

Multi-scale and multi-technique analysis of the thermal degradation of poly(ether ether ketone)



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ABSTRACT

The thermal degradation of PEEK has been studied in rubbery state in wide ranges of temperature (between 180 and 320 °C) and oxygen partial pressure (between 0.21 and 50 bars). On one hand, the thermal ageing mechanisms have been analysed and elucidated by FTIR spectrophotometry and by differential scanning calorimetry (DSC) on sufficiently thin PEEK films (between 10 and 60 μm thickness) to be totally free of the effects of oxygen diffusion. Oxidation occurs on aromatic rings causing the growth of five new IR absorption bands centered at 3650, 3525, 1780, 1740 et 1718 cm⁻¹ and attributed to the stretching vibrations of the O-H bonds of phenol and benzoic acid, and the C-O bonds of benzoic anhydride, phenyl benzoate and fluorenone respectively. In addition, oxidation leads to a large predominance of crosslinking over chain scissions resulting in a sharp increase of T_g. This reduction in molecular mobility prevents the annealing of PEEK, in particular when the temperature of exposure is higher than the onset of the melting endotherm. 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 PEEK 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 crystallinity and macromolecular architecture determined at lower scales. The validity of the Tobolsky's relationship is demonstrated.

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 ether ketone) (PEEK) appears as a serious candidate. Indeed, it is a semi-crystalline

polymer with a highly aromatic structure giving it not only high thermo-mechanical performances (glass transition temperature and melting point are T_g ≈ 153 °C and T_m ≈ 343 °C respectively), 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 PEEK has been studied under inert or slightly oxygenated atmosphere (typically in air), mostly in molten state (between 340 and 485 °C), but rarely in rubber state (between 300 and 320 °C) and never, to our knowledge, in glassy state.

The oxidation of PEEK occurs on the only hydrocarbon groups available in the monomer unit, i.e. on the aromatic rings, in spite of the very low lability of their H atoms. Indeed, the dissociation energy of the aromatic C-H bond is of the order of 465 kJ mol⁻¹, against 393 and 378 kJ mol⁻¹ for the methylenic and methynic C-H bonds respectively [1]. Above 400 °C, oxidation would be mainly initiated by the breakdown of the ether and ketone bonds of the monomer unit [2–4]. It leads to the disappearance of the ketone groups (at 1653 cm⁻¹), but also to the formation of a wide variety of degradation products detected by FTIR spectrophotometry. They include macromolecular products such as phenols (between 3400 and 3700 cm⁻¹), phenyl benzoate (at

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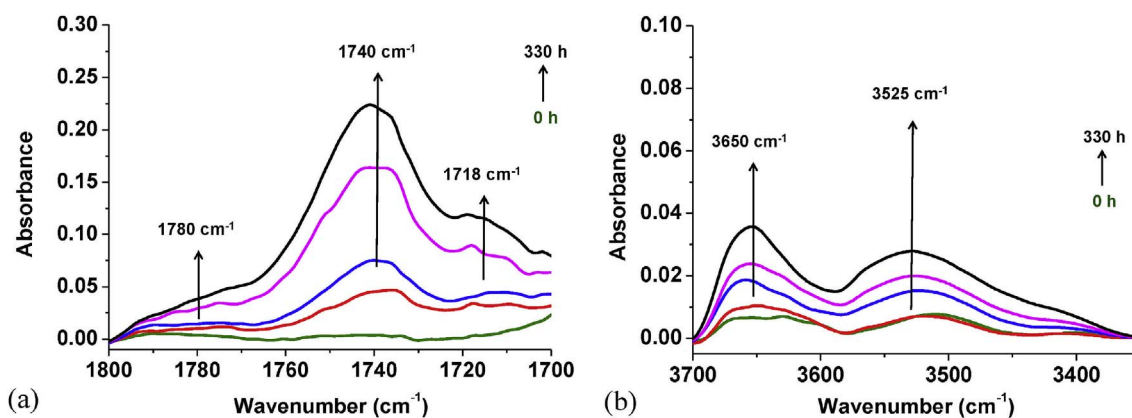


Fig. 1. Changes in the regions of C=O (a) and O-H bonds (b) in the FTIR spectrum of PEEK during its thermal ageing in air at 300 °C.

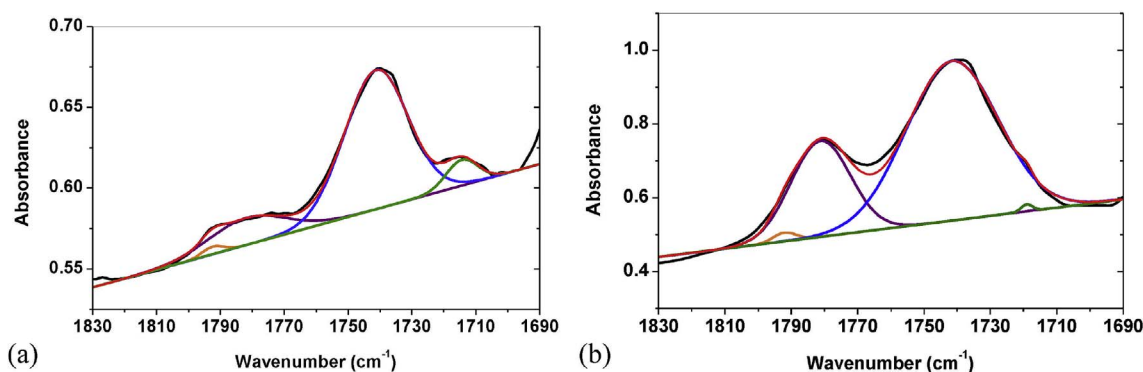


Fig. 2. Deconvolution of the region of C=O bonds in the IR spectrum of PEEK after 324 h of exposure at 300 °C under 0.21 bar of oxygen (a) and after 196 h of exposure at 250 °C under 10 bars of oxygen (b).

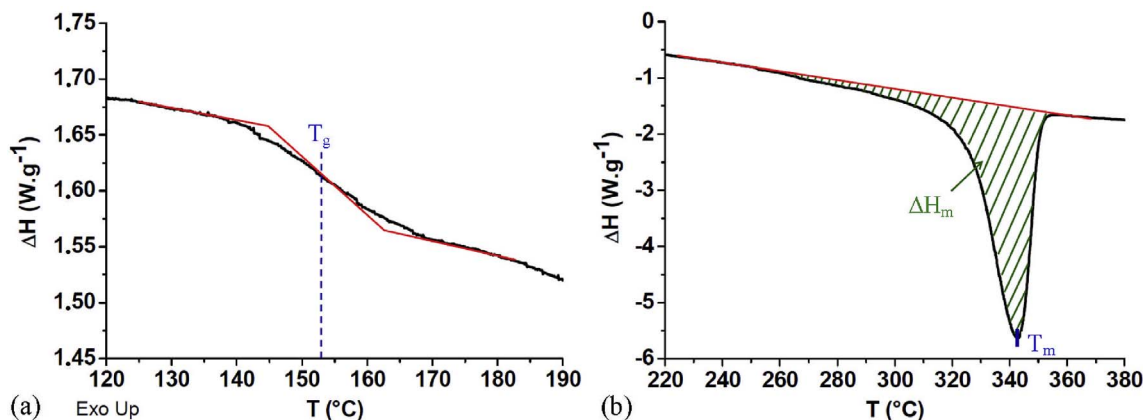


Fig. 3. DSC thermogram of unaged PEEK zoomed around the glass transition temperature (a) and the melting endotherm (b). Determination of T_g , T_m and ΔH_m .

1739 cm^{-1}) and fluorenone (1711 cm^{-1}) [2–4], but also many volatile compounds [4–6]. Hardly detectable below 430 °C, volatile compounds have been clearly evidenced above 450 °C by thermogravimetry coupled with gas chromatography (TGA-GC) or mass spectrometry (TGA-MS). They include quinones, phenols, carbon monoxide and dioxide, benzene, but also aromatic ethers and ketones [4,6].

Mechanisms which involve the rearrangement of phenoxy and acyl radicals, resulting from the breakdown of the ether and ketone bonds respectively, have been proposed to explain the formation of most degradation products. However, these purely thermolytic mechanisms do not explain the acceleration of the oxidation kinetics when raising oxygen partial pressure. Between 360 and 460 °C, a second important source of radicals, which may also explain the accumulation of several degradation products, is the unimolecular decomposition of

hydroperoxides [7].

Changes in the macromolecular architecture of PEEK have been also detected by steric exclusion chromatography (SEC or GPC) [5], and by viscometry in solution [3] or in molten state [5,7,8]. Between 300 and 485 °C, crosslinking predominates largely over chain scissions, this relative predominance being amplified when raising the oxygen partial pressure. Crosslinking causes the increase in the molecular weight [3,5,7,8], gel fraction [3,4] and glass transition temperature [5,8,9]. The most probable crosslinking mechanism is the bimolecular recombination of phenyl radicals [3–6].

Finally, the changes in the crystalline morphology of PEEK have been evidenced by differential calorimetry (DSC). Between 380 and 440 °C, crosslinking limits crystallization when PEEK is cooled to room temperature from its molten state, resulting in a decrease in both the

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