Observations on Structural Changes under Thermal Ageing of Cross-linked Polyethylene Used As Power Cables Insulation

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A B S T R A C T

The widespread use of cross-linked polyethylene (XLPE) as insulation in the manufacturing of medium and high voltage cables may be attributed to its outstanding physical, chemical, mechanical, and electrical properties. However, it is well known that degradation under service conditions is the major problem in the use of XLPE as cables insulation. Especially, thermal oxidative degradation produces low molecular weight and oxygenated products. Several diagnostic measurements have been used in this study in order to characterize XLPE behaviour under thermal ageing. Firstly FTIR has been conducted on fresh and aged samples in order to reveal the effect of thermal ageing on the chemical changes which take place in the XLPE structure. The main changes are the formation of carbonyl groups (aldehyde, ketone, etc.). Use of DSC analysis shows the effect of ageing on the melting peak temperature T_m, melting enthalpy ΔH_m and lamellar thickness. In the last part we have applied X-ray diffraction to reveal the variations in percentage of XLPE crystallinity or addition of any new crystalline phase under thermal ageing. The obtained results showed that thermal ageing at temperatures above the melting temperature of XLPE has a great effect on the material structure.

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INTRODUCTION

Polyethylene (PE) is a non-polar polymer, it is found in semi-crystalline form at room temperature. The crystalline fraction is formed when the material is cooled down from the melting state. The lamellae structure formed during solidification depends on the characteristics of thermal treatment and the conditions of crystallization. In the normal conditions, lamellae grow radially resulting in spherulites and forms the crystalline and amorphous regions of the polymer [1].

In industrial applications, PE is commonly used as an electrical insulation. Specifically, it constitutes the base compound for cable

insulation manufacturing due to its outstanding insulating characteristics and its low price. Cross-linked polyethylene (XLPE) is gradually replacing the polyethylene in such applications due to its greater mechanical and thermal stabilities, and it maintains the good dielectric property of the original polymer (low density polyethylene) [2]. This material used to be employed as an insulating material for the 3-6 kV rated distribution power cables in 1960's and now it is successfully used as the main insulation for the EHV power cables rated from 275 kV to 500 kV because of its superior electrical and mechanical properties [3].

Under its working conditions, the cable is permanently subjected to thermal ageing which can cause an irreversible damage to the cable insulation. Chemical composition of XLPE may change under temperature stress over a period of time. Consequently, some of its properties may alter and produce limitations on the effective service life of the cables. Much work has been carried out on the analysis of chemical modifications generated by ageing [4,5]. It is well known that XLPE conductive properties are governed by its morphology [6] and the insulation degradation under service conditions can be related to volume space charge [7] and propagation of water tree inside it [8]. Some changes in physical properties of polymer such as discolouration, volume shrinkage, and brittleness have been observed [9]. The overall results of thermal ageing are the oxidation reactions, cross-linking, chain scission, variation in crystallinity and variation in heat of fusion and melting point [2]. Thermal ageing can also lead to the deteriorations of electrical and mechanical properties of polymers [9-12].

Usually, performance characterization of XLPE as an insulation material in power cables is managed by employing electrical and mechanical techniques. However, more detailed information on the polymeric material and its ageing can be achieved employing complementary techniques such as thermal analysis, infrared spectroscopy, optical and electric microscopy.

This paper has focused on two objectives, the first concerns presentation of some results of characterization of XLPE under thermal ageing using several complementary techniques (FTIR, DSC, and X-ray) in order to highlight the main structural changes in the polymer under thermal ageing. In the second step, we

try to make some correlations between the dielectric and mechanical properties that we have presented in previous papers [9,13-15] and the observed structural changes reported here. Such correlations certainly lead to better understanding of the degradation and ageing processes.

EXPERIMENTAL

Materials
The selected material for this study is commercial XLPE Union Carbide 4201 which is used as insulation in medium voltage cables (18/30 kV) manufactured by ENICAB firm of Biskra (Algeria). This material, in the granule form, contains polyethylene blended with 2% of dicumyl peroxide (DCP) as cross-linking agent and 0.2% of IRGANOX 1035 as an antioxidant. The analyzed samples were moulded and cross-linked at 180°C under pressure of 300 bars using pressurized heat press.

Thermal Ageing
Press moulded XLPE samples of 2 mm thickness were aged at four different selected temperatures according to the IEC 216 publication [18]. Two samples were aged below the melting temperature of XLPE: 80°C and 100°C, and the other two samples above the melting peak: 120°C and 140°C. The time of ageing was 5000 h for the two first temperatures, and 2500 h and 1500 h at 120°C and 140°C, respectively. The ageing process was carried out using forced air-circulating oven, with an exchange rate of 10 exchanges/h and could maintain the average temperature of the samples within ±2° C. The samples were vertically suspended in the oven in order to be in contact with the circulating air and homogeneous ageing. After each ageing time, five samples were taken and then subjected to different characterization techniques that are described in the next sections.

FTIR Spectroscopy Measurement
The structural changes in XLPE during ageing were analyzed with FTIR spectrometer model FTS-60A. The XLPE films were microtomed from the fresh and aged samples. Each sample was performed at 32 scans in the range 400-4000 cm^{-1} with a resolution of

4 cm^{-1}. To increase the accuracy of the results, the FTIR spectra present the average of five spectra obtained using five small samples taken from different aged samples. One PC was connected to the spectrometer in order to receive and analyze data. The obtained data were analyzed using BIO-RAD software.

DSC Measurement

Thermal properties of the XLPE specimens were studied using DSC 2010 TA Instruments with computer data system. Specimens of about 10-20 mg, removed from the fresh and aged samples at different temperatures were analyzed by heating and cooling at constant rate of 10°C/min under nitrogen atmosphere to avoid thermal degradation. The heating interval was 20-160°C. Each thermogram represents the average of five thermograms for each case. The obtained data were analyzed by TA Universal Analysis software.

X-ray Diffractometry: Wide Angle X-ray Scattering

To make clear any changes in the crystalline phase of XLPE during ageing, we have used X-ray diffraction. The X-ray spectra were made with Cu-K$_\alpha$ radiation with wavelength K$_\alpha$ = 1.54056 Å in a Phillips X'Pert X-ray diffractometer. The operational interval of Bragg angle was 2θ = 5-90° by step of 0.04° with 0.4 s/step scan rate. The measurements were carried out on samples of 10 × 10 × 2 mm in size which make a turn on itself in order to avoid any influence of the preferred orientation of the crystallites and surface defects. The diffractometer was connected to a computer in order to receive and analyze the data. The obtained data were analyzed by X'Pert Graphics Identify software.

RESULTS AND DISCUSSION

FTIR Analysis

The oxidation phenomena in polyethylene and cross-linked polyethylene have been already investigated by many authors [5,12,17,18]. Thermal ageing of XLPE results in significant changes in the infrared absorption spectra. The major by-products of thermo-oxida-
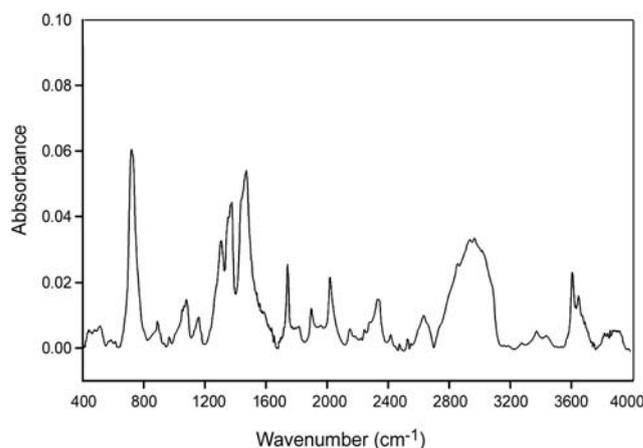

Figure 1. FTIR Spectra before ageing.

tion are carbonyl groups. FTIR Spectra of unaged XLPE specimens and those aged at 80°C and 100°C are very similar and for the sake of brevity only the spectra of virgin is shown in Figure 1. The peak appearance at wavelength of 720 cm^{-1} corresponds to the rocking methylene groups (-CH$_2$). This peak is the most characteristic of the XLPE [19,20], and it is confirmed by other peaks which appear at 1471 cm^{-1}, 2856 cm^{-1} and 2937 cm^{-1}. These peaks correspond to wag vibration, symmetric stretching vibration, and asymmetric stretching vibration of (-CH$_2$) group [18,21,22]. The observed peaks at 889 cm^{-1}, 966 cm^{-1}, and 1635 cm^{-1} are assigned to the unsaturated groups absorptions: vinylidene, *trans*-vinylene, and vinylene groups, respectively [17,21,23]. Methyl group absorption give peaks at 1377 cm^{-1} (wag vibration), 2150 cm^{-1}, 2632 cm^{-1} and 2953 cm^{-1} (symmetric stretching vibration) [18,21,22]. As claimed by the supplier, the Irganox 1035 antioxidant presents absorption bands which occur at about 1078 cm^{-1}, 1159 cm^{-1} and 3604 cm^{-1} [24,25]. This additive substance was incorporated in the polyethylene resin by the manufacturer. The crystalline part of the polymer presents peak at 1898 cm^{-1}, whereas the amorphous one absorbs at 1305 cm^{-1} [26].

According to reference [27] the peak at 1305 cm^{-1} corresponds also to the acetophenone absorption. The thermo-oxidative products present peaks between 1650 cm^{-1} and 1800 cm^{-1}. Our material presents three peaks; the first one appears at 1701 cm^{-1} attributed to carboxylic acid absorption, the second is revealed at 1718 cm^{-1} which characterizes ketone absorption and
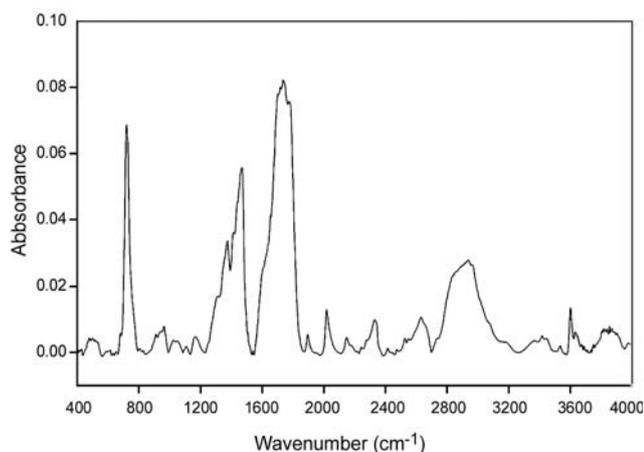
Figure 2. FTIR Spectra after 1500 h at 140°C.

Figure 3. FTIR Spectra between 1650 cm^{-1} and 1850 cm^{-1} at different ageing tempertaures.

the third one is situated at 1741 cm^{-1}. This absorption peak corresponds to the aldehyde or ester [21,23,28,29]. The presence of these carbonyl groups in the unaged sample indicates that oxidation process has taken place during manufacturing process. The hydroxyl groups (-OH) present an absorption area between 3300 cm^{-1} and 3500 cm^{-1} [23].

The thermo-oxidation is one of the main changes caused during thermal ageing, and its behaviour in the tested XLPE insulation samples can be observed in all spectra of the aged samples at different temperatures. The carbonyl concentration in samples tested after 5000 h of ageing at 80°C and 100°C is slightly different from the unaged specimens. There exists, however, a significant increase of the carbonyl concentration after 2500 h of ageing at 120°C and 1500 h at 140°C (Figures 2 and 3).

Figure 2 presents spectra of sample aged at 140°C and is similar to the one obtained at 120°C. This concentration presents strong absorption area which has appeared between 1500 cm^{-1} and 1900 cm^{-1}. This strong absorption indicates that thermo-oxidative process is in very advanced stage after ageing at 120°C and 140°C. Furthermore, as it can be seen from Figure 2, the high concentration of carbonyl groups is accompanied by diminishing antioxidant (decrease in the antioxidant peaks intensities). The thermal degradation of cross-linked polyethylene has been attributed to an antioxidant loss. This additive plays an inhibiting role in the degradation mechanisms. During the process of polymer cross-linking, volatile products are formed in small vacuoles.
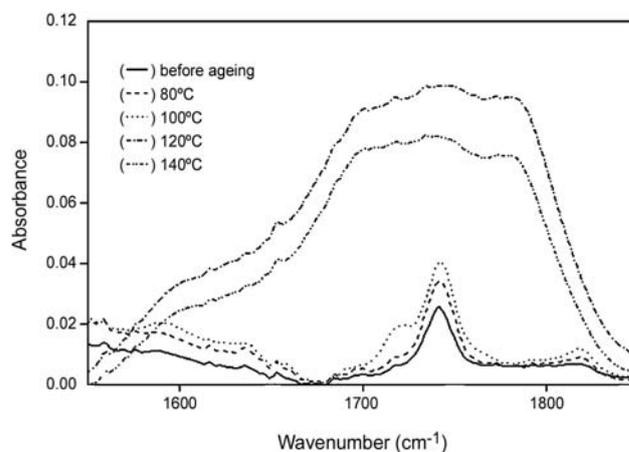
During thermal ageing, a part of trapped gases (hydrocarbons, ketones, and alcohols) can be released and replaced by water or oxygen.

We have reported recently [9] that degradation of the studied material took place in 3 phases. During the first one the degradation is done with a relatively significant speed. The second one is characterized by an increase in degradation speed. During the third one, the speed is reduced and we note a saturation condition, i.e., the antioxidant is being almost completely consumed. The other modification that has appeared in the infrared spectra of samples aged at 120°C and 140°C is the disappearance of peak at 1305 cm^{-1} which presents acetophenone absorption. This volatile cross-linking by-product has presumably evaporated during thermal ageing process. The last observed changes concern vinylene group absorption. This unsaturated group presents peak at 910 cm^{-1} instead of 1635 cm^{-1} after ageing.

Oxidation Evaluation
As the carbonyl groups usually account for most of the oxidation products on thermo-oxidative degradation of cross-linked polyethylene, the concentration of carbonyl groups can be a sign of the existing unsaturated groups (double band index), to monitor the process of degradation. Two indexes were evaluated to obtain quantitative information on thermo-oxidative degradation. These two indexes are [30]:
 - Carbonyl index which is the relative intensities of the carbonyl band at 1741 cm^{-1} (aldehyde absorp-

Table 1. Carbonyl and double band indexes.

Sample	Carbonyl index ($I_{1741/1471}$)	Double band index ($I_{1635/1471}$)
Before ageing	0.4728	0.1150
After 5000 h at 80°C	0.6549	0.2303
After 5000 h at 100°C	0.6061	0.2022
After 2500 h at 120°C	1.5038	0.6634
After 1500 h at 140°C	1.4781	0.5814

tion) to the methylene band at 1471 cm^{-1}.

- Double band index which presents the relative intensities of the unsaturated group at 1635 cm^{-1} to the methylene band at 1471 cm^{-1}.

The obtained results are summarized in Table 1. The first observation leads to the presence of the carbonyl and double band indexes in all the aged samples and in the non-aged XLPE as well. The growth of the two indexes was almost small for samples aged at 80°C and 100°C. They are multiplied by 1.5 for the carbonyl index and by 2 for the vinyl groups. However, there exists a significant increase in the values of two indexes after ageing at 120°C and 140°C, which were multiplied by five. The last observation is an indication of the existence of proportional variation between the two indexes with a correlation between oxidation process and formation of the unsaturated groups. This result is in good agreement with the decomposition process of polyethylene under thermal ageing proposed by Blazsó et al. [31]. The chain scission, which is favoured by the presence of oxygen under thermo-oxidation reactions, contributes to the formation of unsaturated groups. In oxygen-rich conditions, the main scission occurs successively from the first broken chain by auto-oxidation, possibly forming large voids, which are considered to be the origin of the electrical tree channel [32].

DSC Results

With a constant rate of 10°C/min, we have run two consecutive scans on each sample. The first scan began by heating from 20°C to 160°C and then followed by cooling from 160°C to 20°C. The second scan was operated in the same way as the first one. The two consecutive scans were performed on both fresh and aged samples in order to know the effect of
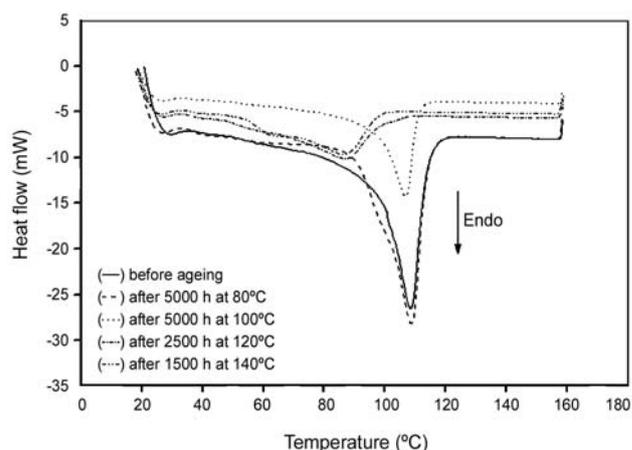

Figure 4. DSC Heating thermogrammes of fresh and aged samples (1st scan).

thermal ageing on crystallinity, the melting temperature, the heat of fusion and crystallization, the lamellar thickness, and the endothermic shape. Thermal ageing may promote cross-linking simultaneously with chain scission and oxidation reactions which cause some changes in the position and shape of peaks. Typical DSC thermograms obtained during the first and second heating runs on the fresh and aged samples are displayed in Figures 4 and 5.

Figure 4 shows thermograms of the first heating run before and after ageing at different temperatures. An endothermic peak, corresponding to the melting temperature of the crystalline part of the polymer, was observed. The main DSC peak is narrow before and after ageing at 80°C and 100°C. It is well known that annealing the semi-crystalline polymer at tempera-
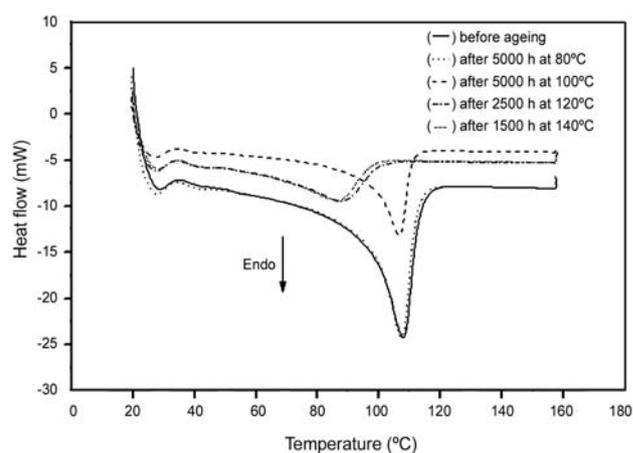

Figure 5. DSC Heating thermogrammes of fresh and aged samples (2nd scan).

tures below the melting point favours the alignment of chains' mobility, narrowing the endothermic peak, small increase in the crystallinity degree and a slight displacement of the melting peak towards higher temperatures [33]. Thermal ageing at 120°C and 140°C causes decrease in intensity, broadening and shifting the maximum melting peak towards lower temperatures. This phenomenon is attributed to the presence of the smaller chain segment, resulting from the bond scission in the backbone of the XLPE macromolecules at high temperatures. Chain scission is favoured by oxidation process [12,19]. It is normally accepted that the degradation, though taking place mainly in the amorphous phase, may also occur at the lamellar fold surfaces, and causes an increase in the surface free energy of the crystals resulting in reduced melting temperature [34]. In this case the surface free energy e may vary significantly because, at elevated temperatures, the crystalline part is in the rubbery state and therefore a larger amount of a rigid amorphous phase remains in the interfacial regions.

According to the well known Thompson-Gibbs equation (eqn 1) and the fact that the lamellar thickness is essentially constant it may be determined by the high degree of branching in the original polyethylene. As a significant increase in the surface free energy leads to the diminution of the term inside the brackets in eqn (1) which subsequently causes the reduction of the melting temperature of the lamellae.

From Figure 4 it is clear that some secondary peaks or shoulders at lower temperatures are present. These peaks or shoulders reflect the thermal history or the characteristics of the samples resulting from the degradation and give indication on the stress formed and morphological changes occurring during degradation. These new thermal energy absorption peaks (shoulders) observed and a broadening of the endothermic graph are due to degradation.

These results can be attributed to changes in crystallite sizes, molecular weight differences that are brought about by chain breakage and secondary recrystallization. These shoulders are noticed between 100°C and 102°C, between 95°C and 103°C, between 50°C and 60°C and between 55°C and 65°C for the unaged sample; after 5000 h of ageing at 80°C, after 2500 h of ageing at 120°C and after 1500 h of ageing at 140°C, respectively. The difference in the shape of

the curves, the position and heat of melting of the different secondary peaks are related to the distribution of the thickness and perfection of the lamellar crystals [28]. This behaviour is certainly attributed to the increasing mobility of lamellar crystals, while on the other hand could be attributed to the recrystallization tendency [19,28,35] as well.

The role of crystallization in this phenomenon indicates that during ageing at elevated temperatures a fraction of the molten polymer cannot crystallize, but it is crystallized only upon cooling. The crystals grown at the lower temperatures during cooling can induce a wide range of lamellar thickness and considerable imperfection. Local variation of lamellar thickness can occur and may be more in cross-linked polyethylene because of local variation in branching and cross-link density. Therefore, these crystals show low melting peaks or shoulders in DSC thermograms.

On the other hand, with increased ageing temperature, the recrystallization process involves the formation of thin lamellae between the primary lamellae. The recrystallization phenomenon can be also explained by the fact that recrystallization phenomenon may be induced by the formation of shorter segments with greater mobility due to chain cleavage during the ageing process. Corroborating the hypothesis that in aged materials, some types of crystals with different sizes and/or of perfect type may coexist and melt at distinctly lower temperatures. This is indicated by the appearance of shoulders in DSC traces and a widening in the melting peak of the polymer.

Figure 5 displays the second heating run on each sample after controlled annealing conditions. These thermograms compare the characteristics of the samples themselves. The second heating thermograms show that the lower melting point components of the first heating stage have disappeared in the second heating stage. This is the result of reorganization of the lower melting point components of the polymer. The low temperature shoulder components become part of the higher melting fraction.

Thermograms of the first and second cooling runs are displayed in Figures 6 and 7. A sharp exothermic peak, which characterizes the XLPE crystallization temperature, has appeared in all thermograms. This peak becomes broader in shape, smaller in intensity, and displaces towards lower temperatures after ageing
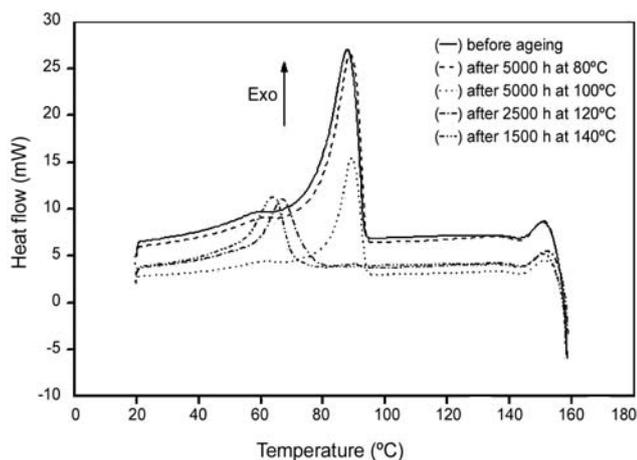
Figure 6. DSC Cooling thermograms of fresh and aged samples (1st scan).

Figure 7. DSC Cooling thermograms of fresh and aged samples (2nd scan).

at 120°C and 140°C. The depression in melting and crystallization temperatures at these ageing temperatures suggests that the specimens have undergone severe deterioration, probably due to very high cross-linking and chain scission, induced by the intensive thermal ageing condition. This behaviour indicates that strong bulk degradation occurs in the molecular structure which as a consequence has progressively decreased the molecular chain length. In these recrystallized curves, both fresh and samples aged at 80°C
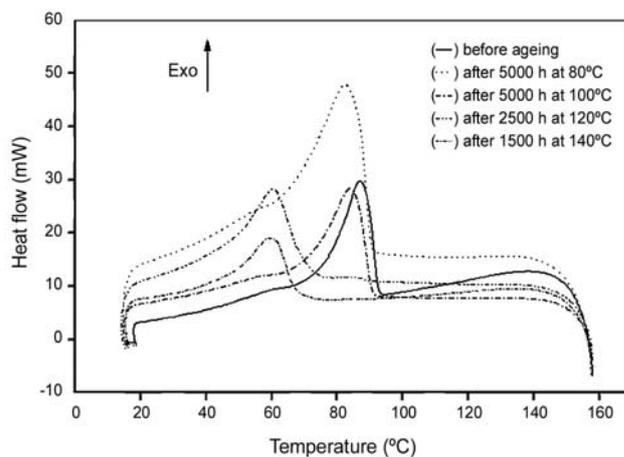
and 100°C show a shoulder at about 60°C because of some secondary relaxations.

Crystallinity and Thermal Parameters of XLPE
The influence of thermal ageing on the crystallinity, melting and crystallization temperatures, specific enthalpies of fusion and crystallization of XLPE is evident from the first and second DSC scans. The obtained results are summarized in Tables 2 and 3. Where $\chi(\%)$ is the crystallinity, ΔH_m is the enthalpy

Table 2. Parameters obtained from DSC measurement (1st scan).

Sample	T_f (°C)	ΔH_f (J/g)	χ (%)	T_c (°C)	ΔH_c (J/g)
Before ageing	108.5	-103.9	37.1	87.7	99.2
5000 h at 80°C	108.7	-115.8	41.4	88.6	100.1
5000 h at 100°C	106.8	-109.6	39.1	89.2	103.1
2500 h at 120°C	86.5	-86.2	30.8	66.7	70.4
1500 h et 140°C	86.4	-71.8	25.6	63.8	59.6

Table 3. Parameters obtained from DSC measurement (2nd scan).

Sample	T_m (°C)	ΔH_m (J/g)	χ (%)	T_c (°C)	ΔH_c (J/g)
Before ageing	107.9	-105.7	37.8	86.4	109.6
5000 h at 80°C	107.3	-106.0	37.9	82.4	267.8
5000 h at 100°C	106.7	-108.0	38.6	83.8	260.5
2500 h at 120°C	87.5	-58.5	20.9	60.3	213.5
1500 h et 140°C	86.3	-63.8	22.8	59.8	114.1

of fusion, ΔH_c is the enthalpy of crystallization, T_m is the melting temperature and T_c is the crystallization temperature.

Minor changes in the crystallinity of samples aged at 80°C and 100°C have been observed in the results of 1st scan. After reorganization of the polymer structure by the 2nd heating run, the crystallinity maintains practically the same value of the unaged sample. The slight increase in crystallinity is probably due to the scission of tie molecules traversing the amorphous regions. The chain scission allows the resulting freed segments to crystallize. Significant drop of the crystallinity degree after ageing at 120°C and 140°C indicates that strong bulk degradation has occurred in the XLPE molecular structure which disrupts the crystalline order of the polymer.

Lamellar Thickness Distribution of XLPE
DSC Endotherms indicate a range of melting temperatures that can be related to the lamellar thickness variations. Changes in the shape of the melting endothermic peaks after ageing at different temperatures reflect modification in the lamellar thickness distribution. The Thompson-Gibbs equation was used to calculate the average lamellar thickness:

$$T_m = T_{m0}\left(1 - \frac{2\sigma_e}{\Delta H_m L}\right) \tag{1}$$

where T_m is the observed melting temperature (K) of lamellar of thickness L, T_{m0} is the equilibrium melting temperature of an infinitely thick crystal, σ_e is the surface-free energy per unit area of basal face, ΔH_m is the enthalpy of fusion of an ideal polyethylene crystal per unit volume, and L is the lamellar thickness. The used values for calculation were as follows [36]: T_{m0}= 414,6 K, ΔH_m= 2,88×10^8 J.m^{-3} and σ_e= 93×10^{-3} J.m^{-2}. The lamellar thicknesses obtained at the main endothermic peaks are displayed in Table 4.

We can see that the average lamellar thickness on the main endothermic peak is affected by thermal ageing. It has increased slightly after 5000 h at 80°C and its distribution has become more homogeneous. This phenomenon occurs even when polyethylene is treated below its main melting point because polyethylene is composed of various lengths of crystals that have their own corresponding melting temperature. By

Table 4. Lamellar thickness at the main endothermic peak.

Sample	Lamellar thickness at the main endothermic peak ($\times 10^{-10}$) (m)
Before ageing	80.89
After 5000 h at 80°C	81.39
After 5000 h at 100°C	76.94
After 2500 h at 120°C	48.60
After 1500 h at 140°C	48.51

heating at some fixed temperatures, the crystals that have lower melting temperatures than the applied heat can be melted and the amount of crystals that can melt at treated temperature become part of the higher temperature's fraction, which explains the shift of the melting peak towards higher temperatures (Table 2). After ageing at 100°C, 120°C and 140°C the lamellar thickness decreases with 4.88%, 39.9%, and 40%, respectively. In this case the chain scission is predominant in degradation phenomenon.

X-ray Diffractometry Analysis
We have used X-ray scattering to analyze fresh and aged XLPE samples in order to identify any new emerging crystalline phase in the material structure under thermal ageing. On the other hand we have studied the crystallinity degree variation according to the ageing time as well.

The X-ray diffraction patterns of XLPE samples aged at different temperatures (80°C, 100°C, 120°C, and 140°C) and at different ageing times are also similar, and to avoid long arguments, we have displayed only the X-ray plot before and after ageing at each temperature in Figure 8. The X-ray plot of fresh sample shows an amorphous halo and two major crystalline peaks at $2\theta = 21.82°$ and $2\theta = 24.06°$ which are characteristic of the (110) and (200) lattice planes [37,38]. One small peak can be observed at $2\theta = 36.5°$ which corresponds to the plane lattice of 020 as Miller indexes [39].

After ageing, the X-ray spectra do not appear to show any changes in the position of peaks or in their splitting. This means that thermal ageing does not lead to any new crystalline phase in the material structure, except variation in the intensity of peaks which indicates that hardly any change has occurred in the
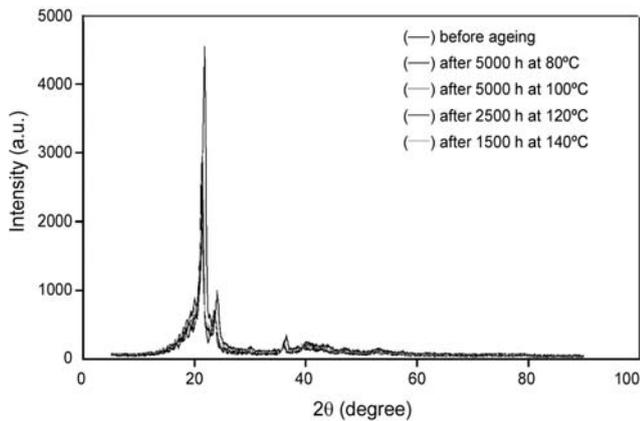
Figure 8. X-ray Diffraction patterns of XLPE before and after ageing.

percentage of crystallinity of XLPE.

The crystallinity of XLPE according to the ageing time was calculated using Hinrichsen's method. This method is based on fitting the diffractogram into three Gaussian functions (Figure 9) using ORIGIN 5.0 software and the crystallinity is given by the following relationship:

$$\chi(\%)= \frac{area1+area2}{area1+area2+area3}\times100 \qquad (2)$$

where:

$\chi(\%)$: crystallinity percentage.

area 1: area under the amorphous halo.

area 2: area under the principal crystalline peak at $2\theta=21.82°$.

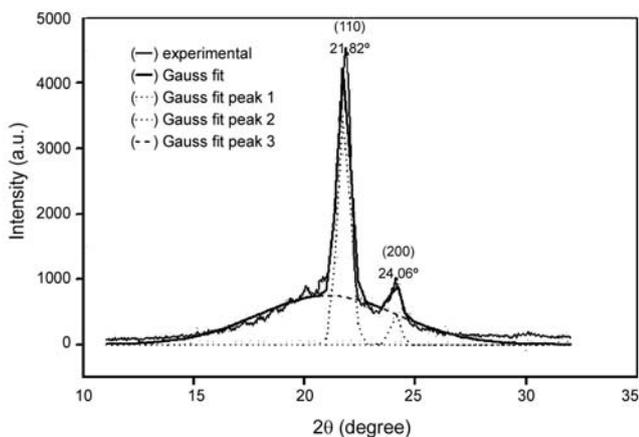area 3: area under the secondary crystalline peak at $2\theta=24.06°$.

Figure 9. Gaussian fitting of the crystalline peaks and the amorphous halo.
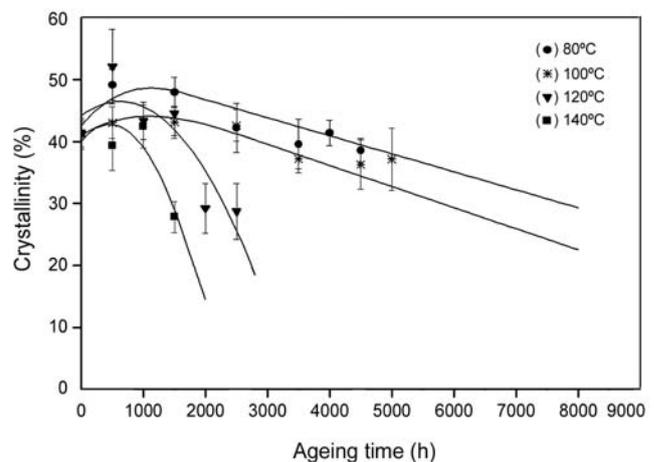

Figure 10. Crystallinity variation according to ageing time.

In Figure 10 we present the variations of crystallinity according to the ageing time at different temperatures with presentation of significant intervals (error bar). For more precision in the determination of crystallinity, the relevant statistical analysis for each temperature is presented in Table 5. The crystallinity increases at first time and then it decreases. The reduction in the crystallinity is more accentuated than the ageing raised temperature. The increase in crystallinity at the beginning of ageing is probably due to scission of tie molecules traversing the amorphous regions, followed by re-arrangement of released segments which favours the alignment of the chains imperfectly crystallized at the manufacturing step to increase crystallinity [34]. Sebaa et al. [40] have reported that creation of new intermolecular polar bonds, due to carbonyl groups leads to the crystallinity increase. The annealing effect at the oxidation temperatures may also contribute to increase in crystallinity [28,33].

With reference to thermal ageing at 120°C and 140°C, i.e., at temperatures higher than the XLPE

Table 5. Statistical analysis of crystallinity determination.

Ageing temperature	Number of readings	Standard deviation	P-value
80ºC	5	2,48039	0,12662
100ºC	5	1,00699	0,02057
120ºC	5	5,74956	0,11357
140ºC	5	5,07364	0,43633

melting point, the sharp drop in crystallinity, the reduction of the melting enthalpy measured with DSC (Table 2), the intensity decrease, broadening, and shifting of the maximum melting peak (DSC thermograms) towards lower temperatures after a short time of ageing indicates that strong bulk degradation occurs in the material caused by different mechanisms such as thermo-oxidation reaction, chain scission, etc. Due to continuous heating, the crystalline parts of XLPE become amorphous which make oxygen diffuse easily and therefore undergo thermo-oxidative chain scission readily. The same mechanism can be proposed also for thermal ageing at 80°C and 100°C, however, at these temperatures thermal degradation phenomena take place at lower rates as the crystalline parts of the material do not melt at these temperatures and need longer heating time.

Ageing Compensation Effect (ACE) Validity in the Crystallinity Variation
The ageing compensation effect (ACE) has been observed and introduced for first time by David [41] in the thermal ageing of polymeric materials of electrical interest, by studying some electrical and mechanical properties. It has been deduced from the Dakin theory based on the Arrhenius law which is given as follows:

$$\log(t) = a + \frac{b}{T} \tag{3}$$

The AEC effect is expressed by single linear relationship between the slope b (activation energy) and the ordinate intercept a (pre-exponential term) of the endurance lines obtained for different end-point criteria. The ageing compensation effect (ACE) thus derived is expressed by [41]:

$$a = \alpha + \beta b \tag{4}$$

Montanari [42] has deduced a new life model based on the ACE which can be written from eqn (4) as:

$$\log t = a + \frac{1}{T}\left[\frac{a}{\beta} - \frac{\alpha}{\beta}\right] \tag{5}$$

This model can be considered to be a general case of the commonly-used one. An interesting feature of the
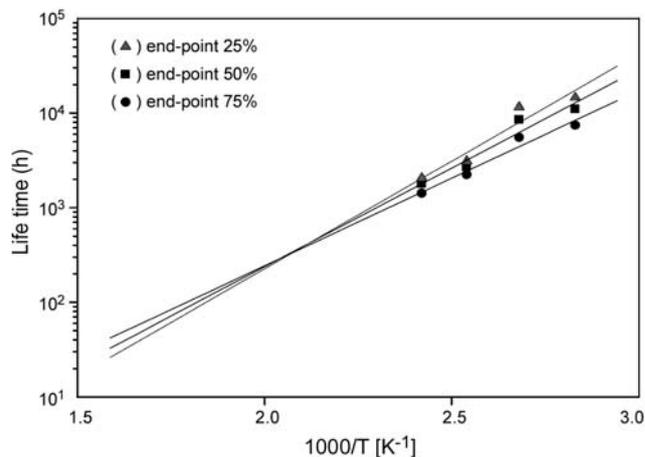

Figure 11. Thermal endurance lines according to the crystallinity for different end-points.

proposed model is that the life lines pertinent to the chosen property and different end-points are not parallel but convergent. David [41] shows that one of the consequences of the ACE is the presence of common point of intersection, known as "isokinetic" point, which corresponds to the "isokinetic" temperature T_{is}.

In order to verify the validity of life model derived from the ageing compensation effect theory [42], we have used crystallinity variation to determine the thermal endurance characteristic for different end-points. The chosen end-points are 25 %, 50 %, and 75% of the initial crystallinity value. The results are presented in Figure 11 where the variation of the insulation lifetime is given versus reciprocal absolute temperature. The obtained curves are non-parallel
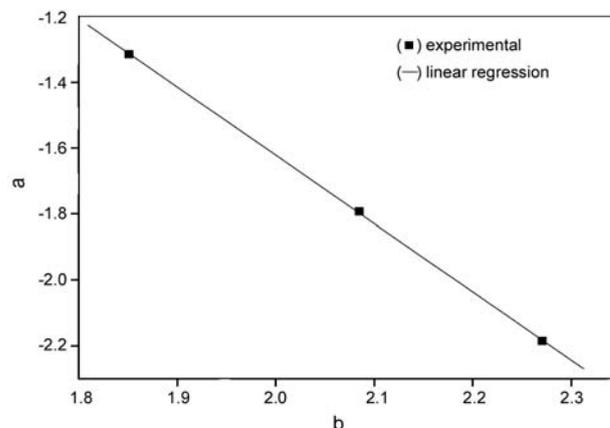

Figure 12. ACE Line obtained from thermal endurance of XLPE for different end-points.

straight lines. In Figure 12 the slope b (activation energy) is shown according to the ordinate intercept a (pre-exponential term) of the endurance lines obtained for different end-point criteria. The obtained data can be described by a single linear relationship which confirms the existence of the ACE effect. The Arrhenius parameters present a good linear regression ($R^2 = 0.9999$) and the ACE parameters have in our case the following values: $\alpha = 2.52322$ and $\beta = -2.07258$.

Correlations between Structural Changes and Performances of XLPE as Insulation Cables

Firstly, one can state that cable ageing process is a very complex phenomenon. It would be very useful to measure the ageing rate without knowing which particular ageing process takes place. The key goal of all ageing studies is to find out which process is the dominant one in cable ageing. A lot of insulation properties can be used to estimate the degradation degree. In addition to the highlighted structural changes above, we have investigated dielectric properties (loss factor, volume resistivity, and relative permittivity) and mechanical properties (elongation-at-break and tensile strength) [9,13-15]. Secondly, we may admit that the detailed interpretation of the observed structural changes must be in the light of specific use of the polymer as cable insulation.

Correlation between the obtained results may be discussed, in this point of view, as follows: After 5000 h of ageing at lower temperatures (below the melting temperature of the insulation), the dominant ageing process is the so-called physical ageing which as a consequence of increase in degree of crystallinity (post-crystallization) leads to higher homogeneity in crystalline part of the polymer.

However, the oxidation degradation has a limited effect in this case and concerns mainly the amorphous fraction of the insulation because oxygen diffusion across the compact crystalline domains is almost impossible. The dominant process in this case has a small effect in the changes of the mechanical and electrical properties of XLPE. Elongation-at-break and tensile strength [9,13,15], and volume resistivity [13,14] maintain their values practically at the end of ageing period. Furthermore, we have even noticed an improvement of dielectric loss factor. This

characteristic presents distinctly lower values after ageing at these temperatures [13,15].

According to the morphological structure, polyethylene and cross-linked polyethylene are polymers which consist of two mutually intermixed phases, the amorphous and crystalline phases. It is found [43] that the crystallinity degree has some influence on the following properties of the insulation: the softening and melting temperatures, dielectric losses, electrical breakdown, resistivity, and the resistance to partial discharges. Andjelkovic et al. [44] have reported that tensile strength, elongation-at-break and crystallinity degree of cable samples may age under thermal stress changes in a similar way according to the ageing time, for which some correlations can certainly be made.

After a short time of ageing, compared with the previous ageing time, at 120°C and 140°C (above the melting temperature of XLPE) two dominant mechanisms can be associated with the ageing process. At the beginning of ageing (after a few hundreds of hours), the particular ageing process which takes place is the physical ageing and leads to increased crystallinity (Figure 10). The overriding mechanism for crystallinity increase in the first stage of ageing is the secondary crystallization. This mechanism occurs since the regions remaining amorphous still have the potential to partially crystallize. The newly formed lamellae are constrained by those formed during primary crystallization. They are thicker as they are formed at higher temperatures. Consequently this ageing process results particularly in the diminution of the dielectric loss factor [13,15].

In fact, as the ageing goes on, and regarding the intensive ageing conditions the main crystalline regions, which are practically antioxidant free, are melted during ageing and makes oxygen diffusion proceed easier. The oxidation process is then begun and auto-accelerated. The oxidation process has been followed by chains scission, and formation of smaller chain segments leads to the intensity weakening, broadening and shifting of the maximum melting peak towards lower temperatures in the DSC thermograms (Figure 4). This disruption of the crystalline order of the polymer causes an abrupt decrease of the crystallinity degree after a short ageing time at these temperatures.

The processes summarized in this picture are responsible for the observed performance changes. Chains scission leads to the diminution of the mechanical properties (elongation-at-break and tensile strength) [9], drops in molecular mass and cross-linking degree (increase of hot-set-test) [9,14]. On the other hand, chains scission reactions contribute to the formation of vinylidene and vinyl groups and other unsaturation groups in XLPE chains. These groups are responsible for the colour changes of the material under thermal stress.

As we demonstrated above, with increasing ageing time and stress, FTIR absorption spectroscopy has revealed an intensity increase of the peaks over the range 1500 cm^{-1} and 1900 cm^{-1}, thus indicating an increase in concentration of the carbonyl groups (Figures 2 and 3). These findings can help to explain the significant disruption in the dielectric properties of the material. The significant incremental increase in carbonyl groups concentration leading to the sharp decrease in the volume resistivity and significant increment of dielectric loss factor and relative permittivity would finally lead to the failure of the insulation. [13,14].

Since thermal deterioration is due to the acceleration of chemical reactions produced by increasing temperature, the ageing rate can be assumed proportional to the rate of chemical reactions. Kim et al. [12] have reported the existence of similarity in variation of carbonyl index and loss factor (tan δ) of XLPE during thermal ageing. Volume resistivity decreases from 10^{14} Ω.cm to 10^{12} Ω.cm after 1500 h at 140°C and 2500 h at 120°C. However, the loss factor increases from about 12×10^{-4} to 50×10^{-4} after 2500 h of ageing at 120°C and reaches 500×10^{-4} after 1500 h of ageing at 140°C.

CONCLUSION

The diagnosis of accelerated thermal ageing of cross-linked polyethylene was investigated in this study. From the obtained results, it can be stated that some chemical changes like oxidation were detected. The main changes are the formation of carbonyl groups (aldehyde, ketone, etc.). It can be concluded that thermal ageing at temperatures under the melting one

have a little effect on the XLPE structure. However, significant changes of thermo-oxidative products are more evident in samples aged at temperatures above 120°C.

Thermal ageing of XLPE may promote chain scission and oxidation reactions, which modify the position and shape of peaks in DSC thermograms. The obvious changes of the DSC parameters (crystallinity, melting peak, and heat of fusion) can be observed in samples aged at different temperatures. The significant observed changes after ageing at 120°C and 140°C suggest that material underwent severe deteriorations, due to the chain scission, induced by the intensive thermal ageing conditions. This deterioration is revealed by crystallinity decrease, broadening and shifting of the main melting peak towards lower temperatures.

The use of X-ray diffraction in studying the effect of thermal ageing on the crystallinity of cross-linked polyethylene makes it easy to indicate that thermal ageing has not any effect on the crystalline phase of XLPE. However, thermal ageing conditions have a great effect on the crystallinity degree. It increases at the beginning of ageing and then it decreases. Reduction in crystallinity degree is more pronounced with higher ageing temperature.

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