

Effects of thermal oxidation on an epoxy–amine thermoset studied by mechanical spectroscopy

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ABSTRACT

The structure and behavior changes of an epoxy–amine thermoset (glass transition around 478 K) oxidized at 423 K in air and under oxygen pressure (0.5 MPa) for various durations have been investigated mainly by DMA (dynamic mechanical analysis). After oxidation the strength of the β secondary relaxation (located at $T_{\beta} \approx 210$ K at 1 Hz) decreases, which leads to an increase in the storage modulus above T_{β} . It is thus an internal antiplasticizing effect due to oxidation; this effect explains the unexpected increase in the elastic modulus of indentation with oxidation time. The specimens oxidized in air are characterized by two glass transitions, one corresponding to the glass transition of the virgin material (478 K at 1 Hz), and the other one, at lower temperature (468 K at 1 Hz), being associated with the oxidized part of the sample. The samples oxidized under oxygen pressure are characterized by a new glass transition located at even lower temperature (450 K at 1 Hz) and attributed to “saturated” oxidized zones near the surface. Therefore, the oxygen pressure does not merely have an accelerating effect.

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1. Introduction

Organic matrix composites, especially carbon fiber/epoxy matrix composites, are currently used in aeronautics, where they could be employed for future applications at high temperature and consequently undergo thermal oxidation. This thermal oxidation induces a catastrophic acceleration of the damage mechanisms of carbon/epoxy composites. This damage is mainly due to matrix oxidation [1].

Thermal oxidation of a bulk polymer leads to the existence of a superficial oxidized layer and, therefore, to a heterogeneous material with a skin–core structure linked with oxygen diffusion inside the material [2]. This has notably been observed for epoxy–amine thermosets [3]. Oxidation involves a weight loss and a density increase, which leads to a superficial shrinkage, and also an embrittlement of the oxidized layer [4]. At the level of the network of thermosets, and more particularly of the epoxy–amines, thermo-oxidation mainly leads to chain scissions [5], which implies a decrease in the glass transition temperature (T_g).

A study in progress at LMPM aims to establish a predictive model of the first damage in carbon/epoxy–amine composites, which require more thorough characterization of the neat matrix oxidation. Oxidation of the epoxy–amine thermoset has been realized

at 423 K in air and under oxygen pressure (0.5 MPa) to accelerate the process [6]. The present work aims to characterize, by dynamic mechanical analysis (DMA), the effects of thermal oxidation, in air and under oxygen pressure, on this epoxy–amine thermoset.

2. Experimental procedure

2.1. Material

The studied thermoset polymer is an industrial epoxy–amine (977-2) obtained by mixing two aromatic epoxy–prepolymers (DGEBF/TGPAP) cross-linked with an aromatic diamine (DDS). Plates 1 mm thick, provided by EADS Innovation Works, were fabricated according to a specific polymerization cycle: a 3-h gelation period at 423 K and a 2-h curing at 453 K under a pressure of 0.7 MPa, followed by a post-curing at 483 K under vacuum for 1.5 h to achieve a cross-linkage as complete as possible.

Before any treatment or testing, all epoxy–amine samples were dried at 373 K for 15 days under primary vacuum. This dried thermoset, called virgin material, is characterized by a main mechanical relaxation at about 478 K (at 1 Hz) corresponding to the glass transition. Two secondary relaxations are observed (at 1 Hz): the β relaxation located at about 210 K and another weaker one around 320 K. Epoxy–amine samples were aged at 423 K: some in air (atmospheric pressure) for 600 h and 1000 h and others under oxygen or nitrogen pressure (0.5 MPa) for different durations (18 h, 48 h, 96 h and 430 h).

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2.2. Experimental techniques

Dynamic mechanical experiments were performed with a TA Instrument Q800 DMA in single cantilever bending mode, in which mainly the external layers are strained. Experiments were performed at 1 Hz with a 0.02% strain, between 133 K and 523 K with a temperature ramp of 2 K/min. The tested parallelepiped samples had a 17.5 mm free length, a 1 mm thickness and a 10 mm width. This technique allows the determination of the storage and loss moduli (noted E' and E'' , respectively); the glass transition and β relaxation peaks were identified and analyzed from the loss modulus E'' curve.

An instrumented Ultra-Micro Indentation (UMI) device, Fischerscope H100C, was used to determine, at room temperature, the elastic indentation modulus (EIT) with a micrometer spatial resolution. The specific sample preparation, as well as the principle and conditions of the UMI measurements, are detailed in another paper [7].

3. Results and interpretation

It must be noticed that aging treatments performed under 0.5 MPa of nitrogen in the same conditions as the aging under 0.5 MPa of oxygen show no modification in the DMA spectra and EIT values in comparison with virgin material. Therefore, all the observed effects shown in this paper have to be ascribed to oxidation.

3.1. Influence of oxidation on the β relaxation/Internal antiplasticizing effect

The epoxy–amine thermoset is characterized by a β secondary relaxation located at $T_{\beta} \approx 210$ K at 1 Hz. This relaxation, observed in all epoxy–amine networks, mainly involves motions of the hydroxypropylether units $-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O}-$ [8–10]. It is characterized by a broad composite mechanical relaxation peak: the low-temperature part should involve isolated movements whereas the high-temperature part should correspond to short-range cooperative motions [9].

After oxidation in air or under oxygen pressure, the strength of the β relaxation decreases. Fig. 1 shows E' and E'' spectra of epoxy–amine samples oxidized under 0.5 MPa of oxygen for various durations. With increasing oxidation time, the strength of the

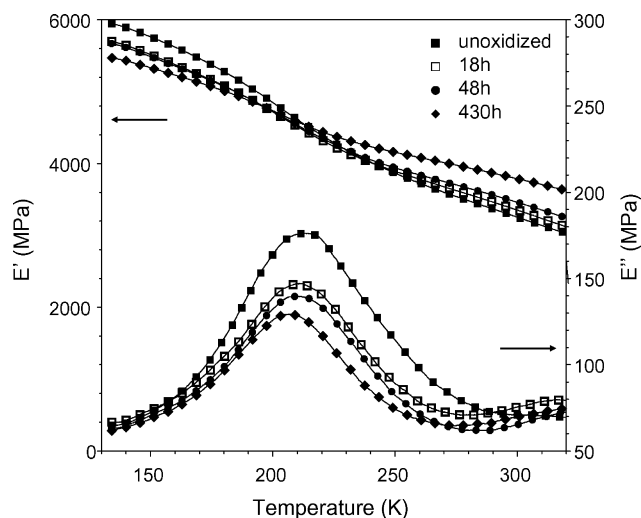


Fig. 1. β relaxation: storage modulus E' and loss modulus E'' versus temperature at 1 Hz for increasing oxidation time at 423 K under oxygen pressure of 0.5 MPa.

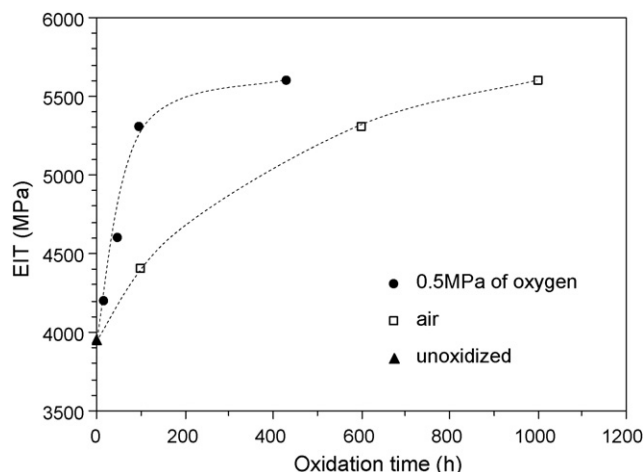


Fig. 2. Elastic indentation modulus (EIT) at a depth of 20 μm at ambient temperature versus oxidation time for material oxidized at 423 K in air and under oxygen pressure (0.5 MPa).

relaxation peak decreases; the high-temperature part of the peak is reduced whereas the low-temperature part is not affected. Therefore, as shown in Fig. 1, the amplitude of the storage modulus drop related to this relaxation also decreases with increasing oxidation duration; this leads to an increase in the storage modulus above T_{β} and especially at ambient temperature. These effects of oxidation on the β relaxation are accompanied by a decrease in the glass transition temperature when compared with the unoxidized thermoset (cf. Fig. 3). These phenomena are characteristic of an internal antiplasticization [11]. Internal antiplasticization has notably been observed when the cross-link density of epoxy–amine networks decreases [10–11]. In the present study, chain scissions due to oxidation lead to a less densely linked network.

This internal antiplasticizing effect therefore explains the unexpected increase in the elastic modulus of indentation at 293 K at a depth of 20 μm with the oxidation time for samples oxidized at 423 K in air and under oxygen pressure (Fig. 2). This increase in EIT near the material surface therefore indicates a superficial oxidation depending on the oxidation time.

Moreover, Fig. 2 shows an accelerating effect of the oxygen pressure regarding the superficial oxidation.

3.2. Influence of oxidation on the main relaxation (glass transition)

3.2.1. Oxidation under oxygen pressure

The influence of the oxidation time under 0.5 MPa of oxygen on the main relaxation is shown in Fig. 3. After 18 h of oxidation, DMA spectrum is characterized by a single glass transition peak (468 K at 1 Hz) located at lower temperature than for the unoxidized material. This peak corresponds to the glass transition of the oxidized zone. After 48 h of oxidation, there are two components in the E'' peak: the previous peak is strongly reduced and a new component located at lower temperature (450 K at 1 Hz) appears. It is noticeable that this low-temperature component already exists for the 18-h oxidation as a weak shoulder. With increasing oxidation time, this component increases in intensity to the detriment of the other component at higher temperature. After 430 h of oxidation, the relaxation peak is almost reduced to this low-temperature component at 450 K with a slight shoulder at higher temperature.

This component is located at low temperature (450 K at 1 Hz) in comparison with the T_g of the unoxidized material and so can be attributed to the glass transition of highly oxidized zones; this low T_g implies that there were many chain scissions and that the net-

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