



## Thermo-oxidative aging of epoxy coating systems

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### ABSTRACT

The thermo-oxidative behavior of unformulated (unfilled) samples of epoxy coatings has been studied at five temperatures ranging from 70 °C to 150 °C. Two epoxy networks based on diglycidyl ether of bisphenol A (DGEBA), respectively, cured by jeffamine (POPA) or polyamidoamine (PAA) were compared. Infrared spectrophotometry (IR), differential scanning (DSC) and sol–gel analysis (SGA) were used to monitor structural changes.

Thermal oxidation leads to carbonyl and amide formation in both systems. POPA systems appear more sensitive to oxidation than PAA ones. Thermal oxidation leads to predominant chain scission as evidenced by the decrease of glass transition temperatures ( $T_g$ ) and increase of sol fraction.

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## 1. Introduction

Epoxy networks cured by aliphatic diamines are commonly used as coatings in nuclear industry where durability is a key property. Typical exposure conditions are a constant temperature of about 50 °C and 0.1 Gy h<sup>-1</sup> of irradiation dose rate, in air.

In a study of polyethylene insulating materials exposed in these conditions, Khelidj et al. [1] proposed a kinetic approach which can be widely generalized. It is based on the graph of Fig. 1 in which the polymer lifetime is plotted against dose rate, both in logarithmic scales.

Three kinetic regimes can be distinguished as following: regime I in which radical initiation results almost exclusively from polymer radiolysis. This regime corresponds to a linear asymptote of slope unity in the simplest cases. Regime III, in which initiation by polymer radiolysis is negligible in front of initiation by hydroperoxide thermal decomposition. This regime corresponds to a horizontal asymptote of which the ordinate is the lifetime in thermal aging at the temperature under consideration.

Regime II is a transition phase between regime (I) and (III). In this regime, initiation by polymer radiolysis predominates at the beginning of exposure, it creates hydroperoxides which accumulate until the time where their concentration reaches a critical value. At

this point, their thermal decomposition becomes the predominant radical source and the polymer undergoes a thermal aging process. Indeed the boundaries between these kinetic regimes sharply depend on different factors such as the radiochemical yield for radical formation ( $G_i$ ), the stability of hydroperoxides, the occurrence of anaerobic radiochemical processes in the sample core, etc.

In a recent publication [2], we have reported results of an investigation aimed to explore essentially the regime (I) for both systems under study. Some peculiarities of POPA and PAA structures were put in evidence and it was shown that, for the dose rates of practical interest ( $\leq 0.1$  Gy h<sup>-1</sup>), aging is dominated by thermal oxidation (regime III), that justifies this work.

There is some literature on thermal aging of epoxy networks [3–8] in a wide temperature range, using analytical tools such as DSC [9], ATG [10], DMTA, FTIR, UV [11] and XPS [12]. Some recurrent features of aging behavior are: the eventual occurrence of post-cure reactions coexisting with oxidation [13,14], carbonyl growth [15,16,10,17], and chain scission [18,19]. This latter process is especially important owing to its role in polymer embrittlement [20].

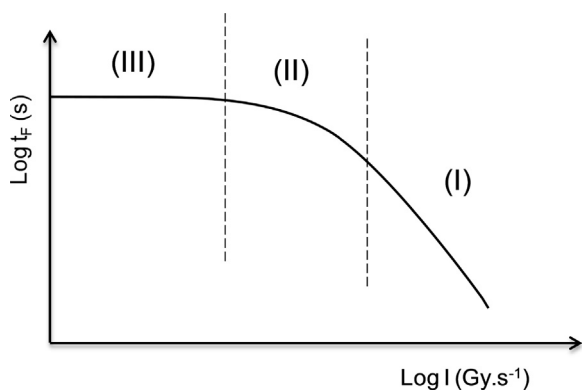
The aim of this article is to compare the thermal oxidative stability of POPA and PAA systems using free films.

## 2. Experimental part

### 2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA) used in this study has an epoxide concentration of 1.71 mol kg<sup>-1</sup> corresponding to

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**Fig. 1.** General shape of the log (lifetime) – log (dose rate) curve at a given temperature.

a number average molar mass  $M_n = 1170 \text{ g mol}^{-1}$  and a degree of polymerization  $n = 3$ .

The polyamidoamine (PAA) has a number average molar mass close to  $1230 \text{ g mol}^{-1}$  corresponding to a degree of polymerization  $j = 3.9$ .

The polyoxypropylene (POPA) has a number average molar mass  $132 \text{ g mol}^{-1}$  corresponding to a degree of polymerization  $x = 3$ .

The structure of these components is shown in Fig. 2.

Stoichiometric epoxide-amine mixtures were used to obtain films of  $100\text{--}150 \mu\text{m}$  in thickness. These films were cured at room temperature (RT) for 3 days to be post-cured at  $110^\circ\text{C}$  under vacuum later on for 48 h. The aim of the post curing is to reach a fully cured network structure as close as possible to the ideal one (only elastically active chains, no dangling chains).

They are transparent (no significant phase segregation) and slightly yellow (limited oxidation during processing).

## 2.2. Aging

Thermal aging was carried out in ventilated ovens under 70, 90, 110, 130 and  $150^\circ\text{C}$  range of temperature. The films were regularly removed from ovens to be analyzed.

## 2.3. Characterization

FTIR spectrophotometry was performed in ATR mode with a Bruker IFS 28 spectrophotometer in the  $4000\text{--}600 \text{ cm}^{-1}$  spectral

range, averaging 64 scans for a resolution of  $4 \text{ cm}^{-1}$ . A defined base line has been fixed for all FTIR spectra. Absorbance values are measured by the height of peak from the defined base line for a given wavenumber. Quantitative measurements were made using the following relationship:

$$[\text{Species}] = \frac{\varepsilon_{\text{Ar}}[\text{Ar}] A(\text{Species})}{\varepsilon_{\text{Species}} A(\text{Ar})} \quad (1)$$

where  $A$  (species) and  $\varepsilon$  species are the absorbance and the molar absorptivity of the species, respectively. The peak at  $1606 \text{ cm}^{-1}$ , whose intensity is invariant throughout degradation, has been taken as reference. The carbonyl and amide concentration were determined by using the Beer–Lambert law in which molar absorptivity usual value of  $500 \text{ L mol}^{-1} \text{ cm}^{-1}$  for carbonyl at  $1730 \text{ cm}^{-1}$  and  $470 \text{ L mol}^{-1} \text{ cm}^{-1}$  for amide groups at  $1658 \text{ cm}^{-1}$  and  $240 \text{ L mol}^{-1} \text{ cm}^{-1}$  for aromatic bands at  $1606 \text{ cm}^{-1}$  [21].

DSC measurements were carried out using a Q1000 modulated differential scanning calorimeter (TA instruments) in a nitrogen flow ( $50 \text{ ml min}^{-1}$ ). Samples weights were ranged between 5 and 10 mg. A temperature ramp of  $2^\circ\text{C min}^{-1}$  was used from 0 to  $170^\circ\text{C}$ . A temperature modulation of  $0.318^\circ\text{C}$  with a period of 60 s was superimposed to the main signal to record simultaneously reversible and irreversible heat flows.  $T_g$  values were assessed from the reversible heat flow curve, since the reversible signal is associated to physical modifications.

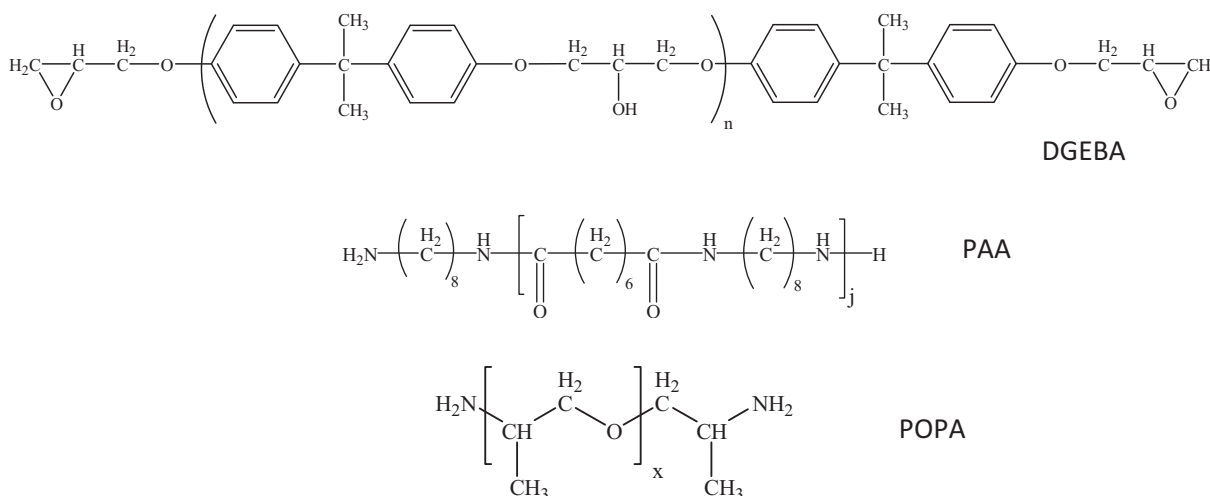
The sol fraction in tetrahydrofuran (THF) was determined in soxhlet for 24 h. During thermal exposure, chain scissions occurring increase the soluble fraction by increasing the number of chains that are no longer related to the network. In order to assess sol fraction, samples have been weighted before and after extraction. Initial weight ( $m_i$ ) of sample ranged from 70 to 100 mg. After 24 h of extraction, the samples were dried during 24 h at  $70^\circ\text{C}$  and weighted ( $m_f$ ). Soluble fraction ( $w_s$ ) was calculated by the following equation:

$$w_s = \frac{m_i - m_f}{m_i} \quad (2)$$

## 3. Results and discussion

### 3.1. Amide formation

The most spectacular changes of IR spectrum occur in the  $1630\text{--}1690 \text{ cm}^{-1}$  interval (Fig. 3), and can be attributed to amide formation. For long exposure times, both systems display their



**Fig. 2.** Chemical structure of “monomers”.

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