The effects of moisture and physical ageing on the elastic behaviour of a structural epoxy

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SUMMARY

Three point bending tests indicate that elastic modulus diminishes linearly with moisture content, at a rate dependent of the ageing time. On the other hand, it seems that any curve modulus versus time of ageing for specific moisture content can be vertically shifted to coincide with other curves. A comparison of the DSC and bending tests data in the present work suggests that the ageing rate constants are not the same.

Keywords: Theromosetting resin; physical ageing; higrothermal effects; mechanical properties.

INTRODUCTION

The cooling of an epoxy resin from its rubbery state to a temperature lower than the glass transition temperature results in a non-equilibrium glassy state. Under constant external conditions, this glassy state spontaneously evolves toward a temporally distant equilibrium, via slow molecular motions. During this process, known as structural relaxation or physical ageing, the physical and mechanical properties change continuously [1]. A deep knowledge of this phenomenon is of significant practical value considering the widespread application of epoxy resins as structural materials and the need of optimum long term material performance. Hence, a huge amount of studies have been devoted to physical ageing in the past years, but only few papers addressed the effect of water absorption on the ageing behaviour [2]. The present paper is focused on the influence of moisture on the physical ageing of an epoxy resin, observed in terms of a change of enthalpy and a change in the elastic modulus as a function of ageing time, under constant hygrothermal conditions.

Before the ageing experiments, the specimens were dried and rejuvenated at 120ºC for 30 minutes, in order to erase any previous thermal history. Then, the specimens were placed in several constant relative humidity atmospheres, at 50ºC: 0%, 30.5%, 45.4%, 74.4%, 84.6% and 95.6%. When the steady state of moisture content (M_e) was achieved, the specimens were subjected to a second rejuvenation and quenched to the ageing temperature, thus defining the initial ageing time. Afterwards, the experimental protocol follows on specimens with several constant moisture contents at 50ºC isothermal ageing, over 350 hours.

Fast Fourier infrared spectroscopy analysis was performed on a UNICAM system and the results confirmed the absence of chemical effects during the environmental exposure programme. A SETARAM DSC-131 differential scanning calorimeter was used to follow the evolution of fictive temperature (T_f) and enthalpy relaxation (ΔH) with the ageing time (t_a). The enthalpy lost on ageing is an exponential function of ta which can be described by the empirical equation of Cowie-Ferguson. Moreover, the equilibrium value of ΔH (ΔH_∞) reduces linearly with the increase of M_e (Figure 1).

Three point bending tests were performed using a Micro Tester (INSTRON) testing machine. The results indicate that elastic modulus (E) diminishes linearly with M_e, at a rate dependent of the ageing time (Figure 2). On the other hand, E increases with t_a according to a Cowie-Ferguson type law and it seems that any curve E -t_a for a moisture content M_e can be vertically shifted to coincide with other curves.

A comparison of the DSC and bending tests data in the present work suggests that the ageing rate constants are not the same. In addition, the results of calorimetric and mechanical tests proved the effectiveness of conditioning procedure to uncouple the moisture effects (i.e. plasticization effects) from the physical ageing effects.

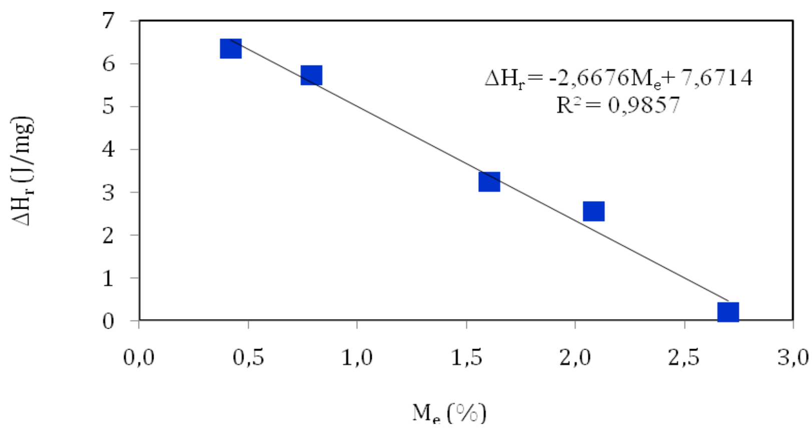

Figure 1 Dependency of $\Delta H\infty$ with M_e.

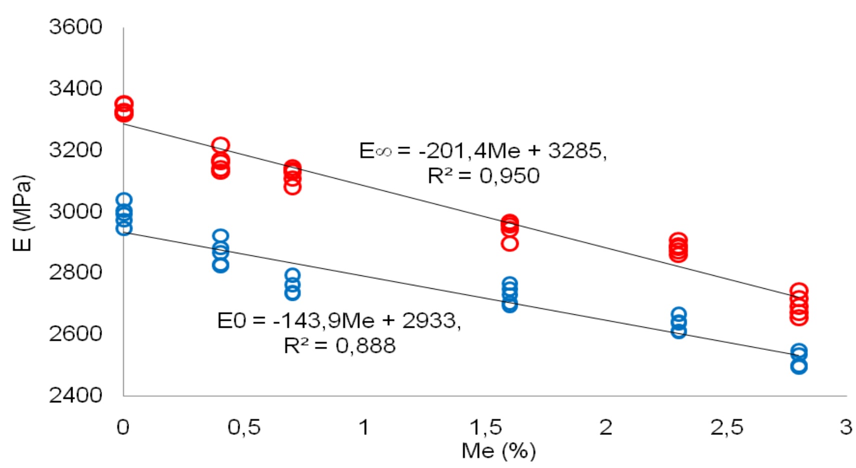

Figure 2 Evolution of E with the M_e (E_0: unaged elastic modulus; E_∞: full aged elastic modulus)..

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