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# Thermal oxidation of epoxies: Influence of diamine hardener

# Esteve Ernault, Emmanuel Richaud<sup>\*</sup>, Bruno Fayolle

PIMM UMR 8006, Arts et Métiers ParisTech, CNRS, CNAM, 151 bd de l'Hôpital, Paris, France

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## 1. Introduction

Epoxy resins are commonly used for coatings, matrices for composite materials or adhesives. There is a wide variety of prepolymer/hardener pairs adapted for each sort of process (laminating, prepreg, injection, hand lay-up...) that lead to thermosets with elevated mechanical properties (modulus ca 3 GPa, flexural strength ca 125 MPa) and electrical insulating properties. It is however known that epoxys are sensitive to thermal oxidation which can limit their long term use [1-5].

Oxidation of epoxy/diamine systems has been covered by several papers (see for example [6-10]), the main conclusions are of which:

- (I) Thermal-oxidation of epoxies follows a general autoxidation mechanism in which the main source of radicals is the decomposition of hydroperoxides [7,11]. Even though oxidation can be described by classical kinetic models, it is not clear if the kinetic parameters associated to elementary reactions are common to all epoxy resins or not.
- (II) Among the main molecular modifications, the appearance of several sort of amide and carbonyl species was shown by FTIR [6,9,12]. It seems that they originate from isopropanol groups being systematically involved in radical attack.
- (III) The changes at macromolecular scale during thermooxidation have been investigated by Tg change (measured

#### ABSTRACT

This work reports the thermal oxidation of DGEBA resins totally cured with cycloaliphatic (isophorone diamine) or with linear aliphatic (trioxa-tridecanediamine or TTDA) diamine hardener. Chemical changes (carbonyl build-up) were monitored by FTIR and macromolecular changes (chains scission and cross-linking) from  $T_g$  variations measured by DSC. Exposition at several temperatures and under several oxygen pressures showed that DGEBA/IPDA has systematically the highest oxidation rate. It was also observed that DGEBA/IPDA undergoes mainly chain scissions whereas DGEBA/ITDA undergoes a predominant crosslinking under air being partially suppressed under enhanced oxygen pressure. Results were discussed on the basis of the possible influence of the structure of hardener.

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by Differential Scanning Calorimetry) or  $T_{\alpha}$  (measured by Dynamic Mechanical Analysis). In aromatic epoxies, a decrease of  $T_{\alpha}$  is attributed to a predominant chain scission phenomenon [13,14]. The so called "internal antiplastification" [13,15] is also observed and would come from the destruction of isopropanol moiety associated to  $\beta$  transition [16].

Since there is, to our knowledge, no definitive conclusion on the link between structure, oxidizability and consequences of oxidation on thermo-mechanical properties, the aim of this work is to study the thermal oxidation of DGEBA/isophorone diamine (IPDA) and DGEBA/4,7,10-Trioxa-1,13-tridecanediamine (TTDA). By comparing the degradation of these two systems, we aim to answer the following questions:

- Are chemical changes observed in both these epoxy systems similar to those already reported in the literature?
- What is the influence of molecular mobility on oxidation kinetics, knowing  $T_g$  of the two chosen systems is quite different?
- What is the influence of the hardener part on the thermooxidation of epoxy/amine?

# 2. Experimental

## 2.1. Materials

The bisphenol A diglycidyl ether DGEBA (DER 332 - CAS 1675-

<sup>\*</sup> Corresponding author. E-mail address: emmanuel.richaud@ensam.eu (E. Richaud).

54-3 - ref 31185 supplied by Sigma Aldrich) has a degree of polymerization n = 0 and a number average molecular mass equal to 340 g/mol. Two kinds of hardeners have been chosen:

- the isophorone diamine here denoted by IPDA (CAS 2855-13-2 ref 118184 supplied by Sigma Aldrich, M = 170.3 g/mol).
- the 4,7,10-trioxa-1,13-tridecanediamine here denoted by TTDA (CAS 4246-51-9 ref 369519 supplied by Sigma Aldrich, M = 220.3 g/mol).

The structure of chemicals is given in Fig. 1.

These components were mixed in stoichiometric ratio i.e. 100 g of DER 332 + 25 g IPDA and 100 g DER 332 + 29 g of TTDA. DSC scans of those mixtures display the classical exothermal peak with a specific cure enthalpy ca 400 J/g for both systems respectively and a maximal temperature of 117 °C for DGEBA/IPDA (consistently with [17,18]) and 114 °C for DGEBA/TTDA.

The systems were fully cured (as checked by DSC from the total disappearance of exothermal signal and by FTIR from the loss of 914 cm<sup>-1</sup> peak attributed to epoxide group) according the following conditions:

- curing at 60 °C during 2 h and post curing at 160 °C under vacuum for 2 h for DGEBA/IPDA
- curing at 60 °C during 1 h and post curing at 80 °C under vacuum for 2 h for DGEBA/TTDA.

In order to obtain 10–30  $\mu$ m films so as to avoid the so-called Diffusion Limited Oxidation [3–5]. The glass transition temperatures of the networks were found to be ca 166 °C for DGEBA/IPDA and 69 °C for DGEBA/TTDA. Their DSC thermograms (Fig. 12) are shown in Appendix and confirm they are fully cured.

### 2.2. Ageing

Thermal ageing under atmospheric air was performed in ventilated ovens (calibrated at  $\pm$  3 °C) at 110 °C, 150 °C and 200 °C. Films were periodically removed for analysis.

The influence of oxygen pressure on oxidation rate was studied by performing ageing tests in autoclaves under 50 bars of pure oxygen at 110  $^{\circ}$ C.



**Fig. 1.** Chemical structure of (a) bisphenol A diglycidyl ether (DGEBA), (b) isophorone diamine (IPDA) (c) 4,7,10-Trioxa-1,13-tridecanediamine (TTDA).

#### 2.3. Fourier transform infra-red spectroscopy (FTIR)

FTIR spectroscopy in transmission mode was performed on free standing films using a Frontier spectrophotometer (PerkinElmer) in the 550 to 4000 cm<sup>-1</sup> wavenumber range by averaging 16 scans with a 4 cm<sup>-1</sup> resolution. Spectra were interpreted using the Spectrum software (PerkinElmer) in order to determine the absorbance value from which the concentration of oxidation products was calculated with the Beer Lambert law:

$$A = \varepsilon_{\lambda} \times l \times C_{\lambda} \tag{1}$$

A being the absorbance (corrected by the baseline value),  $\varepsilon_{\lambda}$  (l/mol/cm) being the molar absorptivity taken equal to  $\varepsilon_{1660} = 470$  l/mol/cm for amides [9], and  $\varepsilon_{1730} = 350$  l/mol/cm for carbonyls [19], l (cm) the thickness of the film and  $C_{\lambda}$  (mol/l) the concentration of the considered species.

## 2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were made with a DSC Q1000 (TA Instruments). Samples with mass ranging between 3 and 5 mg and sealed in aluminum pans were heated from 0 °C to 250 °C at a 10 °C/min ramp under nitrogen flow (50 ml/min). Results were interpreted using TA Analysis software. DSC analyses were done to check the total cure of samples and to measure the value of the glass transition temperature of aged samples. T<sub>g</sub> values were measured during the second heating ramp (i.e. after having removed the thermal history of samples). Two samples of the same resin have been analyzed for each exposure time to control measurements reproducibility.

#### 3. Results

# 3.1. Effect of temperature on the stable oxidation products formation

The main changes induced by thermal oxidation are detected in the 1550-1850 cm<sup>-1</sup> wavenumber range for both systems (Fig. 2). An increase of 1656 cm<sup>-1</sup> peak is observed in DGEBA/IPDA as well as in DGEBA/TTDA. This peak is associated with the appearance of amide groups [6,9,12,20]. A band grows around 1725 cm<sup>-1</sup> for DGEBA/IPDA and around 1736 cm<sup>-1</sup> for DGEBA/TTDA. These bands are usually attributed to the vibration of carbonyl groups. Mechanisms responsible for the formation of oxidative products will be discussed in the next section.

The concentrations in each kind of oxidation products were assessed from Beer Lambert law and their changes were plotted versus time for each exposure conditions (Fig. 3, where the arrows correspond to the time at which samples cannot be handed anymore).

From Fig. 3, the following comments can be drawn:

- No significant induction period is witnessed for both systems whatever the exposure temperature, as commonly observed for comparable systems [9,21]. Oxidation rate is defined as the highest slope of each curve. At 150 °C and 200 °C, the maximal oxidation rate is equal to the initial rate whereas a slight auto acceleration is noticed at 110 °C and is more visible on DGEBA/ IPDA system.
- Oxidation rate values are reported in Table 1. It appears that the oxidation rate for amide groups formation is always equal or

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