EUROPEAN MECHANICS SOCIETY
COLLOQUIUM 607
MARINE AGING OF POLYMERS
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AGEING OF EPOXIES BONDED ASSEMBLIES

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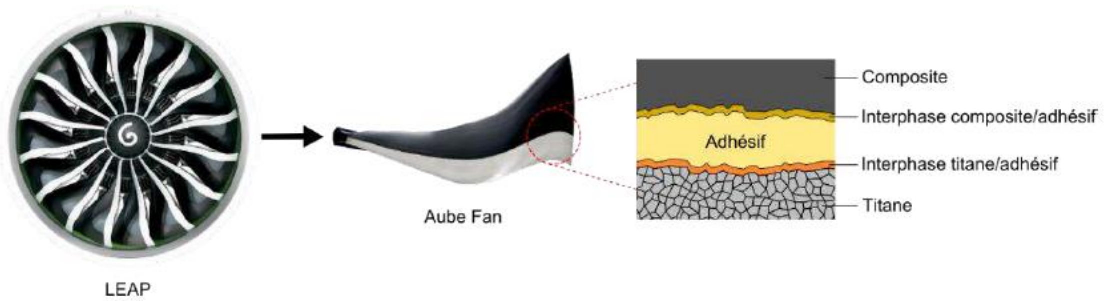
INTEREST OF BONDED ASSEMBLIES IN AERONAUTICS

- CleanSky program

  - 90% NOx (compared to 2000).
  - 50% CO_2/customer/km in 2020, then -75% in 2050

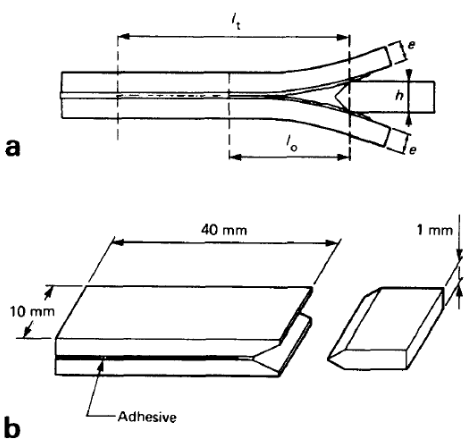
  LEAP engine / FAN blades

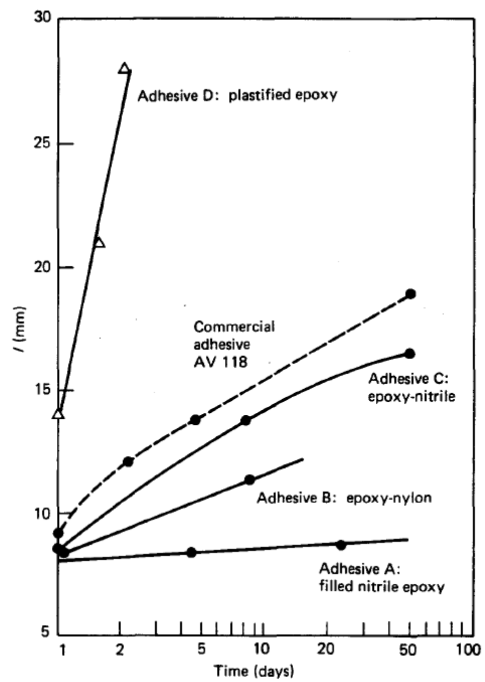


Lifetime of epoxy adhesives submitted to humid and thermal ageing

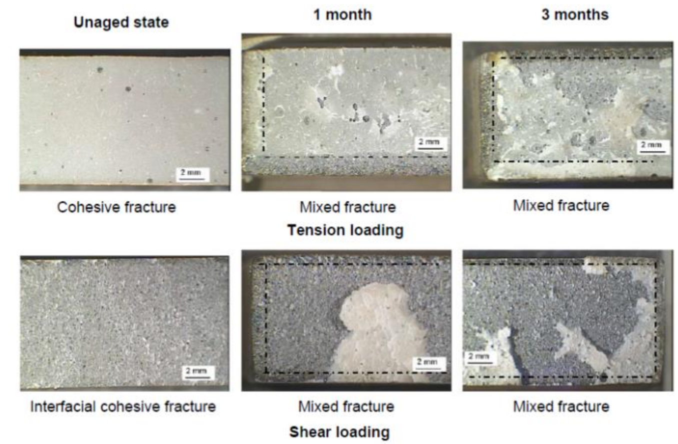
INTRODUCTION - STATE OF THE ART

- Some limits of accelerated tests for lifetime prediction





Crack propagation in bonded assemblies submitted to ageing at 40°C - 90%HR



Bonded assembly steel/epoxy/steel before and after ageing

R. Leger et al. International Journal of Adhesion and Adhesives 44(2013), 66-77.
J. Cognard. International Journal of Adhesion and Adhesives 6(4), 1986, 215-220.
M. Bordes et al. International Journal of Adhesion and Adhesives 29(6), 2009, 595-608.

AIMS OF THE STUDY

- Some grey zones

  Case of thermal oxidation

  Physico-chemical interpretation of failure

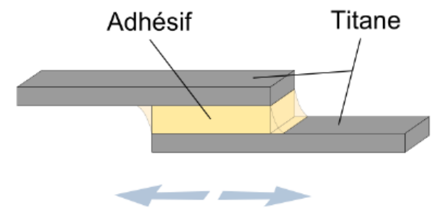
  Representativeness of accelerated ageing tests (nature of the mechanims)

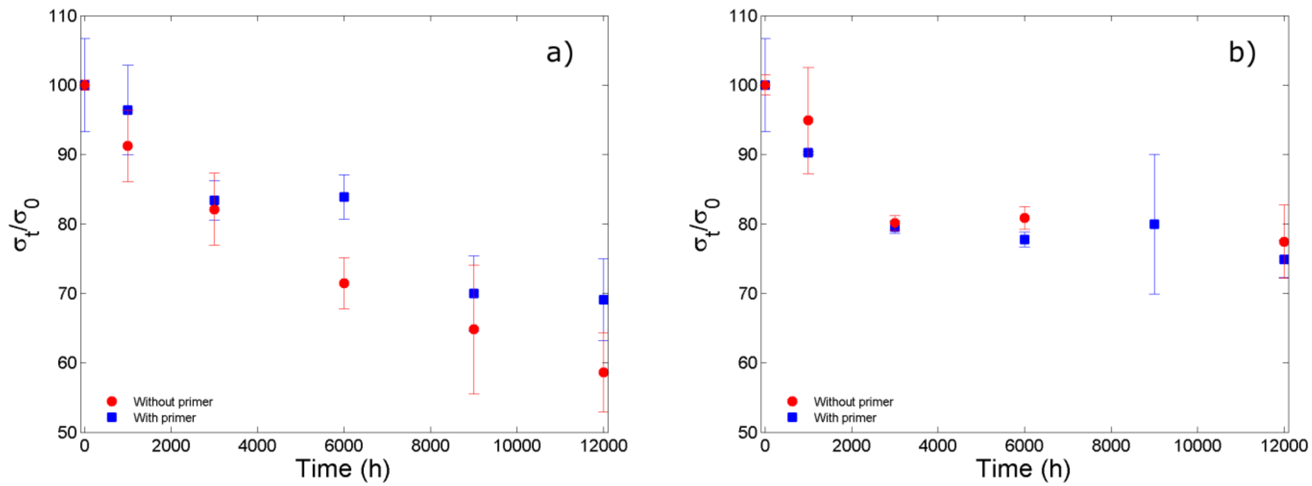
- Comparison of thermal (120°C) and humid (70°C – 85%HR) ageing of titanium / epoxy / titanium bonded assemblies
- Discussion with relevant physico-chemical parameters expressing the epoxy stability towards humid and thermal ageing

AGEING OF BONDED ASSEMBLIES (THERMAL VS HUMID)

MECHANICAL FAILURE OF BONDED ASSEMBLIES

- Comparison of thermal and humid ageing





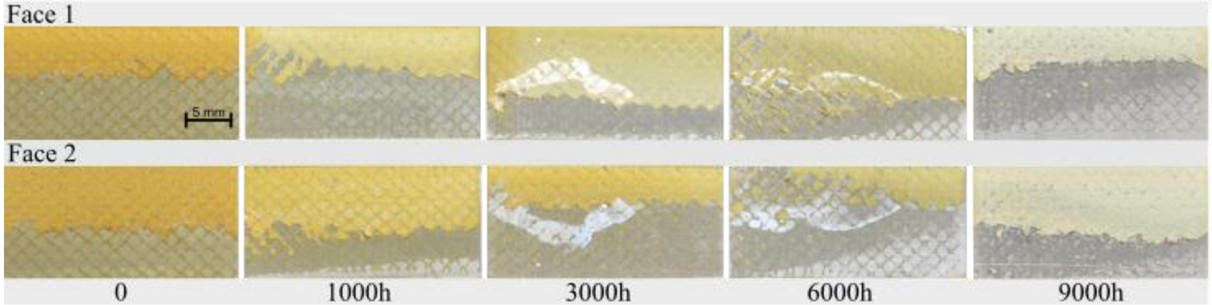
70°C-85% HR | **thermal ageing (120°C)**

-30% during the first 6000 h
-15% between 6000-12000 h

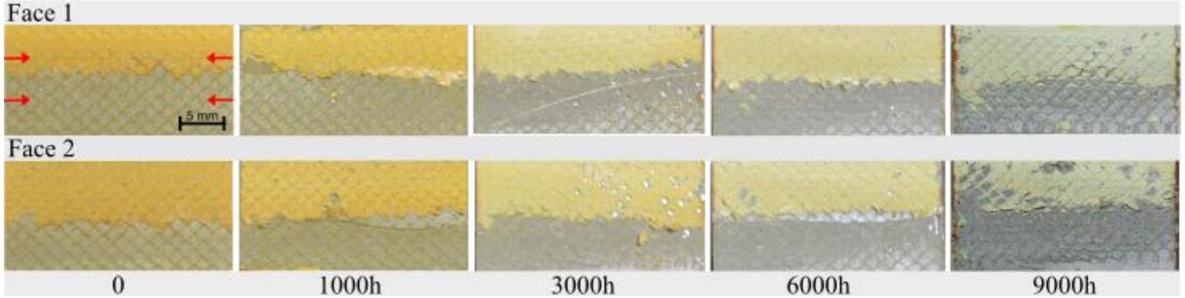
A plateau

MECHANICAL FAILURE OF BONDED ASSEMBLIES

- Nature of failure process



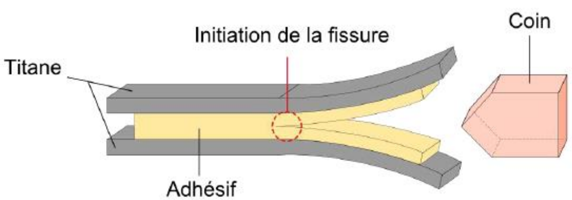
Humid ageing → Becomes adhesive (~ 40%)



Thermal ageing → cohesive

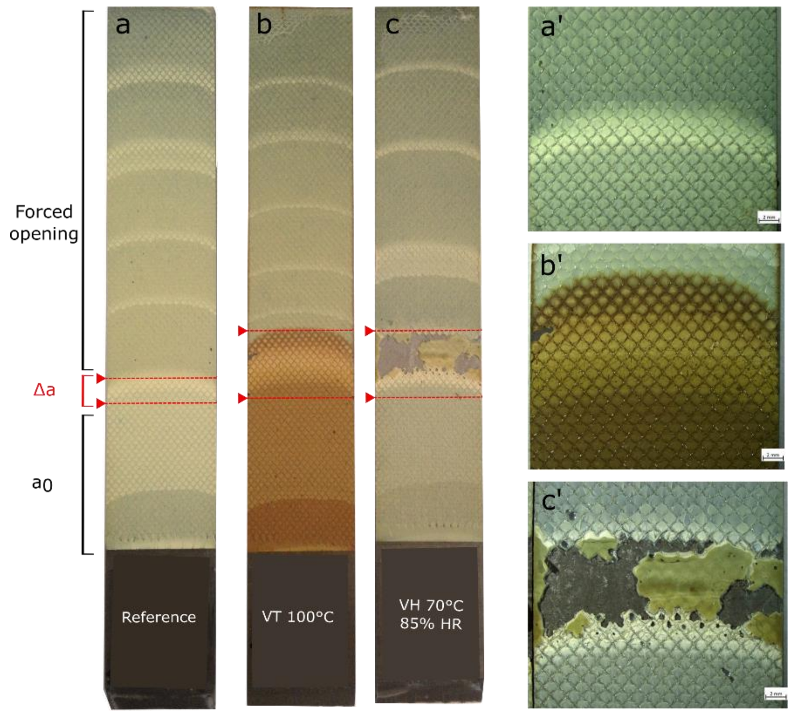
MECHANICAL FAILURE OF BONDED ASSEMBLIES

- A wedge test study



crack position at t_0 and at the end before the forced opening.

3700 h of ageing



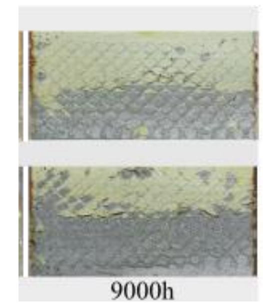
zoom of the damaged areas (Δa).

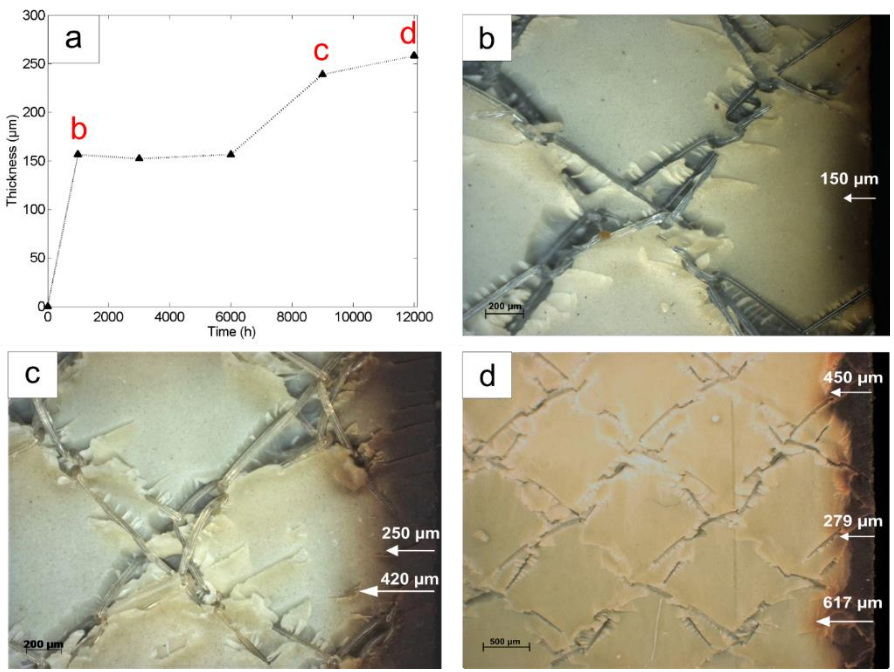
Thermal ageing → cohesive

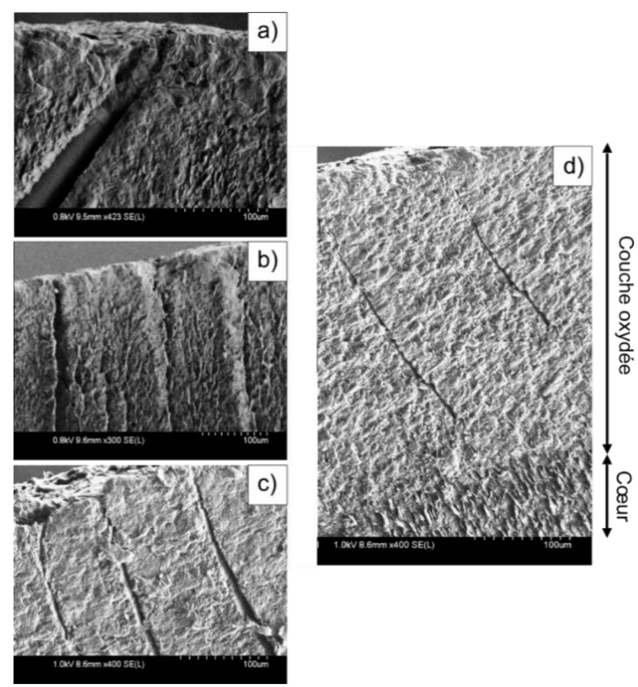
70°C – 85%HR → adhesive

DEGRADED LAYER IN THERMALLY AGED SAMPLES

- Existence of an oxidized layer (single lap shear specimens)



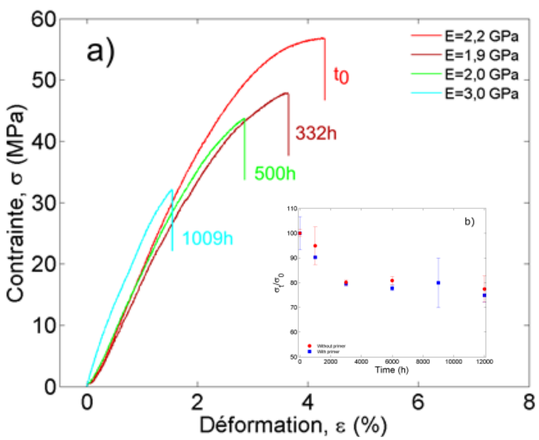


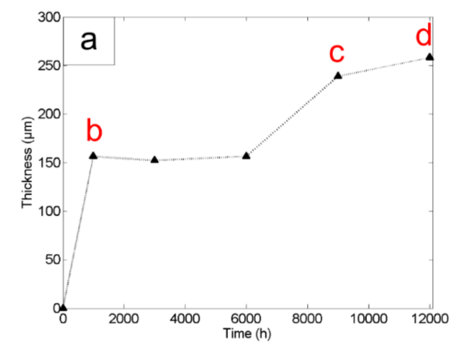


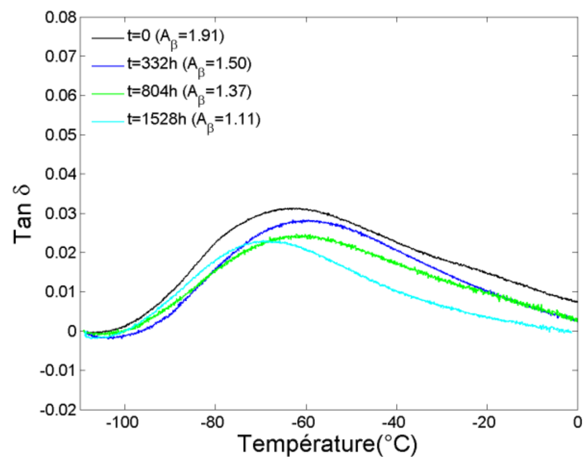
Further increase in oxygen penetration
Decrease in toughness

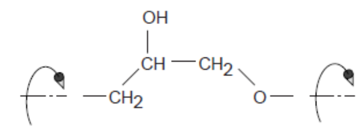
PROPOSAL OF AN EMBRITTLEMENT SCENARIO

- From thin film (120 µm) to bulky bonded assembly



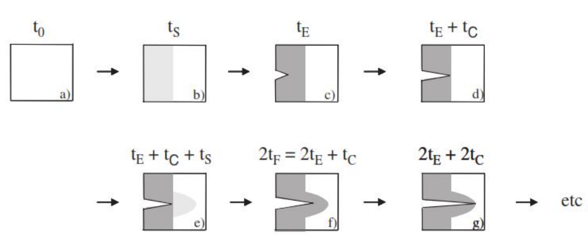






L. Heux et al./ Polymer 38 (1997) 1767-177

Embrittlement of epoxy film
Depletion of β relaxation

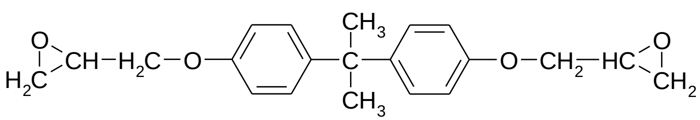


X. Colin et al./ Journal of Composite Materials 39 (2005) 1371-1389

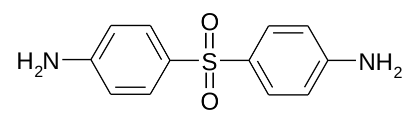
KINETICS AND MECHANISMS OF THERMAL OXIDATION

KINETICS AND MECHANISMS OF THERMAL OXIDATION

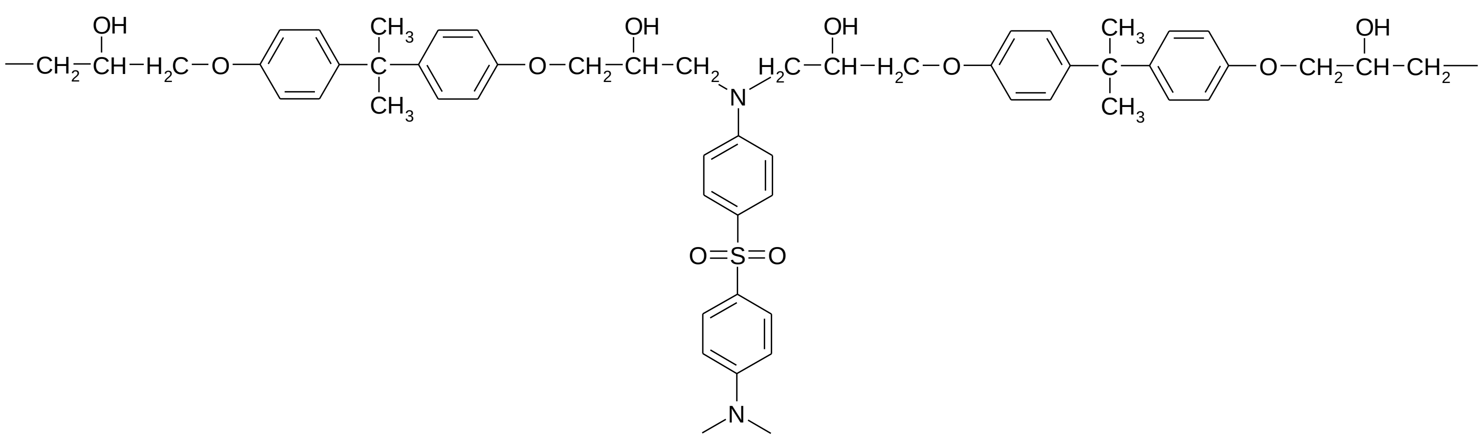
- Study of thermal oxidation of DGEBA-DDS system



DGEBA

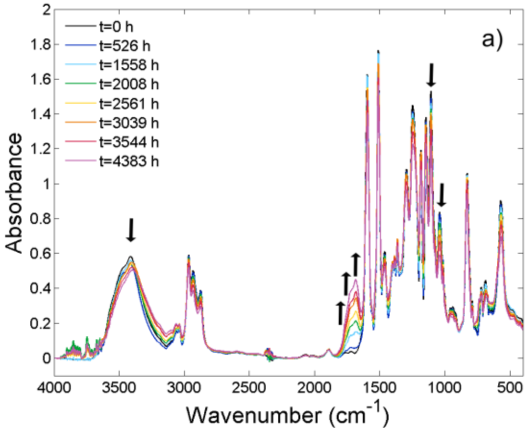


DDS



KINETICS AND MECHANISMS OF THERMAL OXIDATION

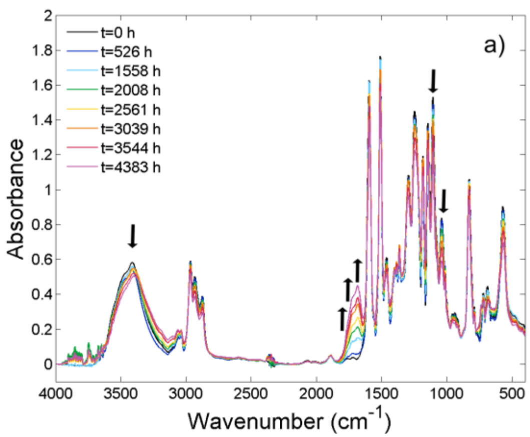
- Some structural changes

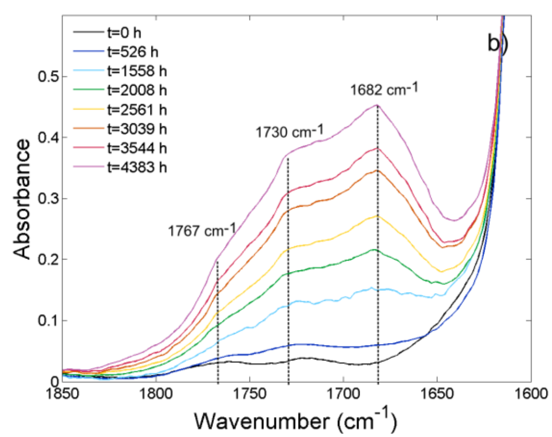


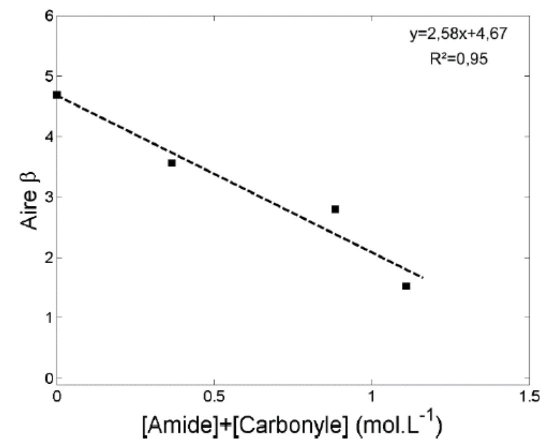
Ageing at 120°C

KINETICS AND MECHANISMS OF THERMAL OXIDATION

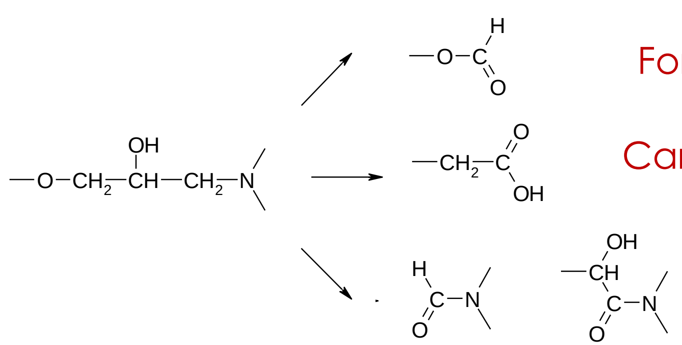
- Some structural changes







Ageing at 120°C



Formate 1765 cm^{-1}

Carboxylic acid 1730 cm^{-1}

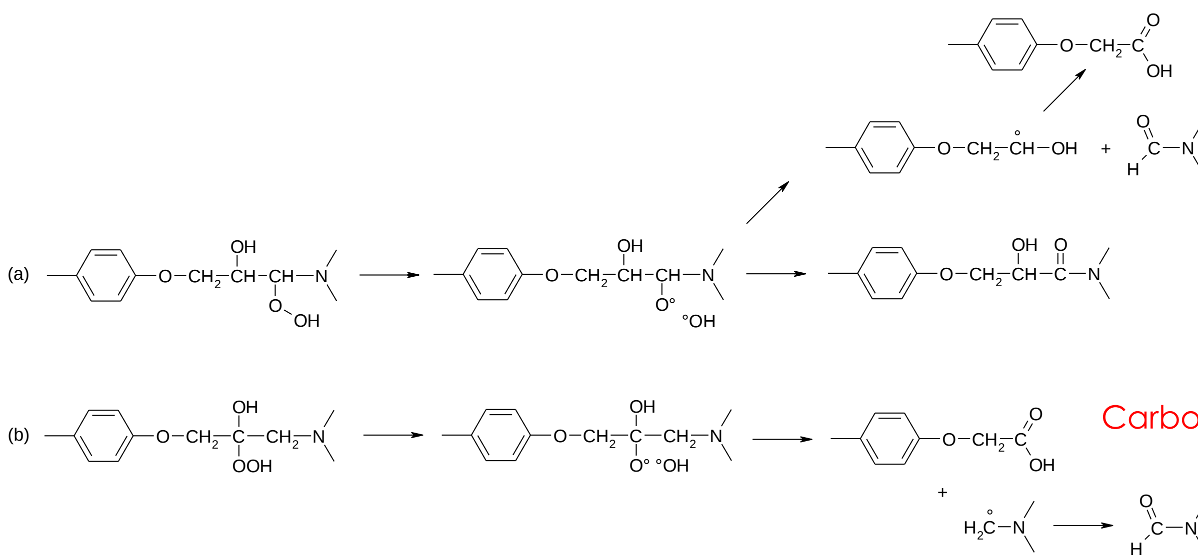
Amide 1680 cm^{-1}

KINETICS AND MECHANISMS OF THERMAL OXIDATION

- Nature of the true oxidation mechanism?

Oxidation of >N-CH_2-

Oxidation of >CH-OH



Distinct sites can generate the same oxidation products

KINETICS AND MECHANISMS OF THERMAL OXIDATION

- Identification of reactive sites from Bond Dissociation Energies of C-H

POO° + PH → POOH + P°

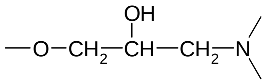
↓

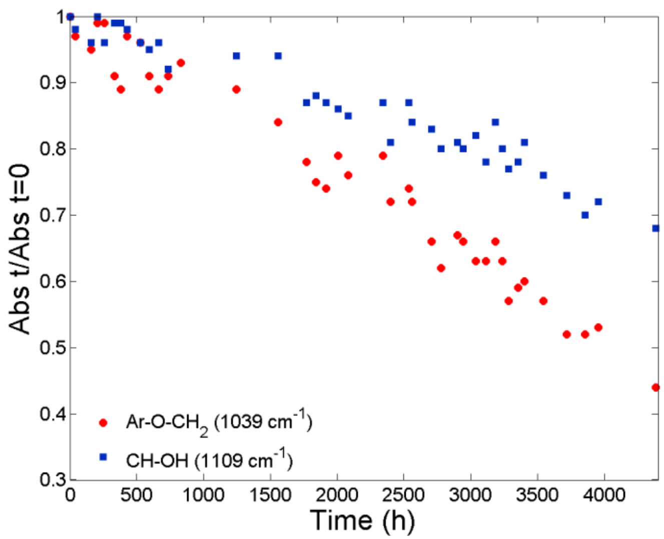
Amides, carbonyls…

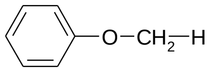
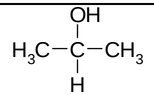
$E_3 = 0.55 \times (BDE - 261.5)$

$\log k_3\ (30°C) = 16.4 - 0.2 \times BDE$

S. Korcek et al / Canadian Journal of Chemistry 50 (1972) 2167-2174





	BDE (kJ mol^{-1})	E_3 (kJ mol^{-1})	k_3(120°C) (l mol^{-1} s^{-1})	k_3(200°C) (l mol^{-1} s^{-1})
	385	67.9	4.8	160.0
	390.5	70.9	3.4	134.4

E.T. Denisov, I.B. Afanas'ev, Oxidation and Antioxidants in Organic Chemistry and Biology, Taylor & Francis Group, 2005.

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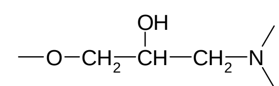
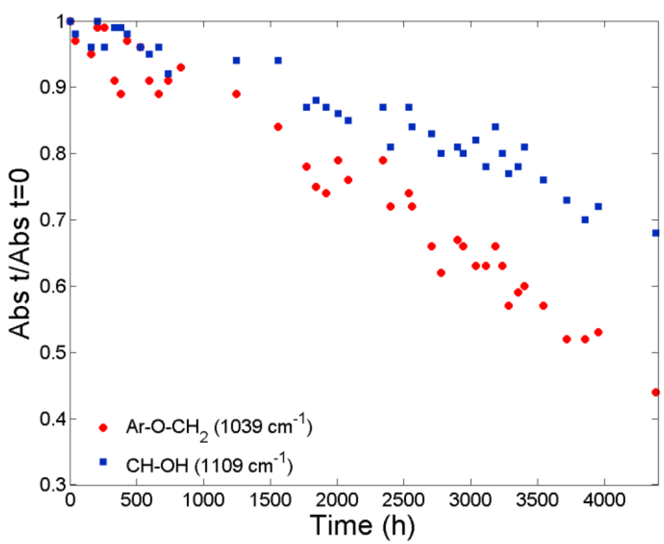
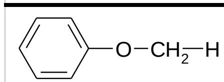
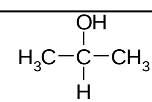
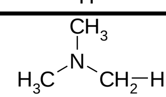




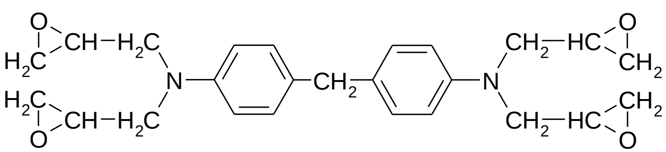
	BDE (kJ mol^{-1})	E_3 (kJ mol^{-1})	k_3(120°C) (l mol^{-1} s^{-1})	k_3(200°C) (l mol^{-1} s^{-1})
	385	67.9	4.8	160.0
	390.5	70.9	3.4	134.4
	376.6	63.3	7.9	208.7

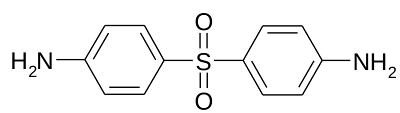
-O-CH_2- and >N-CH_2- are the weakest sites.

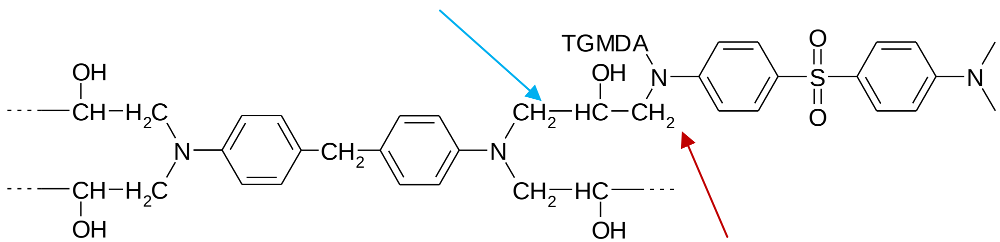
E.T. Denisov, I.B. Afanas'ev, Oxidation and Antioxidants in Organic Chemistry and Biology, Taylor & Francis Group, 2005.

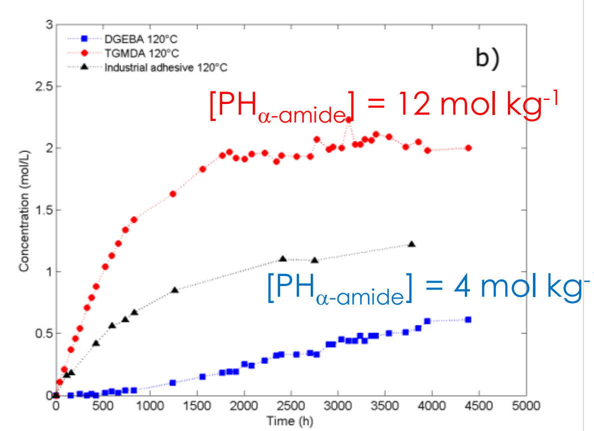
KINETICS AND MECHANISMS OF THERMAL OXIDATION

- Comparison with TGMDA-DDS system









Comparison of amide concentration a 120°C for TGMDA-DDS (●), DGEBA-DDS (■), and the adhesive (▲).

$M = 670\ \mathrm{g\ mol^{-1}}$

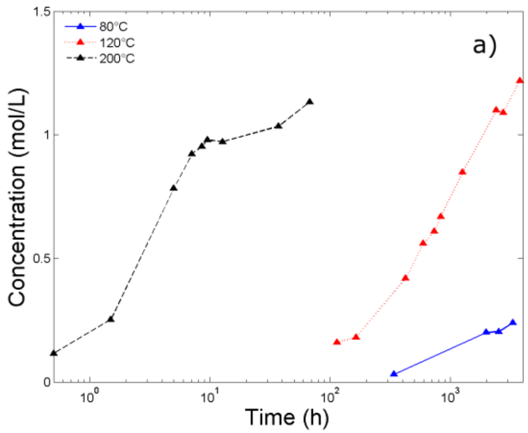
N = 4 (TGMDA) + 4 (α-DDS)

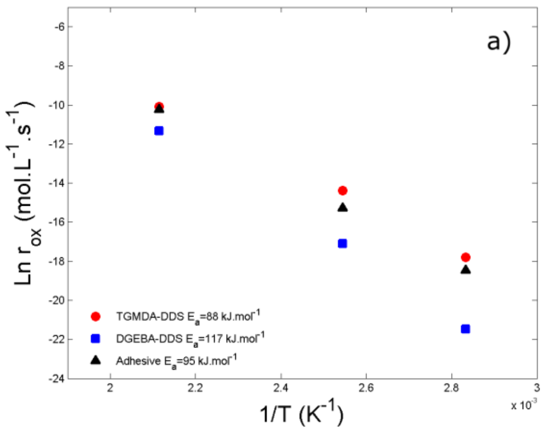
→ $[PH_{\alpha\text{-amide}}] = 6 + 6\ \mathrm{mol\ kg^{-1}}$

KINETICS AND MECHANISMS OF THERMAL OXIDATION

- Oxidation rate for amide formation

$$r_{ox} = r_0 . \exp\left(-\frac{E_{ox}}{RT}\right)$$



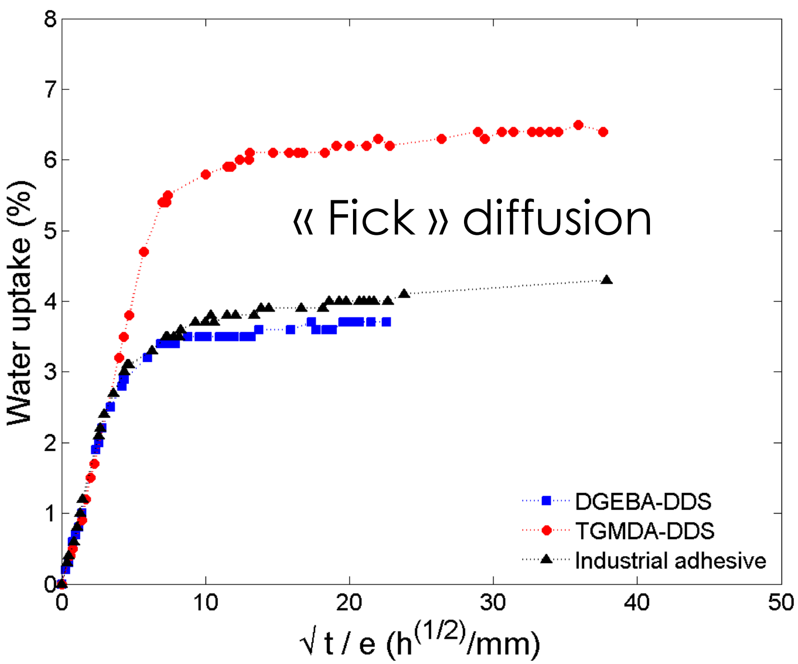


- The behavior of epoxy adhesive can be approximated from DGEBA-DDS and TGMDA-DDS
- The (oversimplified) Arrhenius approach allows to predict the changes in oxidation rate with temperature

KINETICS AND MECHANISMS OF WATER DIFFUSION

WATER AGEING

- Water diffusion



Sorption curves in immersion at 70°C

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot exp\left(-\frac{D.(2n+1)^2.\pi^2.t}{4e^2}\right)$$

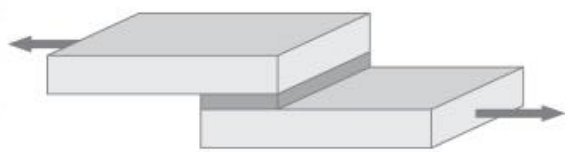
$$\frac{M(t)}{M_\infty} = \frac{4}{e^2} \cdot \sqrt{\frac{D_{app}.t}{\pi}}$$

$$\mathrm{D}_{H20} = \mathrm{D}_0.\exp\left(-\frac{\mathrm{E_D}}{\mathrm{RT}}\right)$$

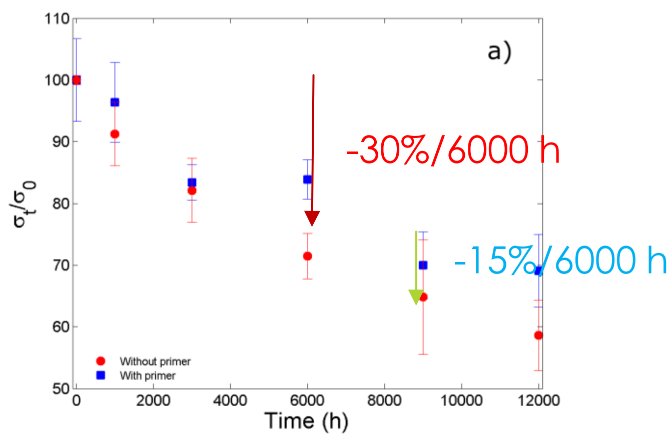
Systems	M_∞ (%)			D (cm² s⁻¹)	E_D (kJ mol⁻¹)	E_S (kJ mol⁻¹)
	70°C	50°C	37°C			
DGEBA-DDS	3.8	3.4	3.3	2.0×10^{-8}	~ 24	~ -0.6
TGMDA-DDS	6.4	6.0	6.3	6.1×10^{-9}	~ 27	~ -0.4
Adhesive	4.2	3.5	3.1	2.1×10^{-8}	~ 22	~ -0.3

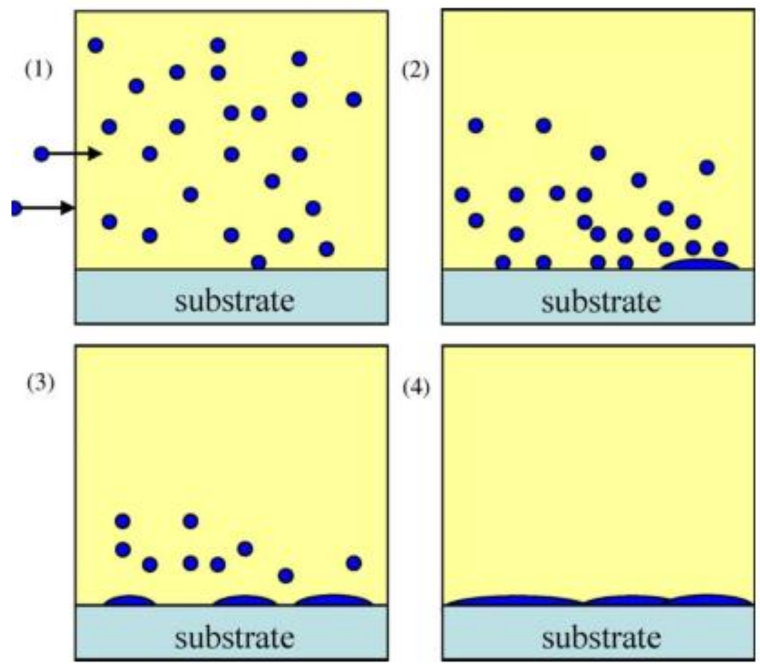
WATER AGEING

- Proposal of failure mechanism



$$t_{diff} \sim \frac{\pi e^2}{16 \times D_{H2O}} \sim 5000\ h$$





J. Cognard. Le Vide, les Couches Minces 251, 1990, 93.

ON THE REPRESENTATIVENESS OF ACCELERATED AGEING TESTS

ASSESSMENT OF « CRITICAL TIMES »

$$t_{diff} \sim \frac{\pi e^2}{16 \times D_{H2O}} \sim 5000\ h$$

$E_D = 25\ kJ\ mol^{-1}$

$$r_{OX} = r_0 . \exp\left(-\frac{E_{OX}}{RT}\right) \qquad E_{TOL} = \frac{1}{2} \cdot (E_D - E_{OX})$$

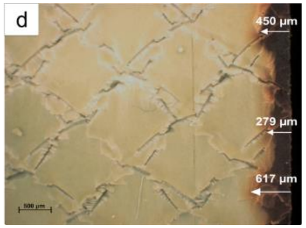
$E_{DO2} \sim 20\ kJ\ mol^{-1}$

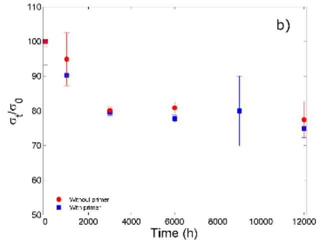
$E_{OX} \sim 100\ kJ\ mol^{-1}$

TOL ↓ if T ↑

Temperature (°C)	t_{diff} (h)
90	2700 (extrapolated)
70	5000
20	22000 (extrapolated)

Temperature	t_{ox} (h) to reach 1 mol L^{-1}	TOL (µm)
120	2000	150
90	22000 (extrapolated)	400 (extrapolated)
70	> 100000 (extrapolated)	900 (extrapolated)





ASSESSMENT OF « CRITICAL TIMES »

$$t_{diff} \sim \frac{\pi e^2}{16 \times D_{H2O}} \sim 5000\ h$$

E_D = 25 kJ mol^{-1}

$$\mathrm{r_{OX}} = \mathrm{r_0}.\exp\left(-\frac{\mathrm{E_{OX}}}{\mathrm{RT}}\right)$$

$$E_{TOL} = \frac{1}{2} \cdot (E_D - E_{OX})$$

E_{DO2} ~ 20 kJ mol^{-1}
E_{OX} ~ 100 kJ mol^{-1}

TOL ↓ if T ↑

Temperature (°C)	t_{diff} (h)
90	2700 (extrapolated)
70	5000
20	22000 (extrapolated)

Temperature	t_{ox} (h) to reach 1 mol L^{-1}	TOL (µm)
120	2000	150
90	22000 (extrapolated)	400 (extrapolated)
70	> 100000 ((extrapolated)	900 (extrapolated)

- At low temperature: water ageing is predominent at short time but oxidation will accumulate at longer times
- Accelerated test at enhanced temperature = risk of « crossover » between humid ageing vs thermal ageing

CONCLUSIONS AND PROPECTS

CONCLUSIONS

- Bonded assemblies are subjected to a complex humid + thermal ageing
- Water ageing → adhesive failure
- Thermal ageing → cohesive failure with oxidized layer favoring the propagation of degradation to the bulk
- Structure-oxidizability relationships: oxidation occurs at the crosslink nodes (>N-CH_2-) and induces β-relaxation depletion and later toughness loss
- Thermal ageing is negligible in early ageing times but « accumulates » within exposure time

PROSPECTS

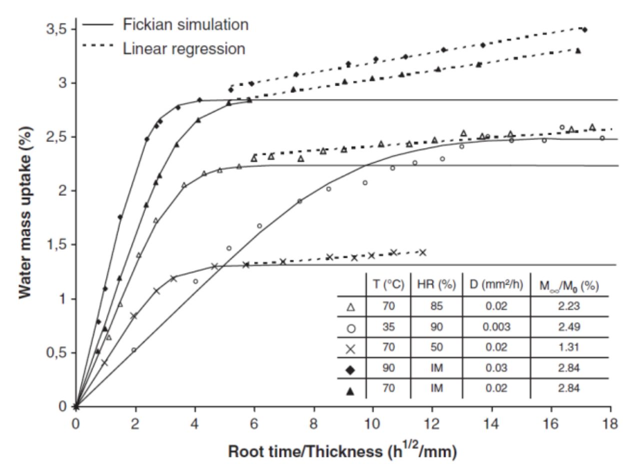
- Develop a reliable kinetic modeling for an accurate prediction of thermal oxidation

$POOH \rightarrow 2P° + P{=}O$	k_1
$P° + O_2 \rightarrow POO°$	k_2
$POO° + PH \rightarrow POOH + P°$	k_3
$P° + P° \rightarrow$ inact. prod.	k_4
$POO° + P° \rightarrow$ inact. prod.	k_5
$POO° + POO° \rightarrow \ldots + \gamma_6 P{=}O + O_2$	k_6

External conditions (T, P_{O2}..) → k_i ← Material formulation

Boundaries conditions → k_i → Differential system → Structure = f(time)

- Coupling between thermal and humid ageing



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