

Effect of peroxide ratio on crosslinking of cable materials

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ABSTRACT

Cross-linking by dicumyl peroxide of three ethylene-propylene terpolymers containing a similar fraction in ethylidene norbornene units (EPDM-ENB) was studied by real-time differential scanning calorimetry (DSC) and Fourier transform infrared spectrophotometry (FTIR). DSC shows clearly that crosslinking rate is an increasing function of peroxide concentration. However, the fully network structure seems to be peroxide concentration independent. FTIR spectrophotometry confirms the thermal decomposition of peroxide into acetophenone, leading to a dramatic decrease in the double bond concentration, as previously observed in literature. However, the complete crosslinking mechanism remains to be established.

KEYWORDS

Ethylene-propylene terpolymer, ethylidene norbornene, dicumyl peroxide, differential scanning calorimetry, Fourier transform infrared spectrophotometry, cross-linking, glass transition temperature.

INTRODUCTION

Monitoring and predicting the durability of critical polymeric parts in nuclear power plants is a crucial issue for EDF. The main objective is to propose a new lifetime prediction approach allowing anticipating the problem of obsolescence of polymer formulations leading, in general, to heavy and costly campaigns of experimental tests.

The partnership of EDF with "ARTS ET METIERS PARISTECH" during the last decade resulted in the development of a kinetic model for lifetime prediction of electric cable insulators and sheaths made of polyethylene or ethylene-propylene copolymers (EPR) containing a high fraction of ethylene units (typically higher than 70 wt%). Today's challenge is to extend this model to peroxide crosslinked ethylene-propylene terpolymers (EPDM) containing a residual fraction of insaturations.

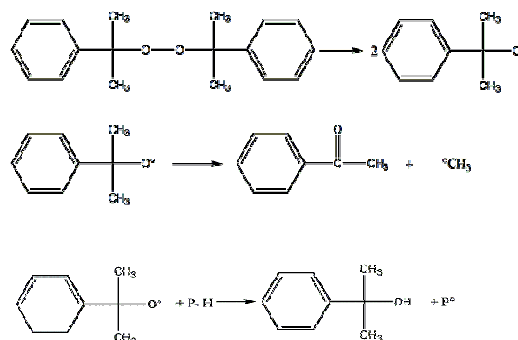
Thus, an accurate lifetime prediction requires a precise knowledge of initial structure of EPDM networks. On one hand, double bonds can readily react with existing radicals and anticipate the ageing. On the other hand, the presence of residual peroxide would initiate an additional localized degradation, for instance at the vicinity of filler-matrix interfaces [1].

The crosslinking of EPR has been intensively studied in the literature [2-6]. It is now well established that reactive sites are both the methinic and methylenic carbons. In the case of EPDM, however, two additional highly reactive sites must be privileged: allylic carbons and double bond.

The crosslinking by dicumyl peroxide begins by the homolytic scission of its O-O bond [7]. This thermal decomposition is followed by a series of rearrangement

reactions leading either to the formation of acetophenone and methyl radical, or to cumyl alcohol [8] (Scheme.1). The ratio between the cumyl alcohol and acetophenone concentrations seems to be substrate independent for a same hydrocarbon family [8,9]. However, this ratio increases with the substrate reactivity when two different hydrocarbon families are compared. In addition, the fraction of dicumyl peroxide converted into cumyl alcohol is a decreasing function of temperature [10].

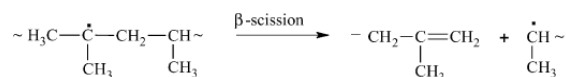
The resulting (alkoxy and methyl) radicals can either graft to polymer by opening a double bond or abstract hydrogen to create a macroradical. Hydrogen abstraction usually takes place on the most labile hydrogen, which ranges preferentially in order: allylic > tertiary > secondary > primary hydrogen. On the contrary, the reactivity of these radicals varies in the reverse order [2,11].



Scheme.1: Decomposition of dicumyl peroxide and formation of by-products

The crosslinking mechanism of EPDM depends on several factors. The polymerisability of the unsaturated fraction depends on the position of the double bonds, the number of allylic hydrogens, the accessibility and relative stability of the resulting allylic radicals [12,13].

A NMR study of the crosslinking by peroxide of an ethylene-propylene terpolymer containing ethylidene norbornene as diene monomer (EPDM-ENB) has shown a 40% conversion of double bonds [8]. Based on these results a crosslinking mechanism has been proposed in which methinic hydrogen of propylene units as well as allylic hydrogen of ENB units are sites primarily attacked by alkoxy radicals. Several authors (e.g. Dickens 1982) have studied the reactions of methinic radicals. It has been proposed that these radicals can rearrange by a β scission (Scheme.2).



Scheme.2: β scission of a methinic radical