

# Study of Epoxy and Epoxy–Cyanate Networks Thermal Degradation to Predict Materials Lifetime in Use Conditions

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**ABSTRACT:** Composite materials are used more and more for aeronautical applications and they have to be as thermally stable as possible. The thermostability of carbon-fiber/epoxy–cyanate composites elaborated with an autoadhesive and autoextinguish prepreg were tested. Dynamical and isothermal aging tests were carried out to evaluate the composite thermal stability. Thermal degradation products were identified by chromatography/mass spectrometry analysis and the results obtained were compared with data known on the material network structure. The physicochemical network structure evolutions and the thermal aging data are correlated with the interlaminar shear strength (ILSS) mechanical results. For epoxy–cyanate composites, cracking appears after a longer time of aging than for epoxy composites. This new epoxy–cyanate material isothermal stability seems to be good and particularly good if it was postcured after processing. The comparison of chemical, mechanical, and crack formation results obtained by accelerated aging tests allowed us to determine models to predict long-term behavior. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3142–3153, 2000

**Key words:** epoxy; epoxy–cyanate; composites; aging; thermostability; lifetime

## INTRODUCTION

The use of high-temperature organic matrix/carbon-fiber composites has increased in the last few years following great requests in the aeronautics and spacial fields. The power of helicopter engines in perpetual progression implies the use of increasingly thermostable composite structures. For example, the engine cowl and fuselage of helicopters are submitted to continuous heat flows, as the temperature is increasingly raised.

Currently, for structural applications, epoxide resins generally strengthened with glass or carbon fibers represent the basis of an important number of organic matrices. The chemical struc-

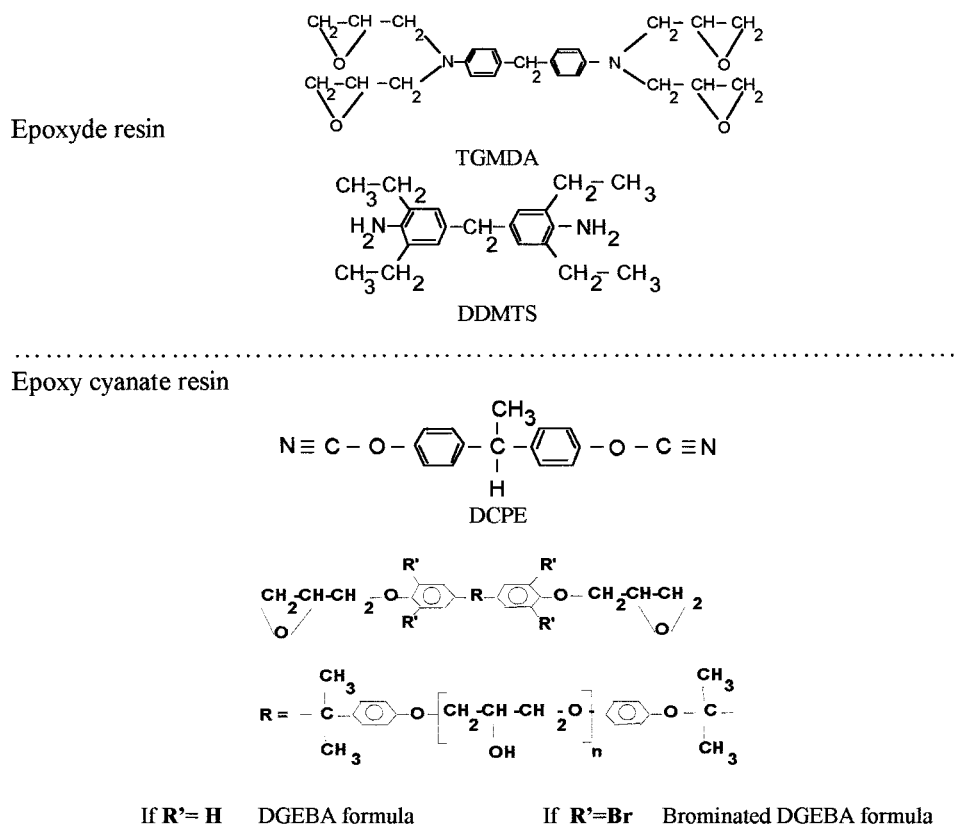
ture of these aromatic epoxide resins (mainly glycidylethers of bisphenols) is not intrinsically thermostable, especially near the glycidyl chemical function. The thermal use limit of materials for a long time situates under 180°C. If we want to use these materials, the higher use temperature is 180°C. Structure technologies developed in the last few years have allowed the development of new resin employed for composite structures of helicopters with higher thermal properties.<sup>1</sup> Nevertheless, if the material autoextinguish property is obtained, the bonding property necessary to decrease the sandwich structures process costs for the manufacture of the engine cowl is not reached. A new formulation based on epoxide and cyanate monomers seems to approach the researched goal.

New organic composite materials based on cyanate resin seem to show a good compromise between usual epoxide resins and bismaleimide resins. The functional epoxide group conjugated with

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**Figure 1** Monomers chemical structure of epoxy and epoxycyanate resins used in this study, before crosslinking.

the polyfunctionality of coreactants (aromatic amine or cyanates) allows for the creation of highly crosslinked networks.<sup>2</sup> Unfortunately within these systems, oxidation-sensitive sites constitute network thermal fragility zones.<sup>3</sup>

This work aims to study the thermal behavior of the composite with epoxy-cyanate matrix and to compare results obtained with those of an epoxy-matrix composite to determine a correlation with the mechanical properties' evolutions. These works will allow access to reliable and complete data on the behavior in the temperature of these composites. They will anticipate the long-term behavior in use conditions of these composite materials.

## EXPERIMENTAL

### Materials

The materials studied are prepregs with 3K HR carbon-fiber reinforcement and thermostable matrices with autoextinguish property, namely ep-

oxy M18-1 resin (Hexcel, France) and epoxy-cyanate 786 resin (Cytac, USA). The main constituting molecules of these resins are described in the Figure 1.

The resin composition, determined by liquid chromatography (HPLC) with a UV detector and using the ratio between the identified peak and the area of all the eluated peaks, allows us to find:

For M18-1 resin: 28% DDMTS (diamino diphenyl methane tetra substituted), 34% TGMDA (tetraglycidyl ether methane diphenyl aniline), 20% PEI [poly(etherimide)] used as a plasticizer to increase the mechanical properties at break ( $K1c$ )<sup>4</sup> and impurities coming from residues of monomer synthesis and as result of polymerization products.

For 786 resin: 27% DCPE, 35% DGEBA (diglycidyl ether of bisphenol A), 12% brominated DGEBA, 20% of a monofunctional polyimide used as a plasticizer. Some impurities are also present in the resin formulation.

Monolithic composite plates are obtained from nine prepreg plies oriented to 0°, dimensions 70 × 80 mm, and 2-mm thick. Eurocopter Company processes these materials by using an autoclave oven with a cure cycle, including a 1-h cycle at 180°C plateau, and with a 2°C/min thermal temperature increase from ambient temperature to 180°C. The content of carbon fibers for the composite plates is near 65 wt % for M18-1 and 60 wt % for 786.

### Network Structure

The determination of chemical-reaction mechanisms acting during the polymerization of epoxy-cyanate systems gives capital information to understand second-time thermal-degradation mechanisms.

It is an essential step to understand thermal-degradation results and to work with methodology as to certify results. Indeed, to understand a loss of mechanical property coming from material-chemical degradation by oxidation, by thermolytic break, etc., and to identify the most fragile sites of the chemical structure, it is necessary to know the network structure well.<sup>5</sup>

### M18-1 Epoxide System

The main reactions of epoxide resin crosslinked with the primary amines are the polyaddition reactions, which are well described in the literature.

Basis mechanisms depend on the addition of TGMDA oxirane cycles and on the hydrogen-function mobility. The primary amines are very reactive; the secondary amines formed are less reactive than the primary amines, nevertheless they play an important role in the polyaddition reaction and lead to the formation of tertiary amine.

Hydroxyl groups coming from the oxirane-cycle opening can react with epoxide functions to form etherification reaction products. These reactions only take place if epoxide functions are in excess. Alcohols can catalyze these different reactions by giving an autocatalytic character to the first stages of polymerization. In addition, the presence of tertiary amine catalyzed the etherification reaction. However, due to steric volume of the DDMS, it is unlikely that the tertiary amine obtained influence this reaction. The homopolymerization reaction of epoxide groups can also take place to form a polymer with zones rich in ether functions.<sup>5-9</sup>

At the end of the crosslinking cure cycle, all the epoxide functions were consumed, but a high quantity of free-residual amine (50%) exists. The evolution of epoxide and amine function concentration during crosslinking reaction was determined by using infrared absorption bands assigned at 906 and 1614 cm<sup>-1</sup> (primary amine), respectively.

### Epoxy-Cyanate 786 System

The mechanism of epoxy-cyanate polymerization presents several stages.

The first stage (Fig. 2) includes the trimerization reaction of cyanate monomers to form a triazine structure. The polymerization of these triazine structures lead to a material with aryl cyanurate structural groups of which the mechanical and thermal properties are high.<sup>10</sup>

The second reaction stage (Fig. 3) between the cyanate and the epoxy monomers lead to a structure with an oxazoline cycle.<sup>11</sup>

Finally, the third reaction susceptible to act corresponds to an etherification reaction of epoxide functions to form a structure with numerous linear ether functions.

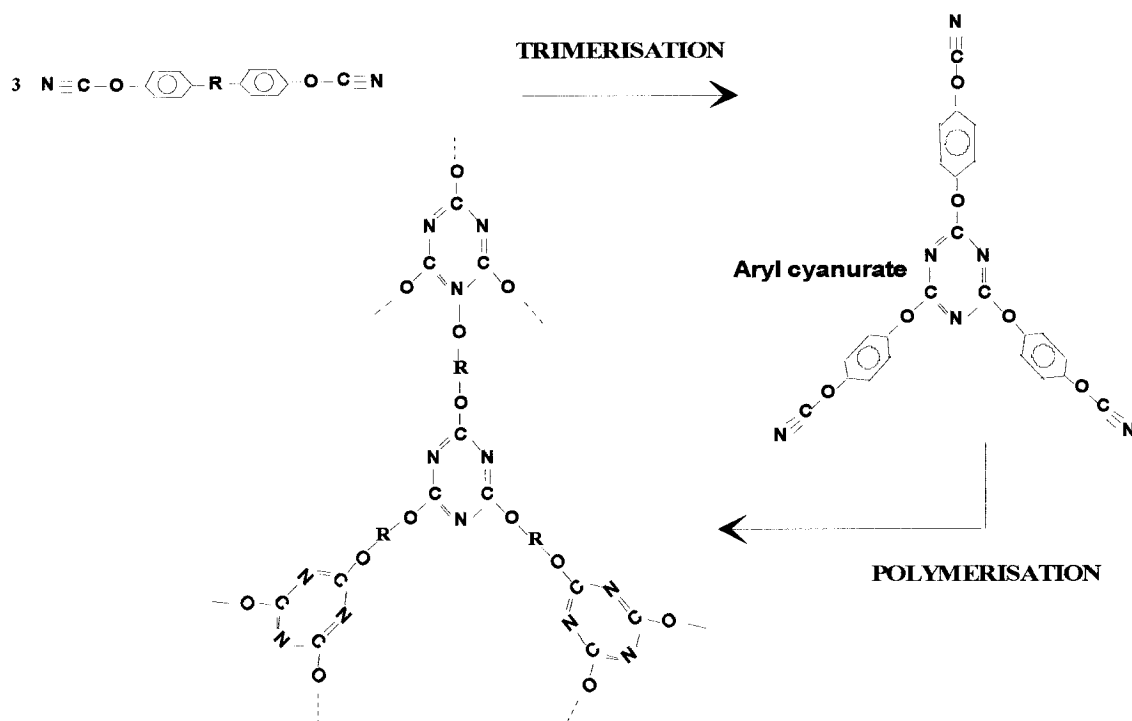
More details on chemical mechanisms of reaction between epoxide and cyanate can be found in works published by Régnier et al.<sup>3</sup> and by Grenier-Loustalot et al.<sup>12</sup>

At the end of the crosslinking cure cycle, the consumption of amine, cyanate, and epoxide groups determined by infrared spectroscopy was full; triazine, oxazoline cycle, and ether molecules are present in the network. All these products begin to be detected by infrared spectrometry when temperature rises to 180°C.

### Analytical Techniques

Thermogravimetric analysis is done in dynamic mode with a heating rate of 10°C/min under inert gas (nitrogen) and under air, with a Shimadzu TGA-50 thermobalance. To determine the thermal degradation kinetics parameter of epoxide and epoxy-cyanate materials, thermogravimetric analyses are also done with a heating rate of 2-5 and 15°C/min. Isothermal stability characteristics have been evaluated by tests in an oven at constant temperature between 150 and 230°C, with an air flow controlled at ±1°C. The samples were periodically weighted with an electronic balance the relative accuracy of which was 10<sup>-4</sup>.

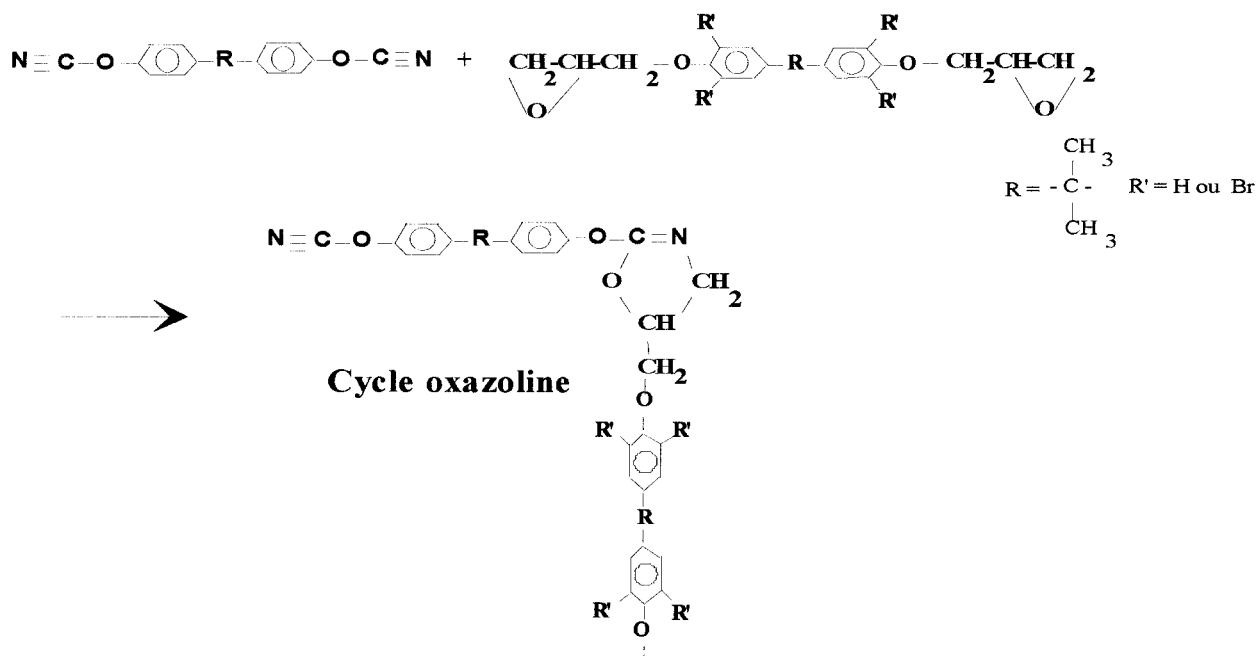
Mechanisms of degradation are studied after material pyrolysis in a Thermolyne F21100 tubu-



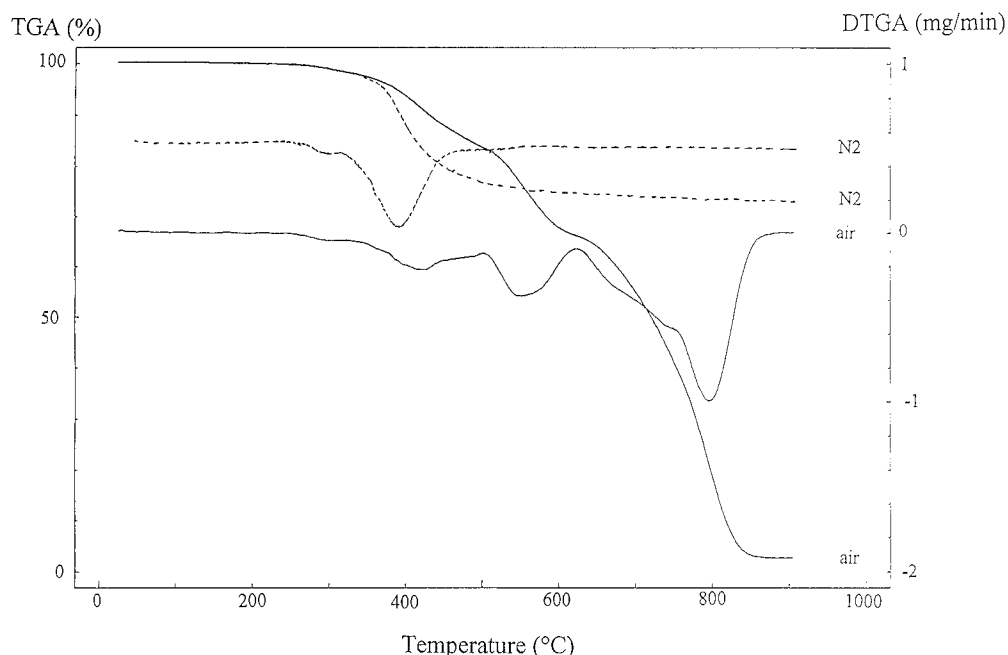
**Figure 2** Chemical reaction of cyanate function.

lar oven at 300, 350, 400, 500, and 600°C under nitrogen atmosphere. Products of degradation are trapped in acetone. The identification of thermal degradation products have been realized with a

Unicam Automass 120 gas chromatography mass spectrometer (GC/MS), in electronic impact mode. The identification of the pyrolysis products is made by using the NIST database. The relative



**Figure 3** Chemical reaction between cyanate and the epoxy monomers.



**Figure 4** Weight loss curve (TGA) and associated derivative curves (DTGA) for M18-1 epoxy composites, during dynamical thermal degradation under air and nitrogen.

molecule amount detected by mass spectrometer represents the surface of the chromatogram peak on the chromatogram total peak area.

The composite mechanical properties evolution is characterized by interlaminar shear strength (ILSS) tests at room temperature according to the NF 17-412 procedure, by using an Instron mechanical test machine.

The viscoelastic properties were recorded against temperature from  $-120$  to  $300^{\circ}\text{C}$  with a scanning rate of  $1^{\circ}\text{C}/\text{min}$  by using a Metravig torsion pendulum with a starting angular deformation of  $1^{\circ}$ . The samples were parallelepiped at  $60 \times 10 \times 2$  mm.

## RESULTS AND DISCUSSION

Many parameters govern the thermal stability of organic composite materials.

As a mechanical point of view, one of the most important parameters is the glass transition temperature ( $T_g$ ), due to the fact that it governs the maximum temperature in the use of the material. As a chemical point of view, the thermal material resistance depends on the atmosphere in which the material is used. Indeed, in an inert atmosphere, the thermal degradation is exclusively a

thermolysis phenomenon. In an air atmosphere, reactions of oxidation become preponderant.

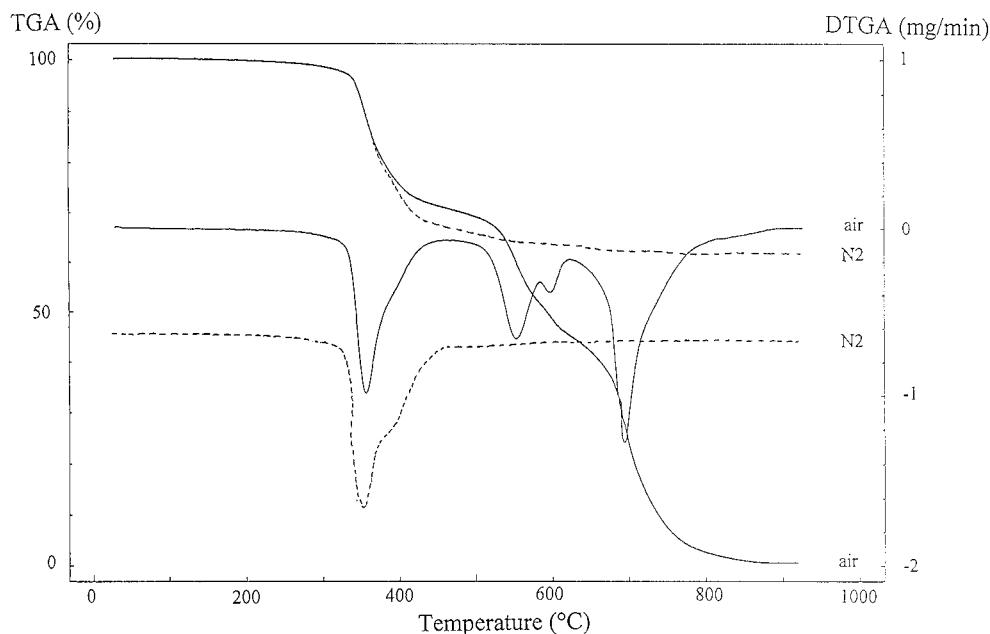
The polymer heat and oxidation resistance is evaluated by thermogravimetric analysis (TGA), which gives comparative results between materials. Furthermore, tests in isothermal for different duration, in a controlled atmosphere, allow us to determine behavioral models and to gain an estimate in the long term. This second technique allows us to evaluate the maximal use temperature in connection with specific factors defined by the manufacturer, such as mechanical properties for a weight loss of a material that generally does not exceed 5 wt % for aeronautical applications.

### Thermogravimetric Analysis

Figure 4 shows curves of weight loss and associated derivatives for M18-1 composite tested under air and under nitrogen.

Figure 5 shows curves of weight loss and associated derivatives for epoxy-cyanate 786 composites tested under air and nitrogen.

Tests under inert gas (nitrogen) indicate that materials have a good thermal stability until  $260^{\circ}\text{C}$ . For high temperatures, the weight loss is rapid in the two cases and shows an unique phase of degradation. The weight loss at the maximum



**Figure 5** Weight loss curve (TGA) and associated derivative curves (DTGA) for 786 epoxy-cyanate composites, during dynamical thermal degradation under air and nitrogen.

of the derivative curve is 10 wt % for the M18-1 material and the noticed temperature corresponds at 400°C, whereas it is 12 wt % for 786 material and the noticed peak temperature is 360°C. At 400°C, the epoxy-cyanate 786 material shows a thermal stability in dynamic inferior to that M18-1 material because the recorded mass loss is approximately 27 wt %. Between 600 and 900°C, the M18-1 residue is 74 wt % and the 786 residue is 60 wt %.

This difference between the two composites can be explained by the weight fraction of resin in the monolithic composite structure. Indeed, the 786 composite is constituted by equal amounts of carbon fibers and organic matrix, whereas the M18-1 composite is composed of approximately 35 wt % resin.

Under air, the dynamic thermal degradation is more complex. The weight loss of the two composites begins at 255–280°C. Between 380 and 550°C, a best thermal stability under air than under nitrogen for the M18-1 material is noted; a similar result is observed for 786 composite, but the phenomenon is less remarkable. For high temperature, materials degrade more rapidly under air than under nitrogen. The fact that the material decomposes more rapidly under nitrogen than under air is rare enough; however, this event has already been noted on other thermostable polymers as polyimides.<sup>13,14</sup> This best ther-

mal stability is due to an oxidized product layer that constitutes a barrier to the distribution of oxygen into the material core.

Under air, the weight-loss curve can be divided into three phases of degradation. The derivative curve shows three zones relatively equivalent for the two composites, the first between 300 and 500°C, the second from 500 to 640°C, and the last one from 640 to 900°C. The third phase of degradation is characterized by a high weight loss in the case of the M18-1 composite.

After 800°C, the obtained residue is very weak and represents < 5 wt % of the sample.

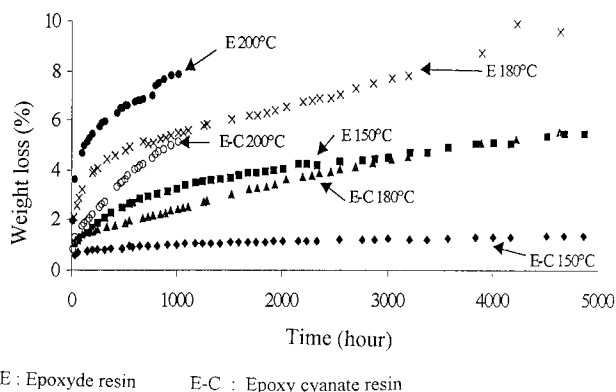
The thermolytic process can be seen under inert or oxidant atmosphere and corresponds to the first phase of degradation between 300 and 500°C. The two other phases are specifically due to a thermo-oxidative process.

To determine thermal degradation kinetic parameters, many theories exist in the literature,<sup>15,16</sup> the most commonly employed being Ozawa's theory. This theory uses a general relationship based on the rate of weight loss ( $da/dt$ ) expressed as a function of the degree of weight conversion ( $\alpha$ )

$$da/dt = \beta f(\alpha)$$

where  $\beta$  is a rate constant depending on temperature according to the Arrhenius law.





**Figure 6** Isothermal weight loss of epoxy and epoxy-cyanate composites (150–180–200°C). The weight loss of composites was calculated by considering the material only with pure resin, without fibers

According to this method, apparent activation energy can be calculated for different sample weight losses.

The thermal degradation of the M18–1 system shows a particularity at the beginning of the degradation. For  $\alpha = 0.1$ , the  $E_a$  is two and one-half times more important under air than under inert atmosphere. This reveals a thermal stability clearly superior under air as compared to an inert environment, whole at least in the first phase of decomposition. After 10 wt % of conversion, the  $E_a$  calculated under air is very stable.

For the thermal degradation of this material under nitrogen, the calculated  $E_a$  increases until a value of 220 kJ/mol for  $\alpha = 0.6$ , then decreases until 35 kJ/mol for  $\alpha = 0.9$ . This corresponds to a thermal degradation, including very numerous thermolytic mechanisms.

The dynamic thermal behavior under inert gas observed for the epoxy-cyanate material is not very different than the observed M18–1 system behavior. The calculated  $E_a$  for this material under oxidizing atmosphere varies between 100 to 140 kJ/mol, all along the degradation ( $\alpha$  between 0.1 and 0.9).

### Thermal Aging in Isothermal Conditions

The interest of studying the thermal behavior of a material at constant temperature by following the weight loss versus time is to establish a lifetime prediction.

The gravimetric evolution of composites aged in isotherm at different temperatures is shown in Figure 6. Curves correspond to the weight loss of

the composite material calculated to 100 wt % of resin versus time.

For the studied temperature range, the thermal stability of the epoxy-cyanate system is superior to the epoxide system. A difference of 3 wt % after 1000 h at 200°C or 3000 h at 180°C is observed. At 150°C, the epoxy-cyanate system presents a very good thermostability; a weight loss of 1.4 wt % is observed after 5000 h. This weight variation has to be compared with the 5.5 wt % measured for the epoxide system tested in the same conditions.

The speed of weight loss ( $k$ ) versus time has been modeled by using an Arrhenius' law to calculate an estimate material lifetime.<sup>17</sup>

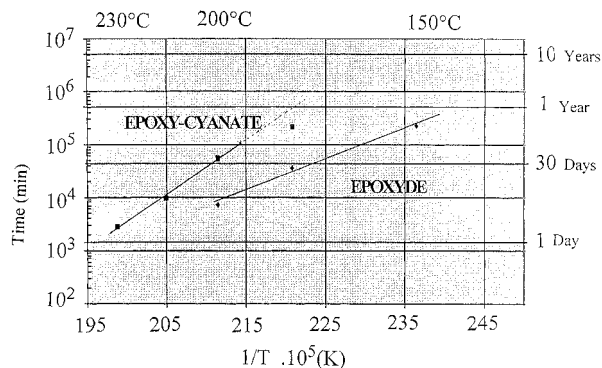
$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad \text{with} \quad k = \frac{\Delta M}{M_0}$$

It appears that the thermal degradation of the constituted epoxide polymer TGMDA and DDMTS seems to present an Arrhenian's behavior. Activation energy ( $E_a$ ) is estimated at 60 kJ/mol; the preexponential factor ( $A$ ) calculated is  $3.1 \times 10^6 \text{ min}^{-1}$ .

On the other hand, the  $E_a$  of the epoxy-cyanate polymer is clearly higher; it is 127 kJ/mol. The preexponential factor ( $A$ ) is  $3.9 \times 10^7 \text{ min}^{-1}$ .

The difference of thermal degradation energy between the two materials has to be connected directly to the different system structures, and corresponding to the crosslinking point formed by the cyanate functions is the formation of triazine nodes.

In the aeronautic field, it is very usual to calculate a material lifetime by using a weight loss



**Figure 7** Lifetime prediction of epoxy and epoxy-cyanate materials, based on a weight loss of 5 wt % for composite.

that does not exceed 5 wt % (Fig. 7). For higher weight loss, the repercussions on residual mechanical properties becomes too extended.

From these results, we can estimate, for example, that the material based on epoxide matrix can stand a thermal aging for 1000 h (approximately 40 days) at 170°C.

For the epoxy-cyanate system, lifetime prediction is more delicate to establish. After 5000 h at 150°C, the time corresponding to a weight loss of 5 wt % has not been reached, because our material is more stable than the epoxide material; however, it does not allow us to locate another point in our Arrhenius' graph. If this graph is studied more precisely, it emerges that points between 230 and 200°C are relatively well lined up, but the point at 180°C seems offset. For thermal degradations with a temperature higher than 200°C, the behavior of the 786 network seems different than for lower temperatures. This can be explained by a change in the structure of the material that we can see on viscoelastic spectra. Indeed, a transition is detected at 185°C.

Nevertheless, in a first approximation, we can try to extrapolate points obtained between 230 and 180°C at the temperature of 170°C to compare the thermostability of our two materials, but we have to remember that it is possible that other degradation phenomena could occur at a lower temperature. This extrapolation equally leads to the estimate that the epoxy-cyanate formulation would support a thermal aging at 150°C for 2 years, which is not in contradiction with our current observations.

From these results it emerges that the lifetime of the composite with epoxy-cyanate 786 matrix is longer than the M18-1 system, knowing that it has been established for material use in isothermal temperature conditions between 150 and 200°C.

### Thermal Degradation Mechanisms

If we wish to obtain an estimation of the long-term material behavior on the basis of models, it is necessary to identify precisely the degradation mechanisms.

To identify the fragile sites of the polymeric structure, we proceeded to pyrolyze the composite materials in a tubular oven and then to separate and to identify the released gases by GC/MS.

### Pyrolysis/GC/MS of the Epoxide M18-1 Composite

At 300°C, the pyrolysis has not induced rupture of chain in the system to form gaseous molecules.

At 350°C, the main released molecules are the aniline in a particularly abundant amount (33%), the methyl aniline (7%), and the *N,N*-dimethylaniline (3%). The 1-cyclohexene molecule, the chlorinated nonane, and the phosphoric ester probably come from resin additives. Finally, a weak amount of tetra-substituted DDMTS aromatic amine (3%) was noticed.

At 400°C, no aniline is detected, as a slight increase in the amount of chlorinated alkane is detected (10%). It appears that a new chemical molecule comes from the epoxide TGMDA degradation and corresponds to 20% of the products released at this temperature. At the end of the analysis, the molecules corresponding to the degradation of the DDMTS reacted on the epoxide functions are detected (15%), as well as the DDMTS (10%).

At 500°C, the pyrolysis degradation leads to the formation of 6% aniline, 2% methyl aniline, 3.5% chlorinated alkane, 3% epoxide groups, and several molecules of which each one represents < 1% but that reflects the degradation of the DDMTS monomer. At the end of analysis, 14% of DDMTS are detected.

At 600°C, 15% of aniline are again detected. In addition to the molecules identified at 500°C, we notice the formation of molecules corresponding to the degradation of the epoxide group and aromatic amine products coming from the DDMTS. At this temperature, many covalent links break, thus creating free radicals that after rearrangement lead to varied chemical structures.<sup>18</sup> Molecules corresponding to the aromatic amine of typical DDM and the aromatic amine of typical DDMTS are also identified.

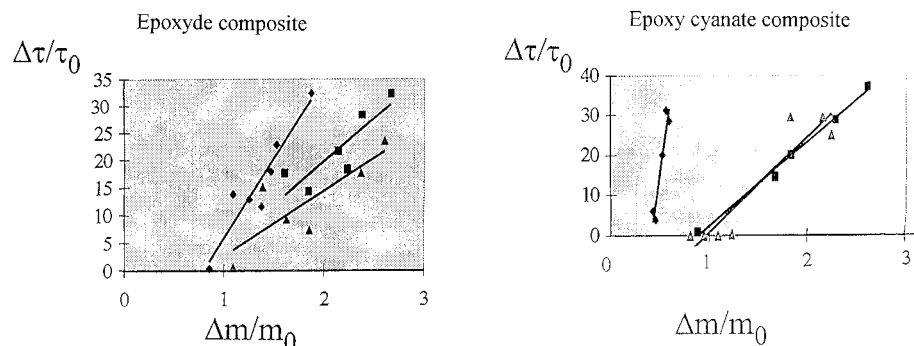
These products are proof of the degradation of the epoxide monomers polymerized with the tetra-substituted aromatic diamine.

### Pyrolysis/GC/MS of the Epoxy-Cyanate 786 Composite

In the case of the thermal degradation at 300°C of the epoxy-cyanate composite, an important production of benzoquinone (31%), chlorinated alkane (14%), and phosphoric ester (10%) is noted. These products are probably additives of the resin. Furthermore, 5% of bisphenol A and 3% of the same chemical structure having lost a central methyl group are identified.

At 350°C, 15% of benzoquinone and 6.5% of phosphoric acid are detected; 9% of phenol are formed. Similarly, we observe the formation of a





**Figure 8** ILSS versus weight loss evolution for epoxy and epoxy-cyanate composites:  $\blacklozenge$ , 150°C;  $\blacktriangle$ , 180°C;  $\blacksquare$ , 200°C.

new relative chemical corresponding to the thermal degradation of the oxazolidone cycle (11%). Then the zone rich in polyether groups begins to degrade. The bisphenol A amount emitted increases slightly (6.5%).

At 400°C, the benzoquinone (18%) and the phosphoric ester (8%) are always present. Five percent of phenol is detected and the amount of oxazolidone degraded is equivalent to that noticed at 350°C. The degradation of the polyether region form molecules of the formula  $C_6H_{10}O_3$ .

At 500°C, the high-pyrolysis temperature provokes many chain splits. Thus, the phenyl isocyanate  $Ph-O-CN$  (1.3%) is detected, as well as a high-phenol production (31%) and molecules derived as 5% of  $HO-PH-CH-(CH_3)_2$ , 7% of  $HO-PH-CH_2-CH=CH_2$ , 6% of bisphenol A, and 15%  $HO-PH-C(CH_3)_2-Ph$ . Bromophenol (3%) is also detected, coming from the bromed DGEBA, second epoxide monomer of the 786 epoxy-cyanate resin.

At 600°C, phenol and allyl phenol are identified, the principal gas of decomposition being bisphenol A (35%), followed by products of degradation of the DGEBA (19%) and bromine DGEBA (12%) groups.

No matter what the degradation temperature, from the total of these results, a great number of similarly detected products were observed. This allows us to consider that degradation mechanisms are the same and to make extrapolations to evaluate the long-term behavior of these composites.

### Mechanical Properties

Values of ILSS ( $\tau$ ) of composites during thermal aging at 200°C show a regularly decreasing evo-

lution without a brutal fall that would indicate in this case an important stratified ruin. Initial properties ( $\tau_0$ ) of epoxy composites are 64 MPa, and 62 MPa for epoxy-cyanate composites.

After 1000 h at 200°C, a decrease ( $\Delta\tau/\tau_0$ ) of 32% for the epoxide system and 37% for epoxy-cyanate is observed.

A degradation at 180°C shows the same tendency as at 200°C after 3000 h. The loss of strength represents 23% for the epoxide system and 25% for the epoxy-cyanate system.

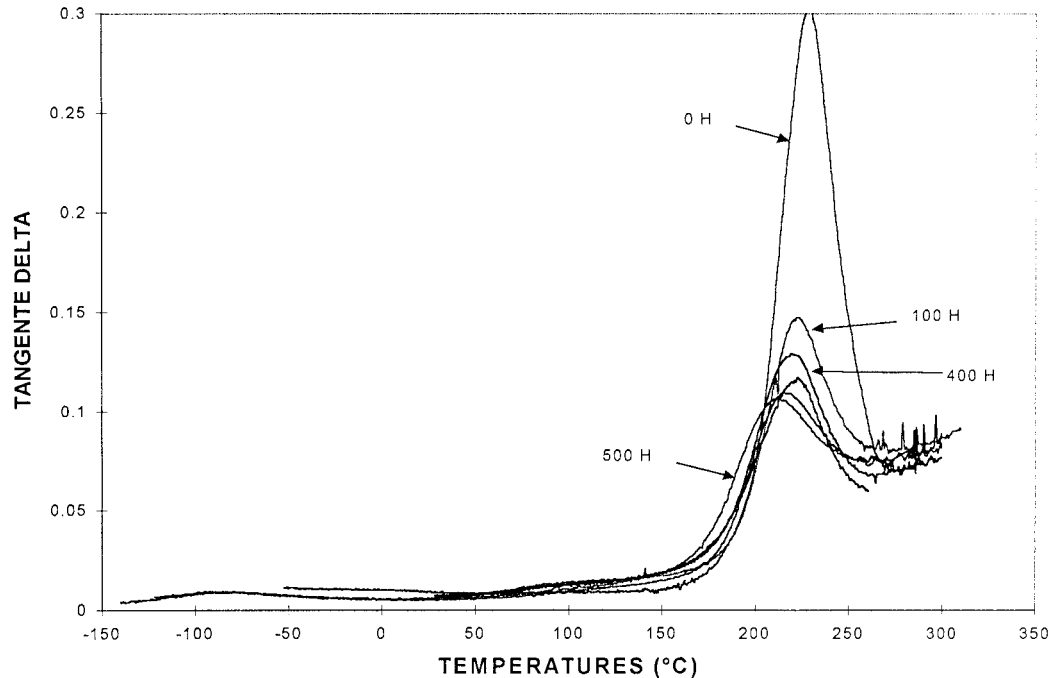
For an isothermal aging at 150°C,  $\tau$  is stable during the first 500 h, then a loss representing 14% after 1000 h for the epoxide material and 20% for the epoxy-cyanate system is observed.

Epoxy-cyanate composite undergoes a fall of  $\tau$  more important at 150°C as compared to an aging at 180°C. One can suppose that at 180°C, rearrangements bring about the organic matrix, whereas for lower temperatures, the phenomenon has not taken place. Triazine cycles convert into cyanurate and oxazolidone chemical groups.

After 5000 h at 150°C, the decrease in properties represents a loss of 32% for the epoxide composite. The case of the epoxy-cyanate composite shows a different behavior, which obviously includes other rupture types than those in interlaminar shear strength and which alters the calculation of ILSS. Nevertheless,  $\Delta\tau/\tau_0$  calculated for 2500 h at 150°C is 28% for the epoxy-cyanate system. This value is equivalent to the value obtained for a composite aged at 180°C for a similar duration.

As a conclusion, values of ILSS obtained on aged samples tested at room temperature show few differences between the two composites.

Figure 8 shows the correlation between the loss



**Figure 9** Tan  $\delta$  curve of epoxy composite aged at 200°C.

of properties ( $\Delta\tau/\tau_0$ ) and the weight loss ( $(\Delta)M/M_0$ ).

Losses of properties according to the composite weight loss at 180 or 200°C each follow a straight line corresponding to an equilibrium between weight loss and loss of mechanical properties. On the other hand, aging at 150°C induces a different behavior. In this case, degradations of the systems induce mechanical property losses without volatile molecule formations. This observation is again more easy to visualize for the epoxy-cyanate composite than it seems to present structure rearrangement when the temperature becomes higher than 180°C. For aging at 150°C, the state of the matrix seems to govern ILLS properties.

At 180°C, thermal degradation in the network are compensated by crosslinking and structural rearrangement of the matrix that allows us to obtain a correlation between the weight loss and the mechanical characteristics.

### Evolution of Viscoelastic Properties

In this part of the work, we look at the evolution of materials' viscoelastic properties. We chose for this test to make aging on a sample at 200°C. Figure 9 shows tan  $\delta$  curves of the epoxy composite after different thermal aging times.

The initial epoxy material ( $T_g$ ) is 230°C. During the thermal degradation, an amplitude diminution of this transition is noticed. The  $G$  modulus measured at room temperature after thermal aging varies between 1.7 and 2.8 GPa. The modulus in rubbery state of the aged composites shows a value far more raised as compared to that the composite not aged. We can suggest that the effect of postcuring due to a long exposition time improves the crosslinking state of the epoxide system. During chemical characterization, we saw that a lot of free amine are present at the end of process. At 150°C, the value of  $G$  into the rubbery state increases by a factor of 5 in 3000 h.

The evolution of the different transitions from the epoxy-cyanate stratified in the case of the thermal aging is very different. Before aging, the tan  $\delta$  curve (Fig. 10) shows two main peaks, the maximum of which are at 185 and 240°C. When we look for the network structure, using microscopy (optical and SEM), we did not see different structural phases in the matrix. The material is, at the observation scale, homogeneous. It is not possible to distinguish either the different chemical structures or the plasticizer incorporated to increase mechanical properties. The only explanation we can find to explain this curve was the coexistence of triazine, aryle cyanurate, and oxazoline cycles with isocyanurate, oxazolidone, and

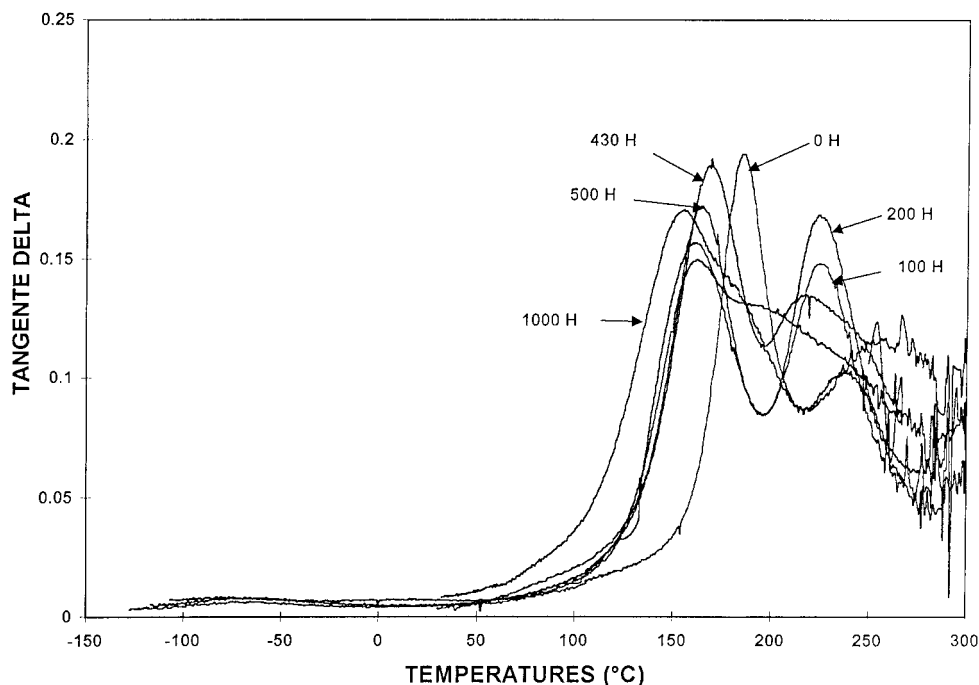


Figure 10 Tan  $\delta$  curve of epoxy-cyanate composite aged at 200°C.

polyether chains forming at the end of network crosslinking and for which the amount of each one changed during aging.

The amplitude of the transition at 240°C tends to increase with aging and reaches its maximum at 200 h. Then this amplitude decreases to lead after 1000 h to the total disappearance of this transition.

The amplitude of the transition at 185°C varies in lesser proportions; on the other hand, the value from this transition decreases strongly (loss 31°C after 1000 h at 200°C).

In the case of the thermal aging at 150°C, the amplitude of the  $T_g$  at 240°C increases in a constant manner but its value is shifted at 218°C after 5000 h. As for the transition at 185°C, the amplitude increases until 1000 h; then it decreases regularly with a loss of 20°C on its initial value. The evolution of the module of shear strength  $G$  is very low during aging.

Epoxide and epoxy-cyanate composite viscoelastic results lead to the following questions.

For the two systems, the constitution of the network after processing tends to a structure that coexists in low- and high-crosslinked zones, microvoids, free molecules, and chain ends.

The physicochemical analysis of the epoxide structure has revealed aromatic amine molecules not having reacted. Furthermore, the analysis by

GC/MS of emitted volatile gases during thermal aging proves the production of composed coming from aromatic diamine as well as a dehydration of the epoxyde system.

The tan  $\delta$  amplitude decrease and the increase of the strength modulus in rubbery state can be explained by the disappearance of dangling chains corresponding to the partially reacted amines. Furthermore, the flexible zone of the system constituted by the crosslinking of the TGMDA disappears during aging. Solid-state NMR and FTIR analysis confirm the rupture of quaternary carbon/nitrogen links with rearrangement of the network.

The case of the epoxy-cyanate polymer seems more complex. It shows two transitions, the first one corresponding to a phase rich in triazine structure coming from the reaction of the cyanate monomers on themselves, the second one to a phase rich in polyether resulting from the addition of epoxide functions. The second one corresponds to the absorbing peak at 240°C. During the material postcuring, or just in the beginning of aging, the network phase corresponding to the transition temperature at 240°C increases, and the material properties are better. Unfortunately, the phase corresponding to the higher  $T_g$  also contains the less thermostable sites. Thermosensitive sites are in the present case, the C—H and

aliphatic C—C of the rich polyether phase. For aging for long periods of time, the rupture of polyether chains reduced the number of links of the thermoset system leading to the decrease of  $T_g$ . The chemical modifications observed could explain the peak evolutions detected during thermo-mechanical analysis used to evaluate materials thermal aging.

## CONCLUSION

The effect of the temperature on mechanical properties and physicochemical effects of epoxides and epoxy-cyanates composites has been studied at constant temperatures between 150 and 200°C. It is possible to make correlations between weight variations of the two composites and ILSS variations determined at room temperature, and therefore it is possible to anticipate evolution of properties in the long term. Nevertheless, for extrapolations, it is again necessary to deepen the study of mechanisms of thermal degradation to separate the different mechanisms that could intervene at temperatures other than those studied.

The epoxy-cyanate composite shows a better thermal behavior than the epoxide composite. During aging, the epoxy-cyanate composite is less damaged. Because of the chemical structure of the epoxide system that contains an important quantity of polyether links (that is, sensitive chemical groups at the temperature), the thermal degradation of this system is more rapid than in the case of the epoxy-cyanate system.

For industrial structural applications, the monolith associated with the core by the adhesive film is intermediary to obtain a sandwich structure. The prevision of lifetime in service at high temperature of sandwiches necessitates the separate study of the different constituents (matrix, reinforcement, adhesive) then in association, to establish their individual behavior, to identify synergistic mechanisms being able to exist and to define the weak point of the structure. From these data, it is possible to determine the most important parameters that govern the structure stability. These parameters will allow us to quantify the properties evolutions and to anticipate the

long-term behavior in conditions of use of the structure.

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