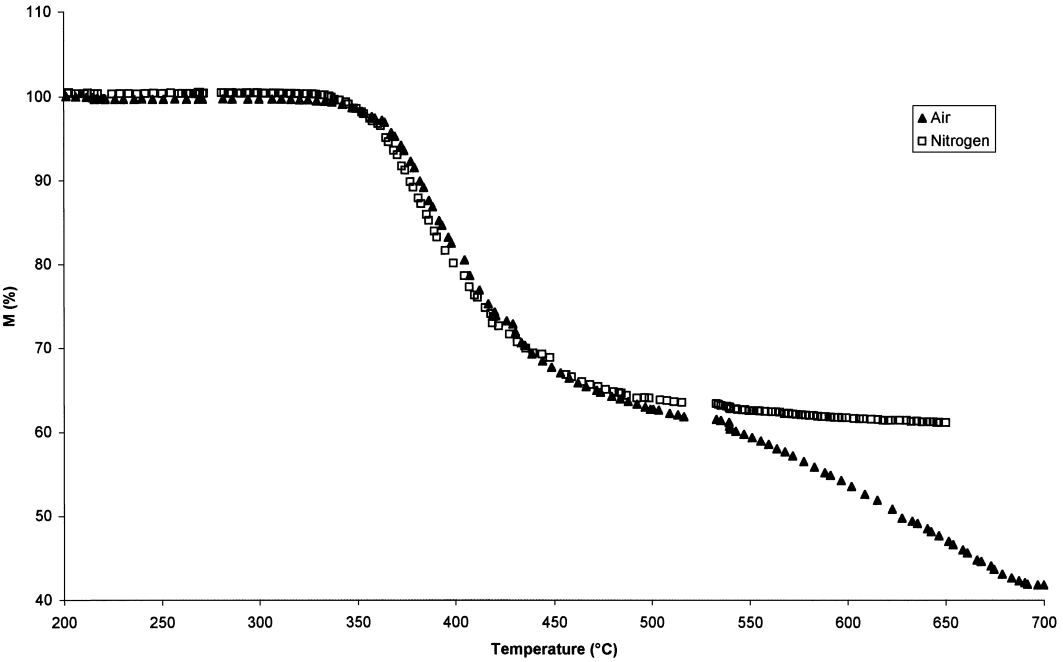

Fig. 3. Residual mass, M, of material during non-isothermal heating at 9°C min^{-1} vs. temperature (▲) in air and (□) in nitrogen.

3.1.4. Determination of kinetic parameters

Analysis has been performed on the results corresponding to the temperature range 300 to 450°C in order to study the first stage of the degradation. The rate of a reaction can generally be expressed by means of the general law:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

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 the 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.

Three methods of analysis have been used: the method due to Kissinger [19], the one due to Flynn and Wall [20], and Ozawa [21] (FWO) and the Invariant Kinetic Parameter (IKP) technique [9,22]. They all present the advantage of being able to be used to calculate the kinetic parameters without involving any consideration of the reaction mechanism(s) directly.

In Kissinger's method, the activation energy, E, can be obtained as follows. Combining Eqs. (1) and (3), we differentiate to obtain $d^2\alpha/dt^2$. Setting the result to zero, corresponding to the maximum of reaction rate, $d\alpha/dt$, we obtain after some algebra:

$$\ln\frac{\phi}{T_m^2} = \frac{-E}{RT_m} + \ln\left[-f'(\alpha_m)\frac{AR}{E}\right] \tag{4}$$

where ϕ is heating rate (dT/dt), the prime represents differentiation with respect to α, and suffix m corresponds to values at maximum reaction rate. A plot of $\ln(\phi/T_m^2)$ vs. $1/T_m$ gives the activation energy, since the slope of such a line is given by $-E/R$, without any assumption of the conversion dependent function [10,19]. This plot is shown in Fig. 4 with the results obtained under air and nitrogen. It is clear from this figure that the activation energy is similar for both gaseous environments. We obtained 180 kJ/mol under nitrogen and 196 kJ/mol under air.

The FWO method, due to Flynn and Wall, and independently Ozawa, is an integral method for determining the activation energies in dynamic heating experiments. They determined a linear approximation leading to the expression [20,21]:

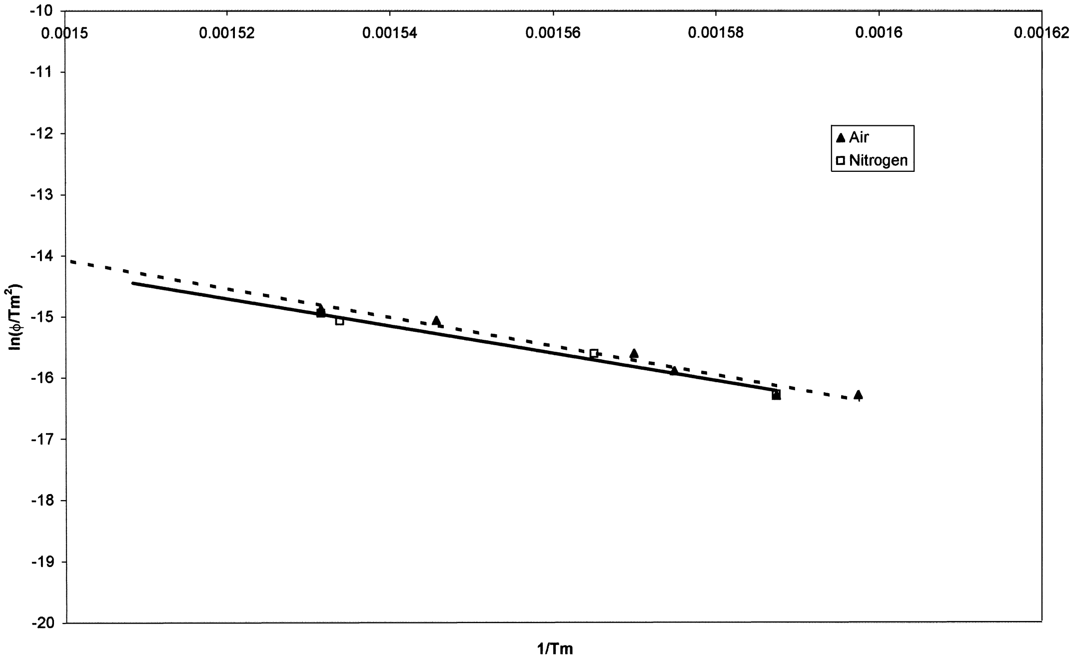

Fig. 4. $\ln(\phi/T_{\mathrm{m}}^2)$ vs. T_{m}^{-1} for interpretation of Kissinger. (▲) In air and (□) in nitrogen.

$$\log(\phi) = \left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \tag{5}$$

This method allowed us to determine the activation energy from a plot of logarithms of heating rates, ϕ, as a function of the reciprocal of temperature, $1/T$, for a constant $g(\alpha)$ [Eq. (2)] (consequently for a constant α), since the slope of such a line is given by $-0.457(E/R)$. This plot is given in Fig. 5 for the different degrees of conversion α and both gaseous environments. The method yields an average value of 193 kJ/mol under nitrogen and 191 kJ/mol under air; we may conclude that the activation energy is the same with or without oxygen.

The last method used is the IKP method. This method, more complex, allows the computation of kinetic parameters considering only residual weight values acquired in the corresponding temperature range. This method was reported in detail in the Appendices of Ref. [22]. We obtained an activation energy of 125 kJ/mol under nitrogen and 124 kJ/mol under air. The value under air is in good agreement with those determined by Rose with TGDDM/DDA (124 kJ/mol) and with TGDDM/DDS (128 kJ/mol) [9]. However, the most interesting result is that the values obtained under air and under nitrogen are similar.

The evidence strongly suggests that the same mechanism(s) occur(s) in the first stage of thermal degradation, at least for the gaseous environments employed here.

3.2. Isothermal results

3.2.1. Influence of oxygen

Examples of mass loss in air and in primary vacuum (0.4 mbar), as a function of the exposure time at 250°C are shown in Fig. 6. Initial mass loss is clearly more rapid in a primary vacuum. We previously suggested [14] that the segments liberated by chain scission need thermo-oxidation to become volatiles under air although they are already volatile under primary vacuum (lower external pressure). These different types of behaviour can explain the difference observed in the mass loss rates. We suggested also that this effect can be partially explained as a result of oxygen reacting at the surface of 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 stage of ageing [12,15,16]. It is also interesting to notice that the shapes of the curves of Fig. 6 are similar to the curves obtained under dynamic conditions. We can suppose that the degradation mechanisms are the same.

3.2.2. Determination of kinetic parameters

In order to determine the activation energy of the thermal degradation process under air at atmospheric pressure, we studied the mass loss at different temperatures. Fig. 7 represents the residual weight vs. time at 180, 215, 230 and 250°C. Eqs. (2) and (3) may be combined and arranged as:

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E}{RT} \qquad (6)$$

According to this expression, the activation energy can be obtained from the slope of the ln*t* vs. 1/*T* plot at a constant conversion level, *α*, without any specific assumption concerning the conversion dependence function. This plot is shown in Fig. 8. The average value obtained for the activation energy of the first stage of degradation under air is *E* = 162 ± 5 kJ/mol. This value is quite close to those calculated above for non-isothermal conditions.

4. Discussion

The synthesis of our results for both isothermal and dynamic ageing leads us to suggest possible mechanisms for degradation. Let us first consider the non-isothermal

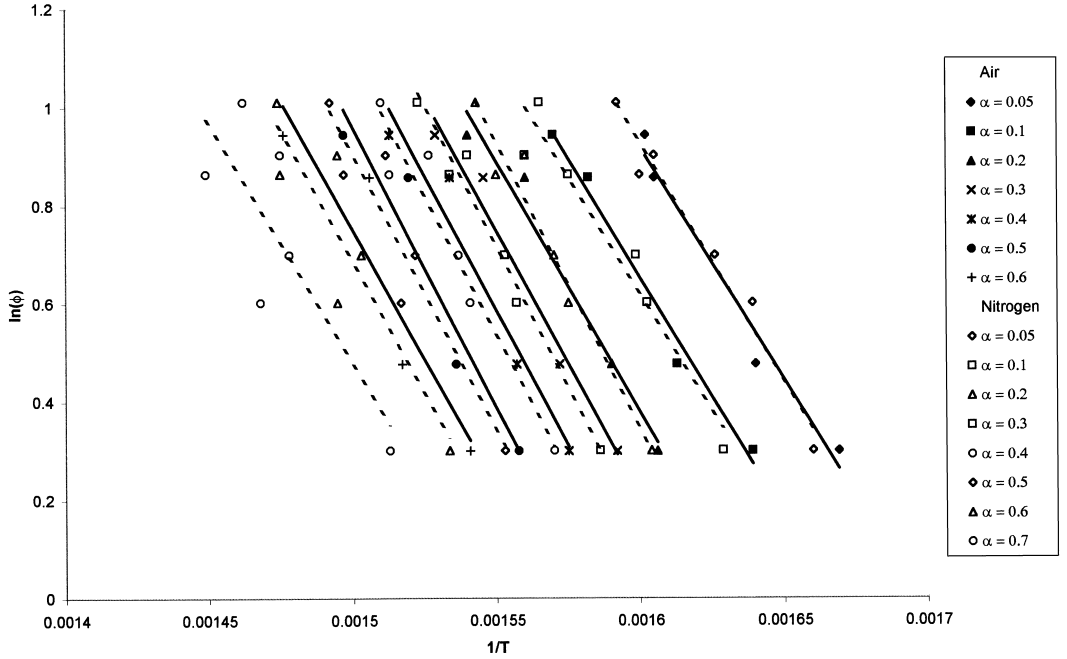

Fig. 5. ln*φ* vs. T^{-1} for different degrees of conversion, *α*, for FWO interpretation. Full symbols and open symbols represent, respectively, ageing in air and in nitrogen.

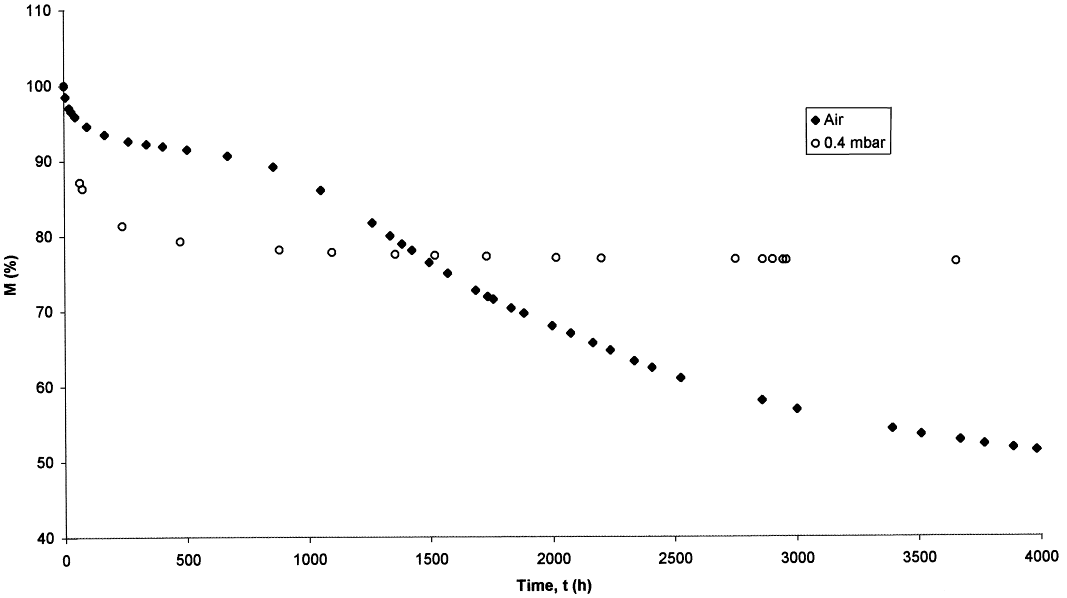

Fig. 6. Residual mass, *M*, of material vs. ageing time, *t*, at 250°C. (▲) In air (atmospheric pressure) and (○) in primary vacuum (0.4 mbar).

results. As did Rose [9], we hypothesise the formation, as a result of degradation in the primary stage, of a thermally more stable compound (or compounds) which we denote X. This process will probably be due to thermolysis, since results strongly suggest that its production is independent of the environments (studied here) and heating rate. Activation energies are very similar (whichever method of calculation is employed) and residual weights at the end of this primary stage coincide, whether an oxygen-containing atmosphere or not is used for ageing. In Ref. [14], we suggested that this first stage was by chain scission by thermolysis. The present results tend to confirm that oxygen is unimportant at this stage: elevated temperature alone leads to degradation. Notwithstanding, under non-isothermal conditions, the temperature corresponding to the

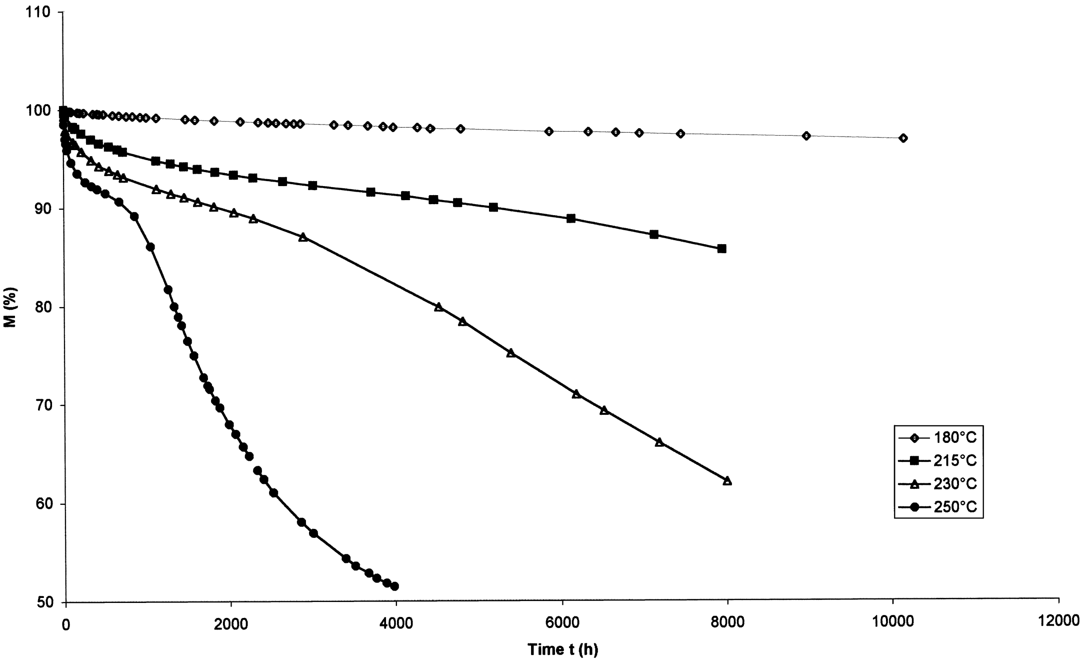

Fig. 7. As for Fig. 6 but only in air at various ageing temperatures. ◇, 180°C; ■ 215°C; △, 230°C and ●, 250°C.

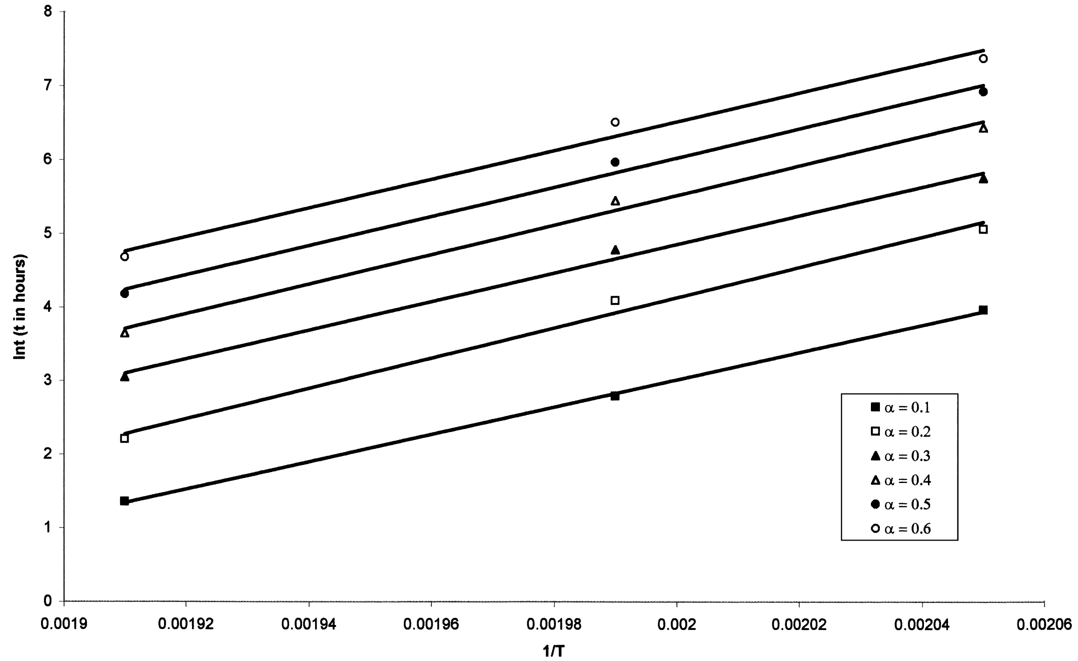

Fig. 8. ln$t$ vs. T^{-1} for interpretation of isothermal results [Eq. (6)] for various degrees of conversion, α.

beginning and to the end of the first stage increase with heating rate: this hysteresis effect is probably related to the rate at which degradation occurs and at which degradation products leave the polymer.

The second stage depends on the environment. In nitrogen, the polymer now remains relatively stable up to ca. 650°C, suggesting that X remains stable also. However, in air a second regime of weight loss occurs, presumably by the thermo-oxidation degradation of X (and/or possibly another chemical entity initially) and the formation takes place of liberated chemical segments, of sufficiently low molecular weight to be volatile.

Let us now consider the isothermal results. Qualitatively, we obtain similar weight loss behaviour as with dynamic conditions. A rapid initial rate of weight loss, the rate being linked to temperature and gaseous environment, decreases, and then increases again, when the environment is air. The junction of these two parts of the curve (see Figs. 6 and 7) corresponds to a local minimum in mass loss rate and can thus be considered to be the end of a first step in the degradation process. In primary vacuum, this deflection does not occur and so we assimilate the two first stages, viz. for isothermal and non isothermal conditions. The second stage of degradation, in air, corresponds to the renewed increase in rate of weight loss: this does not occur for the reduced oxygen environments. However there are differences. The values of residual mass at this point, although similar for different temperatures, are markedly higher than those obtained under non-isothermal conditions. This suggests the formation, presumably also by thermolysis and chain scission, of a (different) thermally more stable compound, denoted Y, during the first step. Migration to the surface of liberated segments and molecular rearrangements may also occur. Fig. 6 shows that compound Y will remain relatively stable in the absence of oxygen. However, in the presence of oxygen, the second stage will correspond to the thermo-oxidation of Y (presumably) continuing until the final total degradation of the polymeric part of the material. Notice also the values of residual weight after the first stage. At reduced pressure (0.4 mbar) this is ca. 75% and under air, ca. 90% [although not shown, the value in nitrogen (4 mbar) is ca. 80%]. Since ageing has been effected at the same temperature (250°C), we assume that the same compound(s) (Y) is (are) formed initially, under the various atmospheric conditions. However, due to the higher, atmospheric, pressure, in air, the low molecular weight species will not leave the polymer so readily compared to the lower pressure conditions. Further degradation is necessary. This could well explain the residual weight differences and also partially explain the (apparently) different kinetics. In addition, surface oxidation could lead to some mass increase. This could possibly explain the small, yet significant, difference in observed residual weight at 0.4 and 4 mbar.

Thus, overall, we suggest that degradation occurs in two steps:

1. Chain scission by thermolysis and partial or total disappearance of liberated segments. Oxygen plays a minor role, except for the thermo-oxidation of liberated segments becoming volatile. The compound formed, Y, is thermally stable in the absence of oxygen.
2. For the second stage, behaviour much depends on the environment. The polymer remains relatively stable in the absence of oxygen, but degrades virtually totally in the presence of oxygen. Similarities in the values of activation energies for the first stage of degradation lend supporting evidence to our hypotheses.

5. Conclusions

This paper illustrates the complexity of the degradation mechanism(s) of a modified epoxy resin and the influence of oxygen during this process. We have shown that the degradation is a two-stage process (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 under air). During this stage, there is formation of a thermally more stable compound by molecular rearrangement. Without oxygen, this compound is relatively stable at high temperatures. The segments liberated by chain scission migrate towards the surface and then either leave the sample immediately as volatiles, if they are already sufficiently volatile (experiments under vacuum or at high temperature) or 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.

We have shown also that the degradation mechanism(s) seem(s) to be very similar under dynamic or isothermal conditions. We think that the compound (Y) formed after isothermal degradation at 250°C could be a precursor of the compound (X) formed under dynamic conditions. The compound (Y) would need more chain scissions and molecular rearrangements to form the compound (X). One fact which emphasizes this idea is the value of the residual weight after the first stage of degradation, this value is ca. 75% for (Y) and only ca. 60% for (X). At present, we have no evidence about the chemical nature of the compounds (X) and

(Y) but we suppose, as did other authors [9], that they are aromatic cyclic compounds.

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