

Oxidative Ageing of Polymers

Jacques Verdu







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General Introduction

Why oxidation?

The yellowing of a polyester-fiberglass hull, the crumbling of paint, the development of a purple coloration at the surface of a PVC extrudate for building are all manifestations of oxidative ageing of polymers. These are examples of changes in the visual aspect of the materials, which may have significant financial consequences but which do not, in themselves, pose a threat to the safe use of the system in question. The embrittlement of a carbon-polyimide part functioning at 200°C in an airplane engine, the hardening of a polybutadeine matrix rocket propeller, and the cracking of a polyethylene electrical cable sheath in a nuclear plant, are also manifestations of oxidative ageing of polymers, but here the resulting failures could have grave consequences on every level. Predicting failures is the main objective of ageing studies. What fails is a system, a structure (in the broader sense). In certain cases, this failure is related to an unforeseen change in the operating conditions (an accident, a fire, etc.). In others, it is related to an inadequate knowledge of the system's capacity to withstand the mechanical loads to which it is subjected (creep, fatigue, etc.). These failures may also result from two incompatible materials being brought into contact, or one material coming into contact with incompatible fluids. Here, we look only at the case of a system failure resulting from the change in the properties of one of its constituent materials, and that change resulting from that material interacting with oxygen. We shall focus on deterministic approaches to the problem, i.e. cases where the system failure can be associated more-or-less accurately with a critical structural state of the material, or at the very least with a critical value of a property of the material. Why limit ourselves to the study of oxidation? For the simple reason that if we lived in a neutral atmosphere, 99% of thermal or photochemical ageing problems would disappear, with the lifespan of polymers being many times higher than it is in the presence of oxygen. However, in many cases oxidation takes place alongside other types of ageing, and there may be significant interplay between these different phenomena. For example,