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Thermal-oxidation of epoxy/amine followed by glass transition temperature changes

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ABSTRACT

Thermal oxidation of three epoxy resins differing by the nature of prepolymer (bisphenol A diglycidyl ether and 1,4-butanediol diglycidyl ether) and hardener (isophorone diamine and 4,7,10-Trioxa-1,13-tridecanediamine) was studied by monitoring changes in glass transition temperature using DSC. Results were discussed using the DiMarzio's approach in which parameters are estimated from an additive group contribution. This theory allowed a fair assessment of T_g values for unaged networks. During oxidation, epoxy networks were shown to undergo chain scissions occurring in great part in hydroxypropyl ether and isophorone groups. However, the exploitation of T_g changes showed the coexistence and even the predominance of crosslinking in materials having linear aliphatic segments. The DiMarzio's approach was used to discuss the possibility of intramolecular cyclization or intermolecular crosslinks which were shown to predominate. Crosslinks were tentatively justified from a mechanistic point of view and quantified depending on experimental conditions.

1. Introduction

Since they are designed for high temperatures applications as matrix for composites, most of the epoxy networks are made of a rigid epoxy and rigid hardener (for example DGEBA/DDS or DGEBA/DDM) [1–13]. Their degradation is very often studied by mass loss [4,6,8,10] which is clearly shown:

- to be associated to the chain scission induced by decomposition of hydroperoxides [7,8].
- to occur quasi instantaneously, since hydroperoxides formed in epoxy amine networks are unstable due to the vicinity of heteroatoms (see for example Table 4.15 vs Table 7.15 in Ref. [14]) which induces the short kinetic chains being an intrinsic characteristic of epoxy resins [8].

It is thus not surprising that mass losses exceeding 10% are measured during thermal ageing [4,6,8] which leads to shrinkage in the oxidized superficial layer in the case of thick samples [15,16].

Some studies also address the consequences of oxidation on the architecture of polymer networks. They show the depletion of glass transition i.e. that rigid networks (with T_g higher than 150 °C) undergo chain scissions [1,11,13,17].

This short literature review suggests the existence of a major or even exclusive chain scission process leading to the loss of mass and ultimate mechanical properties. However, those phenomena were mainly evidenced in rigid epoxy/diamine systems where 2-hydroxypropyl ether is possibly the only reactive site. The case of flexible epoxies (T_g < 100 °C) [18,19] was more scarcely studied so that we were interested in investigating:

- if the above scenario is common to all epoxy networks, or if there are some peculiarities for epoxies with aliphatic linear groups.
- if chain scissions exclusively occur or could they be counterbalanced by crosslinking events ?
- if there is an influence of external parameters (temperature, oxygen pressure) on the consequences of oxidation (at molecular scale i.e. the consequences of the formation of carbonyls or amides), and on the architecture of epoxy networks and later on its thermomechanical properties.

To answers those questions, our investigations will base on a series of epoxy/amine networks differing by their content in aliphatic sequences [20]. Their thermal degradation will be studied at several temperatures and oxygen pressures. A modeling

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approach based on DiMarzio's equation [21] will be first checked on unaged networks and then adapted for taking into account the presence of chain scissions and crosslinks. It will be used to quantify the changes at macromolecular level.

2. Experimental

2.1. Materials

Epoxy/diamine systems were synthesized using the resins and hardeners shown in Fig. 1:

- A Diglycidyl ether of bisphenol A DER 332 resin named here DGEBA (CAS 1675-54-3 – ref 31185 supplied by Sigma Aldrich) has a degree of polymerization n close to 0 and a number average molecular mass equal to 340 g mol^{-1}.
- A Diglycidyl ether of 1,4-butanediol resin named here DGEBU (CAS 2425-79-8 ref 220892 supplied by Sigma Aldrich, M = 202.25 g mol^{-1}).
- An isophorone diamine hardener named here IPDA (CAS 2855-13-2 – ref 118184 supplied by Sigma Aldrich, M = 170.3 g mol^{-1}).
- A 4,7,10-Trioxa-1,13-tridecanediamine hardener named here TTDA (CAS 4246-51-9 – ref 369519 supplied by Sigma Aldrich, M = 220.3 g mol^{-1}).

By combining those resins and hardeners, three systems were chosen: DGEBA/IPDA, DGEBA/TTDA, DGEBU/IPDA. These components were mixed in stoichiometric ratio and fully cured as checked by DSC from the total disappearance of exothermal signal and by FTIR from the total disappearance of epoxide peak at 914 cm^{-1}. Curing enthalpies, curing cycles, final glass transition temperatures are listed in Table 1. In order to avoid the so-called Diffusion Limited Oxidation, films thinner than 100 μm were made using a heating press (Gibrite Instruments).

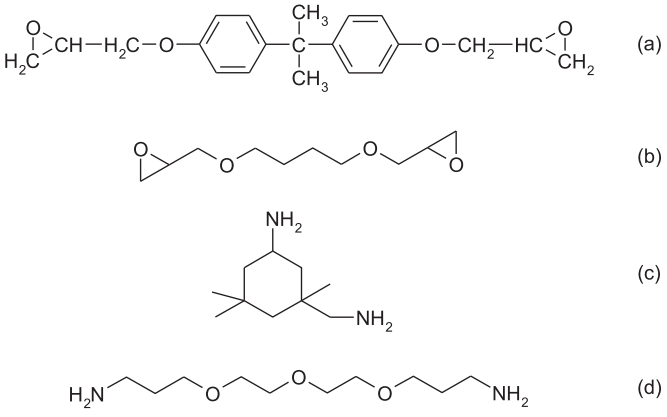

Fig. 1. Chemical structure of monomers DGEBA (a), DGEBU (b), IPDA (c), TTDA (d).

2.2. Ageing

Thermal ageing under atmospheric air was performed in ventilated ovens (calibrated at ± 3 °C) at 110 °C and 200 °C.

The influence of oxygen pressure was studied by performing ageing tests in autoclaves under 50 bars of pure oxygen at 110 °C.

2.3. Characterization

2.3.1. Oxidative products concentrations

FTIR spectroscopy in transmission mode was performed on free standing films using a Frontier spectrophotometer (PerkinElmer) in the 550 to 4000 cm^{-1} wavenumber range by averaging 16 scans with a 4 cm^{-1} resolution. Spectra were interpreted using the Spectrum software (PerkinElmer) in order to determine the absorbance value from which the concentrations in main oxidation products (carbonyls and amides) was calculated according to the method defined elsewhere [20].

2.3.2. Glass transition measurement

Differential scanning calorimetry measurements were made with a DSC Q1000 (TA Instruments). Samples with mass ranging between 3 and 5 mg sealed in aluminum pans were heated from 0 °C to 250 °C at a 10 °C min^{-1} ramp under nitrogen flow (50 ml min^{-1}). 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_g values were measured during the second heating ramp (i.e. after having removed the thermal history of samples) at the inflexion point of the thermogram. Measurements were duplicated to control measurements reproducibility.

3. Results

The measurement of glass transition temperature of the networks is particularly interesting since it is related to the concentration and the flexibility of elastically active chains (those two quantities will be more precisely defined in the “Discussion” section). T_g changes after ageing under air at 110 and 200 °C are given in Fig. 2. It can be observed that:

- DGEBA/IPDA displays a significant T_g decrease under air, suggesting that oxidation induces an increase in the flexibility of segments and/or scissions of elastically active chains.
- DGEBA/TTDA displays a significant T_g increase under air, suggesting that oxidation induces a decrease in the flexibility of segments and/or crosslinking.
- DGEBU/IPDA shows first a slight T_g decrease but reactions responsible for an increase of T_g seem to occur at high degradation level which means that they involve whether oxidation by products or sites with a low reactivity that are « activated » by a sort of co-oxidation process.

Table 1
Characteristics of the epoxy/amine networks.

Epoxy/amine system	Mass of hardener for 100 g of epoxy	Crosslink exotherm	Exotherm onset temperature	Curing cycle	Glass transition temperature
DGEBA/IPDA	25 g	563 J g^{-1} (0.47 J mol^{-1})	80 °C	2 h 60 °C in oven and post cure of 2 h in vacuum at 160 °C	166 °C
DGEBU/IPDA	42 g	400 J g^{-1} (0.98 J mol^{-1})	85 °C	2 h 85 °C in oven and post cure of 3 h in vacuum at 85 °C	60 °C
DGEBA/TTDA	29 g	395 J g^{-1} (0.44 J mol^{-1})	76 °C	1 h 60 °C in oven and post cure of 3 h in vacuum at 80 °C	69 °C