

DEGRADATION DES EPOXYS : APPORT DES METHODES THERMIQUES ET CALORIMETRIQUES

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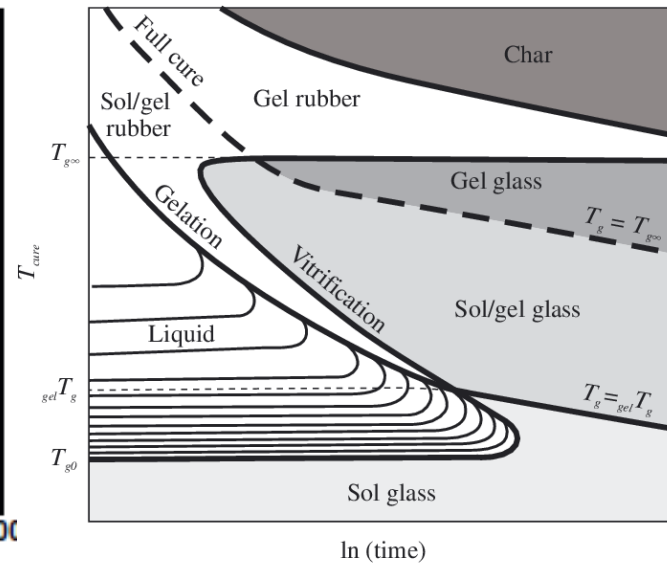
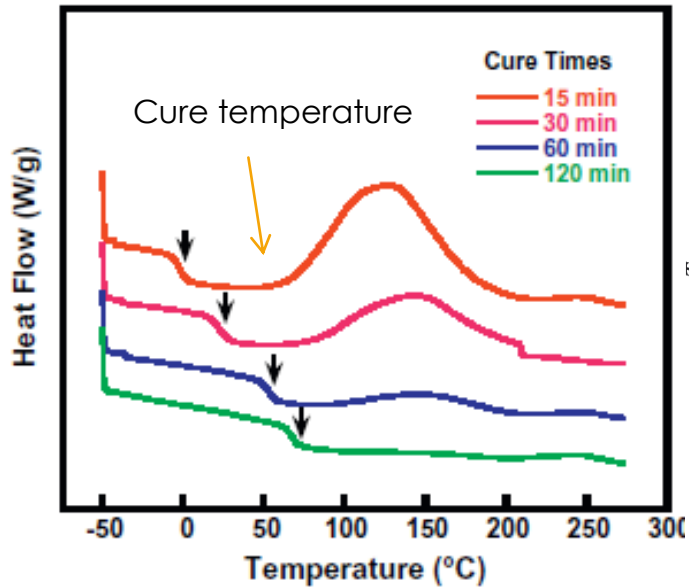
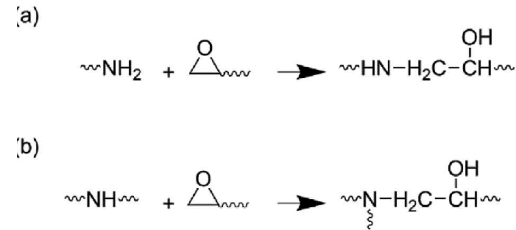


SOMMAIRE

- ▶ Les époxys
- ▶ Le vieillissement physique
- ▶ Le vieillissement chimique
 - dégradation thermique
 - vieillissement thermo-oxydant
- ▶ Perspectives

LES EPOXY

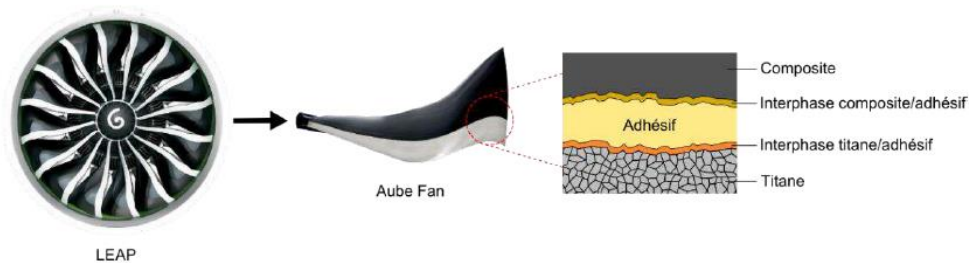
► Généralités



| Type of epoxide | Type of diamine | T _g (1 Hz) (K) |
|-----------------|-----------------|---------------------------|
| | | 489 |
| | | 471 |
| | | 457 |
| | | 442 |
| | | 391 |
| | | 349 |

LES EPOXYS

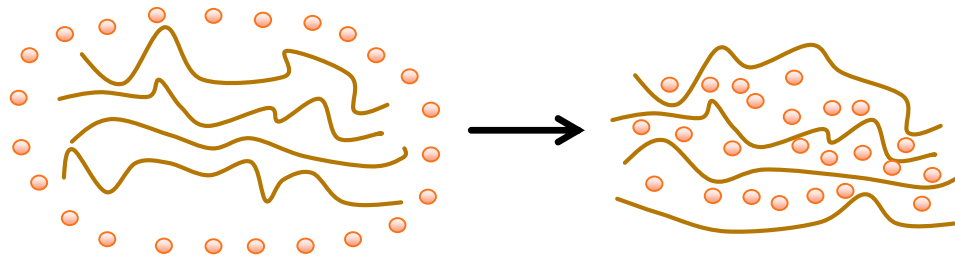
- ▶ Matrices thermodurcissables pour composites hautes performances
 - Bonne adhésion aux renforts = bonne transmission des efforts
Ex: Epoxy + fibres de carbone
 - Faible retrait
- ▶ Applications techniques



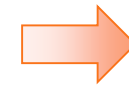
- ▶ ...et plusieurs modes de vieillissement (humide, relaxation physique, oxydation ...)

LES MECANISMES DE VIEILLISSEMENT

► Vieillessement physique

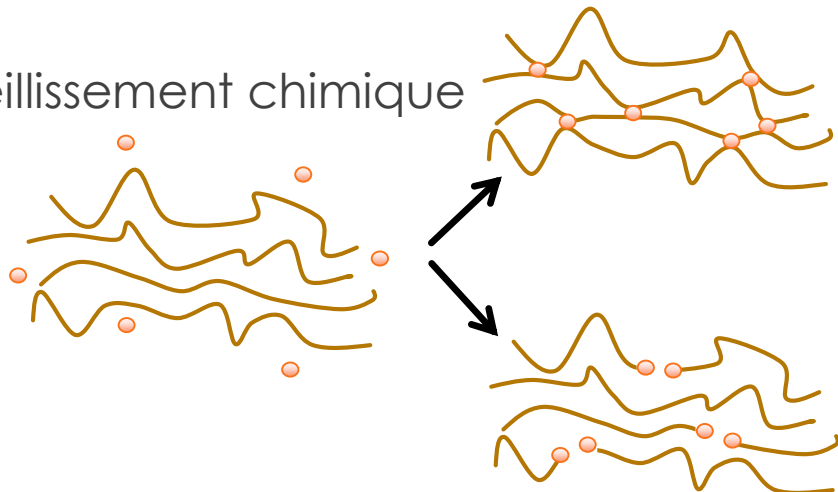


Modification de l'organisation spatiale



Ex: diffusion de l'eau
VRS

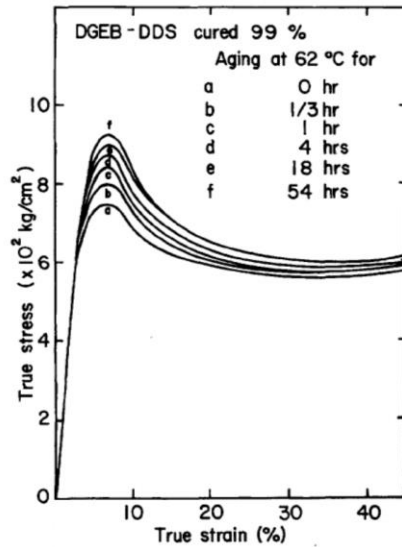
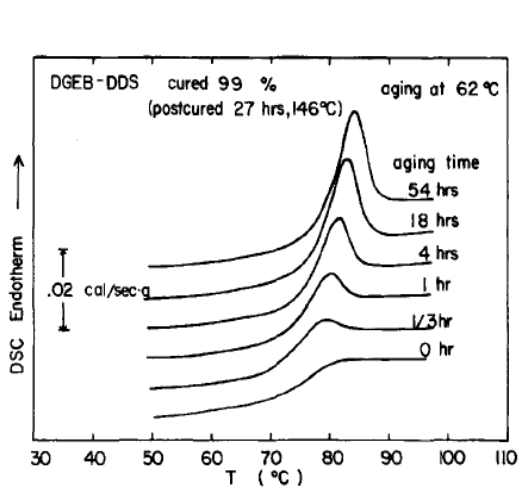
► Vieillessement chimique



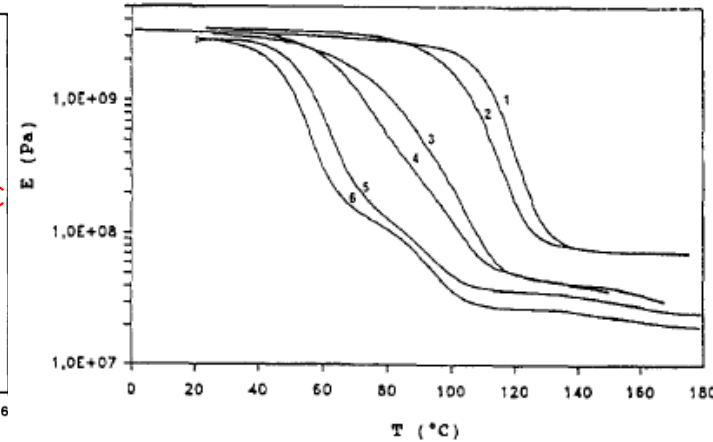
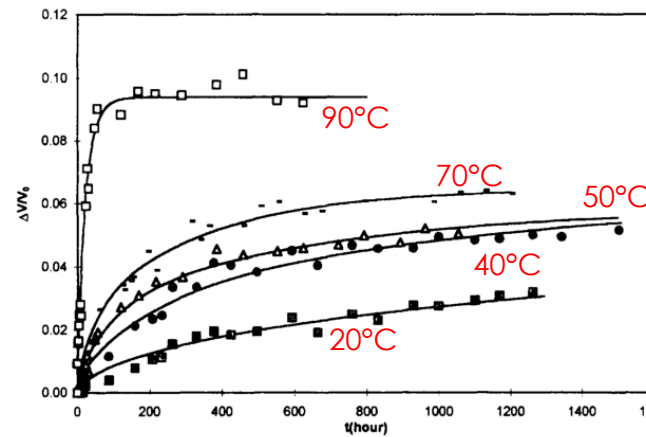
Ex:
Hydrolyse
Oxydation
Thermolyse / vieillissement anaérobie

LE VIEILLISSEMENT PHYSIQUE

► Relaxation structurale



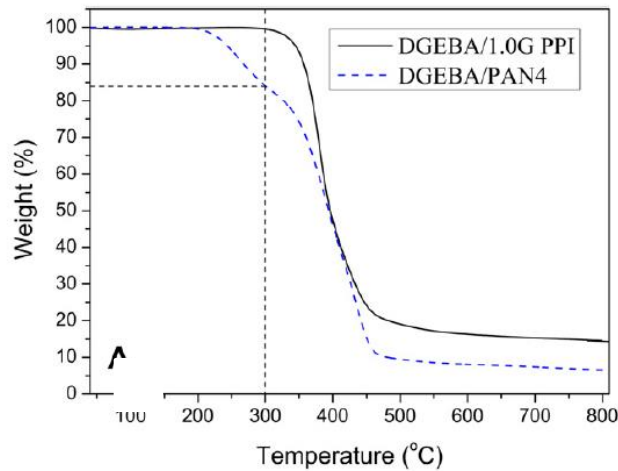
► Perméation de l'eau



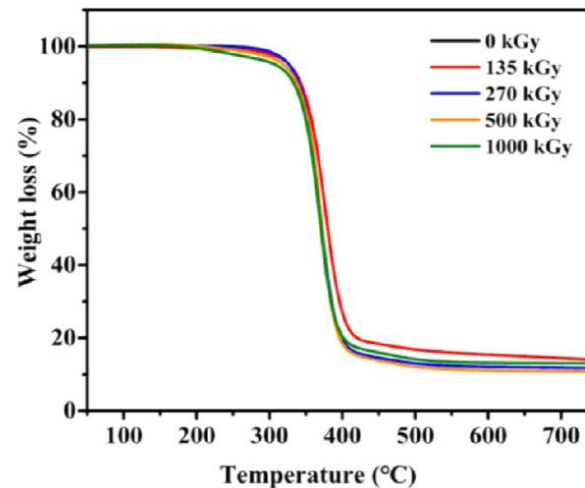
$$T_{g12} = \frac{x_1 \cdot \Delta c_{p1} \cdot T_{g1} + x_2 \cdot \Delta c_{p2} \cdot T_{g2}}{x_1 \cdot \Delta c_{p1} + x_2 \cdot \Delta c_{p2}}$$

VIEILLISSEMENT CHIMIQUE - ETAT DE L'ART

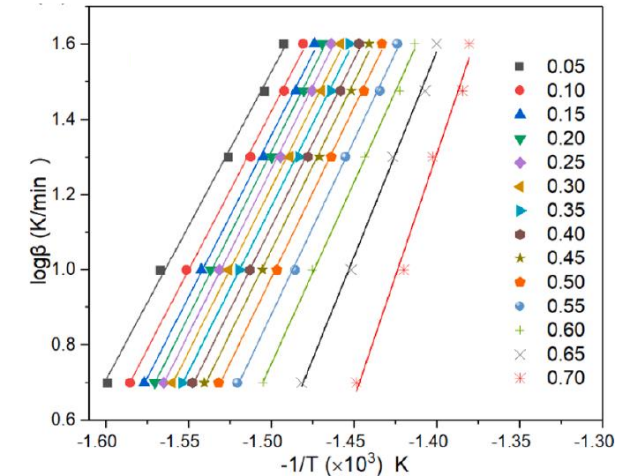
► Vieillessement thermique suivi par TGA



J. Wan et al. Materials Chemistry and Physics 138 (2013) 303-312



Z. Ji et al. Polym. Degrad. Stab. 199 (2022) 109908



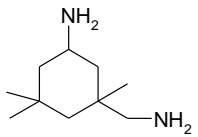
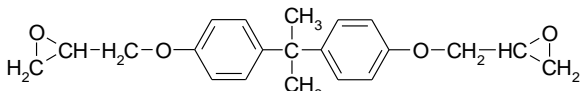
Y. Yang et al. Chemical Engineering Journal 450 (2022) 138424

Classement des systèmes par stabilité thermique
Suivi du vieillissement ? Mais interprétation spéculative
Extraction de paramètres cinétiques apparents

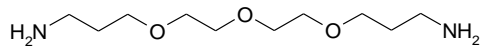
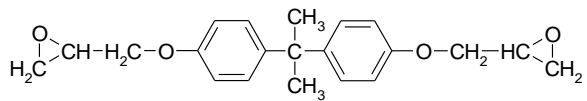
Quid de l'analyse des mécanismes ?

VIEILLISSEMENT CHIMIQUE - ETAT DE L'ART

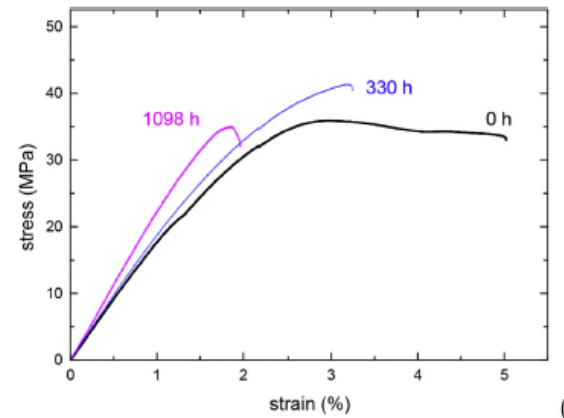
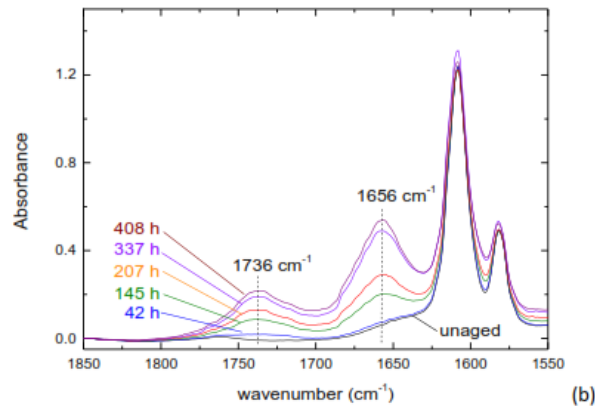
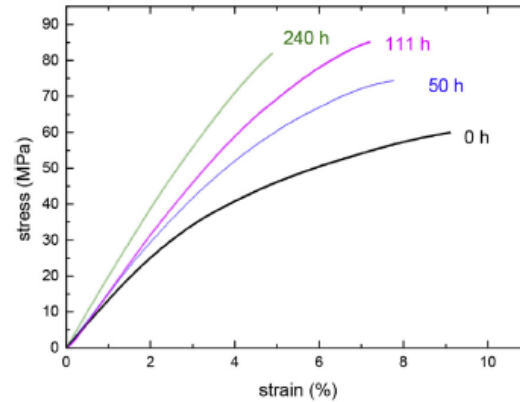
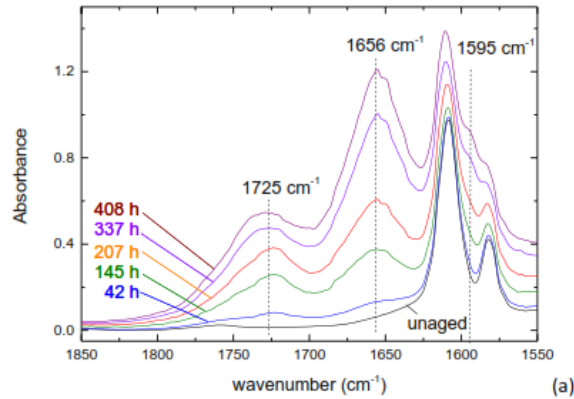
► Oxydation



DGEBA-IPDA



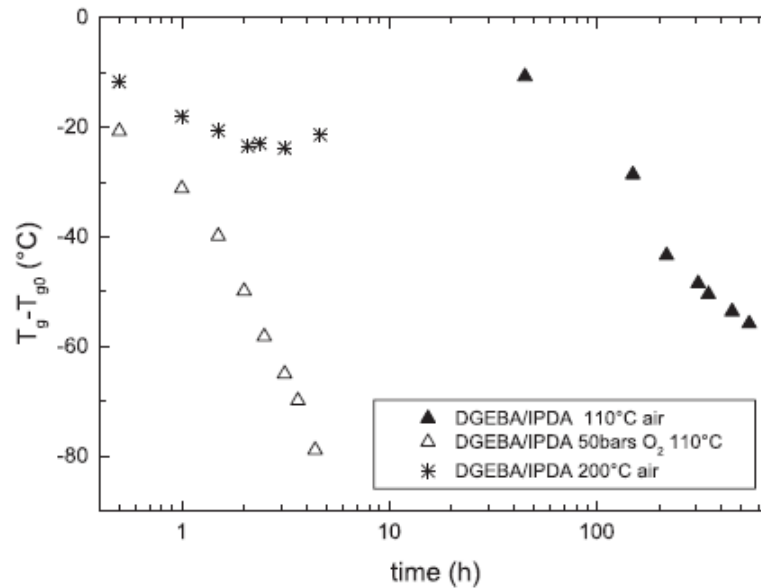
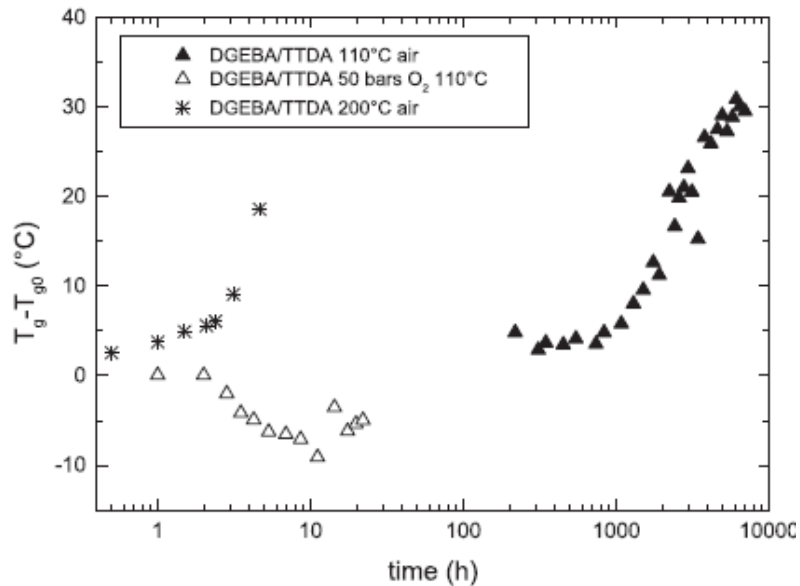
DGEBA-TTDA



- Apparition d'amides (oxydation des $-\text{CH}_2-\text{N}<$)
- Augmentation du module
- Diminution de l'allongement à la rupture

APPORT DE LA DSC

- ▶ Etude de la température de transition vitreuse



$$T_g = \frac{T_{gl}}{1 - (K_{DM}Fn)}$$

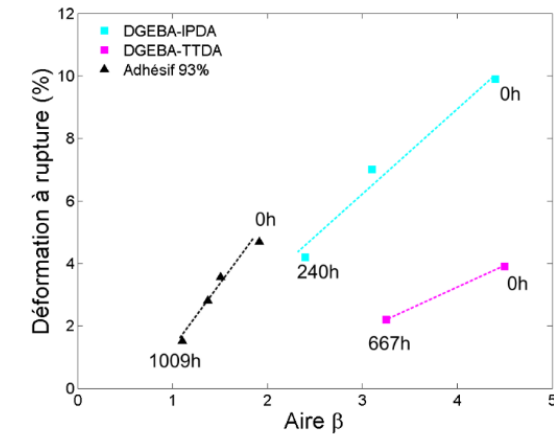
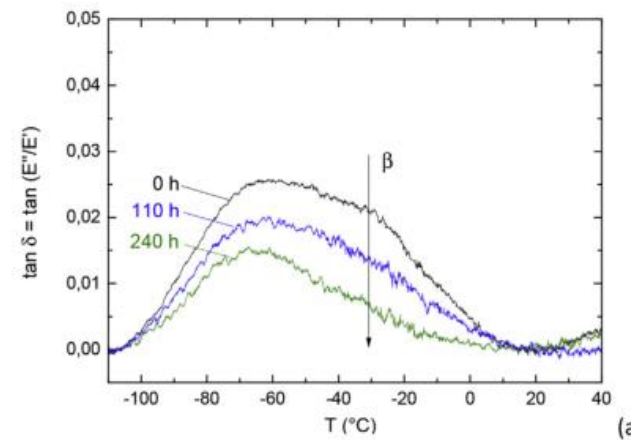
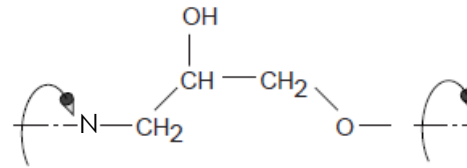
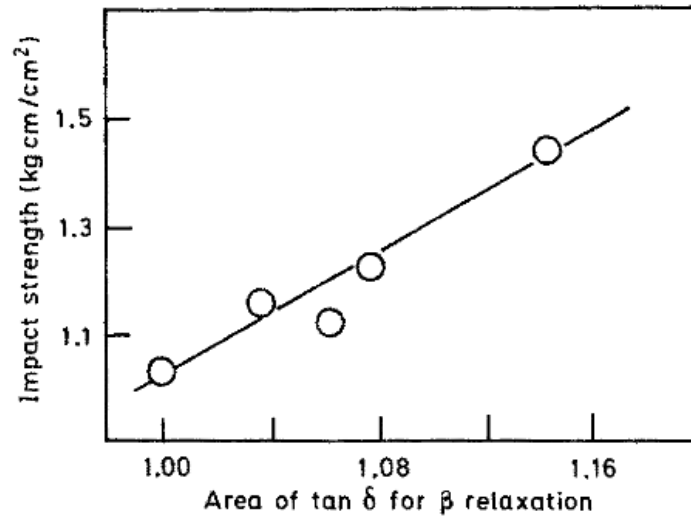
DGEBA-TTDA ($T_{g0} \sim 70^\circ\text{C}$):
soudures si vieillissement sous air

DGEBA-IPDA ($T_{g0} \sim 165^\circ\text{C}$):
coupures de chaînes

Explication + fine de la
fragilisation ?

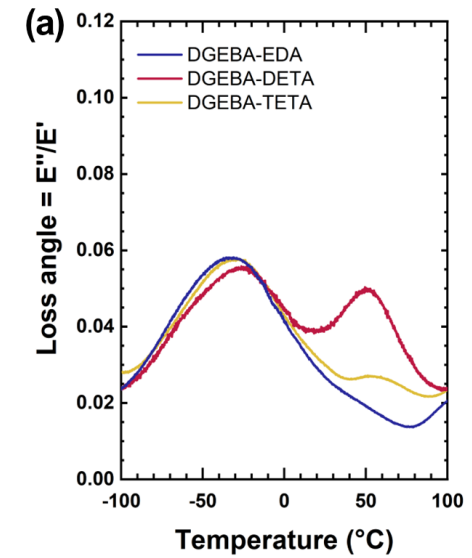
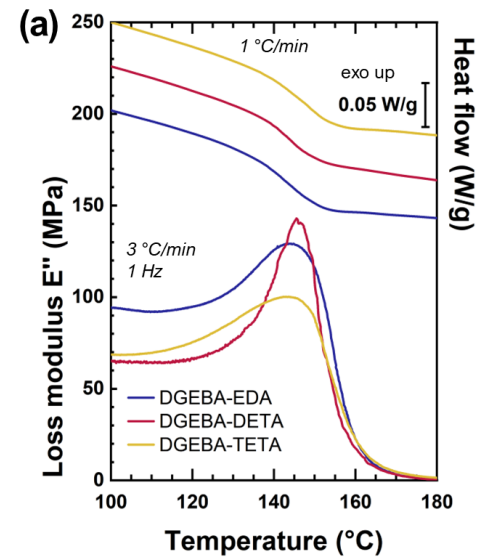
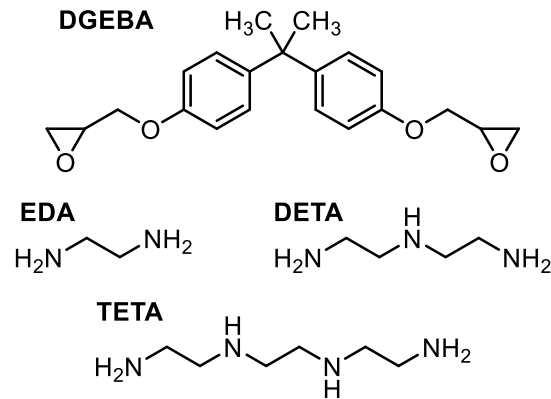
APPORT DE LA DMA

- ▶ Etude de la relaxation sous vitreuse – vers la prédiction de la fragilisation



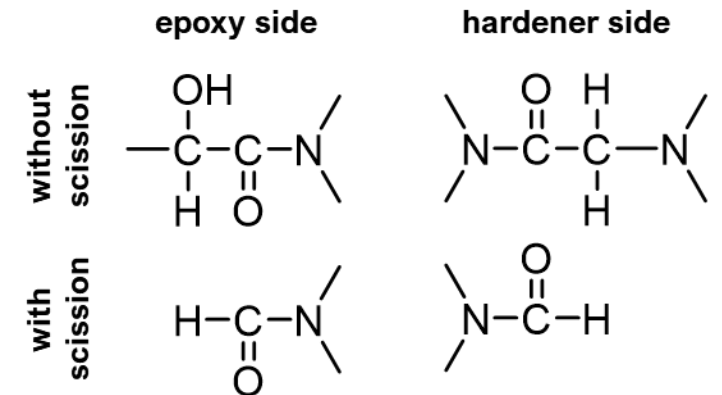
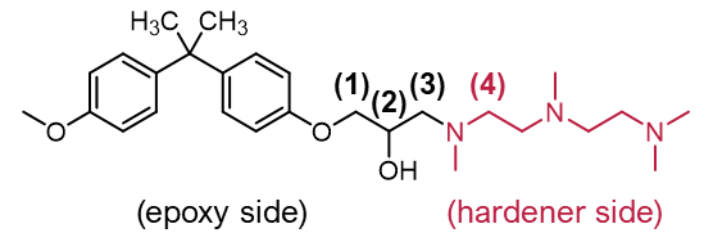
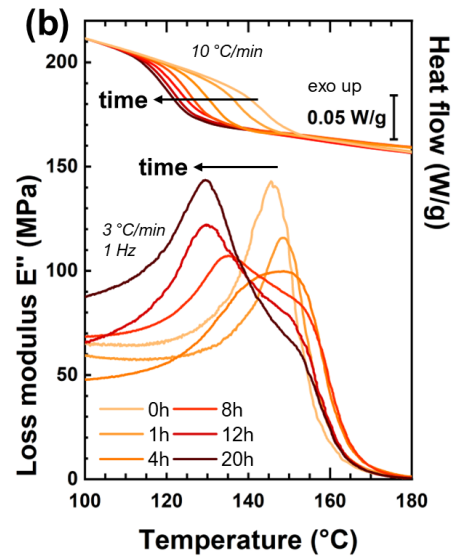
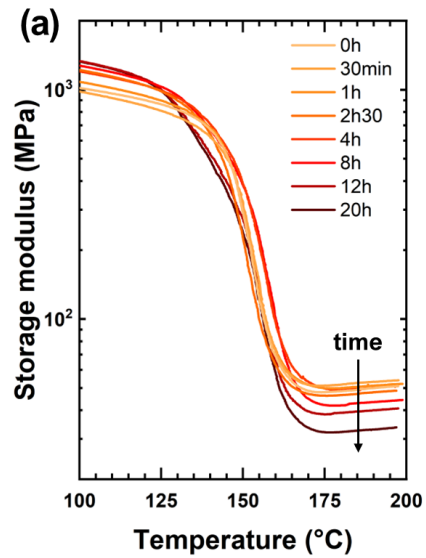
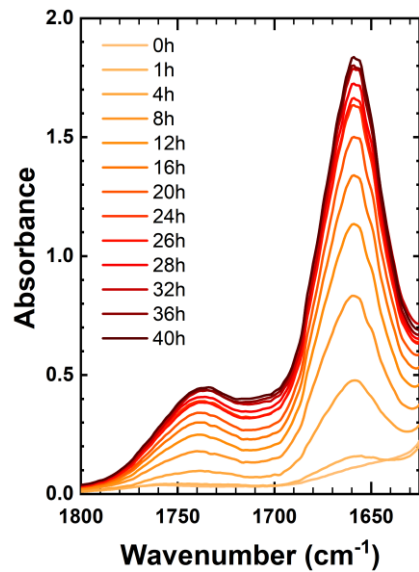
APPORT DE LA DMA

- Compréhension de la réactivité via une étude multi-échelle



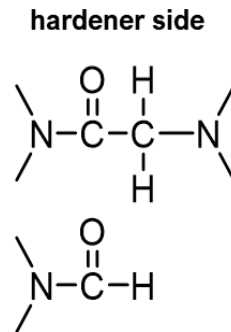
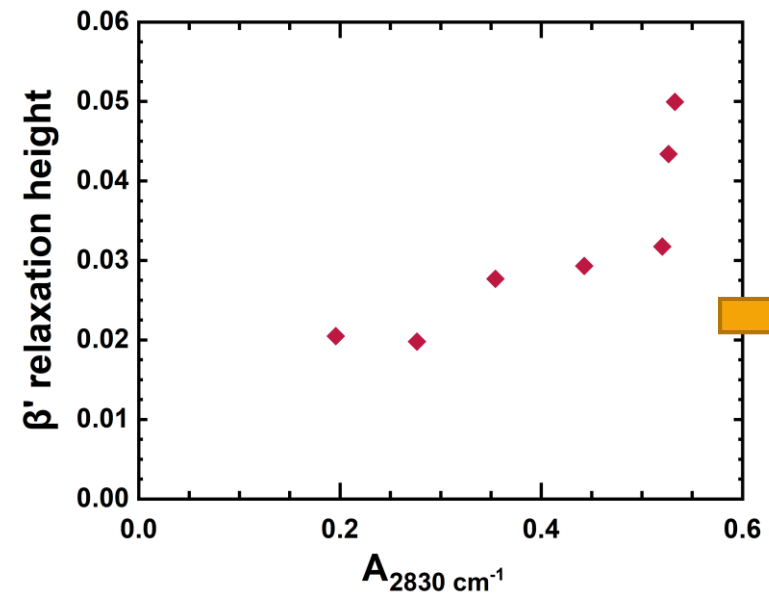
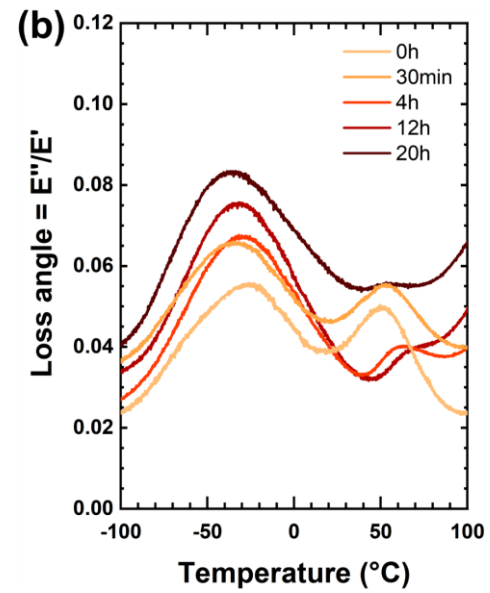
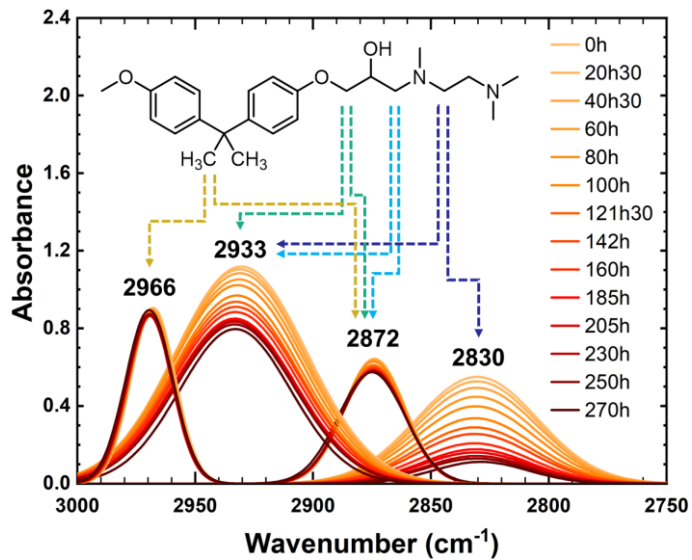
APPORT DE LA DMA

- Compréhension de la réactivité via une étude multi-échelle



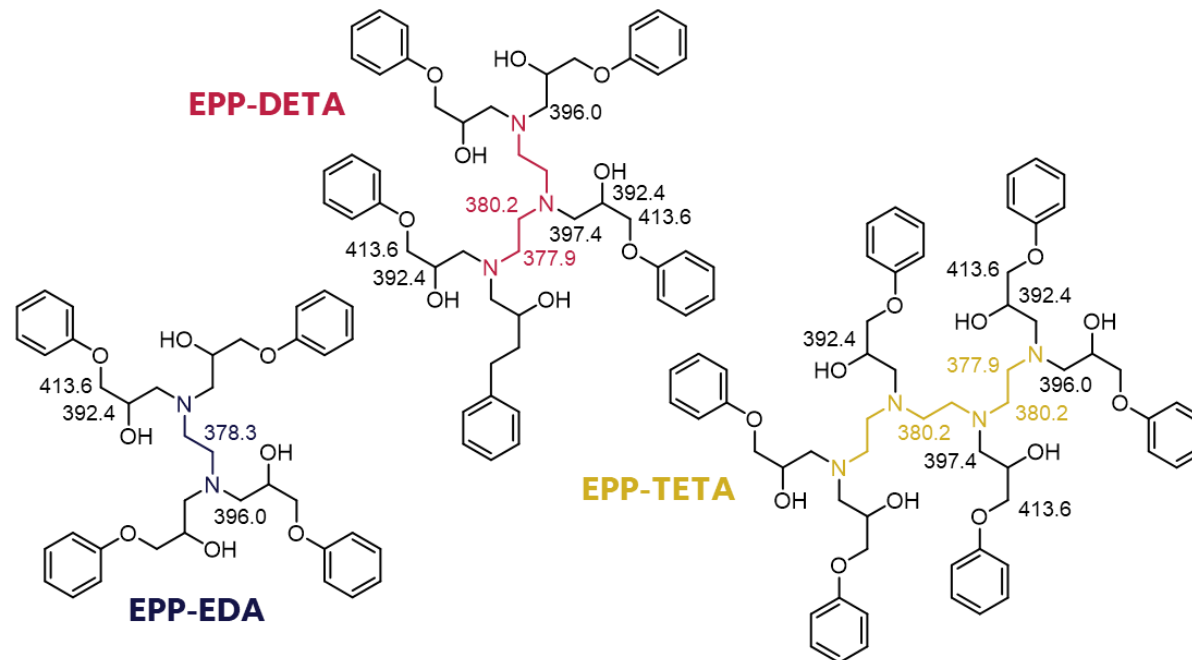
APPORT DE LA DMA

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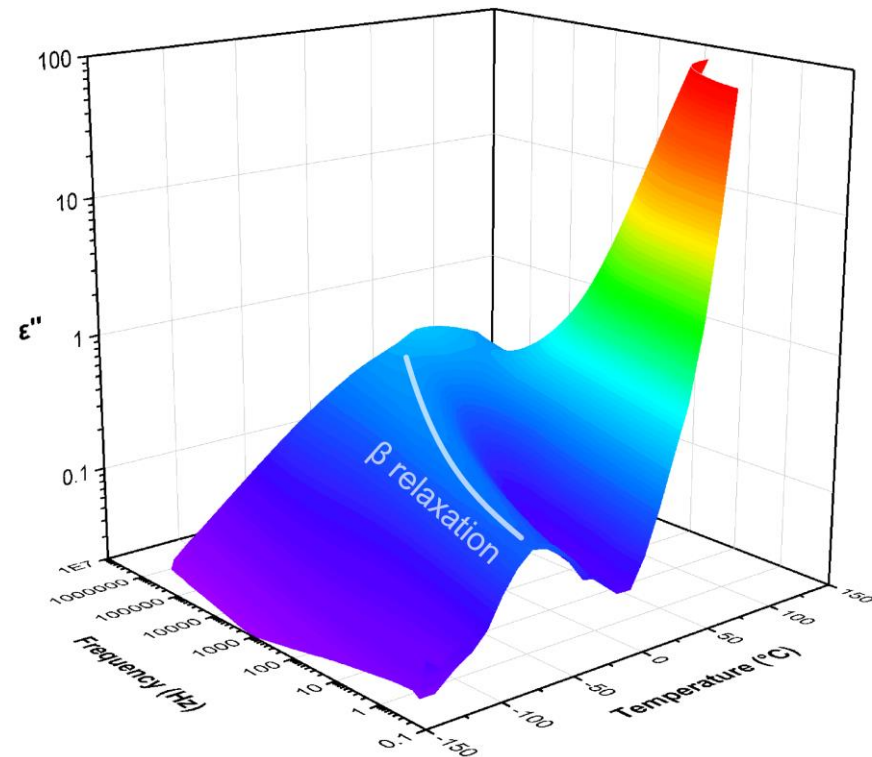
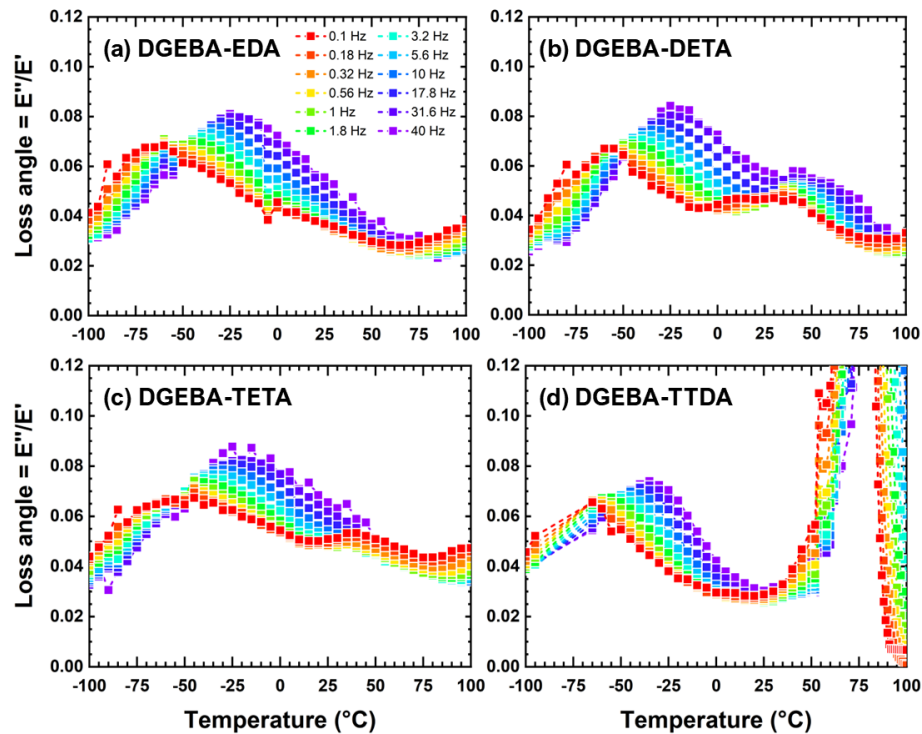
APPORT DE LA DMA

- ▶ Compréhension de la réactivité via une étude multi-échelle
- ▶ Validation par une approche théorique



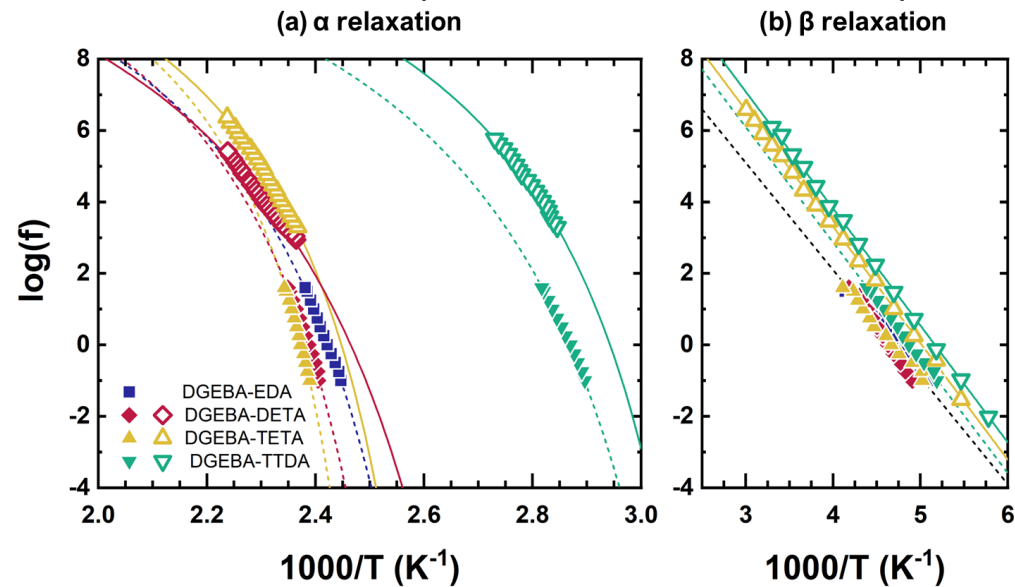
PERSPECTIVES

► Etudes multi-températures / multi-fréquences

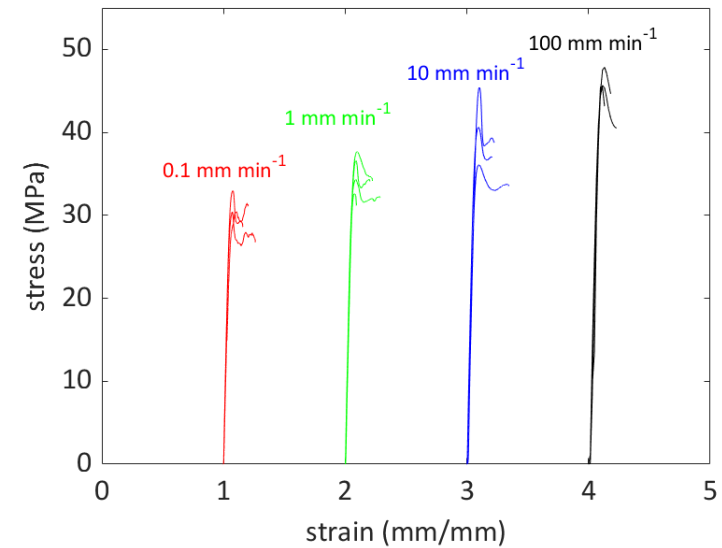


PERSPECTIVES

- ▶ Etudes multi-températures / multi-fréquences



$$\frac{\sigma_y}{T} = \frac{2k}{v} \ln \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right) + \frac{2 \cdot \Delta H}{T \cdot v}$$

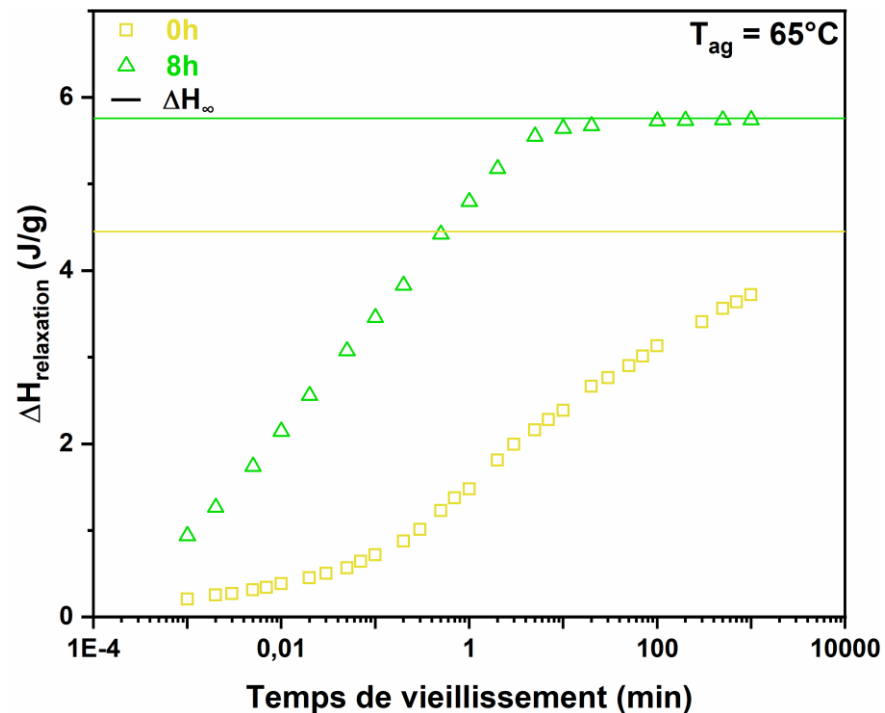


Evolution des paramètres VTFH et Arrhenius des transitions lors du vieillissement

→ Vers une meilleure compréhension des mobilités locales / du volume libre sur les propriétés mécaniques des matériaux neufs et vieillis?

PERSPECTIVES

- ▶ Couplages faibles entre vieillissement chimique et vieillissement physique



$$\Delta H_{\text{relaxation}} = \Delta C_p \cdot (T_g - T_a)$$

$$\text{Ici, } T_{g0} = 79^\circ\text{C} \quad T_{g\text{vieilli}} = 77^\circ\text{C}$$

L'oxydation modifie l'état final (ΔC_p) et la cinétique de VRS (effet des coupures de chaînes)
→ Effet sur les modèles type KAHR ou TNM

A + long terme, effet des couplages forts

CONCLUSIONS

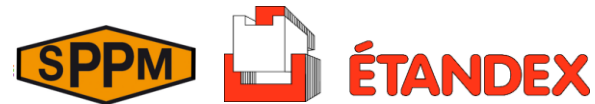
- ▶ Intérêt industriel et scientifique des époxy
- ▶ Intérêt des méthodes thermiques/calorimétriques pour l'étude du vieillissement à l'échelle macromoléculaire
- ▶ Relations entre mobilité sous vitreuse et comportement mécanique
- ▶ Étude des couplages forts et faibles

REMERCIEMENTS

- ▶ Comité des JCAT
- ▶ ANR DUREVE



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