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Study of the thermo-oxidative ageing of cross-linked polyethylene for HVDC applications

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ABSTRACT

We propose to identify different physical and chemical ageing markers due to thermal ageing of the synthetic insulation of HVDC cables. For that purpose, we are interested in the variation of different physical and chemical properties with thermal ageing. The crystallinity, the oxidation and the chain scissions during ageing are key parameters to quantify the XLPE ageing.

KEYWORDS

DSC – FTIR – HVDC - TGA – thermal ageing – XLPE – Cable insulation

1. INTRODUCTION

European governments are aiming at increasing the share of renewable energy; therefore industrial countries are preparing their energy transition. The amount of electricity from renewable energy should reach 20% of supplied energy by 2020. The structure of European power systems must be redesigned to achieve this goal.

Large renewable energy production areas are far away from consumption areas. Point to point long distance connections already exist in some industrialized countries like the USA, China, Japan and Europe. These links are terrestrial or below sea level and directly connected without mesh. These links involve transport under high DC voltage (HVDC). HVDC links can increase the power transmission distance. In fact, we can increase the distance from ten to twenty kilometres with AC cables (HVAC) to hundreds of kilometres with HVDC links.

Reliability and life span of HVDC cables are major issues. The weak point of these new generations of cables is the limited experience of the use of their synthetic cross-linked polyethylene insulation in HVDC. Indeed, local defects in this material will appear and evolve over time based on the history of electric fields and load conditions. Local enhancement of electric fields or thermal runaway may, in particular, be due to the presence of cross-linking by-products.

Ageing studies of cable insulation have already been carried out, focusing on electrical ageing markers like space charges or partial discharges. The identification of physical and chemical markers for the ageing of HVDC cables has been conducted by a succession of complementary approaches to understand the origin of these phenomena. In this paper, we propose several physical and chemical ageing markers to monitor thermal ageing of the insulation.

2. CROSS-LINKED POLYETHYLENE - XLPE

The cross-linked polyethylene is used for XLPE cable insulation due to its good dielectric and mechanical properties. Currently most HVDC cables are based on Mass Impregnated insulation with a relatively long production cycle and manufactured only in a few specific plants in the world. Switching to XLPE extruded cable would allow using the relatively widespread plants for HVAC XLPE cable. The synthetic insulation based on polyethylene has been used since 1960.

XLPE is based on Low Density PolyEthylene (LDPE). The crosslinking consists of creating bridges between polymer chains to obtain a three-dimensional network by forming covalent bonds between polymer chains.

Cross-linked polymers are generally insoluble and infusible. Furthermore, crosslinking enhances the shock resistance, creep resistance and reduces the extent of cracks. In return, it reduces the elongation at break but has no influence on the tensile strength and density.

a. Structure

Cross linked polyethylene is a semi-crystalline material. It is composed of two phases, an amorphous part where there is no long-range organization of molecules and a crystalline part, which is ordered, usually in the form of spherulites (Figure 1).

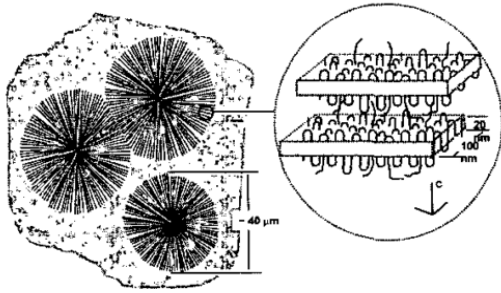


Figure 1 - Semi-crystalline structure showing the spherulites [1]

The size and shape of these spherulites depend on the material type, the cooling rate from the molten state and the presence of nucleating agents. Typically, the diameter of spherulites in XLPE is approximately 10 microns. Cross-linked segments in XLPE are located in the amorphous phase [2],[3],[4]

b. DCP Crosslinking

Cross-linking of polyethylene used in this study is made using peroxide. The peroxides are highly reactive oxidizing chemical species of the R-O-O-R' type which reacts with linear polyethylene (LDPE). The used peroxide is the dicumyl peroxide (DCP - Figure 2), which is organic peroxide. The DCP can be used as a polymerization initiator.

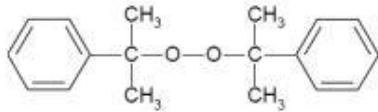


Figure 2 - Chemical formula of DCP

The reaction (Figure 3) [5], [6] begins with the decomposition of peroxides which are added to the low-density polyethylene. The choice of peroxide and extrusion parameters must be considered in order to avoid the start of crosslinking in the extruder when the cable insulation system is produced.

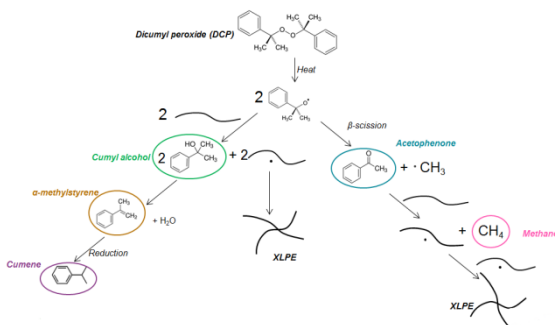


Figure 3 - Cross-linking reaction and formation of crosslinking by-products [6]

During this cross-linking reaction, DCP undergoes homolytic cleavage between two oxygen atoms thereby forming two radicals. This scission is possible if the temperature is about 150 ° C. The formed radicals will snatch labile hydrogen atoms (easily removable with heat) from polyethylene chains. Polyethylene chains therefore have a free electron that will react with another free

electron from another polyethylene chain to thereby form a covalent bond between the two chains. Peroxide decomposition which is the source of free radicals is a slow reaction, which determines the crosslink rate of reaction. During this reaction, the viscosity of the mixture is very high, free radicals are trapped as well as residues from peroxides. This gives rise to the formation of crosslinking by-products such as acetophenone, cumyl alcohol, alpha-methylstyrene, cumene, methane and water. By varying time parameters and temperatures, it is possible to promote a type of by-product, for example cumyl alcohol and acetophenone. Another important by-product which is generated during the crosslinking reaction is methane gas. The cumyl alcohol, acetophenone and alphamethylstyrene increase the conductivity of the material [6]. The acetophenone and alpha-methyl accelerate loads moving within the material.

3. RESULTS

To identify physical and chemical markers due to the thermal ageing of the cross-linked polyethylene, the samples underwent accelerated ageing at a temperature of 135 ° C. Ageing is done in an oven with forced ventilation for better thermal homogenization and to avoid atmosphere saturation by volatile degradation products. Aged samples are plates which have a diameter of 300 mm and are 1 mm thick. These plates are obtained by hot pressing of polyethylene pellets with a temperature profile and pressure similar to those used in the production of extruded cables.

The physical and chemical properties of XLPE were monitored at regular time intervals to identify ageing markers.

Ageing was deliberately pushed beyond the standard limits of commercial XLPE (14 days at 135 ° C, which corresponds to antioxidant dosage), to bring up ageing phenomena which were not visible or detectable in less than 14 days, but potentially having an impact on electrical properties.

a. DSC

DSC is a thermal analysis technique which measures the difference in heat transfer between the analyzed material and a reference, as a function of the temperature.

In our case, it allows us to obtain information on the characteristic temperatures of crosslinked polyethylene. We can identify the melting and crystallization temperatures.

The material crystallinity can be also determined by DSC analysis, the crystallization peak is directly related to the degree of crystallinity (X_c (%)) = $(\Delta H_f) / (\Delta H_{f0})$ with ΔH_{f0} = 285 J/g). XLPE is characterized by a crystallization temperature of 96 ° C and a melting temperature of 95 ° C, its degree of crystallinity in the unaged state is 38%.

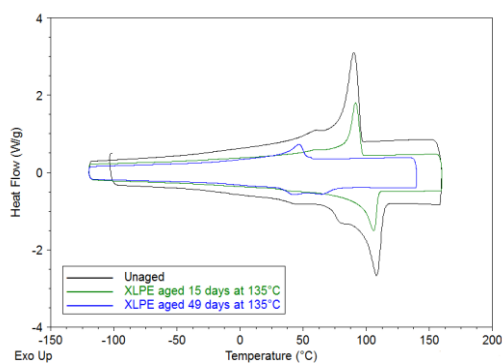


Figure 4 - Thermogram of unaged XLPE and aged XLPE during 15 and 49 days at 135°C

Sample	$T_m(^{\circ}\text{C})$	$\Delta H_f(\text{J/g})$	$T_c(^{\circ}\text{C})$	$\Delta H_c(\text{J/g})$	$X_c(\%) = \frac{\Delta H_f}{\Delta H_{f_0}}$
Unaged	95	102	96	108	38
XLPE aged 15 days at 135°C	95	89	91	105	36
XLPE aged 49 days at 135°C	33	42	52	39	22

Table 1– Melting temperatures ,crystallisation temperatures and associated enthalpy for a unaged XLPE and aged XLPE

The melting and crystallization temperatures (Table 1) are impacted by the thermo-oxidative ageing. Indeed, the melting temperature is shifted downwards, it drops from 95 ° C to 33 ° C and the associated enthalpy is halved. The crystallization temperature is also changed from 96 ° C to 52 ° C.

This change in temperature and enthalpy is due to a very pronounced chain scission after 49 days. When the polymer chains are shorter, their crystallization is slower and their melting temperature decreases.

b. TGA

TGA is a thermal analysis technique that allows us to follow the evolution of the sample's mass depending on the temperature. It can thus obtain the thermal degradation temperature by monitoring the weight loss. It also allows us to identify the change in the degradation kinetics due to material ageing in different atmospheres.

XLPE in the presence in nitrogen atmosphere deteriorates in a single step. A study of aged samples reveals a change in the kinetics of degradation and a modification of associated degradation temperatures.

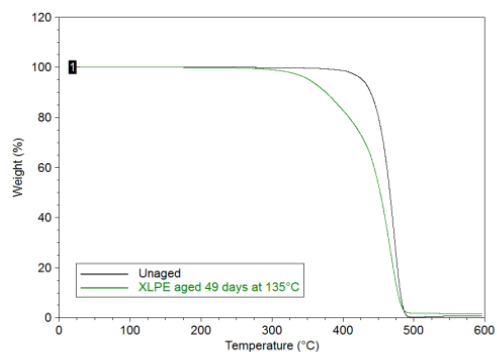


Figure 5 - Thermogram of unaged XLPE and aged XLPE in a nitrogen atmosphere

Thermal ageing modifies the kinetics of XLPE degradation in a nitrogen atmosphere. Indeed, for an unaged XLPE, the material degrades first beginning at 450 ° C and then ending at 489 ° C with a mass loss of 100%. Degradation is completed, it is called thermolysis because oxygen is not involved in the degradation of the material. When XLPE is aged, degradation starts at 300 ° C and ends at 500 ° C. There is a shift to lower temperatures in the starting temperature of thermal degradation between an aged sample and an unaged sample. The thermal degradation starts at 305°C, so 145°C lower.

These changes in degradation temperature and degradation kinetics are related to polymer chain oxidation during ageing as well as chain scission.

c. FTIR

This spectral technique produces a sample of the infrared absorption spectrum. From this spectrum, it is possible to trace the chemical structure and configuration of polymer materials. In the case of polyethylene, we can identify four peaks which correspond to the repeating pattern according to their environment.

Spectral analysis by FTIR (in reflection, ATR Mode - Attenuated Total Reflectance), identifies the peaks associated with the polyethylene matrix before ageing. Indeed, XLPE is characterized by four major peaks (Figure 6) which are representative of the repeating pattern. Some of these peaks are related to the CH₂ groups within the heart of the polymer chain, and others are associated with chain ends. On an unaged XLPE, a peak associated with cumyl alcohol is also visible at 2350 cm⁻¹.

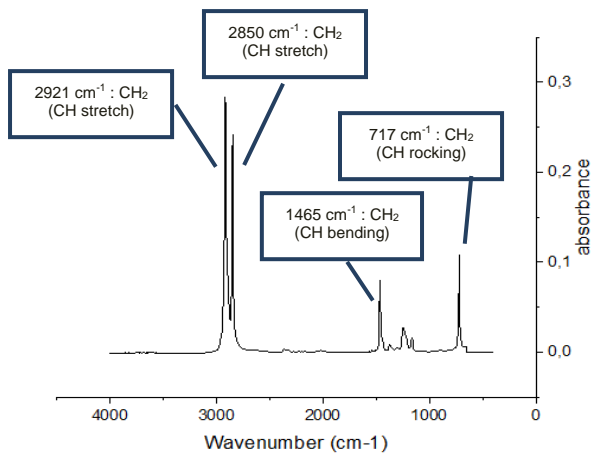


Figure 6 – FTIR spectra of unaged XLPE

The monitoring of ageing by FTIR (Figure 7) allows us to observe the appearance of carbonyl groups at 1690 cm^{-1} (Figure 7) after 28 days at $135\text{ }^{\circ}\text{C}$. These groups are composed of a carbon atom connected by a double bond to an oxygen atom. The amount of carbonyl groups increases with the duration of ageing. The presence of such groups is bonded to a chain oxidation during thermal ageing.

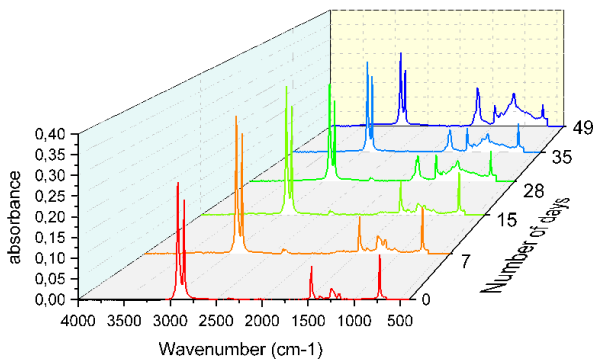


Figure 7 – FTIR spectra of aged XLPE

The intensity of the peaks at 2915 cm^{-1} and 2847 cm^{-1} decreases with ageing time. Conversely, the peak at 1167 cm^{-1} increases. The first two peaks are related to CH_2 groups present in the heart of the polymer chains and the other peak is related to the CH_2 groups of chain ends. Decreasing the amount of chain heart groups is linked to the chain scission. This hypothesis is confirmed by the increase in the intensity of the CH_2 groups of chain ends. Thermal ageing of XLPE causes chain scission.

4. CONCLUSION

Thermal ageing have an irreversible impact on XLPE. Antioxidant content in the mixture has to protect the material during the cable lifetime of 40 years at 90°C equivalent to 14 days at 135°C , that must not modify XLPE. Thermal ageing during 14 days at 135°C shows that the antioxidant quantity is sufficient to protect XLPE and beyond start a measurable change of XLPE.

Different techniques of physical and chemical characterizations allow us to highlight some ageing markers. A crystallinity loss has been identified in DSC, which is due to the presence of shorter chains. We can confirm this chain scission during thermal ageing by FTIR measurements. This irreversible chain scission can potentially affect the mechanical and electrical behavior of cables and affect their life span.

Finally, the ageing causes XLPE oxidation which is visible by TGA and FTIR measurements. , These thermal ageing markers can be correlated to electrical markers.

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