ANALYSIS OF MANUFACTURING PROBLEMS RELATED WITH METAL-METAL AEROSPACE STRUCTURAL JOINTS THROUGH ACOUSTIC EMISSION AND DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Problems experienced during cure cycle of epoxy adhesives in film form concern especially false bonding due to extraneous substances (e.g., protective Teflon layer) or to an incorrect or too long storage of the adhesive.

In addition to these problems, a sudden blackout or a not planar application of the pressure can hinder the performance of a complete polymerisation cycle. Thus, after having collected some information on the most frequent events that reduce joints quality in aerospace industry, all those cases were approximately reproduced in laboratory with a hot-plates press and materials really used in practice (2024 T3 aluminium alloy treated with chromic acid anodization). Acoustic emission monitoring followed the whole period of cure cycle, indicating in real time occurrence of adhesion and/or polymerisation phenomena. A wide database was so created with all the cases of concrete industrial interest, so to allow a statistical evaluation of AE data, leading to a reliable quality evaluation.

Results obtained by acoustic emission were confirmed submitting adhesive specimens to a DSC (Differential Scanning Calorimetry) analysis so to measure the degree of polymerisation and finally with shear tensile tests.

INTRODUCTION

NDE on adhesive joints means to connect outputs from in-production monitoring, aiming to localisation of voids and non-bonded zones, and durability investigations, able to determine the service life of the structure (1).

Some ultrasonic techniques have a strong capability to reveal disbonds and voids in the joints after their production. It is still difficult however to determine their cohesive strength or ageing. The discernment of well-bonded areas from areas presenting different thickness or imperfect adhesion due to a somewhat polluted adhesive is furthermore possible. In this field acousto-ultrasonic technique can play a relevant role too and was successfully associated with pattern recognition (2).

All the usual techniques applied in aircraft industries (ultrasonics, low frequency vibrations, thermography) have though some difficulties in characterising all areas of poor wetting (3, 4). In many cases durability data are thus not provided by a continuous monitoring of joint structures, but rather by ageing model structures.

Mechanical tests (shear lap stress, fatigue tests) on an adhesive joint cannot provide of course information on stresses, due to environmental and effective conditions, that have however some influence on its durability and efficiency.

An alternative way can be so to forecast joint quality from the behaviour during joint preparation of the materials involved. The cure cycle can be simulated in laboratory, producing then some variations on its temperature, time, presence of defects in the joint, unsuitable surface treatment and whatever can influence joint quality (5,6). The problem is to find a NDT technique able to monitor in real time any difference between the standard cycle and modified procedure joints and to correlate these variations with final quality of adhesive structure.

The meaning to monitor an out-of-standards cure cycle can be also to ponder whether and in what sense the real industrial cycle could be modified, totally preserving the safety of structure together with a relevant reduction of costs.

In the past acoustic emission has been successfully used to monitor a cure cycle of polymers, in support with electrical methods (e.g., potential drop measurements). Available results (e.g., from (7)) confirm that a relation between phenomena occurring during cure and AE features can be found, although this has not lead up to now to statistical models. Of course AE data interpretation requires a continuous physical feedback so to supply a believable picture of the behaviour all the critical parts involved in the conception of the final structure.

Some experiences (8,9) have convinced us of the opportunity and the feasibility to relate AE signals detected during the polymerisation cycle with the occurring phenomena. These experimentations lead us to the concept that AE monitoring is able to discern the three phases of cure cycle with their respective prevalent physical phenomena. The possible links of AE data with C-Scan image analysis had also been revealed (10) in particular about the incorrect or insufficient application of pressure on the joint that can generate finally local disbonds.

DSC outputs (11,12) add to our data a quantitative measure of enthalpy exchanges due to polymerisation process. They can so be useful to evaluate the effects on the adhesive of applying non-standard cure cycles.

EXPERIMENTAL

This work has been carried out, proceeding to the same type of evaluation (in-process monitoring of acoustic emission + calorimetry) both from JRC-ISIS and from CIRA and UdN laboratories together.

The joints were produced with 2024T3 aluminium alloy single overlapping on a surface of 25.4 x 12.7 mm according to ASTM D1002 standard. The surfaces were prepared with CAA (chromic acid anodization) and primer, and the adhesive was a modified epoxy (AF163-2K by 3M). Standard cycle guidelines, supplied by Italian aircraft industries, are reported here below.

Pressure = 0.25 (±0,035) MPa
Medium heating rate: 2-3°C/min
Phases: 1. Heating from 49 to 117°C
2. 90 minutes-holding at 117 (±3°C)°C
3. Natural cooling from 117 to 66°C

The results obtained by each laboratory are presented separately through this paper. This aims especially to show whether and in what measure previous research experiences in this field can affect the interpretation of acoustic emission data.

Finally, a discussion is reported to try to lead to a common red wire the whole experimentation.

JRC Ispra

Calorimetry

A Perkin Elmer's DSC7 differential calorimetry was used to test 50 µl adhesive samples.

Two types of tests were carried out:
a. isothermal: 5 minutes at 49°C, then heating with a 2°C/min rate (Scan Rate) and again constant temperature, finally automatic return at 49°C.
b.scanning: heating of adhesive from 40 up to 250°C with a 10°C/min rate (Scanning Rate), then automatic return at 40°C.

In detail, beyond to system calibration, the following tests were performed:
Scan on uncured adhesive (test A)
Ideal isotherm:90 min at 117°ΣC (B)
Low T isotherm: 90min at 83°ΣC(C)
Short isotherm: 10 min. at 117°C (D)
A scanning has followed each of the four tests (tests AS,BS,CS, DS).

Scan on uncured adhesive (test A; fig.1) was carried out so to conceive a first idea about the polymerisation. This curve presents a negative peak signal of exothermic reaction (polymerisation) starting at 127°C and completed at 207°C (max. activity at 150,33 ° C). Let's observe then the scanning effected after the performance of ideal isotherm at 117°C (test BS; fig.2). This curve presents still a weak negative peak, indicating that at the end of ideal cycle the polymerisation was not yet completed. We pass then to consider how polymerisation is modified during the modified cycles. After 90 minutes at 83°C the very slow polymerisation showed by the decreasing behaviour of the calorimetry curve (fig.3; test C) is very far from its conclusion; the same indication was given by test D (10 min. at 117°C).

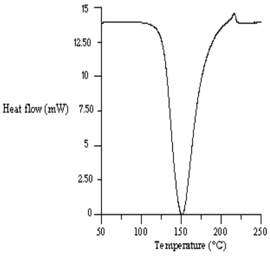

fig.1

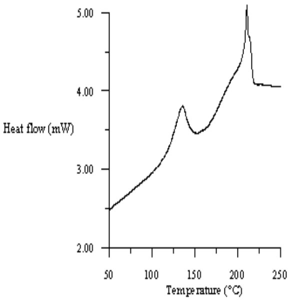

fig.2

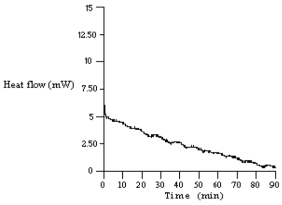

fig.3

Released thermal energy is however greater for the 83°C x 90 minutes cycle than for the 117°C x 10 minutes (see Table 1): this means that in this last case the polymerisation has proceeded further than for the other cycle.

Table 1

Action	Enthalpy (J/g)	Polymerisation
No cure	181,50	Absent
90 min at 83°C	142,18	Very low
10 min at 117°C	54,69	Low
90 min at 117°C	1	High

Our considerations can be then centred on two facts:

1.The ideal cure cycle does not lead to a complete polymerisation of the adhesive. This may signify that, in order to have a good adhesion, the effect of the pressure and of the cooling down period plays surely a critical role.

2.The two alternative cure cycles proposed lead effectively to a scarce quality polymerisation.

ACOUSTIC EMISSION

A LOCAN-AT apparatus was used with a threshold of 28 dB, so to acquire a very high sensibility and a total gain of 60 = (40+20) dB.

Definition times of the signal were PDT=20 µs, HDT=500 µs and HLT= 300 µs, obtained after calibration and verification with an oscilloscope.

The two sensors were placed at both sides of the joint with a distance between them of 161 mm.

AE hits with less than 5 counts and less than 2 energy units were excluded as well, because they are strongly affected by electrical and environmental noise.

Five series of processes have been monitored, leading respectively to:

- correctly produced joints (AA)
- joints with a defect of 5x5 mm in the centre of the bonded area (CA)
- joints with the same defect at the boundaries of the bonded area(CB)

- joints produced with lamina not treated with CAA (chromic acid anodization) (BB)
- joints produced with a holding temperature lowered at 90°C (DA)

So to schematise and simplify the description of our situation, phenomena that can generate acoustic emission throughout the production of such joints can be:

- contractions and dilatations of aluminium lamina, compared also with the different dilatation of the press plates
- pressure effect (gas bubbles, voids closure in the adhesive, air trapping and liberation)
- change in viscosity of the adhesive due to the creation of crosslinking through the adhesive
- shrinkage of adhesive on aluminium lamina, beginning when percentage of adhered joint becomes significant

What we observed was that for all the joints the most of AE was detected during the heating, very few AE instead during the holding period and especially from 0 to 10 min. and from 80 to 90 min. of the II phase of the cycle. Some AE was detected again all along the cooling down period, except for DA (90°C holding) specimens. In this case the absence of any important AE phenomenon during cooling down indicates really, as then confirmed by tensile tests, the little shrinkage due to weak adhesion.
Nevertheless, about 80 % of AE activity revealed by all the samples during the heating period has probably to be ascribed to the heat transmission effects between press, weight and aluminium lamina and to some initial pressure effects. In addition to that, the activity during the "core" of the holding phase (10 to 80 minutes) is very scarce and does not present any particular trend.

So, our attention was attracted by the last part of the test, from about 80 min. during temperature holding up to the end of the test. Here, though some bursts to be related to the metal are still present, the effect of polymer shrinkage consequent to adhesion is clearly discernible.
After some discussion, the type of events to be attributed to adhesive shrinkage seem to present the following "finger-tip" profile:

- Discontinuous events and not great bursts (rather related with the contractions and dilatations of metals)
- Avg. frequency[1]: 50-300 kHz, thus around the natural peak frequency of sensors, so to minimise the insurgence of reflections (high avg. frequencies) or of multiple events in a large time domain (low avg. frequencies). A somehow complex AE event is not justified for a shrinkage.
- Duration: 50-300 µs so to have single events, but far from the risk of detecting short bursts due to electrical disturbs.
- Amplitude not exceeding one order of magnitude above the threshold, i.e. about 50 dB.

The period when we found most of these "shrinkage signals" was in particular during cooling down from 100°C up to 66°C with significant events somewhere at the very last minutes of temperature holding.
Ideal specimens (AA) are characterised by the presence and the quite constant number of these events (about ten per test in the indicated period), some of which are characteristically present always when lowering the temperature below 80°C.
Joints with defects (CA and CB), independently from their position, not always show these events, in some cases present them in very little number and only in the last minutes. This needs however further investigations, because AE does not seem able to discern the position of the defect neither to provide a sufficient discrimination.
The absence of the protective oxide layer on aluminium creates instead in BB specimens a wide amount of these shrinkage effects, that seem to be due to the penetration of the adhesive through the discontinuities of the surface, so to produce a false and inefficient bonding.

Finally, the most believable indication of adhesive quality seem to be ascribed to the

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[1] In LOCAN-AT (but also in some other instruments!) this is: (counts/duration)*1000

detection of a constant number of these shrinkage events for all the specimens of a series.

Table 2 resumes some results for each series of 5 specimens, regarding only the events considered as shrinkage effects (see above criteria) and observed than from the 80° minute of temperature holding and the end of the test. We can observe the little number of critical events on DA specimens and their considerably inferior avg.number of counts.

	Hits	Avg.Counts	Avg.Energy
AA	37	18.16	11.24
CA	19	15.63	8.79
CB	24	17.92	11.63
BB	41	17.17	10.05
DA	10	11.60	7.90

Some tensile tests were carried out both on joints produced with the ideal cycle (AA) and on that produced with 90°C holding (DA).

The results confirmed the great difference of quality between these two series of samples: AA joints showed in fact an average ultimate stress of 35.1 MPa; their failure is of cohesive type and comes when the adhesive breaks.

DA joints came to failure instead simply by serrating test machine grips on the specimen, due to the unavoidable little bending stress to be applied (the joint area has a thickness more than twice the thickness of the remaining part of the specimen). So, no measurement was possible, but such a resistance cannot be satisfying.

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Calorimetry

Setup

This laboratory used a METTLER DSC30 apparatus, with liquid azote cooling.

Adhesive weight tested was each time 10 mg. Four isothermal tests at 110,115,120 and 130°C and a scanning from 20 to 250°C (rate=10°C/min) (fig.4) were carried out.

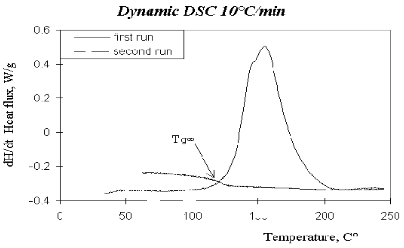

fig.4

Experimental procedure

Assuming that the heat evolved during the polymerisation reactions is proportional to the extent of reaction α, it is possible to characterise the reaction rate (dα/dt) directly from DSC thermogram by measuring heat generation rate (dH/dt).

Thus $(d\alpha/dt)=(1/H_t)(dH/dt)$, where H_t is the total heat developed during polymerisation. The total amount of heat has been calculated by using dynamic DSC tests. Fig.4 shows dynamic tests performed on adhesive specimen. Cure reactions ends at about 220 ° C. The integration of exothermic peak gives H_t=175.6 J/g, this value was averaged over three different tests. Second run has been performed on totally cured adhesive: inflection in the heat flow signal corresponds to the glassy transition temperature $T_{g\infty}\approx120°$ C.

Passing to the isothermal tests, thermograms, reporting the heat flux as a function of time, have been worked out to obtain the degree of conversion as a function of time at constant temperature (fig.5). The total reaction heat calculated by integration of the isothermal thermograms is significantly lower than that obtained in dynamic tests, since during low temperature isothermal tests polymerisation is not completed and the final value α_{max} is an increasing function of the test temperature.

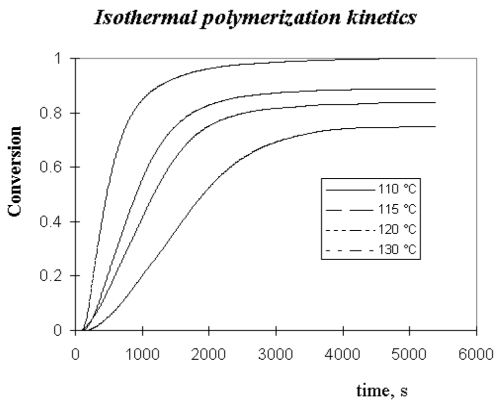

fig.5

Incomplete reaction has to be attributed to the loss of mobility of the reacting molecules within the developing network (13). The fitting in the range of temperatures on study gave: $\alpha_{max}(T) = \alpha_0 + \beta T$ where α_0=-3.88 and β=0.01213 [K^{-1}]. Here below the experimental data are reported (Tab.2).

Table 2

Temperature, K	α_{max}
383	0.75
388	0.84
393	0.89
403	1.00

Kinetic model

Kinetic behaviour of epoxy system has been extensively studied and several kinetic models are available(14). Experimental data relative to isothermal tests were used to fit the kinetic model {1}:

$$[(d\alpha/dt)(T,\alpha)]=K_0 \exp(-E/RT)\alpha^m(\alpha_{max}(T)-\alpha)^n$$

Parameters have been verified by comparison with the dynamic DSC data, these data were not used to fit the kinetic model. Fig.6 aims to compare experimental data calculated from DSC dynamic thermogram, where:

$$T(t) = 20[^\circ C] + 10\left[{}^\circ C/_{min}\right] t$$

and the model results obtained by numerical integration of {1}.

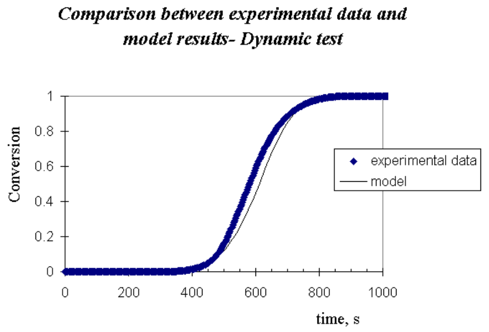

fig.6

The model has been used to evaluate the curing reaction during the standard temperature cycle in the joint production. Fig.7 shows the model predictions in terms of degree of conversion as a function of the processing time, the processing temperature has been also reported. The dwell temperature 120°C does not allow the total curing of adhesive, the maximum degree of conversion compatible with the temperature cycle is 0.89. Model predicts the end of curing after about 90 mins.

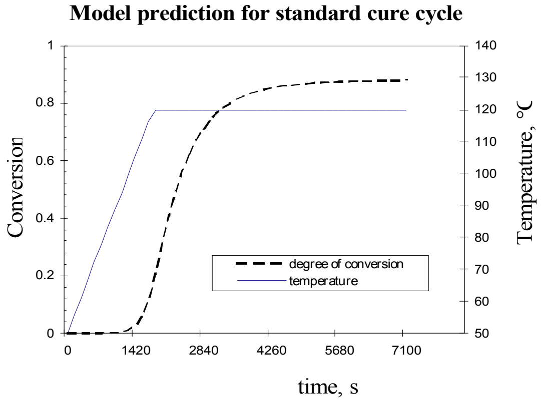

Fig.7

Table 3
Parameters of kinetic model.

K_0 [1/s]	E/R[K]	m	n
2 10^7	9020	0.37	1.18

Acoustic emission

The acoustic emission was acquired by CIRA with a LOCAN 320 apparatus by PAC .Its gain was 80=(40+40) dB, and the threshold was set at 40 dB. PDT was 300 μs, HDT was 600 μs and HLT was 900 μs. Events with a number of counts<6 and with energy <2 units were locked out using a front end filter.

The tests that we consider here are the following:

1.Ideal cycle
2.¼ surface covered by Teflon
3.½ surface covered by Teflon
4.¾ surface covered by Teflon
5.Whole surface covered by Teflon

Here is reported (fig.8) the ideal cure cycle diagram plotted by AE system itself.

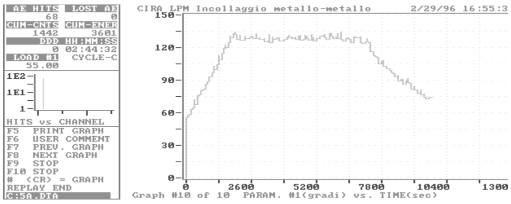

fig.8

In fig.9 we can observe the behaviour of cum.counts vs. time curves. Here the three phases are evident and we can easily observe that the most vivacious phase is the cooling down, with an increasing activity at the end part of the test.

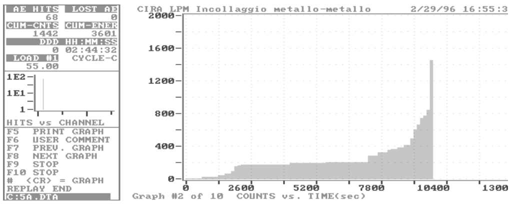

fig.9

Progressively increasing the surface covered by Teflon, that gives so a false adhesion, we can note that also a clear distinction among the three phases is lost (fig.10, referred to a 75 % Teflon covered surface) although the cycle is aprreciably the same than for the ideal case (fig.11).

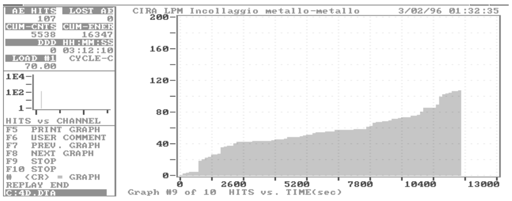

fig.10

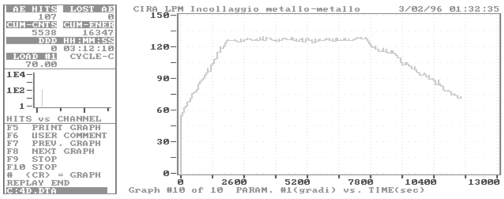

fig.11

To quantify better this reduction of importance of cooling down (when shrinkage effects are detected) with the gradual reduction of adhered surface, we produced then another tool of analysis from a statistical point of view.

“Tie” analysis

We called tie the period of cooling down of our joints, when adhesion has to be produced effectively.
The events during the “tie” (Table 4) represent the most of AE phenomena in ideal and 25% covered surfaces. Instead they are not so concentrated in the other cases, when increasing Teflon covering.
So acoustic emission seems to be very sensible to shrinkage effects and potentially to the presence of defects, simulated by Teflon interposition.

Table 4

TEST TYPE	Tie events/ Total events
A(ideal)	0.61
B(teflon 25%)	0.58
C(teflon 50%)	0.20
D(teflon 75%)	0.25

DISCUSSION & CONCLUSIONS

AE technique has a particular sensibility to the correct adhesion, efficaciously integrating information provided by mechanical testing. Shrinkage effects are always revealed and their different emphasys from test to test due to the particular conditions of performance and to the presence of some disbonding is strongly promising for an use of this technique with statistical goals, with the aim to produce an automatic screening of AE outputs, leading immediately to the identification of joint quality.

The close correlation with calorimetric results has furthermore supplied the conscience of the importance to apply a suitable bonding technology to pass from the completion of the polymerisation to the real adhesion process. Calorimetry has reported our analysis close to real microscopic processes, to provide the knowledge of phenomena whose experimental effects are studied analysing AE data so to reduce the worrying incertitude about “what we are really hearing”.

Much has to be done however to automatise this NDT process and to apply it also on the real process. From bare technical problems, such as the indisponibility of expressly tailored high temperature sensors, to other more industial questions, such as the “scaling effect” have in fact to be considered.

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