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Dielectric Properties and β -Relaxation in Cross-linked Polyethylene: Effect of Thermal Aging

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Abstract- The present paper aims at investigating the influence of thermal aging on the crystallinity, the permittivity and β -relaxation of cross-linked polyethylene (XLPE) used in power cables. For this, accelerated thermal aging is performed on circular XLPE samples for 5040 h (210 days) at 80, 100 and 120 °C and for 1512 h (63 days) at 140 °C. Changes in the crystallinity of XLPE are assessed by Differential Scanning Calorimetry (DSC). Frequency domain dielectric spectroscopy is used to analyze the variations of real and imaginary parts of the permittivity, before and after aging. Moreover, β -relaxation is investigated through loss factor (ϵ_r'') analysis in the temperature range from 0 to 100 °C at several different frequencies 10, 10², 10³ and 10⁴ Hz. We show that dielectric spectroscopy is not the best suite method to reveal the earlier steps of aging.

Keywords: cross-linked polyethylene, dielectric relaxation, thermal aging, differential scanning calorimetry, permittivity.

I. INTRODUCTION

With the advent of synthetic insulating materials in the middle of the 20th century, cross-linked polyethylene (XLPE) continues to be extensively used in underground cables manufacturing due to its excellent dielectric properties [1, 2]. Nevertheless, cables could be exposed to severe thermal constraints during their operating conditions. Consequently, insulation may suffer degradation and structural changes due to thermal oxidation [3]. In a previous work [4], it has been found that at the beginning of aging, the mechanisms of degradation are inhibited by the antioxidant introduced into the material. Also, post-cross-linking reactions could occur leading to a decrease of orientation polarization in the material due to the recrystallization of some parts in XLPE. On the other hand, the chemical degradation of XLPE during prolonged thermal stress consists mainly in the consumption of the antioxidant followed by the generation of polar groups such as carbonyl, peroxide and hydroxyl groups.

In polyethylene material, three principal relaxation modes can be observed. The α relaxation is generally observed in crystalline polymers and it is usually related to the motion of chain units within the crystalline portion [5]. The α -process was reported as dielectrically active due to the reorientation of carbonyl groups in the chains in the crystalline phase [6]. However, space charge processes seem to be at play as well. Therefore, it cannot be easily used as an aging marker. In

contrast, β and γ processes have their origins in the amorphous phase [5].

Several studies were performed to investigate dielectric relaxation modes of polyethylene in the perspective of aging diagnosis development. D. Kostoski *et al* [7] studied the effects of gamma irradiation in air and accelerated aging on low-density polyethylene (LDPE) using thermally stimulated discharge current (TSDC) measurements. Results show the increase of the intensities of the β and γ dielectric relaxations and the shift of their positions due to the influence of radiation dose and accelerated aging. Moreover, E. Suljovrujić *et al* [8] showed that the decrease of the β relaxation intensity can be related to a decrease of the amorphous fraction in LDPE. Besides, irradiation and accelerated aging induced a decrease of the activation energy of this relaxation mode.

In the current work, we focus on β -relaxation of XLPE and its changes produced due to a different aging method, which is accelerated thermal aging. For this, XLPE samples have been subjected to aging for 5040 h (210 days) at 80, 100 and 120 °C and for 1512 h (63 days) at 140 °C. The evolution of the loss factor, ϵ_r'' , associated with the β -relaxation is proposed as a parameter to reflect aging degree. Therefore, frequency domain dielectric spectroscopy measurements have been performed. In fact, the variations of phase transitions of XLPE due to thermal aging have been monitored in our previous work [4] using differential scanning calorimetry (DSC). Some results will be discussed in this study in order to show the correlation between the crystalline structure and the dielectric relaxation. This will also lead to a better understanding of aging and degradation mechanisms and to assess the relevance of using the changes in the β relaxation process as an aging marker.

II. EXPERIMENTAL SECTION

A. Material and Samples Preparation

The studied material is used for extruded ac power cables of nominal voltages $U_0/U = 18/30$ kV. First, the pellets of cross-linkable resin (LE4201R from Borealis) are provided with 2 wt. % of di-cumyl peroxide (DCP) as cross-linking agent. The material contains also di-tert-butyl peroxide and Irganox antioxidant.

For manufacturing the XLPE samples, the pellets were preheated for 5 minutes at 125 °C then molded and cross-linked at 185 °C under a pressure of 300 MPa using a heating molding press. These conditions (300 MPa and 185 °C) are maintained for about 10 minutes to ensure complete cross-linking of the material. At the end, the press is cooled with water with maintaining always the same pressure.

Finally, XLPE plates were cut into circular shape samples with a diameter of about 46 mm and a thickness of (2 ± 0.2) mm. Samples were cut using a cutting press with a circular cutting die tool.

B. Thermal Aging Experiments

Accelerated thermal aging tests were carried out by arranging the XLPE circular samples vertically inside air-circulating ovens for 5040 hours (210 days) at 80, 100 and 120 °C. Moreover, since the degradation process is very fast at 140 °C, samples have been aged for a maximum duration of 1512 hours (63 days).

C. Frequency Domain Dielectric Spectroscopy

Real and imaginary parts of the permittivity were measured using Novocontrol Alfa-A High Performance Analyzer dielectric spectrometer with a ZGS active sample cell. The system can control the temperature under N₂ atmosphere by a Quatro cryosystem within ± 0.1 °C. Prior to the dielectric measurements, gold electrodes were deposited onto both surfaces of XLPE circular samples by sputtering. The diameter and the thickness of the sputtered electrodes are respectively 35 mm and 30 nm. Real and imaginary permittivity, ϵ_r' and ϵ_r'' were analyzed before and after aging in the temperature range from 0 to 100 °C at 10, 10², 10³ and 10⁴ Hz.

III. RESULTS

A. Dielectric constant ϵ_r'

Dielectric constant values are presented in Fig. 1 versus temperature at different frequencies. From the obtained results, before and after aging at temperatures of 80 and 100 °C, ϵ_r' remains practically constant as the temperature increases from 0 to 85 °C. Then, ϵ_r' starts to decrease slowly from 85 to 100 °C. In fact, at lower temperature, the segmental motion of the chain is practically null and the dielectric constant is not affected. However, at sufficiently higher temperature, the dielectric constant is again reduced due to strong thermal motion which disturbs the orientational polarization [9].

Also, a slight decrease of ϵ_r' was observed in the case of aging at 100 °C at all frequencies from 0 to 85 °C. As already discussed in our pervious report [4], the post-cross-linking could optimize the crystallinity of the aged samples at 100 °C, leading to make the orientation of dipoles more difficult. Furthermore, it has been found also that the crystallinity of XLPE slightly increased from 39.8 % before aging to 42.4 % after aging at 100 °C for 5040 h, as given in Table 1.

In contrast, at aging temperatures of 120 and 140 °C, ϵ_r' rises significantly compared to other aging temperatures. Moreover, thermal agitation could be enhanced from 0 to

about 40 °C since the intermolecular forces between polymer chains are broken [9].

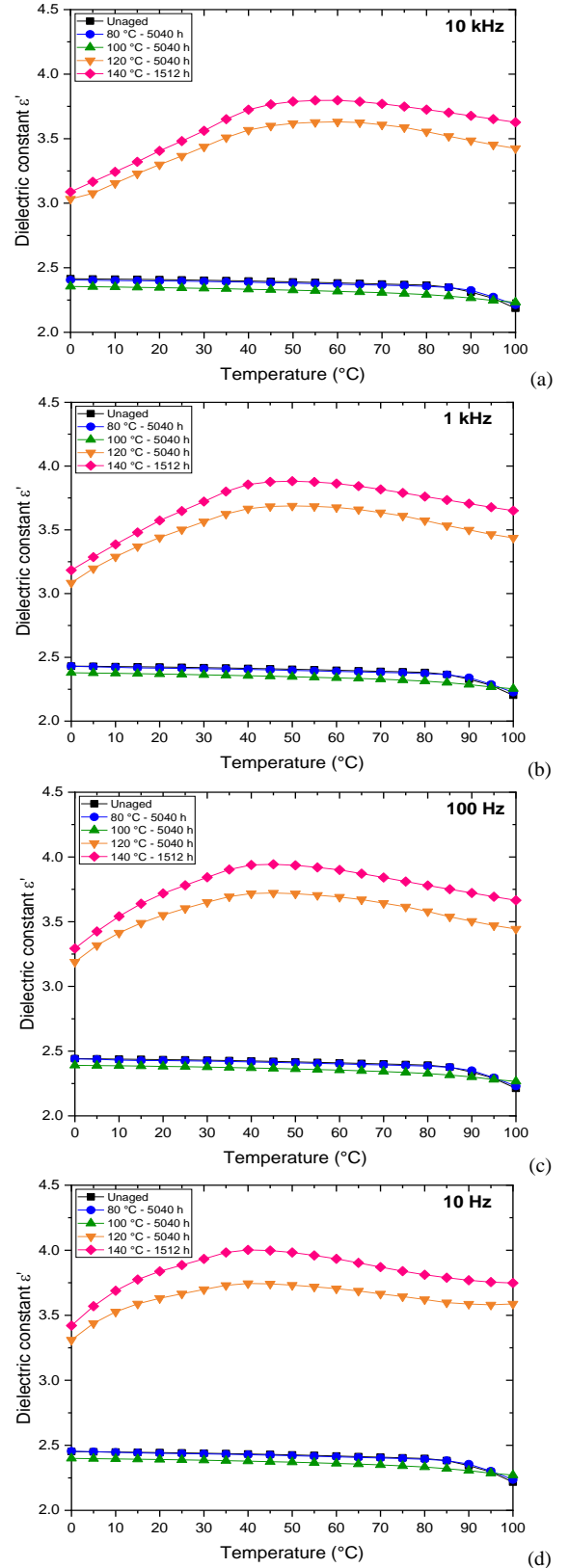


Fig. 1. ϵ_r' variations with temperature and for different aging temperatures at: (a) 10 kHz, (b) 1 kHz, (c) 100 Hz and (d) 10 Hz

Consequently, the dielectric constant increases with the temperature and then it decreases. The observed threshold temperature (40 °C) is lower than that at other aging conditions. This may be related to the shift of the XLPE melting peak toward lower temperatures after aging at 120 and 140 °C [4].

TABLE I
RESULTS OBTAINED FROM DSC MEASUREMENTS (SECOND SCAN)

	Unaged	80 °C, 5040 h	100 °C, 5040 h	120 °C, 5040 h	140 °C, 1512 h
T_m (°C)	104.43	104.41	104.80	82.77	70.09
ΔH_m (J.g ⁻¹)	111.30	112.70	118.70	67.40	35.87
χ_c (%)	39.75	40.25	42.39	24.08	12.81

T_m is the melting point, ΔH_m is the enthalpy of fusion and χ_c is the crystallinity rate

B. Imaginary part of permittivity ϵ_r'' and β -relaxation

In this section we have chosen to study the evolution of ϵ_r'' in order to investigate the influence of aging on the β -relaxation of XLPE. Fig. 2 presents ϵ_r'' curves versus temperature at different frequencies before and after aging. The results before and after aging at 80 and 100 °C show that the imaginary part of the permittivity remains nearly temperature-independent (from 0 to 100 °C) at 1 and 10 kHz and the relaxation peak could not be noticed. As the frequency decreases, the curves are shifted to lower temperatures and a minimum appears at 80 °C for the frequency 10 Hz. Also, ϵ_r'' decreases with the decrease of the frequency in the case of aging at 100 °C which is most likely a consequence of reduced mobility of the chain segments due to the enhancement of the crystallinity [8].

When the degradation becomes more advanced, at 120 and 140 °C, ϵ_r'' drastically rises and the peak attributed to the β -relaxation can be easily observed at lower temperatures. At these aging conditions, chain scission by thermal oxidation is the dominant process and the crystallinity decreases as shown in Table 1. As a result, the amorphous phase becomes more important which makes the macromolecule chains more flexible to interact under the polarization effect. This result remains very important indicating how dielectric losses in XLPE cables could be very significant, even below 40 °C, depending on the frequency. In accordance with previous works [7], [8] and [10], β shifts toward lower temperature with decreasing frequency, however its intensity is not significantly affected. As shown in Fig. 2c and 2d, a dielectric loss peak occurs at a higher temperature than the β process. The beginning of the α -relaxation peak can be well observed at 10 and 100 Hz. Furthermore, the frequency-temperature shift of the β -relaxation could be fitted by the Arrhenius equation (1) in the cases of aging at 120 and 140 °C:

$$f_{\max} = f_0 \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where E is the activation energy, k is Boltzmann's constant, T is the absolute temperature and f_0 is a constant. The results are plotted in Fig. 3. On the basis of the imaginary part of permittivity, the activation energy for sample aged at 120 °C is 2.22 eV compared to 1.93 eV for aging at 140 °C.

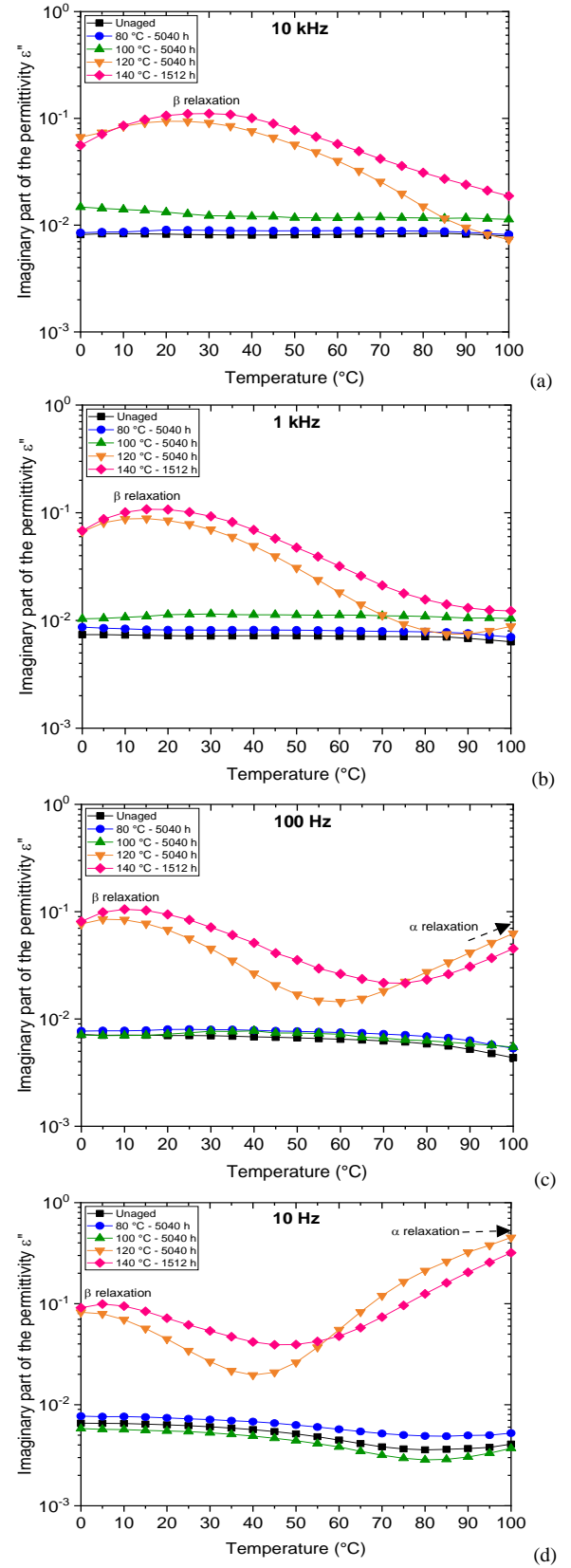


Fig. 2. ϵ_r'' variations with temperature and for different aging temperatures at: (a) 10 kHz, (b) 1 kHz, (c) 100 Hz and (d) 10 Hz

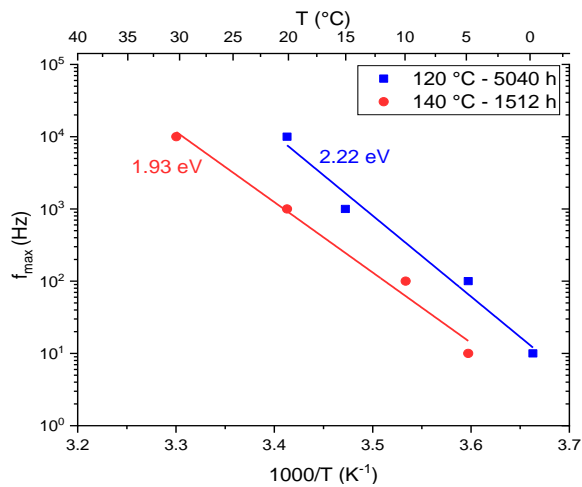


Fig. 3. Arrhenius plot of β -relaxation peaks for aging at 120 and 140 °C

IV. DISCUSSION

A large change in the dielectric behavior of XLPE was observed when changing the aging temperature from 100 to 120 °C. One of the reasons could be the fact that the temperatures are at both sides of the melting point, hence the oxidation kinetics would be slowed down in the partially crystalline state. To bring some light on this point, we have plotted in Fig. 4 the dielectric loss factor measured at 20 °C as a function of aging time at 120 °C. Very clearly, the losses increase abruptly between the last two aging times and so does the dielectric permittivity [4]. Similar trends were observed at 140 °C indicating that a critical degradation state exists in the material. Comparatively, the carbonyl index (Fig. 4) follows a more progressive rise before a final step [4]. The abrupt changes in properties can reasonably be ascribed to the end step of antioxidant consumption and the subsequent attack of the polymer chains by oxidation.

Regarding activation energies, Geng *et al.* [11] reported on the change in high temperature dielectric losses in XLPE aged in the same temperature range but with much shorter times (up to 240 h) than herein. Activation energies of the same order as here were obtained, without a clear trend vs. aging degree. Conduction processes were advocated related to these losses. According to the variation of permittivity and losses, the aging degree after 1512 h at 140 °C would be higher than after 5040 h at 120 °C. With the increase in degradation, the activation energy has significantly decreased, and the peak position has changed. However, monitoring the aging degree through this parameter does not seem feasible as the relaxation is very weak at low degradation degree.

V. CONCLUSION

This paper highlights the evolution of ϵ_r' and ϵ_r'' in XLPE samples with thermal aging. Also, β -relaxation process is studied and correlated to the physical structure changes of the material. The main conclusions of this study can be summarized as follows:

i/ XLPE properties remain practically unchanged in the case of aging at 80 °C whereas some improvement of the crystallinity

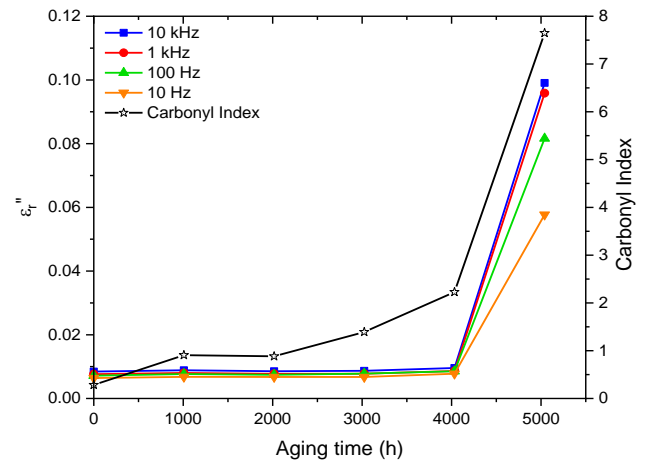


Fig. 4. Evolution of loss factor and carbonyl index as a function of aging time at 120 °C

and the dielectric behavior of XLPE can be noticed at 100 °C. Physico-chemical degradation is effective when aging at 120 and 140 °C, leading to substantial increase of ϵ_r' and ϵ_r'' .

ii/ Dielectric losses in degraded XLPE cables could be large near operating temperatures (10 to 40 °C).

iii/ β -relaxation peak intensity and position are strongly dependent upon the changes of the amorphous phase. This could be a good indicator of the severe deterioration of XLPE structure. For revealing the earlier stages of degradation, the carbonyl index seems to represent a better parameter.

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