

## Effect of heat treatment on morphology and dielectric properties of PE cable insulation material

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### Abstract

It is known that the heat treatment process in the production of extruded cables, affects the electrical properties of polymeric insulation materials; this effect is via two main phenomena; first, it leads to diffusion and removal of polar substances from the system; second, it affects the polymer morphology by increasing the polymer chain relaxation and creation of crystallites, hence increasing the crystallinity of the material.

In this study, thick pressed samples with additive free low density polyethylene (LDPE) insulation material were heat treated at different conditions for different periods of times. Differential scanning calorimetry (DSC) measurements confirmed that heat treatment leads to higher crystallinity and higher lamella thickness in LDPE. Dielectric properties of the material was studied by conduction current measurement and dielectric spectroscopy.

Conduction current of samples with different heat treatment times was measured at high electric fields which shows that the conduction current of LDPE is affected by heat treatment. Generally, the apparent conductivity decreases by heat treatment.

Dielectric spectroscopy measurements show that heat treatment does not have a significant effect on real and imaginary permittivity of the polymer. Interestingly, an increase in the sample thickness via heat treatment, was observed both by sample thickness related to the memory effects in the polymer which needs to be taken into consideration for accurate capacitance measurements.

### 1. Introduction

The application of high voltage DC cables with extruded insulation has increased considerably since its first introduction in the late 90's [1]. Today extruded HVDC cables with cross-linked Polyethylene (XLPE) insulation for voltages as high as 525 kV is available [2]. Although research on new insulation concepts is ongoing in many academic and industrial institutes, today XLPE is the predominant insulation technology used in extruded HVDC cables.

For the reasons above, different types of Polyethylene and specifically cross-linked polyethylene is between the most well studied materials, when it comes to

electrical properties such as polarization and conduction properties. Nevertheless, due to the still growing importance of this insulation material, a better understanding of the relation between chemical and electrical properties of Polyethylene is valuable.

XLPE is produced by creating cross-links between Polyethylene by reactions mediated commonly via decomposition reactions of peroxides; Dicumyl Peroxide (DCP) is the most common peroxide used in production of XLPE cable insulation. The cross-linking reactions from decomposition of DCP leads to formation of volatile species in the insulation such as Methane, Acetophenone, Cumyl-Alcohol, Alpha-Methyl-Styrene and Water, also known as cross-linking by-products, from which the polar species are known to influence the electrical properties of the insulation under DC electric field [3]. In order to remove the Methane all XLPE insulated cables (AC or DC) are heat treated with ventilation (also known as degassing). In case of DC cables, degassing helps to remove the polar species and decreases their influence on conductivity [4].

Generally, degassing of XLPE leads to reduction of its conductivity [5] and generally it has been attributed to the removal of polar species from the insulation. But it is well-known that heat treatment, also affects the morphology of PE [6], [7]. It has been shown that heat treatment leads to formation of new thin crystallites and thickening of existing crystallites in PE [7]. Heat treatment at higher temperature or longer heat treatment time at a certain temperature leads to creation of thicker crystallites; such changes in morphology can be detected using DSC.

Besides, the morphology and by-products, heat treatment in presence of air, may lead to oxidization of the polymer. Although oxidization at normal heat treatment temperatures (70-90 °C) may be small [8], it has to be taken into account. Effect of oxidization and Carbonyl content on electronic structure of LDPE has been detected in different studies for example [9].

Since during degassing, both chemical composition of XLPE and its morphology are affected, it is hard to associate the effect of degassing on conductivity only to removal of polar cross-linking by-products.

The purpose of this study is to specifically study the effect of heat treatment on the morphology and electrical properties of PE. For this reason, clean additive free LDPE without any peroxide nor

Antioxidant has been used to isolate the effect of heat treatment only to morphological changes which is studied using DSC. The electrical properties of the LDPE has been then studied by dielectric spectroscopy and high field conduction measurements. Finally, the results are analyzed and conclusions are made.

## 2. Experiments

Studies are performed on clean additive free LDPE insulation material. Thick samples (1 mm) have been used to minimize surface effects associated to chemical reactions, degassing, or on electrical measurements. The samples have been heat treated either in vacuum oven or in Aluminum foil to minimize effect of oxidization. To see the effect of oxidization, one sample was heat treated in normal oven and results were compared with other references.

Morphological effects are studied by DSC while electrical tests were done by dielectric spectroscopy and high field DC conduction. The thickness of the samples were also accurately measured before and after heat treatments and tests.

### 2.1. Sample preparation

LDPE granulates were pressed in a Fontijne Grotnes hydraulic polymer press to prepare circular plaque samples for the experiments. The samples were 1 mm in thickness and 14 cm in diameter. The press molding was done by heating from room temperature to 130 °C under 20 kN pressure between two metal plates in the press to melt the granulates before increasing the pressure to 200 kN and forming the samples; pressure was maintained for 18 minutes before the samples were again cooled down to room temperature using the water cooling feature of the press.

The samples were packed tightly in Al foil and stored in a freezer before they were taken to heat treatment. The first set of samples used for DSC and dielectric spectroscopy studies, were heat treated in vacuum oven at 50 °C for different time periods to achieve different levels of annealing. The heat treatment times for these studies were chosen as 0, 1, 2, 4, 8, 16 and 64 h.

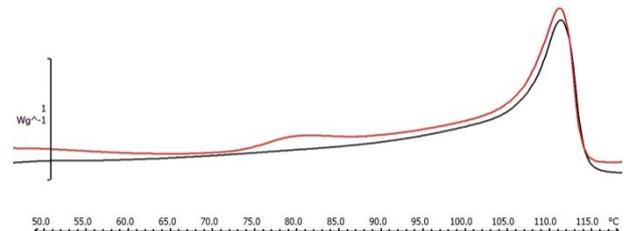
A second set of samples used for conductivity measurement were heat treated in normal oven at 50 °C for different time periods. In this set, the samples were tightly wrapped in Al foil to minimize effect of degassing or oxidization. One sample was heat treated in normal oven at 50 °C for 74 h without any diffusion barrier for comparison.

All electrical measurements were done immediately after heat treatment was completed and no further storage was done; and each sample is used only for one measurement and no sample is reused.

### 2.2. DSC results

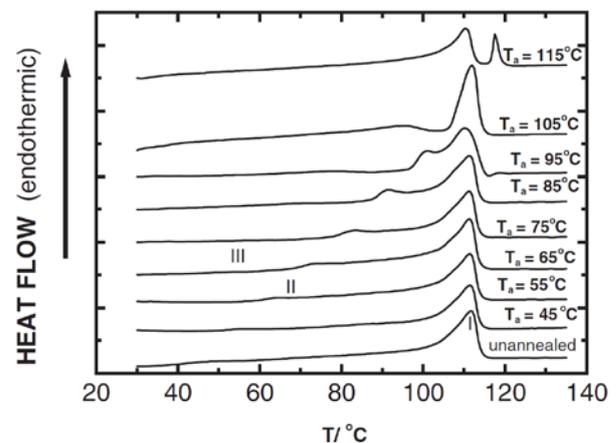
Differential scanning calorimetry (DSC) was employed with a Mettler Toledo DSC 1 thermal analysis

equipment to estimate the crystallinity of the samples with different levels of heat treatment. The effect of heat treatment can be observed from the DSC output curve. For example, in Fig. 1 the black curve is for a sample without any heat treatment and the red curve is for a sample that was annealed at 80 °C. A peak is observed in the DSC curve from the heat treated sample around the heat treatment temperature.



**Fig. 1** – Example DSC output curve for LDPE before (black) and after (red) heat treatment at 80 °C; an extra peak appears in the curve due to the heat treatment.

This phenomenon has been observed and reported in other publications as well. Fig. 2 from [6] shows the relation between the temperatures of the DSC curve versus the heat treatment temperature. The peak is associated to the thickening of crystallites and usually is seen at temperatures slightly higher than the heat treatment temperature. It is also observed that longer heat treatment time leads to a shift of the peak in the DSC curve to higher temperatures. The results of DSC measurements in this study were in agreement with the aforementioned reports.



**Fig. 2** - Thermograms of LDPE after annealing at different temperatures from [6]; a peak in the curve is observed at a temperature slightly higher than the annealing temperature.

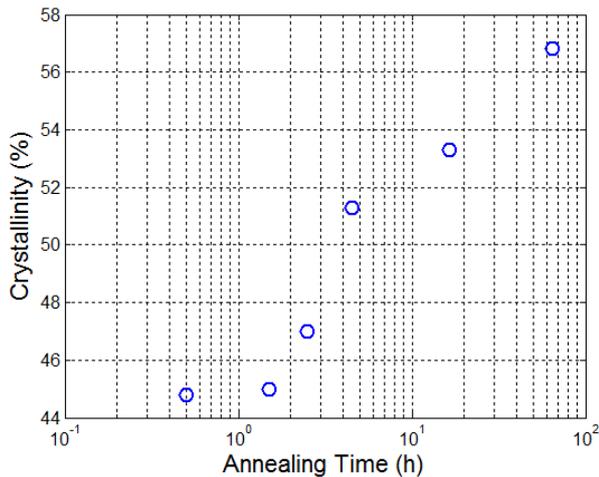
In this work the total enthalpy method [10], [11] has been used to determine the degree of crystallinity. The crystallinity,  $W_c$  was calculated from Eq. 1:

$$W_c = \frac{\Delta h_{exp}}{\Delta h_f(T) - \int_{T_1}^{T_m} (C_{pa}(T) - C_{pc}(T)) dT} \times 100 \quad \text{Eq. 1}$$

Which relates  $W_c$  to the enthalpy of the samples,  $\Delta h_{exp}$ ,  $T_m$  (Desired temperature to find the crystallinity, 290 K

used in this study),  $T_1$  (Lower limit of integration, 243 K),  $\Delta h_f(T)$  (Heat of fusion of 100% crystallized PE, 290 J/g [6]),  $C_{pa}(T)$  (Heat capacity of amorphous PE) and  $C_{pc}(T)$  (Heat capacity of crystalline PE).

The crystallinity of samples annealed (heat treated) at 50 °C for different times, is plotted in Fig. 3. It is observed that the crystallinity of the samples increases by longer heat treatment times. This means that heat treatment at 50 °C affects the morphology of LDPE by facilitating the movement and relaxation of polymer chains into the crystallites which leads to higher crystallinity of the sample.



**Fig. 3** – Effect of annealing time at 50 °C and calculated crystallinity from DSC measurements.

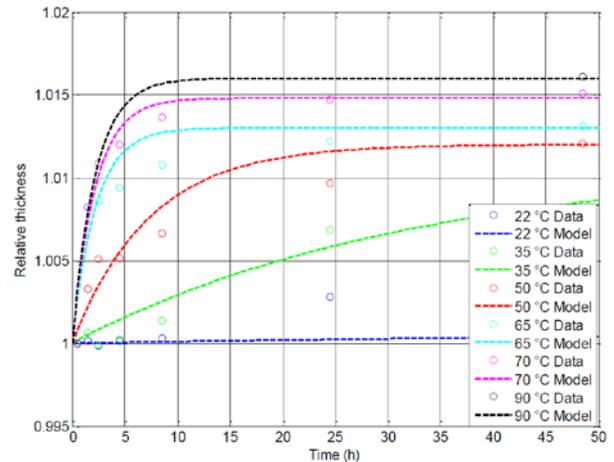
### 2.3. Thickness variation

During the calibration measurements, a general decrease in the capacitance of the samples was observed by heat treatment. After careful measurement of sample thickness, before and after heat treatment, it was observed that the thickness of the samples increased marginally by heat treatment [12]. This is attributed to the fact that since granulates with 1,5 -2 mm in diameter are used to press 1 mm thick plates, a small residual of “history” remains in the polymer which lead to slight “swelling” of the samples upon relaxation at moderated temperatures. For example, Fig. 4 shows the relative change of sample thickness normalized to the original thickness of approximately 1 mm thick LDPE press molded samples, after heat treatment at different temperatures and times.

It is notable, that all thickness measurements are done at stable room temperature conditions, hence the thermal expansion effect is excluded.

Although such small change of thickness may be irrelevant to most measurements, but in accurate dielectric measurements, it is necessary to pay careful attention to this effect in order to avoid wrong conclusions. If not corrected, 1 % increase of sample thickness, leads to 1 % lower measured capacitance which may be interpreted as decline of permittivity which is wrong due to geometrical effects. Therefore, in

all electrical measurements in this study, the thickness of the samples before and after tests was measured and taken into account in the analysis of the results.

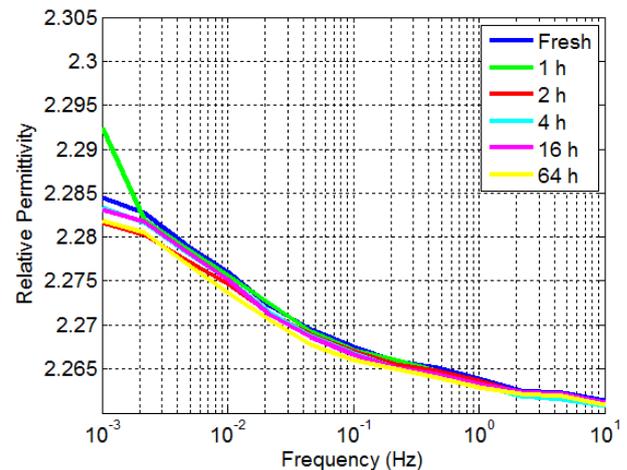


**Fig. 4** – Relative change of sample thickness after annealing at different temperatures for different times [12].

The sample thickness variation, is dependent to the type and size of granulates, pressing conditions such as temperature, pressure time, and geometry of the sample; therefore the conclusions from this study cannot be expanded to other cases, instead such effects should be evaluated for studies with different sample material, preparation and geometry.

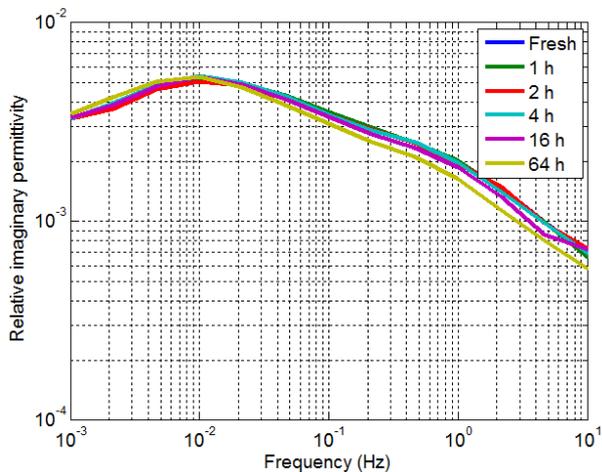
### 2.4. Dielectric spectroscopy

Dielectric spectroscopy measurements were conducted on samples with different heat treatment times to study the changes in dielectric response due to different levels of crystallinity. The real and imaginary relative complex permittivity was calculated and presented in Fig. 5 and Fig. 6 respectively, for samples with different levels of heat treatment tested in the frequency range of 1 mHz to 10 Hz under 500 V.



**Fig. 5** – Relative permittivity measured on 1 mm thick samples annealed at 50 °C for different times measured with 500 V. The permittivity does not change significantly.

The main conclusion from these studies was that within the accuracy of the dielectric spectroscopy measurement in this study, no considerably change was detected neither in real nor the imaginary permittivity of the samples. Therefore, it seems that although heat treatment at 50 °C causes morphological changes in the polymer, these changes are not large enough to affect the dielectric properties of clean LDPE for frequencies between 1 mHz and 10 Hz. For certain measurements done with higher field level (6 kV/mm) not included in this paper, implications of change of dielectric loss and frequencies below 1 mHz were done (see [12]).



**Fig. 6** – Relative imaginary permittivity ( $\epsilon''/m$ ) of 1 mm thick samples annealed at 50 °C for different times measured with 500 V. The change is insignificant.

### 2.5. Conductivity measurement

Effect of heat treatment time on high field conductivity of LDPE was studied by heat treating 1 mm thick press molded LDPE samples at 50 °C in normal oven. Although the samples were produced from clean additive free LDPE and they should be free of mobile polar chemical species, the samples were tightly wrapped in Al foil to minimize their contact with air which may facilitate degassing and also may cause oxidization. The samples were heat treated for different times from 0 to 70 h; one sample was heat treated without Al foil for 74 h to see the effect of contact with air. After heat treatment, the samples were mounted in the electrode system (for details of the setup see [13]), heated in an oven up to 50 °C, then 30 kV was applied on the samples and the charging current was logged every 5 seconds for 1 day. For each study one new sample was used and no sample was reused.

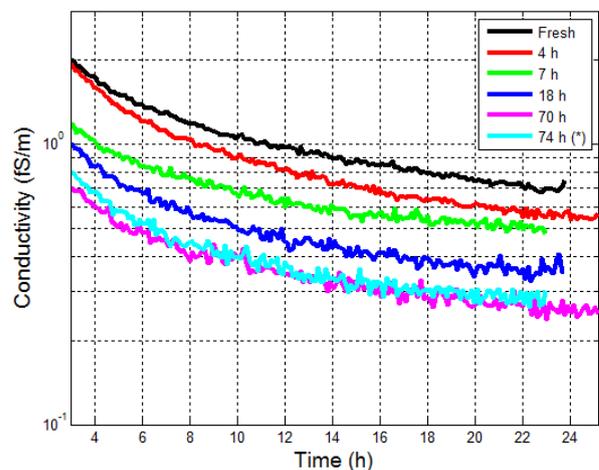
The measured leakage current is converted to apparent conductivity using:

$$\sigma = \frac{I}{U} * \frac{d}{A} \tag{Eq. 2}$$

Where,  $I$  is the measured current,  $U$  is the DC voltage,  $d$  is the sample thickness and  $A$  is the area of the measurement electrode.

Which after relaxation of polarization dynamics, will tend to conductivity of the samples.

The measured apparent conductivity of the samples is plotted in Fig. 7. The first few hours of are strongly affected by polarization currents therefore the data is only plotted after 3 hours. It is clear that heat treatment leads to a decrease of conductivity of the samples. For example, 70 h of heat treatment at 50 °C leads to a decrease of the high field conductivity by a factor of 2,0 which is considerable. The sample heat treated without Al foil for 74 h, shows very similar apparent conductivity as that the sample with Al foil and 70 h. This means that the effect of degassing and oxidization is negligible and therefore this decrease of conductivity is attributed to the morphological changes (increased crystallinity) of the polymer. It is in line with other studies [8] which found that unless exposed to much higher temperature (90 °C) and for longer periods of time (few weeks) the oxidization of LDPE during heat treatment is negligible.



**Fig. 7** – Apparent conductivity of 1 mm thick LDPE samples, annealed at 50 °C for different duration of time and measured at 50 °C with 30 kV during 24 hours. The conductivity decreases with longer heat treatment time.

**Table 1** – Apparent conductivity (fS/m) of samples with different heat treatment times measured after different times under voltage.

\*Heat treated without diffusion barrier.

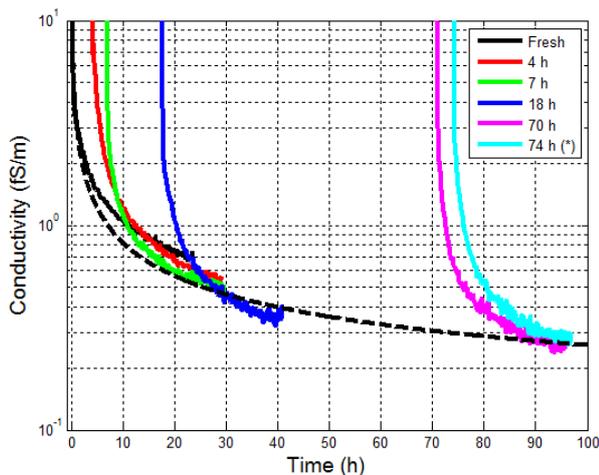
	4 h value	8 h value	12 h value	16 h value	20 h value	23 h value
4 h	1,75	1,20	0,99	0,84	0,76	0,69
7 h	1,60	1,05	0,81	0,70	0,60	0,56
18 h	1,04	0,76	0,64	0,56	0,53	0,48
70 h	0,84	0,60	0,50	0,41	0,35	0,35
74 h *	0,60	0,40	0,35	0,31	0,26	0,26

The measured apparent conductivity shown in Fig. 8 is presented in Table 1 for quantitative comparison. Using the measured data from different heat treatment times, efforts was paid to find a function to fit to the measured data. The best fit was found with:

$$\sigma = \sigma_t * t^{-0,6} + \sigma_s \tag{Eq. 3}$$

In which, steady state conductivity was found to be  $\sigma_s = 0,07 \left[ \frac{fS}{m} \right]$  and the transient conductivity is  $\sigma_t = 3 \left[ \frac{fS}{m} \right]$ .

Finally, the measured apparent conductivity of samples are plotted in Fig. 8 shifted in time in accordance to their heat treatment time, together with the fitted function in Eq. 3. All measurements show a transition in the measured leakage current after voltage application associated to polarization and charging processes, but after decay of these transients, the conduction current is in good agreement with the general decline of conductivity with heat treatment time.



**Fig. 8** – Apparent conductivity measured of samples plotted including their heat treatment time as a time lag. A clear trend can be observed in the decline of apparent conductivity by heat treatment.

Based on the results obtained from this study, it is concluded that heat treatment at 50 °C, affects the morphology of LDPE and the crystallinity increases by longer heat treatment. The change of morphology does not seem to have a strong influence on the polarization behavior of the polymer at frequencies above 1 mHz since permittivity and dielectric losses are not affected by heat treatment. Heat treatment may cause variations in the sample thickness due to the geometrical history of the polymer; this change should be evaluated for each material and sample preparation technique and considerations should be made on the sample thickness change to obtain correct dielectric spectroscopy results. Apparent conductivity of LDPE is found to be sensitive to heat treatment. Heat treatment at 50 °C leads to reduction of apparent conductivity. Since the presence of diffusion barrier does not seem to affect the conductivity, it is concluded that change of morphology affects the conductivity; in this case, longer heat treatment led to higher crystallinity and lower conductivity.

Since even heat treatment of clean additive free LDPE affects the measured apparent conductivity, the reduction of conductivity of XLPE due to heat treatment cannot be purely attributed to reduction of its polar

chemical content. Instead it can be explained as a combination effect of changes in the morphology and chemical content of XLPE. Besides, change of morphology will affect the distribution and dispersion of volatile chemicals in XLPE, so inter-coupled effects can also be expected. Therefore more studies need to be done on XLPE with and without polar chemicals and with different heat treatments to evaluate different processes on its DC conduction physics.

### 3. Conclusions

In this work, the effect of heat treatment on crystallinity and dielectric properties of clean additive free LDPE is studied.

1 mm thick press molded samples were heat treated at 50 °C for different durations of time; crystallinity was studied by DSC, dielectric spectroscopy was used for polarization studies and high field conduction current was measured at 50 °C and 30 kV, i.e. 30 kV/mm.

The results show that heat treatment at 50 °C, leads to an increase in the crystallinity of the samples which relates to heat treatment time. Dielectric spectroscopy did not detect any significant change in the dielectric response of the material in the range of 1 mHz to 10 Hz. It was detected that a small change in thickness happens in the samples which is attributed to the memory effect of the polymer in granulate form. This change needs to be evaluated and taken into account in capacitance measurement studies.

High field conduction measurement of samples with different heat treatment times show a clear relation between longer heat treatment time and a decline in apparent conductivity of the samples. Therefore there seems to be a relation between higher crystallinity of the samples due to heat treatment and their decline in high field conductivity.

Since heat treatment of XLPE, besides removal of polar volatile species from the polymer, leads to morphological changes, the effect of degassing on XLPE high field conduction cannot be purely attributed to the polar chemical content; instead a combination of morphological changes and the change of chemical content should be considered together with other combinational effects. Further studies need to be done on better understanding of effect of heat treatment on conduction in XLPE via different processes.

### 4. References

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