

PREDICTION OF THE CAVITATION DURING THE THERMAL AGEING OF AN ORGANIC MATRIX COMPOSITE AND THE CONSEQUENCES ON MECHANICAL BEHAVIOR

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Abstract

This communication is devoted to the thermal ageing in air between 160 and 220°C of a composite core made of an epoxy-anhydride matrix reinforced by unidirectional carbon fibers used for stiffening an aluminium electrical wire. Microscopic examinations of polished composite cross-sections have revealed the formation and accumulation of microcavities of gases in the composite bulk responsible for a monotonous decrease in elastic modulus. After a certain duration (depending of the aggressiveness of ageing conditions), these microcavities connect and lead to the formation of "apparent" large micro-cracks responsible for a dramatic decrease in fracture properties when the size of the damage area reaches a critical value. The resulting structure/mechanical property relationships have been interfaced with a non-empirical model giving the main features of the thermolysis kinetics of the polymer matrix. In particular, this model predicts the accumulation of organic molecules responsible for cavitation in the composite bulk when their concentration exceeds their solubility threshold.

1 Introduction

The request for electricity increases constantly in Europe. Faced to environmental and societal pressures opposed to the construction of new overhead power lines, electricity companies need new technical solutions for increasing the current rating without changing the sag of the present lines. Several potential solutions are under investigation. Nexans Research Center (NRC) has developed a solution based on aluminum electrical wire stiffened by an organic matrix composite core (OMCC) made of epoxy-anhydride matrix and unidirectional carbon fibers. However, this solution will be selected by electricity companies only if the OMCC long-term durability (typically for at least 50 years) is clearly demonstrated.

At the present time, the average working temperature of the overhead power lines is located between 80 and 90°C. However, during maintenance operations, temperature can rise up to 160-180°C for very short durations. At these temperatures, ceramic fibers (glass and carbon) are stable. As a result, OMCC may only perish by thermal ageing of their weakest organic component: polymer matrix or fiber/matrix interface (or interphase). Two thermal ageing mechanisms can compete:

- Thermal decomposition of the organic component due to its own instability in the absence of molecular reagent (i.e. oxygen). This mechanism is often called “thermolysis”. It is initiated by the cleavage of weak chemical bonds. In the case of epoxy-anhydride matrices, one suspects that ester groups rearrange according to a 6-membered reaction, as previously evidenced, for instance, for linear polyesters at high temperature (typically for $T > 200^{\circ}\text{C}$) [1].
- Thermal oxidation of the organic component due to the presence of labile hydrogen atoms. According to well-known structure/propagation rate constant relationships [2], in the case of epoxy-anhydride matrices, oxidation would take place preferentially on methylene groups located in a α position of electronegative atoms (oxygen or nitrogen).

Recently, the durability of another type of OMCC, also made of epoxy-anhydride matrix, but reinforced both by unidirectional carbon and glass fibers, has been evaluated by Barjasteh and coll. [3, 4]. According to these authors, the thermal oxidation of the polymer matrix would be the main degradation mode, although it affects only a very thin superficial layer of about 100-150 μm thickness between 150 and 200°C , i.e. only 2-3% of the core diameter. This thin oxidized layer would not alter the tensile behavior because, in this direction, the entirety of the applied stress is supported by the fibers [3], but would lead to a progressive collapse of the shear behavior [4]. However, to our opinion, these conclusions must be considered with caution, because they ignored totally the important values of weight losses (about 10%wt after 200 hours at 200°C) observed by these authors in the absence of oxygen [3, 4].

Preliminary studies made in our laboratory, on OMCCs elaborated by Nexans NRC, have shown that there is a first order effect of thermolysis on the OMCC mechanical behavior. Indeed, at 200°C , the quasi-linear decrease with exposure time of the flexural stress at break is almost independent of the oxygenation degree of the ageing atmosphere (nitrogen or air). The stress drops to about 50% of its initial value after only 2400 hours at 220°C . Starting from these observations, a non-empirical kinetic model for OMCCs lifetime prediction has been elaborated. This model is constituted of two elements:

- The chemical step describes the main features of the thermolysis kinetics of epoxy-anhydride matrices. It is derived from a realistic mechanistic scheme checked from a very powerful and sensitive analytical technique: high resolution mass spectrometry, of which the basic principle has been presented in a recent publication [5]. This step predicts the accumulation of organic molecules coming from thermolytic chain scissions and a condensation reaction and, when the concentration of these molecules exceeds their solubility threshold, the formation of micro-cavities of gas in the polymer matrix.
- The mechanical step predicts the consequences of the multiplication and connection of these micro-cavities on the OMCC flexural behavior. It is composed of a couple of structure/property relationships allowing to calculate the change (against time of exposure) of the flexural modulus and stress at break in function of a single and very simple damage criterion: porosity fraction X_p . These relationships have been established from a careful analysis of the damage development in OMCC and its consequences on the engineering flexural curves.

By interfacing both chemical and mechanical steps, it becomes possible to determine the time for OMCC embrittlement in given thermal ageing conditions.

The aim of the present communication is to give an overall view of this non-empirical kinetic model and to check the validity of its different constitutive elements from a relevant selection of experimental data.

2 Experimental

2.1 Materials

The OMCC under study is a rod of circular cross-section of 7 mm diameter processed by pultrusion. It is made of epoxy-anhydride matrix and unidirectional carbon fibers (Figure 1). Prior to thermal ageing exposures, the OMCC was characterized by conventional laboratory techniques. In particular, polished cross-sections were examined by optical microscopy. The volume fraction of fibers and porosity ratio were determined by thermogravimetry and image analysis (ImageJ software) respectively. Their respective values are about 72% and 0.7%. Moreover, the onset of the principal mechanical relaxation T_{α} (onset), often assimilated to the glass transition temperature T_g , was determined by viscoelasticimetry in a torsion mode (DMTA, Rheometrics RDA3 viscoanalyzer) using the conventional operative conditions (ramp temperature between 40 and 300°C, 5°C/min, 1 Hz) and graphical method described in standard ISO 11359-2. T_{α} (onset) is about 214°C.



Figure 1. Aluminum electrical wire stiffened by an OMCC developed by Nexans NRC.

Let us remember that, below 250°C, carbon fibers are stable. As a result, thermal ageing may only occur in organic components, i.e. in polymer matrix and fiber/matrix interface.

The determination of the thermal ageing mechanisms and kinetics of both components requires the realization of additional experiments (e.g. thermal ageings, exposures in chemical environments, physicochemical characterizations, etc.) at least on neat matrix samples. Of course, the study of simplified composite structures (e.g. two carbon fibers bonded together by a thin resin join) would be very useful, in particular to directly access to information on the fiber/matrix interface. But, in this case, it would be difficult (because of the low detection threshold of current chemical analytical techniques) to guarantee the correct reproducibility of the initial characteristics of the industrial OMCC. For this reason, neat epoxy-anhydride films and plates (of about 200 μm and 1 mm thick respectively) were processed by casting in a Teflon mold. They were cured in an air-circulating ventiled oven according to the temperature cycle recommended by Nexans NRC, in order to reach a crosslinking density relatively close to the OMCC matrix one. The validity of these processing conditions was checked from the determination of T_{α} (onset) by viscoelasticimetry (see above). T_{α} (onset) is about 217°C.

2.2 Ageing conditions and tests methods

OMCC sections of 700 mm length were subjected to isothermal exposures between 160 and 220°C for several hundred days in air-circulating ovens and were removed intermittently to be carefully examined by 3D- and 2D-imaging microscopic techniques.

A global view of the damage development in the OMCC volume was obtained by X-tomography (Nanotom Phoenix X-Ray tomograph). The snapshots were post-treated by the VG Studio MAX software before to be analyzed. They reveal the initial presence of microcavities of gases in the OMCC bulk at the end of the processing operation, and the multiplication and growth of these latter during thermal ageing.

A further examination of these microcavities was performed by optical microscopy (Leica DM 4000M microscope) after polishing of cross-sections. Porosity ratio was determined by image analysis (ImageJ software) after binarizing and thresholding micrographs.

OMCC residual mechanical properties were determined by 3-points bending tests with an INSTRON 5881 machine equipped by a 10 N load cell. The experiments were performed at 23°C in 50% RH with a speed fixed at 5mm/min. The load was applied with an indenter (of 10 mm radius) in the center of OMCC barrels of 100 mm length positioned on supports (of 4 mm radius) spaced of 80 mm. A peculiar attention was paid on the changes in the flexural modulus and stress at break versus exposure time.

In parallel, neat matrix samples were exposed in different ageing environments in order to better understand the thermal ageing mechanisms and kinetics of the OMCC matrix.

The effect of thermolysis was determined by high resolution mass spectrometry (HR-MS, Alyxan BTrap analyser) and thermogravimetry (TGA, TA Instruments Q500 Apparatus). In both cases, neat matrix films were subjected to isothermal exposures between 120 and 240°C under a nitrogen flow of 50 ml.min⁻¹ in the apparatus cavity, and the signal (concentration of main volatile compounds for HR-MS, weight changes for TGA) was recorded continuously versus exposure time for each temperature.

The transport properties of the main volatile compounds in the OMCC matrix were determined by sorption experiments. In the case of water, neat matrix films were exposed in various water vapors (ranging from 0 to 90% RH) between 30 and 60°C in a peculiar sorption oven (SMS apparatus) equipped by an ultrasensitive microbalance of Cahn with an electromagnetic compensation in order to access to weight changes up to 0.1 µg. The water uptake was recorded continuously versus exposure time for each temperature.

For other volatile compounds, neat matrix plates were directly immersed in pure solutions of volatile compounds at 120°C. But, in this case, the samples were intermittently removed from the solutions to be weighted manually.

3 Elaboration of the kinetic model

3.1 Mechanical step

Careful examinations of initial OMCCs by X-tomography and optical microscopy reveal the presence of microcavities at the end of the processing operation. The corresponding initial porosity ratio is about 0.7%. These microcavities are in the form of long microchannels parallel to the carbon fibers. Most of them are continuous along the entire OMCC length. Since the temperature cycle of OMCC processing finishes with a plateau of 10 minutes at 220°C, it is suspected that the matrix thermal ageing has started during the processing operation and thus, is responsible for this damage.

An example of micrographs of composite cross-sections obtained before and after 118 days in air at 200°C is presented in Figure 2.

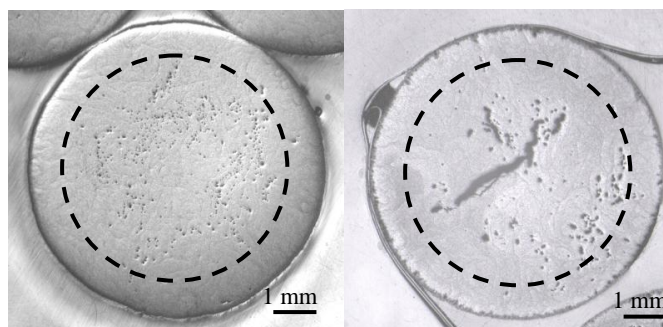


Figure 2. Micrographs of composites cross-sections before (left) and after 118 days in air at 200°C (right). Evidence of a nonporous superficial layer of about 1.1 mm thick.

It appears clearly that the number and size of microcavities increase with exposure time, especially in the matrix richest regions of the composite bulk (Figure 2, right). Since these regions are located far from the composite surface, they are inaccessible to atmospheric oxygen. It can be thus concluded that these microcavities may only result from matrix thermolysis. It is possible to define a nonporous superficial layer ℓ_{np} of about 1.1 mm thick. When they are sufficiently close to each other, microcavities coalesce to form apparent large cracks (Figure 2, right). A magnification of these cracks confirms that they are in fact formed of microcavities juxtaposed against each other, like a pearl necklace (Figure 3).

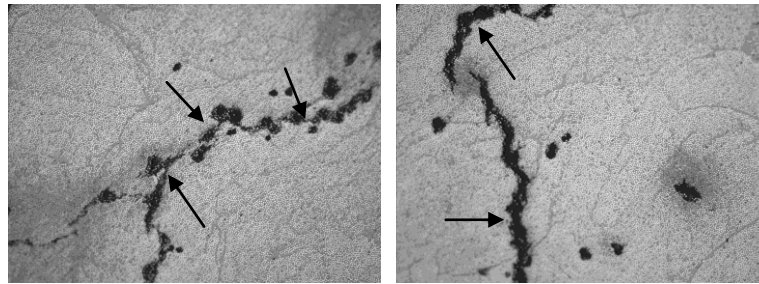


Figure 3. Magnification ($\times 100$) of some apparent large cracks formed in the transverse direction of fibers after 20 days in air at 200°C . Evidence of microcavities coalescence (left) and formation of thin microcracks connecting neighboring microcavities (right).

Engineering flexural curves obtained before and after OMCC thermal ageing in air between 160 and 220°C shown clearly that thermolysis leads to a decrease both of elastic and fracture properties with exposure time. Values of flexural modulus E and stress at break σ_R have been plotted versus porosity ratio X_p in Figure 4.

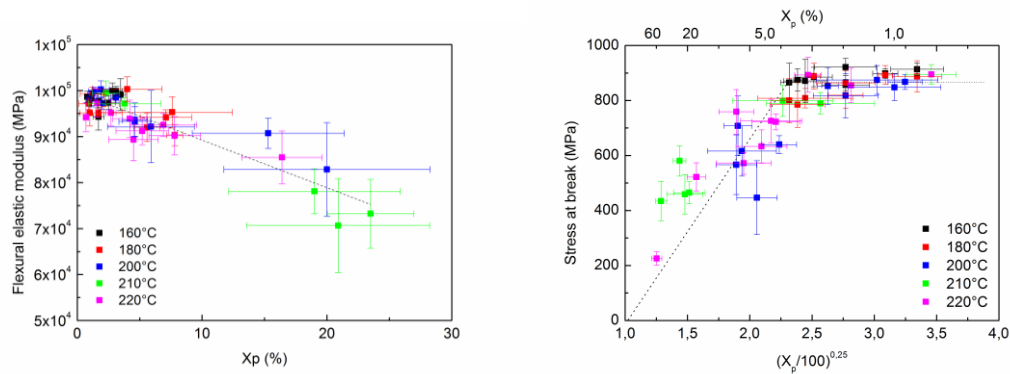


Figure 4. Flexural modulus versus porosity fraction (left) and stress at break versus quadratic root of porosity ratio (right) for OMCCs aged in air between 160 and 220°C .

It can be seen that, in both cases, all experimental points are placed around a single master curve independent of thermal ageing conditions. E is a decreasing function of X_p (Figure 4, left). It can be thus written:

$$E = E_0(1 - X_p) \quad (1)$$

where E_0 is the flexural modulus of the virgin OMCC, i.e. free of any microcavities. The value of E_0 can be determined graphically by intersecting the straight-line of Equ. 1 with the y-axis. One finds: $E_0 = 99.6$ GPa.

In contrast, as X_p remains lower than a critical value $X_{pC} \approx 3.6\%$, the composite is slightly damaged. Its fracture behavior is not affected by thermolysis and its stress at break remains almost constant:

$$\sigma_R = \sigma_{R0} = 867 \pm 26 \text{ MPa} \quad (2)$$

But, when $X_p > X_{pC}$, σ_R is a linear function of $X_p^{-1/4}$ as predicted by the fracture mechanics theory [6]. A relatively simple equation can be proposed:

$$\sigma_R = \sigma_{R0} \frac{X_p^{-1/4} - 1}{X_{pC}^{-1/4} - 1} \quad (3)$$

3.2 Chemical step

Thermolysis of epoxy-anhydride matrices would consist, at least, in two elementary reactions:
 - It is well known that ester groups are very unstable at high temperature (typically, for $T > 200^\circ\text{C}$). Indeed, in linear polyesters, they rearrange according to a 6-membered reaction and thus, lead to the formation of carboxylic acid and vinyl end-chains [1]. There is no reason that this reaction does not occur in epoxy-anhydride matrices. In this case, it may also lead to the formation of diacid fragments which can rapidly condense into cyclic anhydrides and thus, liberate water (Figure 5).

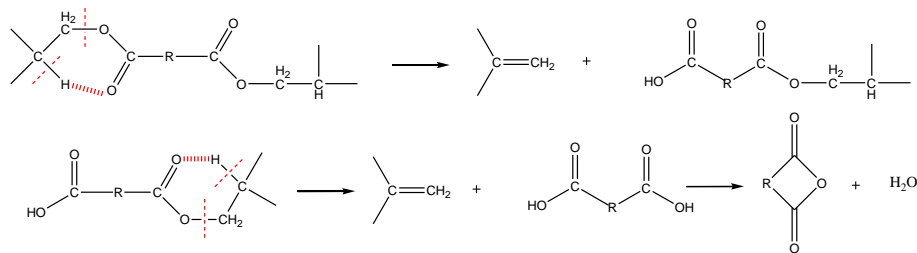


Figure 5. Cleavage of ester groups in epoxy-anhydride matrices. R represents the hydrocarbon segment of the anhydride monomer.

- Then, pairs of carboxylic acid end-groups can, in turn, condense into anhydride linkages and thus, liberate water (Figure 6) [2].

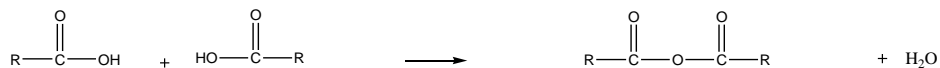


Figure 6. Condensation of carboxylic acid end-groups in epoxy-anhydride matrices.

Finally, the thermolysis mechanism can be summarized as follows:



where Es, An, Ac and F designate respectively ester and anhydride linkages, and carboxylic acid and vinyl end-groups. V designates cyclic anhydrides formed with a yield ν .

The existence of both reactions was successfully checked by high resolution mass spectrometry. Indeed, two volatile compounds: cyclic anhydrides and water, responsible for significant weight losses, were clearly detected at 220 and 240°C in nitrogen.

At this stage, the question which comes to mind is: Which compound is responsible for cavitation? A partial answer to this question may be given by comparing the solubility parameters of these compounds with the solubility parameter of the epoxy-anhydride network under study. These parameters have been estimated using the method proposed by Small [6]:

$$\delta = \left(\frac{E_{\text{coh}}}{V} \right)^{1/2} = \frac{F}{V} \quad (4)$$

where E_{coh} , F and V are respectively the cohesive energy, molar attraction constant and molar volume of the organic substance under consideration. According to Small, F and V would obey an additive law:

$$F = \sum F_i \quad \text{and} \quad V = \sum V_i \quad (5)$$

where F_i and V_i are contributions of structural groups to F and V respectively. Their values at 25°C have been reported, for instance, by Van Krevelen [7] and Fedors [8]. The numerical application of Eqs 4 and 5 leads to the values of solubility parameters reported in Table 1.

Organic substance	F (J ^{1/2} .cm ^{3/2} .mol ⁻¹)	V (cm ³ .mol ⁻¹)	δ (MPa ^{1/2})
Epoxy-anhydride	12 965	570.1	22.7
Cyclic anhydride	1 305	57	22.9
Water	864	18	48

Table 1. Values of solubility parameters of organic compounds and epoxy-anhydride network under study.

It appears that cyclic anhydrides are highly soluble in the epoxy-anhydride matrix since their solubility parameters are very close. On the contrary, water is considerably less soluble. It is thus expected that its equilibrium concentration is relatively low in this polymer matrix. The validity of this assumption was successfully checked from sorption experiments (Figure 7).

The kinetic curves of water weight uptake obtained in 90% RH between 30 and 60°C are reported in Figure 7 (right). These curves call for the following comments:

- The sorption kinetics obeys the second Fick's law. The coefficient of water diffusion (calculated from the initial slope of the curves) obeys an Arrhenius law:

$$D_w = 3.1 \times 10^{-7} \exp(-33500/RT) \quad (\text{m}^2.\text{s}^{-1}) \quad (6)$$

- The equilibrium water concentration (calculated from the final plateau of curves) obeys the Henry's law:

$$C_\infty = S_w \left(\frac{\text{RH}}{100} \right) p_s \quad (7)$$

where S_w is the coefficient of water solubility and p_s is the saturated vapor pressure of water. Since they both obey an Arrhenius law:

$$p_s = 10^{11} \exp(-42000/RT) \quad (\text{Pa}) \quad (8)$$

$$S_w = 8.8 \times 10^{-12} \exp(+43900/RT) \quad (\text{mol.l}^{-1}.\text{Pa}^{-1}) \quad (9)$$

it comes finally:
$$C_{\infty} = 8.1 \times 10^{-1} \left(\frac{RH}{100} \right) \exp(+1900/RT) \quad (\text{mol.l}^{-1}) \quad (10)$$

- The equilibrium weight uptake and water concentration are almost temperature independent: $(\Delta m/m)_{\infty} = 2.3 \pm 0.2 \%$ and $C_{\infty} = 1.6 \pm 0.1 \text{ mol.l}^{-1}$. This is general behavior of moderately polar polymers. It results from the fact that, in these polymers, the water-polymer interactions (through hydrogen bonds) are highly exothermic. Indeed, here, the heat of water dissolution is negative ($\approx -43.9 \text{ kJ.mol}^{-1}$) and its absolute value is close to the heat of water vaporization ($\approx 42 \text{ kJ.mol}^{-1}$). Thus, the activation energy of equilibrium quantities, which is the sum of both contributions, is close to zero ($\approx 1.9 \text{ kJ.mol}^{-1}$).

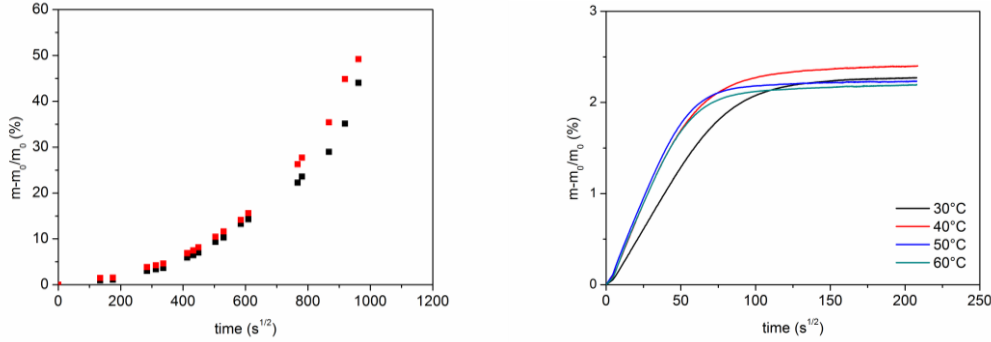


Figure 7. Mass uptake of neat matrix films of about 200 μm thickness in various chemical environments. Left: In a pure cyclic anhydride solution at 120°C. Right: In 90% RH at 30, 40, 50 and 60°C.

Therefore, it was considered that water is the main compound responsible for cavitation. The local water concentration C in the epoxy-anhydride matrix can be calculated from a balance equation expressing that one part of the water, generated at position r by thermolysis, can diffuse in the composite radial direction:

$$\frac{dC}{dt} = r(C) + D_w \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \quad (11)$$

$$\text{with } r(C) = \nu k_1 [Es] + k_2 [Ac]^2 \quad (12)$$

It is expected that cavitation occurs at time $t = t_c$ when $C = C_{\infty}$. Indeed, above the solubility threshold of water in the polymer matrix, it is expected that a phase separation occurs in the water/polymer mixture, leading to the formation of microcavities of gas. At low conversions, the thermolysis follows a zero-order kinetics and $r(C)$ can be approximated by an apparent rate constant K (expressed in $\text{l.mol}^{-1}.\text{s}^{-1}$), so that:

$$t_c = \frac{C_{\infty}}{K} \quad (14)$$

However, the characteristic time for water diffusion is an increasing function of the distance ℓ traveled in the composite radial direction:

$$t_D = \frac{\ell^2}{D_w} \quad (15)$$

Thus, two distinct OMCC regions can be defined:

- Far from the composite surface, $t_D \gg t_C$. Water accumulates rapidly and leads to cavitation.
- In contrast, near the composite surface, $t_D \ll t_C$. Water migrates quasi-instantaneously up to surface where it evaporates.

It is thus possible to calculate a thickness of nonporous superficial layer ℓ_{np} by making equality between both characteristic times: i.e. $\ell = \ell_{np}$ when $t_C = t_D$:

$$\ell_{np} = \left(\frac{D \times C_{\infty}}{K} \right)^{\frac{1}{2}} \quad (16)$$

Finally, porosity ratio corresponds to the gas volume trapped into microcavities when $t > t_C$:

$$X_p = (C - C_{\infty}) \times V_w \quad (17)$$

where V_w is the molar volume of water.

4 Conclusion

A kinetic model has been elaborated for predicting the thermal ageing kinetics and its consequences on elastic and fracture properties of OMCCs between 160 and 220°C. It is constituted of a system of five differential equations derived from a realistic thermolysis mechanism of epoxy-anhydride matrices, including a balance equation for water (Equ. 11), and interfaced with a couple of structure/property relationships (Equs 1-3). This model gives access to the increase in porosity ratio in the composite bulk, responsible for a progressive decrease of the flexural modulus and, when the porosity ratio reaches a critical value of about 3.6%, for a dramatic collapse of the stress at break.

The validation of this kinetic model is now in progress at the laboratory. Attention is focused on three important validation criteria, easily checkable experimentally both on neat matrix and composite samples: weight losses of thin (without any microcavities) and thick samples (with microcavities), global porosity ratio and thickness of nonporous superficial layer.

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