

PHOTO- AND THERMO-OXIDATIVE AGEING OF PE SHEATHS FOR CABLE STAYED BRIDGE APPLICATIONS

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Abstract

High density polyethylene (hdPE) sheaths are commonly used as protective barrier for cable stayed bridges. It is usually admitted that photo-oxidation is the main degradation process for such materials. However, thermal oxidation can also take place and sometimes predominate beyond some critical conditions in the irradiation intensity – temperature map, especially at very low irradiation intensity or at high temperature¹. The main objective of this communication is the non empirical determination of boundaries delimitating the respective domains of both oxidative mechanisms from the domain where no one can be neglected relatively to the other one, at a relatively low temperature (typically close to ambient).

To avoid complications due to a diffusion controlled oxidation kinetics, thin films (200 and 300 μm thick) of unstabilised and unfilled hdPE were prepared by compression moulding. One part of the specimens was subjected to photo-oxidative ageing for a period of 80 days in a Weather-o-meter chamber, under different irradiation intensities (0.35, 0.51 and 0.65 $\text{W}\cdot\text{m}^{-2}$) at a temperature of 40°C in atmospheric air. The other specimens were exposed to thermal ageing in air-circulating ovens at 40 and 100°C, at least during the same period. After ageing, the main structural changes at different pertinent scales, were determined using conventional laboratory techniques: IR spectrophotometry for molecular changes, rheometry in melt state for macromolecular changes, differential calorimetry, X-ray diffraction and densimetry for micro-structural changes, and uniaxial tensile tests for macroscopic changes.

The following trends can be deduced as regard to thermo- and photo-oxidation mechanisms:

- Thermo- and photo-oxidation are characterized by the development of wide hydroxyl and carbonyl peaks on IR spectra. The subtraction of IR spectra obtained before and after NH₃ treatment, clearly shows that the carbonyl peak is composed of several contributions: aldehydes (at 1732 cm⁻¹), carboxylic acids (1710 and 1734 cm⁻¹) and ketones (1713 cm⁻¹)².

- A large part of carbonyl groups results from the β scission of alkoxy radicals. Chain scissions lead to a catastrophic decrease of weight average molecular mass.

- Chain scissions liberate small macromolecular segments from the entanglement network located in the rubbery amorphous phase. These segments migrate easily up to interfaces between amorphous and crystalline zones and thus, lead to an increase of the lamellae thickness and crystallinity ratio. These effects are noticeably higher in the case of photo-oxidation (average increase in crystallinity ratio of 15% after 80 days) than in the case of thermal oxidation (no significant changes).

- Decrease in molecular weight and increase in lamellae thickness are both responsible for a catastrophic decrease of the ultimate mechanical properties (polymer embrittlement).

However, the most interesting result, from a kinetic modelling point of view, concerns the general shapes of kinetics curves obtained for thermal and photo-oxidation. In the case of a "close-loop mechanism", producing its own initiator product (the hydroperoxide group), kinetics curves present an induction period followed by a sharp auto-acceleration, preceding a steady state. It is clearly observed that auto-acceleration is much more progressive in its initial part in the case of photo-oxidation (for which hydroperoxide decomposition is essentially unimolecular) than in the case of thermal oxidation (for which hydroperoxide decomposition is essentially bimolecular).

A simplified kinetic model has been tentatively built from these experimental observations. It is derived from a radical chain oxidation mechanism, of the closed-loop type, initiated both by the thermolysis and photolysis of hydroperoxides. It will be shown that this model simulates satisfyingly the general trends of both thermal and photo-oxidation kinetics.

References

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