DC Conductivity Measurements of LDPE: Influence of Specimen Preparation Method and Polymer Morphology

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Abstract

DC conductivity measurements are important for gaining fundamental understanding of conduction mechanisms of insulation materials, as well as in the development of HVDC power system components, such as extruded cable systems. In this study, the influence of sample processing on the morphology and DC conductivity of low-density polyethylene (LDPE) has been studied. Direct compression moulding of LDPE pellets is commonly used in research laboratories for obtaining plaque samples, whereas extrusion is an additional commonly used technique for dispersion of particles in nanocomposites prior to the compression moulding process. In this study LDPE plaques have been obtained by either compression moulding directly from pellets, or by extrusion followed by compression moulding. The morphology obtained in the first case consisted of banded spherulites, whereas the latter method yielded a morphology of small axialites. The difference in sample processing had also an impact on the DC conductivity. The DC conductivity at 22 °C and 3.3 kV mm^{-1} was of the order of 4x10^{-18} S m^{-1} for the plaques obtained by extrusion and compression moulding whereas the plaques obtained by direct compression moulding exhibited a conductivity of 1x10^{-16} S m^{-1}. In addition, the reproducibility of the performed DC conductivity measurements was also verified in a round robin test performed between the Royal Institute of Technology and Chalmers Technical University.

1. Introduction

Power transmission over long distances enables harvesting of renewable energy sources located far away from the demand, connecting countries and continents by underground or subsea cables. High voltage direct current (HVDC) cable systems are suitable for this purpose compared with alternating current transmission, where the losses become too large at longer distances, due to capacitive losses of the latter [1]. The operating voltage of HVDC cables has been gradually increased over the past decades, with cable systems up to 525 kV available today. The use of higher transmission voltage will further reduce the losses, enabling even longer HVDC lines [2]. The increase in voltage requires improvement of the insulation material properties, e.g. breakdown strength, conductivity and space charge. Low-density polyethylene (LDPE) that is used as insulation materials in HVDC cables today is manufactured as pure as possible in order to minimize the conductivity by reducing the number of charge carriers. However, crosslinking of LDPE by using peroxides is a commonly used method in order to obtain a material with sufficient thermal stability. However, this method yield by-products present in the cable even after degassing [3].

DC conductivity and space charge measurements are two important characterization methods for HVDC cable insulation, both on plaque samples in lab scale as well as on real cables. Characterization of compression moulded samples and samples extracted from a real cable have been shown to yield similar results [4]. However, in order to obtain such results it is important to assess the experimental parameters during the preparation of the compression-moulded samples. Especially DC conductivity characterization can be affected by many parameters that may lead to erroneous conclusions, e.g. changes in morphology, oxidation, protective pressing film used during compression moulding, additives and moisture [4-7].

LDPE is a semicrystalline material with a crystallinity of ca. 50 wt.%. The crystalline lamellae radiate out from the centre of nucleation forming different superstructures such as spherulites or axialites. The morphology is dependent on the molar mass and the degree of chain branching of the polymer; in addition, the superstructure is strongly dependent on the concentration of nucleation points and on the crystallization temperature [8]. Therefore, when producing and characterizing new LDPE materials for HVDC insulation a careful study of the morphology should be included.

In this paper, the morphology of compression-moulded LDPE plaques, prepared in different ways has been investigated. Direct compression moulding of pellets into plaques has been compared with extrusion prior to compression moulding, or extrusion directly into a film.

The latter two methods are normally used for preparation of LDPE composites filled with particles or other additives [9]. Also the influence of protective films (PET or Al foil) during compression moulding has been investigated. Conductivity measurements of the prepared samples is presented by Xu et al. [10] at NORDIS 2017.

2. Experimental

LDPE pellets were provided from Borealis AB. Various sample preparation procedures were used for producing plaque specimens for DC conductivity measurements. Specimens were prepared at the Royal Institute of Technology (KTH) and Chalmers Technical University (CTH). At KTH, LDPE pellets were either directly compression moulded to plaque specimens or extruded prior the compression moulding. At CTH, LDPE pellets were directly compression moulded or directly extruded to a film by using a film die. The thickness of the specimens produced at KTH and CTH was 0.3 and 0.1 mm, respectively.

At KTH, compression moulding (LabPro 400 Press, Frontljne Grotnes) was preformed at 130 °C by first applying a contact pressure for 10 min, followed by a 200 kN press force applied for an additional 10 min period and finally water cooling to room temperature during 7 min, with a maintained compressive force of 200 kN. Polyethylene terephthalate (PET) films or aluminium (Al) foils was used as protective material around the LDPE during the compression moulding. LDPE powder was obtained by cryo-grinding of pellets after immersion in liquid nitrogen for at least 1 h. The LDPE material was then circulated in an extruder (Micro 5cc Twin Screw Compounder, DSM Xplore) at 150 °C, with 100 rpm for 6 min. Compression moulding was also the final processing step for the materials extruded at KTH.

At CTH, direct compression moulding of LDPE pellets was also carried out at 130 °C; first by applying a compressive force of 2 kN for 3 min followed by a gradual increase of the compressive force to 200 kN and finally the moulded material solidified during a water cooling with a maintained compressive force to room temperature during 6 min. Pellets were compression moulded either by using PET films or Al foils as protective pressing material. Extrusion at CTH was performed in two steps: extrusion of the LDPE powder to pellets followed by a second extrusion to a 0.1 mm thick film. A single screw Brabender extruder 19/25D was used with a temperature profile of 115, 130 and 140 °C from the hopper to the die and a screw rotation of 5 rpm.

The morphology of the compression-moulded specimens was investigated with a field emission scanning electron microscope (Hitachi S-4800) after permanganic acid etching for 2 h to reveal the crystalline domains in the bulk. Compression moulded samples were freeze cracked prior to the etching. The permanganic acid etchant contained 4 mL water, 16 mL phosphoric acid, 40 mL sulfuric acid and 600 mg potassium permanganate [11]. The samples were rinsed with water and dried in a desiccator after etching.

Differential scanning calorimetry (DSC) was preformed on 5 ± 0.5 mg pieces obtained from the plaque samples. The temperature profile for the DSC measurements was as follows: cooling to –50 °C, heating to 200 °C, cooling to –50 °C and finally heating to 200 °C at a rate of 10 °C min^{-1}. The time duration of the constant temperatures was 5 min. A nitrogen flow of 50 mL min^{-1} was used. The crystallinity and peak melting temperature were evaluated using the second heating scan, after which the thermal history of the samples had been erased. The mass crystallinity was assessed by the total enthalpy method [12].

$$w_c = \frac{\Delta h_f}{\Delta h_f^0 - \int_{T_1}^{T_m^0} (c_{p,a} - c_{p,c})\,dT} \tag{1}$$

where w_c is the mass crystallinity, T_m^0 the equilibrium melting point of PE, Δh_f the enthalpy of melting, Δh_f^0 the melting enthalpy for 100% crystalline PE at T_m^0 (293 J g^{-1}), $c_{p,a}$ and $c_{p,c}$ are the heat capacities for the amorphous and crystalline components, respectively. The equilibrium melting point is 414.6 K for PE. Published data of heat capacities were obtained from Wunderlich and Bauer [13]. The melting enthalpy was obtained by integration of the melting peak with a baseline drawn from –30 °C to a distinct end of the melting peak followed by a truncation of the integral to 25 °C. Melt flow index measurements (CFR 91 from DGTS) was preformed according to the ISO 1133 standard method using a load of 2.16 kg at 190 °C.

3. Results and discussion

Figure 1 shows scanning electron micrographs of etched cross-sections for two common sample preparation procedures, where compression moulding is the last step for both procedures. Directly compression moulding of pellets to plaques results in a morphology that consists of banded spherulites (Figure 1a). The spherulites are several micrometers in diameter but a distribution of their size is difficult to obtain from SEM images due the low chance to crack them exactly through the spherulites centres. However, an individual spherulite, where the center is visible, is shown in Figure 1b and has a diameter of ca. 5 μm. When the LDPE pellets are grounded to a fine powder, followed by extrusion for 6 min, prior to compression moulding, the morphology is altered to a lamellae structure absent of a clear superstructure (axialites), as shown in Figure 1c. Overview images of extruded samples are not shown since no larger superstructures could be seen in zoomed out images with the same magnification as in Figure 1a. Figure 2a shows the bulk morphology of directly compression moulding of LDPE grounded to a fine powder, which

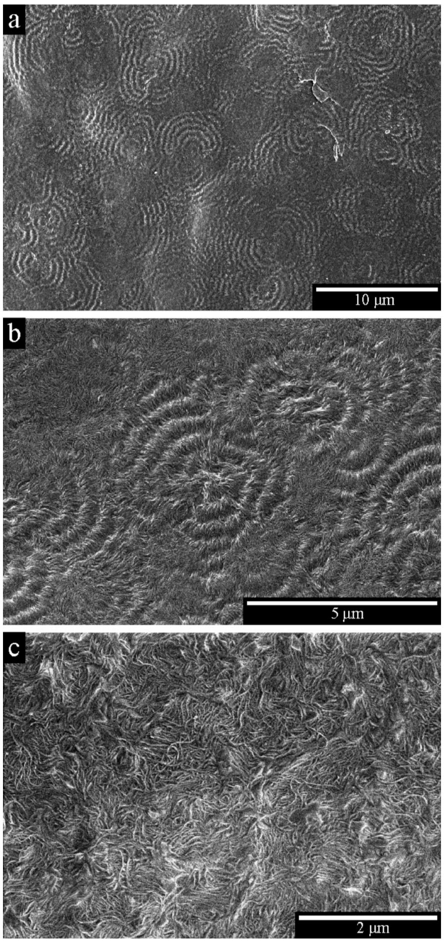

Fig. 1. Scanning electron micrographs of the bulk morphology for (a and b) directly compression moulded pellets and (c) 6 minutes extrusion prior to compression moulding.

also showed banded spherulites. Thus, the grinding of pellets cooled down in liquid nitrogen to a fine powder had no impact on the morphology. However, the morphology is altered similar to as shown in Figure 1c after only 10 s of extrusion prior to the compression moulding (Figure 2 b). The reason for the altered morphology due to extrusion could in principle originate from oxidation during this processing step, resulting in lower molecular mass species that cannot form banded spherulites. An investigation of carbonyl absorption by infrared spectroscopy is ongoing. However, no carbonyl absorption have been observed in compression moulded plaques where LDPE without added antioxidants have been extruded for 6 min prior pressing. The bulk morphology of LDPE containing 200 ppm antioxidants, processed by extrusion for 6 min prior to compression moulding, is shown in Figure 2c. No oxidation should occur during extrusion for this sample containing antioxidants but the morphology is still altered without any sign of banded spherulites. In addition, melt flow index measurements showed a slightly lower value of 1.8 g (10 min)$^{-1}$ for pellets directly compression-moulded than 1.9 g (10 min)$^{-1}$ for 6 min extrusion prior to compression moulding. However, the difference is small and does not indicate a significant lowering in molar mass.

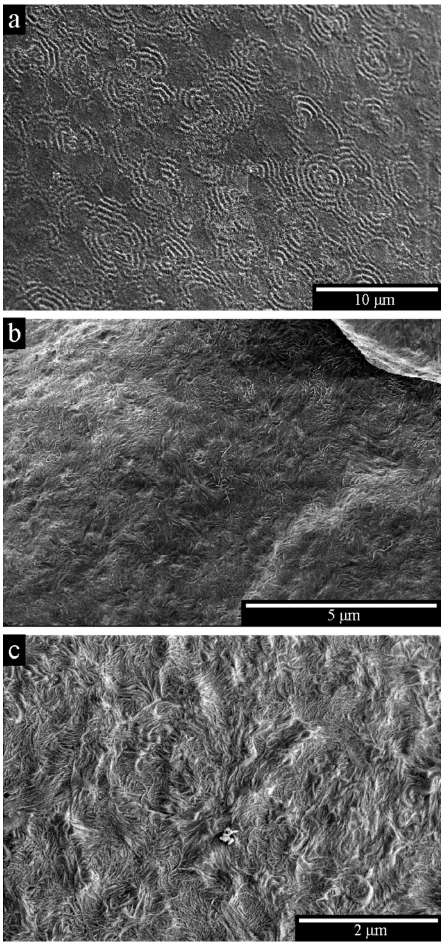

Fig. 2. Etched cross-sections revealed by etching and scanning electron microscopy for (a) directly compression moulding of LDPE powder, (b) 10 s extrusion prior to compression moulding and (c) 6 minutes extrusion of LDPE with 200 ppm antioxidants prior to compression moulding.

The observed bulk morphologies for the studied sample preparation methods are very consistent for specimens prepared at KTH and CTH (presented by Xu et al. [10] at NORDIS 2017). In literature where the morphology of LDPE specimens for HVDC cable applications have been studied, no banded spherulites are seen in the extruded samples [5]. However, when pellets have been directly compression moulded to plaque specimens banded spherulite morphologies have been observed [14, 15]. Abid et al. [16] etched compression moulded LDPE and XLPE plaque specimens that did not show banded spherulites. However, the samples in this study were etched from the compression-moulded surface and not the freeze-cracked cross-section. The absence of banded spherulites on the etched surfaces on LDPE plaques, prepared by direct compression moulding from pellets in the current study indicated that the surface morphology is different to the bulk morphology.

Table 1. Crystallinity, melting and crystallization for different sample preparation procedures prior to compression moulding

Sample preparation procedure	w_c[a] (%)	T_m[b] (°C)	T_c[c] (°C)
No extrusion (pellets)	58	109.4	100.7
No extrusion (powder)	58	110.1	100.2
10 s extrusion	57	110.2	101.6
6 min extrusion	57	110.3	102.5

[a] Mass crystallinity

[b] Melting peak temperature

[c] Onset crystallization temperature

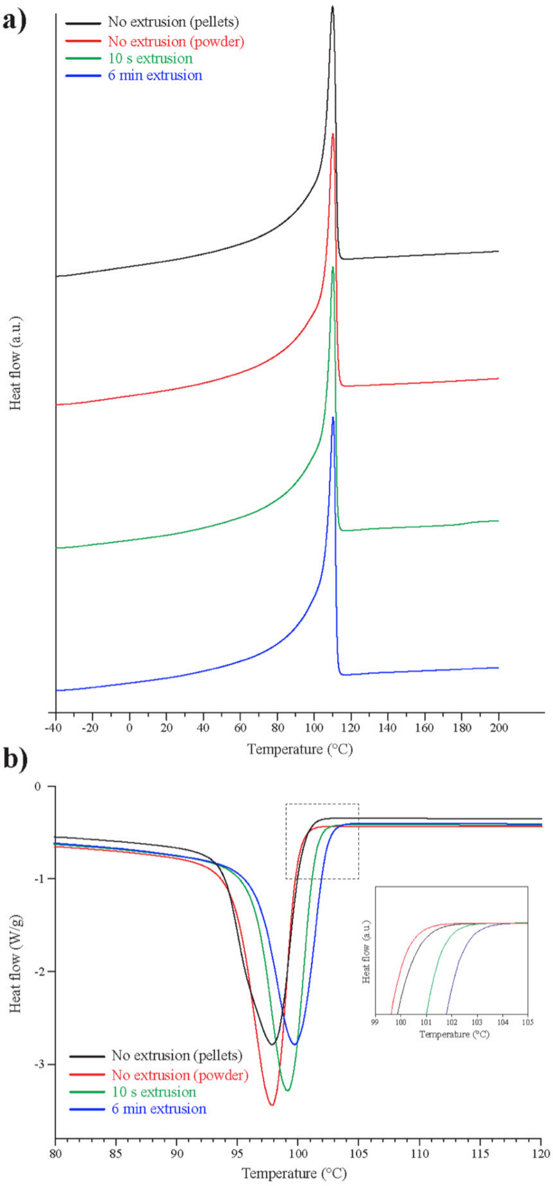

Fig. 3. (a) Melting and (b) crystallization curves of compression moulded films for different sample preparation procedures obtained by DSC.

The difference in bulk morphology of specimens without or including extrusion in the sample preparation procedure seems not to depend on degradation due to no carbonyl absorption after extrusion and similar melt flow index measurements. The reason for the morphology difference could depend on nucleation, which was further investigated using DSC.

Figure 3 shows the melting and crystallization of samples prepared according to the different methods. The second melting curves are showed in Figure 3a, i.e. after erasing the thermal history. The mass crystallinity at 25 °C was 58 ± 1 % for all samples. The melting traces are similar in shape and only a very small difference can be seen in the peak melting temperature (T_m), as can be seen in Table 1. The melting peaks ends for all samples at ca. 118 °C so the compression moulding temperature of 130 °C will melt all material completely, preventing the existence of nucleation sites in the melt. Also a small difference can be seen in the onset crystallization temperature (Figure 3b and Table 1), where directly compression moulded pellets and powder show a similar T_c (100.2-100.7 °C) and extrusion for 10 s and 6 min displayed a T_c between 101.6 and 102.5 °C. The differences in temperature are small but very consistent for several measurements. This indicates that nucleation occur earlier in the extruded samples than for directly compression moulded samples, which provide a possible explanation to the difference in bulk morphology (Figure 1). Nucleation in the bulk is always

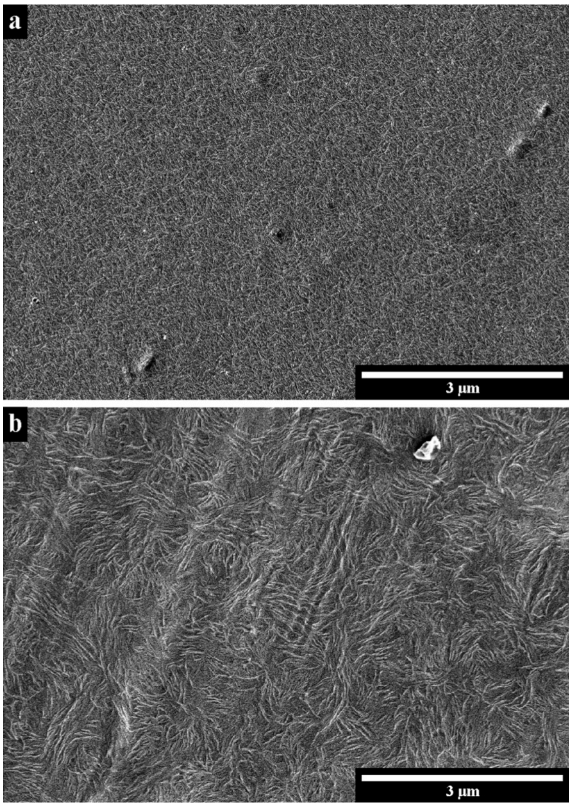

Fig. 4. Scanning electron micrographs of the surface of compression moulded samples pressed between (a) PET and (b) aluminum foil.

heterogeneous, i.e. nucleation is initiated at nucleation sites from particles in the material [8]. These heterogeneous nucleation sites exist in the pellets and are located far away from each other to form several μm large banded spherulites during compression moulding. During extrusion the existing nucleation sites were thoroughly mixed and even fragmentized, which resulted in a good dispersion of nucleation sites that yielded smaller axialites.

Surfaces of compression moulded samples by using either PET films or Al foils on both sides of the LDPE material are shown by the micrographs in Figure 4a and b, respectively. Note that no etching has been performed prior to microscopy of the compression-moulded surfaces. A finer surface structure is obtained by using PET film, whereas clear lamellar structures are shown when using Al foil. The influence of protective film on the DC conductivity is presented by Xu et al. [10] at NORDIS 2017.

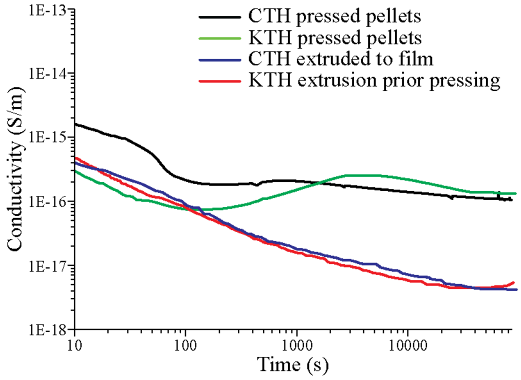

Fig. 5. Influence on the DC conductivity for various commonly used sample preparation procedures for obtaining plaque LDPE samples in research.

Figure 5 shows the results from DC conductivity measurements at 22 °C and 3.3 kV mm^{-1} for the above mentioned sample preparation procedures at KTH and CTH. When extrusion is a part of the preparation procedure the conductivity after 24 h is $4\mathrm{x}10^{-18}$ S m^{-1}, while the conductivity for directly compression-moulded pellets is $1\mathrm{x}10^{-16}$ S m^{-1}. Further investigation regarding the influence of morphology on the DC conductivity is ongoing.

4. Conclusions

Commonly used sample preparation methods for obtaining plaque samples of LDPE for HVDC cable applications show significant different bulk morphologies originating from thoroughly mixing and dispersion during extrusion of nucleation sites existent in the pellets. In addition, a significant difference in DC conductivity has also been observed. The DC conductivity at 22 °C and 3.3 kV mm^{-1} was of the order of $4\mathrm{x}10^{-18}$ S m^{-1} for the plaques obtained by extrusion and compression moulding (morphology dominated by axialites) whereas the plaques obtained by direct compression moulding (morphology dominated by banded spherulites) exhibited a conductivity of $1\mathrm{x}10^{-16}$ S m^{-1}. In addition it was shown that reproducible results in conductivity was obtained between different labs, if the same type of sample preparation procedures was used.

References

[1] J. C. Fothergill, "The Coming of Age of HVDC Extruded Power Cables," *Electrical Insulation Conference (Eic),* pp. 124-137, 2014.

[2] H. Ghorbani, A. Gustafsson, M. Saltzer, and S. Alapati, "Extra High Voltage DC Extruded Cable System Qualification A world record in HVDC cable technology," *International Conference on Condition Assessment Techniques in Electrical Systems (CATCON),* pp. 236-241, 2015.

[3] T. Hjertberg, V. Englund, P. Hagstrand, W. Loyens, U. Nilsson, and A. Smedberg, "Materials for HVDC cables," in *Jicable HVDC'13*, France.

[4] H. Ghorbani, "Characterization of conduction and polarization properties of HVDC cable XLPE insulation materials," Licentiate thesis, KTH, Stockholm, 2016.

[5] M. G. Andersson, J. Hynynen, M. R. Andersson, V. Englund, P. O. Hagstrand, T. Gkourmpis*, et al.*, "Highly Insulating Polyethylene Blends for High-Voltage Direct-Current Power Cables," *Acs Macro Letters,* vol. 6, pp. 78-82, Feb 2017.

[6] Y. Ohki, T. Asada, Y. Umeshima, and M. Ikeda, "Electrical conduction in highly resistive polyolefin films modified by polar groups," *Electrical Engineering in Japan,* vol. 120, pp. 9-16, Aug 1997.

[7] M. Praeger, I. L. Hosier, A. F. Holt, A. S. Vaughan, and S. G. Swingler, "On the Effect of Functionalizer Chain Length and Water Content in Polyethylene/Silica Nanocomposites: Part II – Charge Transport," *IEEE Transactions on Dielectrics and Electrical Insulation,* pp. 1-9, 2015.

[8] U. W. Gedde, *Polymer Physics*. London: Chapman & Hall, 1995.

[9] L. K. H. Pallon, A. T. Hoang, A. M. Pourrahimi, M. S. Hedenqvist, F. Nilsson, S. Gubanski*, et al.*, "The impact of MgO nanoparticle interface in ultra-insulating polyethylene nanocomposites for high voltage DC cables," *Journal of Materials Chemistry A,* vol. 4, pp. 8590-8601, Jun 14 2016.

[10] X. Xu, M. Karlsson, K. Gaska, S. M. Gubanski, H. Hillborg, and U. W. Gedde, "Robust measurements of electric conductivity

in polyethylene based materials: measurement setup, data processing and impact of sample preparation," presented at the NORDIS, 2017.

[11] M. M. Shahin, R. H. Olley, and M. J. Blissett, "Refinement of etching techniques to reveal lamellar profiles in polyethylene banded spherulites," *Journal of Polymer Science Part B-Polymer Physics,* vol. 37, pp. 2279-2286, Aug 15 1999.

[12] A. P. Gray, "Polymer crystallinity determinations by DSC," *Thermochim. Acta,* vol. 1, pp. 563-579, 1970.

[13] B. Wunderlich and H. Bauer, "Heat Capacities of Linear High Polymers," *Adv. Polym. Sci.,* vol. 7, p. 151, 1970.

[14] S. Nilsson, T. Hjertberg, and A. Smedberg, "Structural effects on thermal properties and morphology in XLPE," *European Polymer Journal,* vol. 46, pp. 1759-1769, Aug 2010.

[15] I. L. Hosier, A. S. Vaughan, and S. G. Swingler, "Structure-property relationships in polyethylene blends: the effect of morphology on electrical breakdown strength," *Journal of Materials Science,* vol. 32, pp. 4523-4531, Sep 1 1997.

[16] F. Abid, H. Ghorbani, A. M. Pourrahimi, and H. Edin, "Differences in morphology and polarization properties of heat-treated XLPE and LDPE insulation," *IEEE Conference on Electrical Insulation and Dielectric Phenomena (IEEE CEIDP),* pp. 113-116, 2016.