Influence of Additives on the Dielectric Strength of High-density Polyethylene

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ABSTRACT

In this study, we present the results of the influence of chemical additives (antioxidant and UV stabilizer) and pigments (titanium dioxide and carbon black) on the short-term dielectric breakdown test of high-density polyethylene (HDPE). These additives and pigments are commonly added to polyolefins, which are used as insulating material for medium voltage cables. The incorporation was performed in a single screw extruder and thin films specimens were obtained by hot compression from extruded materials. For the dielectric breakdown test, an automated system has been used. A voltage ramp of 500 V/s was applied to specimens immersed in a silicon oil bath at room temperature. The degree of crystallinity and chemical modification of the formulations were evaluated by X-ray diffraction and Fourier transform infrared (FTIR), respectively. The dielectric breakdown results have been analyzed by a Weibull distribution. The shape and scale parameters of this distribution have been obtained by a graphic and maximum likelihood method. These results showed that the carbon black is the component that affects the dielectric strength, that the β shape parameter from the graphic method can be used to evaluate additive mixing conditions, and that the weakest point for formation of the rupture channel is on the carbon black agglomerate.

1 INTRODUCTION

AMONG the various types of polymeric dielectrics, high-density polyethylene (HDPE) has been standing out as a raw material for the production of insulators, spacers, and also as coating for cable conductors used in electrical power distribution networks. For this type of application, the dielectric strength is one of the properties that must be taken into account in order to check the ability to withstand high electric fields. Dielectric strength is defined as a relationship between the breakdown voltage and the dielectric thickness, representing the maximum field which the material can support indefinitely for a specific experimental setup [1–5].

The use of high purity polymers in engineering applications is technologically not viable. This problem leads to the development of formulations with additives in order to protect the polymers against losses in their properties (for example, mechanical and thermo-mechanical) during the processing stages and/or in service [6]. These additives used in polymers for electrical insulation may or may not harm the electric properties.

Khalil *et al.* [7], studied the step dc breakdown of low-density polyethylene (LDPE) with 1% of titanium dioxide, and showed a loss of 10% in the dielectric strength of doped LDPE (6.5 MVcm) compared with pure LDPE (7.1 MV/cm). They related this fact to the changes in space charge distribution in the doped LDPE, passing from balanced homocharges in the pure polyethylene (PE) to a distribution dominated by negative charges in the PE with TiO_2. This provides an increase in the electric field in one of the electrodes causing the material to break at lower voltages. When testing the PE doped with reversed polarity, they did not find significant changes in the dielectric strength (6.3 MV/cm). According to the authors, the change in the distribution of space charges happens slowly, the space charge remains 'frozen' while the polarity changes in the electrodes, thus providing the increase of the field in the other electrode. In this situation they had the same rupture probability.

An important aspect of the titanium dioxide (rutile type) is its protection against ultraviolet (UV) in polyolefins [8–10]. In the case of the polypropylene, 2.0% of titanium dioxide promotes equal protection that provided by 0.2% of carbon black [9]. However, when combined with a sterically hindered amine (Hals UV stabilizer), it provides a quite pronounced synergism in UV protection [8, 9].

Ku and Liepins [1] showed that the incorporation of 1% carbon black to unknown resins decreases the dielectric strength in 90% of the cases, while levels >1% do not promote any further decrease in the dielectric strength. According to the authors, this behavior is due to the large difference between the conductivity and the permittivity of the resin and carbon black, resulting in low dielectric strength caused by distortions in the electric field.

Okamoto *et al.* [11] studied the effect of the size of carbon black agglomerates present in the interface area, between the semiconductor layer (with 35%wt carbon black) and the insulating (crosslinked PE with-

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Table 1. Concentration of the additives in HDPE.

Sample	N220 %wt	TiO_2 %wt	AO %wt	UV %wt
A00	2.0	0.5	0.05	–
A01	2.0	0.5	0.05	0.20
A10	2.0	0.5	0.20	–
A11	2.0	0.5	0.20	0.20
B00	0.5	2.0	0.05	–
B01	0.5	2.0	0.20	0.20
B10	0.5	2.0	0.20	–
B11	0.5	2.0	0.20	0.20
T11	0.0	2.5	0.20	0.20
N11	2.5	0.0	0.20	0.20
BR	0.0	0.0	0.0	0.0

out carbon black), on the dielectric strength (ac, 50 Hz). To modify the size of the agglomerates, they used different additives and they verified that when the size of the agglomerates was $\simeq$200 nm, high values of dielectric strength were achieved.

Even if variables such as morphology, additives or pollutants and test conditions are under control, scatter in the dielectric breakdown results is inevitable. Thus, it is necessary to use statistical models to treat and obtain the value of the dielectric strength and still evaluate its significance to guarantee the reliability of the data. Among current statistical models, the Weibull model is regarded as the most appropriate for data analysis obtained from breakdown tests [2, 11, 12].

Coppard *et al.* [13] have verified that the shape parameter (β) of the Weibull distribution can evaluate the scatter of the results and this is related to the size distribution of the defects present in the dielectric. The lower the scatter, the higher β will be and the narrower the size distribution of the defects.

Based on these considerations, this study has the purpose to use the Weibull distribution as a tool to study the influence of the additives (carbon black, titanium dioxide, UV stabilizer and anti-oxidant) on the dielectric strength of the high density PE, with the dc breakdown test using the positive ramp voltage and sphere-plane electrodes. The results of the breakdown tests will be evaluated using the Weibull distribution, with the intention of providing more information on the safe use of these additive in systems of electrical insulation.

2 MATERIALS AND METHODS

2.1 MATERIALS

The high-density polyethylene (HDPE) used was supplied by Polialden SA, with a melt flow index of 0.9 g/10 min. (ASTM D1238) and density of 0.953 g/cm^3. The stabilizer system consisted of Irganox™ B215 (AO) and Tinuvin™ 111 (UV), supplied by Ciba-Geigy SA. The carbon black (N220) and the titanium dioxide (TiO_2), in the form of master batch with a concentration of 30%wt, were supplied by Cromex SA. The particle size of titanium dioxide was $\sim$0.20 μm. The master batch vehicle was a high-density PE with melt flow index of 1.1 g/10 min. Table 1 presents the concentration of additives used in this study. The master batch of the antioxidant and UV stabilizer (UV) were developed in our laboratory in a torque rheometer Haake HBI System 90.

2.2 SAMPLE PREPARATION

The additives in masterbatch form were incorporated into the virgin HDPE by extrusion, in a Gerst single screw extruder. The material was extruded and dried for 72 h at room temperature. Then, films with a thickness of 40 to 100 μm were obtained by hot compression. The mold temperature for obtaining the films was maintained at $\sim$180°C and pressure 10 MPa/cm^2.

The formulations used in this study followed the designation 'AXY' and 'BXY' where 'A' indicate the grades with 2.0% of N220 and 0.5% of TiO_2 and 'B' the grades with 0.5% of N220 and 2.0% of TiO_2; 'X' the antioxidant (AO) content (zero for the low and 1 for the high) and 'Y' the UV stabilizer content, following the same designation for 'X'. Table 1 presents the additives concentrations for all formulations.

2.3 DIELECTRIC BREAKDOWN TEST

The dielectric breakdown test was carried out in a self-developed system. The system is interfaced with a microcomputer 486DX2 that controls a power supply, Bertan model 225, whose function is to apply the voltage to the electrodes. This system allows automatic control of the voltage ramp rate and interruption and selection of the voltage waveform. For this study, the type of electric stress was a positive ramp with a rate of 500 V/s applied between sphere-plane electrodes immersed in silicone oil in a controlled environment.

The thickness of the sample was measured after the test in the surroundings of the rupture point using a magnetic induction meter Permascope MPO. To control the thickness parameter in the analysis of the results, the first twenty within 50 to 70 μm were considered for each formulation.

2.4 PHYSICAL CHEMISTRY CHARACTERIZATION

The degree of crystallinity was determined for all formulations using X-ray diffraction data obtained from films with a thickness of $\sim$100 μm using a diffractometer (Phillips X'pert MPD model). The X-ray radiation used was the CuKα ($\lambda = 1.54056\times10^{-10}$ m). The value of the degree of crystallinity used in this study corresponds to the average of three measurements as calculated by Equation (1) [15, 16].

$$W_{c,x} = \frac{S_{(200)} + S_{(200)}}{S_a + S_{(110)} + S_{(200)}} \tag{1}$$

where $S_{(110)}$ and $S_{(200)}$ are the relative areas of the peaks corresponding to the diffraction planes (110) and (200), respectively, and S_a is related to the area of the amorphous band.

Possible modifications in the chemical structure of HDPE, mainly thermal oxidation, during the preparation of the samples (extrusion and hot compression), were meassured by Fourier transform infrared (FTIR) using a Perkin Elmer model Spectrum 1000. The absorption band at 1720 cm^{-1} was used to verify the performance of the stabilization package used in the formulations.

2.5 DISTRIBUTION OF WEIBULL

The two parameters Weibull model parameters (β and E_γ) were used to evaluate the results of the dielectric breakdown test. Equation (2) shows the Weibull accumulated distribution function

$$P_f = 1 - \exp\left[-\left(\frac{E_b}{E_\gamma}\right)^{\beta}\right] \quad (2)$$

where P_f is the failure accumulated probability, E_b is the dielectric strength (MV/cm), E_γ the dielectric strength for $P_f = 63.2\%$, the scale parameter, and β the shape parameter. Commonly, the parameter E_γ is used to compare differences in dielectric strength determined in the breakdown test [1, 2, 11–13].

The parameters of this distribution were determined by the graphic and the maximum likelihood methods.

2.6 THE GRAPHIC METHOD

The parameters β and E_γ were calculated from the linear regression of Equation (2) when linearized

$$\log[-\ln(1 - P_{f,i})] = \beta \log E_{b,i} - \beta \log E_\gamma \quad (3)$$

According to the recommendation of the IEC 56 standards, the rank function F_i used is presented in the Equation (4)

$$P_{f,i} = \frac{i - 0.5}{n + 0.25} \quad (4)$$

where i is the i-th result when the values of E_b are sorted in ascending order and n is the number of points; for this study, $n = 20$.

2.7 THE MAXIMUM LIKELIHOOD METHOD

So far, the Maximum Likelihood is currently considered the most important estimator of parameters [12, 17]. For determination of β and E_γ, Equation (5) must be solved

$$\frac{\sum_{i=1}^{n} E_{b,i}^{\hat{\beta}} \ln E_{b,i}}{\sum_{i=1}^{n} E_{b,i}^{\hat{\beta}}} - \frac{1}{n}\sum_{i=1}^{n} \ln E_{b,i} = \frac{1}{\hat{\beta}} \quad (5)$$

where $E_{b,i}$ is the i-th value of dielectric strength, $\hat{\beta}$ the estimated value of β and n the number of samples.

Having determined the value of $\hat{\beta}$, the scale parameter value is obtained by Equation (6)

$$E_\gamma = \left[\frac{1}{n}\sum_{i=1}^{n} (E_{b,i})^{\hat{\beta}}\right]^{\frac{1}{\hat{\beta}}} \quad (6)$$

To solve the Equations (5) and (6), an interactive method present in the Excel 7.0 program was used. A confidence interval at 95% for E_γ, also was determined.

3 RESULTS AND DISCUSSIONS

3.1 PHYSICO-CHEMICAL CHARACTERIZATION

3.1.1 DEGREE OF CRYSTALLINITY

The degree of crystallinity is a factor that can influence the results of the dielectric strength [1, 3, 4]. Figure 1 shows the percentages of crystallinity $W_{c,x}$, obtained from X-ray diffraction data for the different formulations. The values of $W_{c,x}$ meet between 66 and 68% for all formulations, showing that changes in concentration of the used additives does not modify this variable.

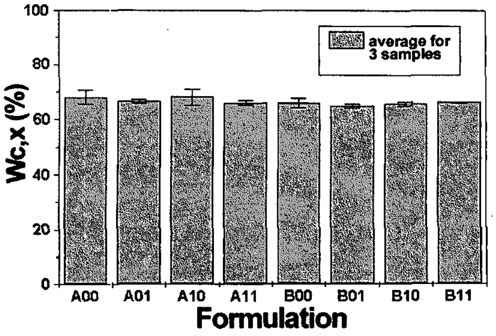

Figure 1. Degree of crystallinity of the formulations.

3.2 FTIR CHARACTERIZATION

Chemical modification of the polymer structure also can affect its dielectric strength. Therefore it is important to observe such modifications. The most significant chemical modification in our case is thermal oxidation during processing of the samples and this fact can be detected by infrared (IR) spectroscopy. The absorption band at 1720 cm^{-1} in the spectra was not observed for all the formulations studied. The missing band in the spectrum suggests that there is no thermal oxidation due to extrusion and hot compression processes, showing the efficiency of the stabilization package used, even at such a low concentration (0.05 wt%) of antioxidant [14].

3.3 ANALYSIS OF DIELECTRIC STRENGTH RESULTS

3.3.1 SCALE PARAMETER

Figure 2 presents the results of dielectric strength (E_{rup}) after linear regression with Equation (3). Initially the formation of three different groups is seen: one for formulations 'AXY' (2.0% of N220 and, 0.5% of TiO$_2$), another for the formulations 'BXY' (0.5% of N220 and, 0.0% of TiO$_2$) and the third corresponding to pure HDPE (BR). We can observe some scatter in the dielectric strength data in all formulations, mainly in A00 and B11.

The three sets of separated data observed in Figure 2 also can be visualized in Figure 3. In the plot, E_γ data with 95% confidence interval for each formulation, as obtained by the maximum likelihood, are presented. By analyzing the values, the E_γ of 'A' samples are not superimposed on 'B' samples and *vice versa* The same argument is valid for BR.

With the incorporation of 0.5% of N220 and 2.0% of TiO$_2$, and verified in both methods, a 35% decrease occurred in the dielectric strength as compared to pure HDPE (~5.9 MV/cm). To 2.0% of N220 and 0.5% of TiO$_2$ a decrease was verified of 57%.

To verify whether the dielectric strength of HDPE is affected or not by the titanium dioxide, two special formulations were developed: one denominated as T11 with 2.5% of TiO$_2$, and another with 2.5% of carbon black denominated N11, both with 0.20% of antioxidant and 0.20% of UV

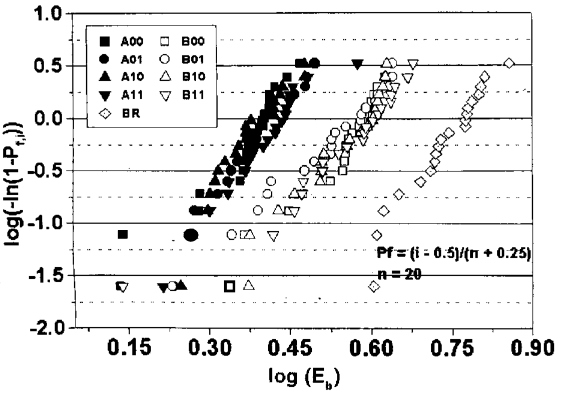

Figure 2. Linear regression of the Weibull model for dielectric strength of HDPE with additives. E_b is the dielectric strength (MV/cm) and $P_{f,i}$ the accumulated probability of failure.

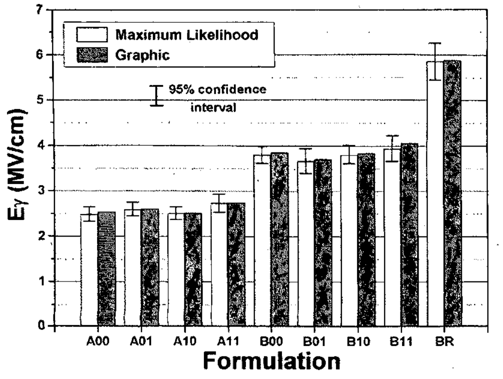

Figure 3. E_γ values determined by maximum likelihood and graphic methods. Data from [18].

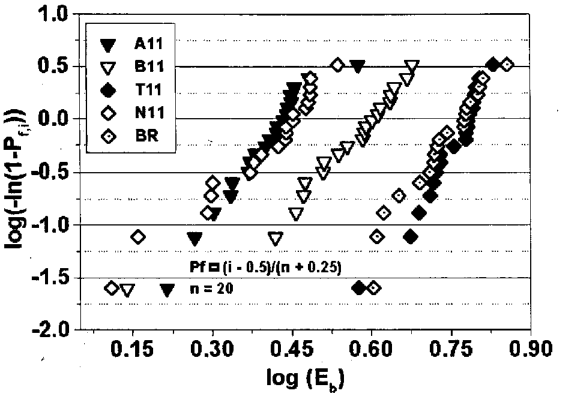

Figure 4. Linear regression of the Weibull model. Comparison between different pigments levels (TiO_2 and N220).

stabilizer. Figure 4 shows the values of dielectric strength of these two new formulations. For comparison, the results of the formulations of the same antioxidant and UV stabilizer levels (A11 and B11) and of pure HDPE (BR) are also presented. It was observed that the lowest value of dielectric strength of the B11 samples was found between the lowest values of A11 and N11. This observation is important because the dielectric rupture always occurs at the weakest point. According to Okamoto [11] and Coppard [13], in practice, dielectric breakdown probably does not occur at the value E_γ ($P_f = 63.2\%$) but at lower values, for example, at E_{rup} for $P_f = 1\%$. Therefore, it is not recommended that E_γ value alone is used to specify the insulation material; it is also necessary to consider any other parameter that represents more adequately the value of electric fields that the insulation can support.

Table 2. E_γ values (MV/cm) determined by the Maximum Likelihood and Graphic methods. $E_{\min}$ is the minimum value obtained experimentally.

Formulation	Max. Likelihood			graphic method	
		95% conf. interval			
	E_γ	E_γ up	E_γ lo	E_γ	$E_{\min}$
A00	2.49	2.67	2.33	2.55	1.37
A01	2.60	2.77	2.45	2.61	1.72
A10	2.51	2.67	2.37	2.52	1.56
A11	2.74	2.95	2.54	2.75	1.64
B00	3.80	3.99	3.61	3.86	2.18
B01	3.67	3.96	3.40	3.71	1.71
B10	3.81	4.03	3.61	3.85	2.32
B11	3.94	4.24	3.66	4.06	1.38
T11	5.99	6.30	5.69	6.04	3.78
N11	2.78	3.05	2.53	2.83	1.29
BR	5.86	6.30	5.45	5.89	4.02

Comparing the E_γ values (Table 2) of the formulations with different concentrations of carbon black (A11 and N11) it is observed that they are similar, showing that an increase from 2.0% to 2.5% in carbon black content does not affect significantly the dielectric strength. Even so both formulations presented E_γ smaller than B11 which again confirms the influence of carbon black in this property.

In relation to the T11 formulation, the E_γ value was slightly higher than that of the BR (~4%), although this was not significant, since both E_γ were simultaneously within the 95% confidence interval. This increase in the dielectric strength contradicts the results obtained by Khalil *et al.* [7] who observed a significant decrease in dielectric strength in the presence of titanium dioxide. This disagreement can be attributed to two factors: the use of a different electrode system and a different polymer used in their work (low density PE). The data of Table 2 were plotted in Figure 5 for better visualization.

By analyzing these results it can be concluded that the most significant component in the dielectric strength is the carbon black content. No significant alterations in the dielectric strength with variations in the level of other components (antioxidant and UV stabilizer) incorporated in the HDPE has been observed.

3.4 SHAPE PARAMETER

Table 3 presents the β values, determined by the graphic and maximum likelihood methods. The values were already corrected for a small number of replica specimens and $\Delta \log E$ (difference between $\log(E_\gamma)$ and $\log(E_{\min})$, *i.e.* the scattering results for each formulation is also shown, with $E_{\min}$ being the lowest dielectric strength determined experimentally. Table 3 shows differences >20% between the β values obtained by both methods. This fact shows the need for a careful choice of the method used to determine the β value, as already observed by Ross [12]. Although the maximum likelihood method is precise enough

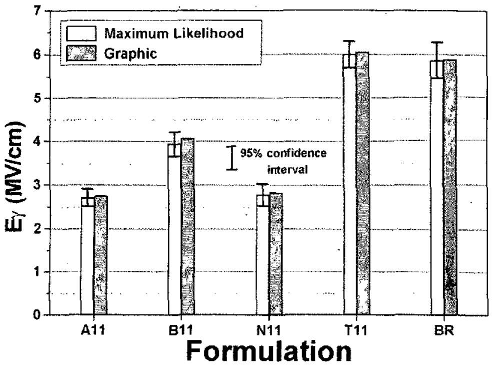

Figure 5. E_γ values determined by the maximum likelihood and graphic methods for formulations with different levels of pigments (TiO_2 and carbon black). Confidence interval of 95% for E_γ obtained by the maximum likelihood method.

Table 3. Parameter β determined by the Maximum Likelihood and Graphic methods.

Sample	Max. likelihood		Graphic method	
	β	$\Delta \log E$	β	$\Delta \log E$
A00	7.3	0.259	5.7	0.270
A01	6.5	0.179	7.3	0.181
A10	6.8	0.152	7.8	0.153
A11	5.3	0.223	6.5	0.224
B00	7.9	0.242	6.4	0.248
B01	5.2	0.332	4.8	0.336
B10	7.1	0.208	6.3	0.213
B11	5.4	0.456	4.2	0.469
N11	5.8	0.333	4.6	0.341
T11	10.7	0.200	8.9	0.204
BR	6.9	0.164	7.4	0.166

to calculate the parameters of the Weibull distribution, it is not very sensitive to the dispersion of the data.

Figure 6 illustrates the values of β and $\Delta \log E$ from Table 3. One may notice that β, determined by the graphic method tends to decrease with increasing of scattering results ($\Delta \log E$), whereas β determined by the maximum likelihood method, presents a random behavior.

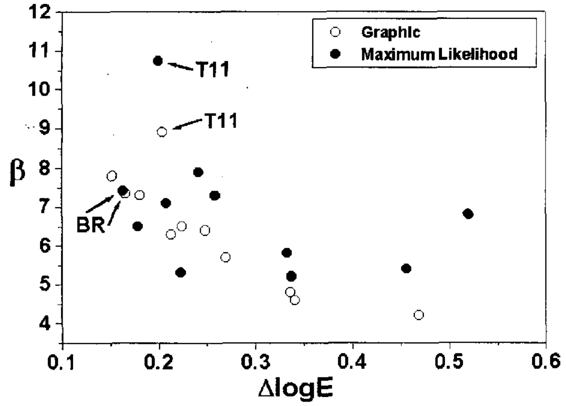

Figure 6. Behavior of β related to scattering results $\Delta \log E = \log(E_\gamma) - \log(E_{\min})$ for formulations presented in Table 3.

Coppard *et al.* [13] demonstrated that β is related to the size distribution of the defects present in the dielectric. Analogously in the case under study, it means that β is related to the distribution/dispersion of additive(s) that affects the dielectric strength, more specifically the carbon black agglomerate size distribution. This conclusion is validated when a rupture channel is observed through an optical microscope. Figures 7(a) to (c) illustrate some of the tested samples. The dark points are carbon black agglomerates and the white arrow indicates the rupture channel produced by the electric discharge showing that the agglomerates are more susceptible points to the rupture. For this analysis, when considering two insulations with the same E_γ and different β, it is possible to infer that the one showing a higher β value, determined by the graphic method, presents higher reliability (quality) during its use when compared with the one with a lower β.

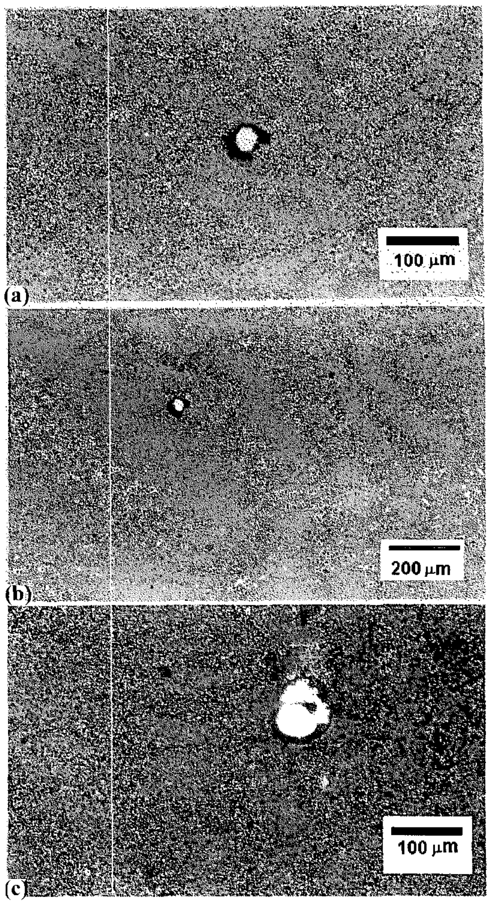

Figure 7. (a) Rupture channel in formulation N11 as observed through the optical microscope. Breakdown voltage is 2817 V. Dielectric strength is 1.76 MV/cm. Magnification is 250×. (b) The same as (a), but with magnification 125×. (c) Rupture channel in formulation A11 as observed through the optical microscope. Breakdown voltage is 4478 V. Dielectric strength is 1.36 MV/cm, magnification is 250×.

Hence, in our case, β is influenced by the incorporation conditions (mixing and homogenization) of these pigments (in this case, carbon black) to HDPE.

It can be seen in Figure 6 that for T11 formulation, the β value does not follow the trend of the formulations containing carbon black, showing a possible change of the rupture mechanism in the samples with only titanium dioxide.

Considering the results discussed so far, it was verified that β is influenced by the variables that affect the mixing conditions of the additive, for example: quality of the master batch [19] and processing conditions. Besides affecting the dielectric strength, the control of the dispersion of additives, such as carbon black, is important to improve the polyolefins protection against UV radiation [19–21].

In another study [22], we verified an improvement from 2.55 to 4.21 MV/cm of E_γ and of β from 5 to 8.1, when additive mixing was done in a twin screw extruder that is most suitable to incorporate and disperse additives in polymers. This fact reinforces the influence of carbon black agglomerates size distribution in the β. The broader the agglomerates size distribution, the lower the β value.

Another factor that could influence the scattering of dielectric strength results is the variation of the degree of crystallinity of the samples in the same formulation. However, it was verified that the larger variation in the degree of crystallinity was not larger than $\sim$5%, indicating that this factor is not as significant as the agglomerate size distribution of the carbon black, on the scattering of the dielectric strength.

Using this analysis, from the viewpoint of the dielectric strength, the reliability of the dielectric during its use, the formulation without carbon black (T11) is the most suitable because it present both β (8.9 for the graphic and 10.7 for the maximum likelihood method). E_γ (5.99 and 6.04 MV/cm in Table 2) are higher than obtained in other formulations.

4 CONCLUSIONS

FROM this study, it can be concluded that among the studied additives (antioxidant, UV stabilizer, TiO_2 and carbon black), carbon black is the most critical one for the dielectric strength of high density PE. This was checked by optical microscope showing that the rupture channels are located in carbon black agglomerates. Titanium dioxide does not cause significant changes in the dielectric strength and is a good choice to replace carbon black in dielectric materials in which it is currently used as a pigment and protection against UV radiation.

It is also possible to conclude that the value of the β shape parameter, when determined by the graphic method, can be used to evaluate the conditions of defect size distribution that decrease the dielectric strength of the insulator. In our case, the β shape parameter is directly related to the dispersion of the carbon black in the HDPE. With higher values of β, there is a lower scattering of the dielectric strength and a better carbon black dispersion and consequently higher reliability of the dielectric behavior of the material.

In relation to the protection against the thermal oxidation, the package of stabilization employed is quite efficient, even for low concentration levels of the thermal stabilizer.

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