

## Multi-scale and multi-technical analysis of the thermal degradation of poly(ether imide)



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### ABSTRACT

The thermal degradation of PEI has been studied in wide ranges of temperature (between 180 and 250 °C) and oxygen partial pressure (between 0.21 and 50 bars). On one hand, the chemical ageing mechanisms have been analysed and elucidated by FTIR spectrophotometry and by differential calorimetry (DSC) on sufficiently thin PEI films (between 10 and 60 μm thickness) to be totally free of the effects of oxygen diffusion. As expected, and by analogy with other aromatic polymers of similar chemical structure, oxidation occurs preferentially on the methyl groups of the isopropylidene unit of the bisphenol A part, thus causing the disappearance of their characteristic IR absorption band at 2970 cm<sup>-1</sup> and the growth of a new IR absorption band at 3350 cm<sup>-1</sup>, attributed to alcohols. In addition, oxidation leads successively to a relative predominance of chain scissions and crosslinking, resulting in a non-monotonic change of T<sub>g</sub>. On the other hand, the consequences of oxidation on the elastic properties have been analysed and elucidated by micro-indentation on polished cross-sections of PEI plates of 3 mm thickness. The diffusion control of oxidation leads to the development of profiles of Young's modulus within the sample thickness, which correlate perfectly with the changes in chemical structure determined by FTIR spectrophotometry. However, the increase in Young's modulus in the superficial oxidized layer is not the direct consequence of oxidation but of a physical ageing.

### 1. Introduction

The competition in the aeronautical market depends both on economic and ecological issues such as the reduction of costs, on-board weight and fuel consumption. That is the reason why since its origin, the aerospace industry has been looking for new lighter materials with high thermo-mechanical properties. In this context, the use of composite materials made of organic matrix reinforced with glass or carbon fibers (OMC) has been amplified with the aim of progressively replacing the metallic materials. Initially designed for the fabrication of structural parts (wing, tail, fuselage, etc.), OMCs are now being considered for applications in increasingly harsh thermo-chemical environments, such as areas near heat sources (typically in environments of aircraft engine). However, they will be used only if their long-term durability is clearly demonstrated.

The use of thermoplastic matrices has several advantages, such as the integration of specific functions, but also the assembly of parts of the same or different nature. Among the thermoplastic matrices that can meet the aeronautical specifications, poly(ether imide) (PEI) appears as a serious candidate. Indeed, it is an amorphous polymer with a highly aromatic structure giving it not only high thermomechanical

performances (T<sub>g</sub> ≈ 217 °C), but also a high chemical resistance to the most usual solvents (acetone, toluene, ethyl acetate, etc.) and aeronautical fluids (in particular, Skydrol). The thermal degradation of PEI has been little studied in the literature, almost exclusively in the rubbery state above 300 °C in inert or in slightly oxygenated atmosphere (typically in air).

The oxidation of PEI, but also of aromatic polymers with a similar chemical structure, occurs mainly at the methyl groups of the isopropylidene unit of the bisphenol A part, which contains the most labile H atoms [1,2]. Oxidation leads to the formation of a wide variety of degradation products detected by FTIR spectrophotometry. These products include carbonyls, especially aromatic (at 1690 cm<sup>-1</sup>) and aliphatic ketones (1724 cm<sup>-1</sup>) and anhydrides (1840 and 1860 cm<sup>-1</sup>), as well as hydroxyls (3553 and 3514 cm<sup>-1</sup>) [2–6]. The disappearance of the IR absorption bands which are characteristic to the isopropylidene unit (C-CH<sub>3</sub> bond at 1186 cm<sup>-1</sup>) and methyl groups (C-H bond at 2870, 2933 and 2970 cm<sup>-1</sup>) has been also observed [3,5].

Mechanisms of chain scission were also proposed to explain the formation of the wide variety of volatile products. Chain scissions occur at the C-C bonds of the isopropylidene unit, but also at the ether bonds

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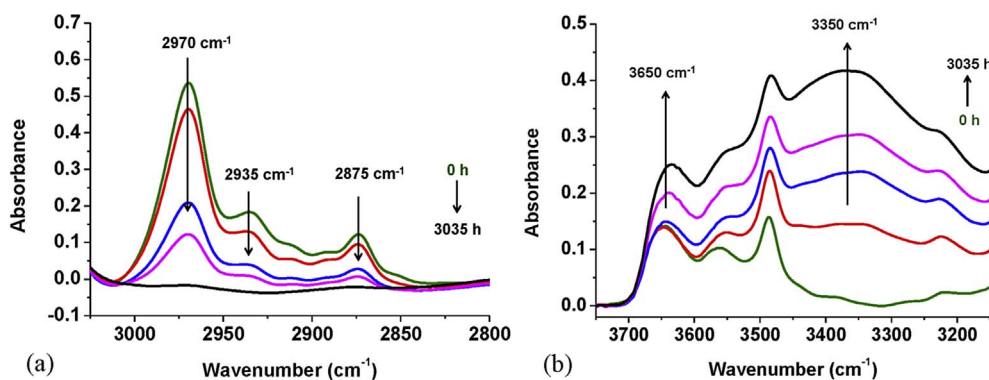


Fig. 1. Changes in the regions of C-H (a) and O-H bonds (b) in the FTIR spectrum of PEI during its thermal ageing in air at 250 °C.

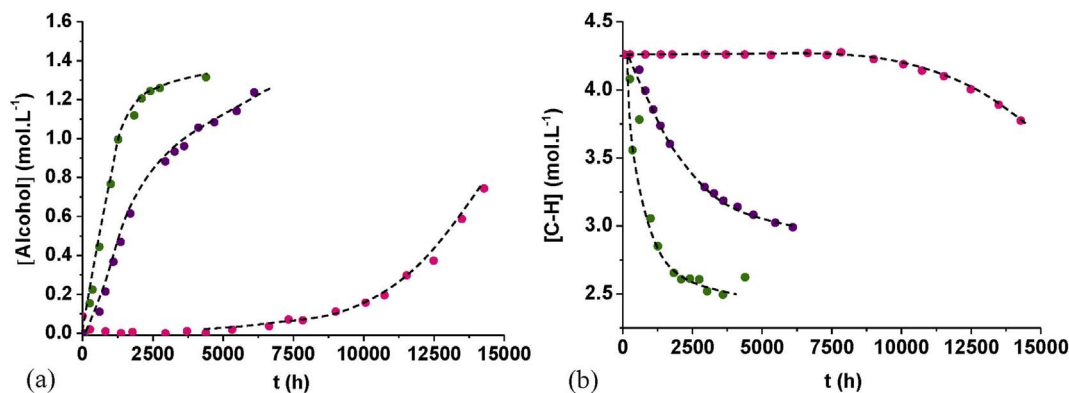


Fig. 2. Changes in the concentration of alcohols (a) and C-H bonds (b) during the thermal ageing of PEI in air at 200 (in pink), 220 (violet) and 250 °C (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

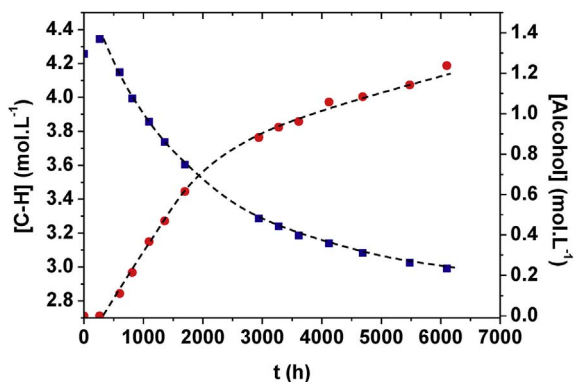


Fig. 3. Comparison between the changes in the concentration of C-H bonds (■) and alcohols (●) during the thermal ageing of PEI in air at 220 °C.

between the phenyl and phthalimide rings [1,6–9]. They predominate largely over crosslinking at the beginning of exposure, but they become finally negligible in comparison to crosslinking at longer term [1,5,7,10,11]. The bimolecular recombination of methylene radicals would be the main source of crosslinking.

The present article provides a detailed multi-scale and multi-technical analysis of the thermal degradation of PEI at lower temperatures and higher partial oxygen pressures than those studied until now in the literature. A peculiar attention is paid to the consequences of degradation on two key thermomechanical properties in the aeronautical field: the changes in the glass transition temperature and Young's modulus.

## 2. Experimental

The material under study is the PEI ULTEM® 1010 supplied by SABIC company in the form of pellets. Plates of 3 mm thickness were

molded by an injection machine from these pellets by the Pôle Européen de Plasturgie (PEP) located in Oyonnax (France). The plates were then cut with a LEICA RM2255 microtome in order to obtain sufficiently thin films (typically between 10 and 60  $\mu\text{m}$  thickness) for ensuring a homogeneous oxidation throughout their thickness. The oxidation kinetics of PEI was studied in the rubber state at 220 and 250 °C, but also in the glassy state at 180 and 200 °C, under oxygen partial pressures ranged between 0.21 bar (in air-ventilated ovens regulated at  $\pm 1$  °C) and 50 bars (in autoclaves). All the films were periodically removed from the ageing chambers and cooled to room temperature in a desiccator containing silica gel for preventing any moisture recovery prior to being characterized. It is noteworthy that much thicker samples (plates of 3 mm thickness) were also exposed in air-ventilated ovens at 220 and 250 °C in order to put in evidence the development of oxidation profiles. In all cases, the consequences of oxidation were analysed by several complementary laboratory techniques from the molecular to the macroscopic scales, via the macro-molecular and microscopic scales.

The changes in molecular structure were followed by FTIR spectrophotometry in a transmission mode. The FTIR spectra of the PEI films were measured before and after ageing for detecting and quantifying the disappearance of chemical groups initially present in the PEI matrix and the formation of the main oxidation products. The analyzes were carried out with a Perkin Elmer Frontier apparatus between 400 and 4000  $\text{cm}^{-1}$ , after having averaged the 16 recordings obtained with a minimum resolution of 4  $\text{cm}^{-1}$ . The thermal ageing of PEI leads to two major changes in the FTIR spectrum (Fig. 1). On the one hand, it can be seen the decrease in intensity of the IR absorption bands at 2970, 2935 and 2875  $\text{cm}^{-1}$ , which are mainly characteristic of the C-H bonds of the  $-\text{CH}_3$  groups of the isopropylidene unit in the early periods of exposure, but also of the C-H bonds of the  $-\text{CH}_2-$  groups formed during thermal ageing at longer term (see Fig. 4). On the other hand, it is observed the appearance and growth of a wide IR absorption band

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