



## Short communication

## Evidence of surface accumulation of fillers during the photo-oxidation of flame retardant ATH filled EVA used for cable applications

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## ARTICLE INFO

## Article history:

Received 4 November 2013

Received in revised form

30 January 2014

Accepted 4 March 2014

Available online 18 March 2014

## Keywords:

Photo-oxidation

UV ageing

Halogen free

Flame retardant

EVA

Aluminium hydroxide

## ABSTRACT

This paper is devoted to the photo-oxidation of a fire retardant polymer used for cable jacketing and an emphasis was put on understanding how highly filled composites (Ethylene-Vinyl Acetate filled with Aluminium Tri-Hydroxide) behave under UV irradiation. Samples have been irradiated during several thousand hours and the degradation has been studied at the surface but also within the polymer bulk. The degradation of the polymer part, because of a massive chain scissions process, leads to a progressive enrichment of the inorganic part at the surface which then acts as a screen for the bulk. Thus, the degradation is very heterogeneous along the polymer thickness and the degradation profiles well correlate with the evolutions of the mechanical properties (i.e. mechanical properties are not influenced if the degradation profile remains small compared with the total sample thickness).

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## 1. Introduction

Materials used in the cable industry (building, shipbuilding, nuclear, automotive, photovoltaic applications...) have to present and to keep their properties during long time under service conditions. Insulation or cable sheathing materials were most of the time highly formulated compounds to be compliant with the numerous requirements: long-term durability, fluid resistance, mechanical properties, fire resistance... Regarding the fire retardancy and because of an increasing need for the customers to use less hazardous materials, Halogen Free Flame Retardant (HFFR) polymers [1–3] were used in several applications. Classical HFFR systems can be based on either inorganic fillers (metal hydroxides, nanocomposites...), phosphorous, nitrogen, silicone-containing systems [4,5], or a mix of these additives to achieve synergistic effects.

The photo-oxidation of Ethylene-Vinyl Acetate (EVA) copolymers has been widely studied in the literature [6–8]. Authors agreed that UV ageing leads to the formation of many photo-products (acids, ketone...). Photo-oxidation degrades both the ethylene and the vinyl acetate parts of the copolymer. A complete

scheme of degradation was given [9] in which a chain scission phenomenon seems to be predominant in the case of the EVA. A loss of the mechanical properties after several hundred hours of photo-ageing is then observed as a direct consequence.

As far as we know, the photo-ageing of flame retardant systems has been sparsely studied, especially the UV ageing of highly filled systems like ATH (Aluminium Tri-Hydroxide) filled EVA. The photo-degradation of polymers containing halogenated (brominated) additives has been studied [4,10,11] and it has been demonstrated that these additives accelerate the degradation and can interact with specific anti-oxidants. Regarding phosphorous and nitrogen based fire retardant systems [4,12], several observations have been made. Without going into details, we mainly noticed that systems based on polyphosphate are highly sensitive to hydrolysis. Studied flame retardant systems using inorganic fillers [4,13,14] are most of the time nanocomposites. The main observations were that the addition of nanofillers (clays, Layered Double Hydroxide ...) decreases the stability of the system because of the absorption of a part of the stabilizers within the fillers and because of the presence of metallic impurities contained in natural fillers. Metallic impurities have indeed a well known catalytic activity [15] to decompose the hydroperoxides and then to catalyse the degradation.

One of the significant papers concerning this topic is the work of Schartel et al. [16]. They observed that there is a blooming of some of these fire retardant additives (talc and melamine

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**Table 1**  
Depth of penetration in infrared in reflexion mode for the degradation profiles.

| Crystal ATR                | $\bar{\nu}$ (cm <sup>-1</sup> ) | dp (μm) | 3 × dp (μm) |
|----------------------------|---------------------------------|---------|-------------|
| Diamond ( <i>n</i> = 2.38) | 3600                            | 0.33    | 1.00        |
|                            | 700                             | 1.71    | 5.14        |

cyanurate) at the surface. They demonstrated that the photo-ageing mainly degrades the surface and that it can impact the fire resistant properties. Another work [17] has demonstrated for nanocomposites (PVA/clays) that an extended period of UV ageing could lead to an accumulation of nanofillers at the exposed surface because of an important degradation/erosion of the organic matrix. As far as we know, this degradation phenomenon (migration or polymer surface elimination) has not been studied for highly filled systems and especially for composites using metal hydroxides (Aluminium and Magnesium oxides) while these systems represent a large volume of the produced flame retardant materials.

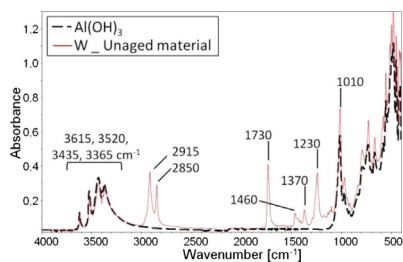
This paper deals with the photo-ageing of a classical HFFR material, i.e. the polymer matrix is an EVA copolymer and the fire retardant additive is ATH. An emphasis was put to identify the chemical and macroscopic evolutions of this material under UV irradiation. It is well known that these materials need to be highly filled to fulfil with fire requirements and the main objective here is to understand how this high filler loading impacts the ageing.

## 2. Experimental

### 2.1. Materials

An industrial Halogen Free Fire Retardant (HFFR) compound used for cable sheathing application has been used in this study. The polymer matrix was a crosslinked Ethylene-Vinyl Acetate copolymer filled with Al(OH)<sub>3</sub> and clays (Kaolin). Residual weight value after a heating ramp up to 800 °C monitored by TGA was ca. 40% which corresponds to a total filler weight percentage close to a total of 55% of which kaolin is approximately 5%. Vinyl Acetate (VA) content was estimated both from FTIR analysis [18] and from the measurement of the melting temperature using DSC [19]. The VA content was found close to 40% in weight in the unfilled matrix.

Test samples were processed as 1 mm thick plates and as 200 μm thin films by means of melt compression. Thick plates of 1 mm, representative of classical sheathing thickness, were used to test the mechanical properties. Films of 200 μm were used to identify the filler accumulation phenomenon. Samples were pressed at 180 °C under 200 bars for 9 min in order to achieve peroxide crosslinking of the EVA matrix (90% of cure according to moving die rheometry results).



**Fig. 1.** Left: Infrared spectra at initial time in the domain 4000–400 cm<sup>-1</sup> of the studied sample (continuous) and of the pure ATH (dash). Right: Assignments of the main IR features for the initial material.

### 2.2. Photo-oxidation

The irradiations were performed under artificial accelerated ageing conditions. The ageing device was an SEPAP 12/24 unit [20] commercialized by Atlas, which was equipped with four medium pressure mercury lamps (Polamp 400W) situated in vertical positions at each corner of the chamber. Wavelengths below 295 nm were filtered by the glass envelope of the sources. Irradiance in the range 300–400 nm is 100 W m<sup>-2</sup>. The temperature at the surface of the samples was fixed at 60 °C.

This device is usually used for UV ageing of cable sheathings (EN 50289-4-17 for example). No specific acceleration factors have already been measured for highly filled EVA between the SEPAP 12/24 and natural ageing but previous work [21] found average acceleration rates of around 20–40 for thermosets.

### 2.3. Analysis

The infrared (IR) spectra were recorded in reflection mode with a Thermo Nicolet Nexus spectrophotometer equipped with a thunderdome-ATR (4 cm<sup>-1</sup>, 32 scans). The thunderdome is a single reflection ATR accessory with a diamond crystal.

The degradation profiles within the material were determined using the infrared spectrophotometer equipped with the ATR accessory. Infrared spectra have been recorded after successive thickness controlled surface abrasion using a buffing machine and a micrometer. In reflexion mode, the depth of infrared beam penetration (dp) [22] within the sample is given in Eq. (1).

$$dp = \frac{1}{2\pi \times \bar{\nu} \times n_1 \times \sqrt{\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}} \quad (1)$$

where *n*<sub>1</sub> and *n*<sub>2</sub> are the refractive index of respectively the crystal and the material (average value of 1.53 is taken),  $\bar{\nu}$  is the wavelength of analysis and  $\theta$  is equal to 45°. Previous works [22] proposed that the real depth of penetration is about 3dp and Table 1 presents results of dp and 3 × dp for the diamond crystal. From Table 1, the IR beam probes thicknesses ranging from 1 to 5 μm (extreme surface) so successive abrasion steps allowed to determine degradation profiles within the bulk.

Mechanical properties have been measured using dumbbell shaped specimens punched from the 1 mm sheets according to the IEC 60811-501. The specimens were tested using a Monsanto T2000 tensile testing machine (max. measuring range of 1 kN) at an elongation rate of 250 mm min<sup>-1</sup> and at 23 ± 2 °C, 50% HR. Five specimens from each reference were tested.

Surface analysis of the materials were performed using Scanning Electron Microscope (SEM), JSM 6700F from JEOL Company. The UV exposed surface of the specimens have been sputter-coated

| $\nu$ (cm <sup>-1</sup> ) | Assignments  |
|---------------------------|--|
| 3615, 3520, 3435, 3365    | $\nu$ (-OH)  |
| 2915, 2850                | $\nu$ (CH <sub>3</sub> ), $\nu$ (CH <sub>2</sub> ) |
| 1730                      | $\nu$ (C=O)  |
| 1460                      | CH <sub>2</sub> bending vib.                       |
| 1370                      | CH <sub>3</sub> bending vib.                       |
| 1230                      | $\nu$ (C-O-C) <sub>s</sub>                         |

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