Dielectric Strength of the Blends of Virgin and Recycled HDPE

S. A. Cruz, M. Zanin

Department of Materials Engineering—DEMa/Universidade Federal de São Carlos—UFSCar, Rodovia Washington Luís, Km 235/São Carlos, SP, Brazil, CEP 13565-905

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ABSTRACT: This work evaluated the incorporation of recycled high-density polyethylene (HPDE) in the virgin polymer by measuring its dielectric strength. Post-consumer containers of HDPE were collected and passed through the basic processes of plastics recovery: washing, grinding, and drying. Formulations were elaborated containing 0, 25, 50, 75, and 100% of recycled material incorporated to the virgin resin by extrusion and injection processes, stabilized with 0.2% Irganox B215. Samples of these materials were submitted to dielectric breakdown analysis by using an electrode-type sphere—plane and ramp of positive electric tension. The data were treated and analyzed by using the statistical distribution of Weibull, and the Maximum Likelihood method. The degree of crystallinity was measured by X-ray diffraction. Atomic absorption spectrophotometry was employed to identify metallic residues present in the samples. The results showed that there is a 17% decrease in the values of the dielectric strength when we compare the virgin HDPE with the 100% recycled. Therefore, formulations containing up to 50% of recycled material may be taken into consideration in the development of products in electric insulating systems. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1730–1735, 2004

Key words: recycling; post consumer; polyethylene; dielectric properties; dielectric strength

INTRODUCTION

The applications of recycled high-density polyethylene (HDPE) are becoming more and more frequent and its use includes paving (recycled HDPE mixed with asphalt), plastic wood, building sites (conduits, etc.), plastics culture (canvases), automobile industry, production of containers for industrial chemical products, bags (plastic carrier bags, etc.), blends with virgin resin for the packaging of cleaning, and plastic crates. Although the polymeric materials are commonly used as dielectric by the industries of the electric section and there is still a diversity of studies on the electric behavior of those materials, the survey in several data bases did not show any reference related to the characterization and application of recycled HDPE for systems of electric insulation, with the exception of conduits, in which the most relevant property is the mechanic one.

Among the various types of polymeric materials that are dielectric, HDPE stands out as a raw material for the production of insulators, spacers, and connectors for low tension and also as coating for cable conductors used in electrical power distribution networks. For polymeric insulators, the dielectric strength is one of the properties that must be taken into account to check the ability to withstand high electric fields. Dielectric strength is defined as a ratio between the breakdown voltage and the dielectric thickness, representing the maximum field that the material can support for a specific experimental setup.[1–5]

Even if variables such as morphology, additives or impurities, and test conditions are under control, scattering in the dielectric breakdown results is inevitable. Thus, it is necessary to use statistical models to treat and obtain the values 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.[2,5–7] Ueki and Zanin[5] used the distribution of Weibull to correlate the form parameter β of this model with the distribution and dispersion of the carbon black particles in the HDPE. They concluded that the larger the value of β, the more homogeneous the system is. Therefore, this work intends to study the viability of recycling the HDPE from containers discarded in municipal solid waste to be employed in electric insulation systems. To this end, five blends were developed containing 0, 25, 50, 75, and 100% of recycled material incorporated in the virgin HDPE and its insulating properties evaluated through the dielectric breakdown test. The statistical model of Weibull was used to treat the dielectric strength data, because they could show a wide dispersal. Also, atomic absorption spec-

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Correspondence to: M. Zanin (dmza@power.ufscar.br).
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trophotometry analyses for Ni, Cr, Al, Mg, V, Ti, and Si were carried out to identify the metallic residues present in the recycled HDPE. Molar mass alterations and the degree of crystallinity were verified through melt flow index (MFI) and X-ray diffraction.

EXPERIMENTAL

Materials

The used virgin HDPE, GM 9450F, supplied by Ipiranga Petroquímica S.A., (Rio Grande do Sul, Brazil) has a MFI of 0.32 g/10 min (norm ASTM D 1238) and a density of 0952 g/cm^3. It comes in the form of pellets with basic stabilization for processing, being used for the manufacture of injected pieces for electric insulation in low tension.

The recycled material used was HDPE, collected in the selective collecting system at the Federal University of São Carlos, (São Paulo, Brazil) composed mostly of personal hygiene and cleaning products. For the stabilization during the reprocessing of the recovered material, a commercial mixture of the antioxidant Irganox B215 was used (2 : 1 Irgafos 168 : Irganos 1010) supplied by Ciba Chemical Specialties Ltda. (Brazil).

Recovery conditions and incorporation of recycled HDPE

The collected HDPE passed through the basic recovery processes of post-consumer plastic: grinding (mill of knives Primotécnica, 738 rpm, and four HP flakes of 0.3 in.), washing (in a washer developed in the 3R-Núcleo de Reciclagem de Resíduos[8] with pure water for 5 min and with 1% caustic soda solution for more than 5 min, the rinsing being done with water for 10 min in the washer itself), and drying (in oven with renewal and circulation of air, MA 037 for 24 h at 50°C).

The recovered material was reprocessed by the extrusion process (Gerst type 25 × 24*D*, $L/D = 24$, temperature profile of 150, 180, 180°C and screw speed of 70–80 rpm) with addition of 0.2% in weight of the antioxidant Irganox B215. After that, this material was added to the virgin HDPE in proportions of 25, 50, and 75%, and injection molded (Arburg 270 V with temperature profile of 160, 180, 180, and 190°C, and mold temperature of 50°C). To facilitate the interpretation and identification throughout the work, the samples were named as shown in Table I.

TABLE I
Nomenclature and Composition (% in weight) of the Blends

Formulation	% of virgin HDPE	% of recycled HDPE[a]
R-0%	100	0
R-25%	75	25
R-50%	50	50
R-75%	25	75
R-100%	0	100

[a] All of the formulation contain 0.2% antoxidant in weight.

Preparation of the samples

Films with a thickness of 30 to 50 μm were obtained by hot compression. The mold temperature to obtain the films was maintained at ~ 180°C and a pressure of 10 MPa/cm^2.

Physical chemistry characterization

The degree of crystallinity was determined for virgin and recycled HDPE by using X-ray diffraction data obtained from injected material in powder form by using a diffractometer (Siemens D 5000 model). The X-ray radiation used was the CuKα (λ = 1.54056 Å) with an angular range of X-ray diffractions patterns of 5 to 45° (2°/min). The value of the degree of crystallinity used in this study corresponds to the average of three measurements as calculated by[9,10]

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

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 halo. S2003[11] was used to determine the individual areas, opting for a Pseudo-Voight-type line format for the amorphous halo as well as for the diffraction lines. The software intrinsically used corrections, such as absorption and Lorentz factor. The background subtraction was based on a second-degree polynomial throughout the measurement interval.

Possible changes in the average molar mass of HDPE derived from the mixing with the recycled material were analyzed by MFI by using a plastometer MFI 10 CB, with a weight of 10 kg at 190°C.

Characterization of the metallic residues

To characterize the metallic residues present in recovered HDPE, analyses of spectrophotometry of atomic absorption with atomization in flame were done. The analyses were accomplished in a spectrophotometer of atomic absorption (Perkin–Elmer, model 4100). The HDPE samples were powdered cryogenically in boron silicate capsules to avoid possible contamination by metal traces present in the ceramic. Then, 5 mL of concentrated nitric acid was added to 3, 4, and 5 g samples of pulverized material, which was heated until dry. Then, 5 mL ethanol solution of 50% magnesium nitrate was added as a chemical modifier. The new solution was heated until dry, pyrolyzed in a muffler at 200°C (10°C/min), and left to rest at this temperature for 2 h. The temperature was raised to 350°C at 1°C/min for approximately 6 h. The residues of the capsules were dissolved in 8 mL of chloride acid/nitric acid solution and diluted to 25 mL. Three readings were performed for each element by using the TITRISOL standards (Merck) to calibrate the equipment. The analyzed elements were Ni, Cr, Al, Mg, V, Ti, and Si, selected because of the possibility of being used in the synthesis process of HDPE.

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 vicinity of the rupture point by using a magnetic induction meter, Permascope MPO.

Distribution of Weibull

The two 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

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

where P_f is the failure accumulated probability, E_b is the dielectric strength (MV/cm), E_γ is the dielectric strength for $P_f = 63.2\%$, the scale parameter, and β is the shape parameter. Commonly, the parameter E_γ is used to compare differences in dielectric strength determined in the breakdown test.[1,6,12]

The parameters of this distribution were determined by the Maximum Likelihood method.

The Maximum Likelihood method

So far, the Maximum Likelihood method has been considered as the most important estimator of parameters.[7,13] For the determination of β and E_γ, eq. 3 must be solved as

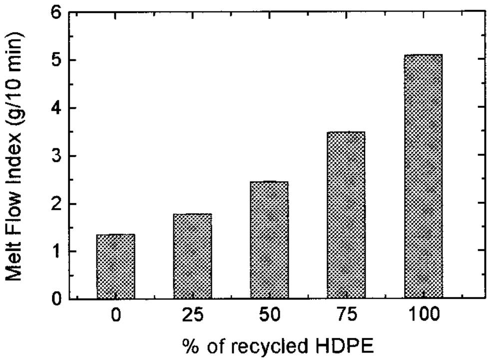

Figure 1 Melt flow index for HDPE containing 0, 25, 50, 75, and 100% of recycled material incorporated to the virgin resin.

$$\frac{\sum_{i=1}^{n} E_{b,i}^{\hat{\beta}} \ln E_{b,i}}{\sum_{i=1}^{n} E_{b,i}^{\hat{\beta}}} - \frac{1}{n}\sum_{i=1}^{n} \ln E_{b,i} = \frac{1}{\hat{\beta}} \tag{3}$$

where $E_{b,i}$ is the ith value of dielectric strength, $\check{\beta}$ is the estimated value of β, and n is the number of samples; for this study, $n = 20$.

Having determined the value of $\check{\beta}$, the scale parameter value is obtained by

$$E_\gamma = \left[\frac{1}{n}\sum_{i=1}^{n} (E_{b,i})^{\hat{\beta}}\right]^{1/\hat{\beta}} \tag{4}$$

To solve eqs. 3 and 4, an interactive method, present in the Excel 7.0 program, was used. A confidence interval at 95% for E_γ was also determined.

RESULTS AND DISCUSSION

Physicochemical characterization

Degree of crystallinity

The degree of crystallinity is a factor that can influence the dielectric strength results.[1–3] The values of crystallinity, obtained from X-ray diffraction data, for the materials were 64% for virgin polymer and 67% for recycled HDPE. The results show that the incorporation of recycled material in HDPE virgin does not modify this parameter and does not interfere in the values of the dielectric strength.

Melt flow index

Figure 1 presents the MFI values for formulations containing 0, 25, 50, 75, and 100% of recycled material incorporated to the virgin HDPE.

TABLE II
Concentration of Metals in the Sample R-100%[14,15]

Metal	[μg/g (ppm)] R-100%
Ni	ND
Cr	13
Al	90
Mg	144
V	ND
Ti	5500
Si	220

ND = not detected.

TABLE III
E_γ, E_γ^+, E_γ^-, and E_{min} Values (MV/cm) Obtained by the Maximum Likelihood Method

Formulation	E_γ	95% Confidence interval E_γ^+	E_γ^-	E_{min}
R-0%	6.23	6.55	5.93	5.32
R-25%	6.07	6.45	5.71	4.64
R-50%	5.45	5.83	5.08	3.63
R-75%	5.11	5.58	4.67	2.49
R-100%	5.20	5.64	4.79	2.55

Characterization of the metallic residues

Table II presents the weight fractions of metallic residues in the 100% recycled material obtained by means of spectrophotometry measurements.

In Table II, it can be observed that the metals Ni and V were not found, perhaps because, in this case, they do not take part in any catalysis process and because they are not usually used in the formulation of colorants or fillers. It is known that HDPE can be synthesized usually through the Phillips and Ziegler processes. In the Ziegler process, the catalyst is composed of Ti, whereas in the Phillips process, it is composed of Cr.[16] In the analysis of metal residues, the presence of Cr is small, 13 ppm, but the presence of Ti is considerable. The high content found for Ti, around 5500 ppm, can be attributed to the catalytic residue and the residue of fillers and pigments, once the titanium dioxide is used to promote white coloration in thermoplastics.

In this analysis of residues, the Si appears as the second more abundant element, around 200 ppm, which can be related to the catalytic residue of HDPE synthesized by the Phillips catalyst. Even with Cr being the base metal for this synthesis, according to studies accomplished by Moss and Zweifel,[16] it was verified that HDPE catalyzed by the Phillips process presents a higher content of Si (85 ppm) than Cr (2.5 ppm).

Although the focus is on these two types of catalysts and their respective transition metals, it can be observed that other metals are present in considerable amounts. For example, Mg and Al could contribute to a decrease in the dielectric strength with an increase of the incorporation of recycled material to the virgin resin.

Dielectric strength

The values of E_γ that correspond to the value of the dielectric strength for the failure accumulated probability of 63%, obtained by the Maximum Likelihood method, the upper (E_γ^+) and lower (E_γ^-) limits of 95% confidence interval, and also the smallest value of the dielectric strength (E_{min}) experimentally measured for each formulation, are presented in Table III.

To better illustrate the influence of recycled material concentration in the virgin HDPE, the values of E_γ and their respective confidence intervals at 95%, observed in Table III, are presented in Figure 2.

The comparison between the E_γ values found for the 100% recycled HDPE and for the virgin HDPE shows a decrease by approximately 17%. The formulation R-100% is slightly superior to R-75%, however, without statistical meaning because both are practically within the confidence interval of 95%. The variation between the formulations R-0% and R-25% is not significant as well. It can be verified, by the results of Table III, that a decrease exists in the values of E_{min} with the weight fraction of recycled material. Many authors[5,7] have observed that considerable differences between the values of E_{min} as compared with E_γ represent inferior electric performance, as in the case of the formulations R-75% and R-100%, which showed approximately a 50% difference between these parameters; for the virgin resin, this value was 16%. This is because, according to Weibull, the weakest point (E_{min}) determines the performance of the whole system.

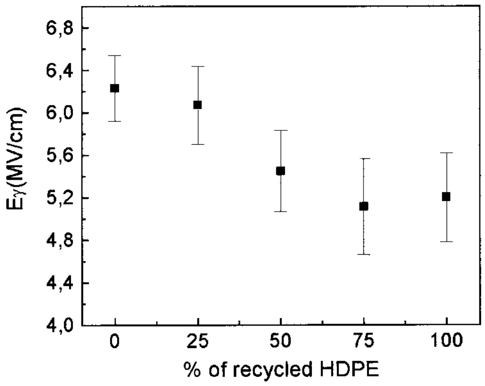

Figure 2 E_γ values obtained by the Maximum Likelihood method for HDPE containing 0, 25, 50, 75, and 100% of recycled material with confidence interval.

TABLE IV
Parameter β Determined by the Method of Maximum Likelihood and Δ log E

Formulation	β	ΔlogE
R-0%	10,90	0.07
R-25%	8,87	0.12
R-50%	7,96	0.18
R-75%	6,09	0.31
R-100%	6,61	0.31

The decrease in the values of E_γ with the recycled material concentration in the virgin polymer can be related to the presence of conductive impurities that remained from the synthesis process, recovery, and processing (fillers, pigments, and additives) of the recycled material. The presence of metals, revealed by the technique of spectrophotometry of atomic absorption, validates this supposition.

Ueki and Zanin[5] verified that for HDPE without additives, the values of E_γ are slightly superior to those containing additives, such as UV radiation stabilizers. The virgin resin used in this work and incorporated to the recycled material did not contain any additive, apart from the ones used for its prestabilization, which can also justify its superior value of E_γ. Another factor that could be associated with the differences observed in the value of the dielectric strength is the degree of crystallinity. However, significant alterations in this property were not verified, which justify the variation in the values of the dielectric strength.

Table IV presents the values of parameter β determined by the Maximum Likelihood method and of Δ log E [difference between $\log(E_\gamma)$ and $\log(E_{\min})$] for each formulation. Figure 3 illustrates the values of β and Δ log E from Table IV.

It can be observed in Figure 3 that there is a decrease in the values of β with the increase of Δ log E. The value of Δ log E represents the dispersion of the data obtained in the dielectric strength tests, and the smaller the value, the more reliable the final measure of E_γ is. On the other hand, according to the literature,[5,17] when β and Δ log E are related to one another in the way observed in Figure 3, these parameters can reflect the homogeneity and dispersion of particles in the polymeric matrix. The decrease of β with the increase of the weight fraction of recycled material reveals a smaller dispersion of pigments, fillers, and/or also a larger amount of impurities, as already described, remained from the washing process, catalysis residue, fillers, and additives (identified in Table II). The increase in the values of Δ log E indicates an increase in the dispersion of the experimental data with the recycled material concentration in the formulations, mainly for the formulations R-75% and R-100%. So, it can be concluded that these formulations present inferior electric performance as compared to the formulations R-0%, R-25%, and R-50%.

The standard NBR 5405 recommends that in the determination of the dielectric strength the results of just five tests and their average value should be considered. Still, it considers that if one of the results differs more than 15% from the average, a new group of tests should be done, which may lead to an erroneous result. Therefore, if the statistical treatment of Weibull is used, more information can be obtained about the dielectric strength of the material according to their parameters and the reliability of the results analysis is increased.

Figures 4 and 5 illustrate the identified rupture types in the five formulations by using an optical microscope. Most of the tested samples, approximately 62%, broke in a punctual way (see Fig. 4). On the other hand, in the remaining samples (38%) the perforation was accompanied by a path on their own surfaces, according to Figure 5. This behavior was independent of the sample composition. These perfo-

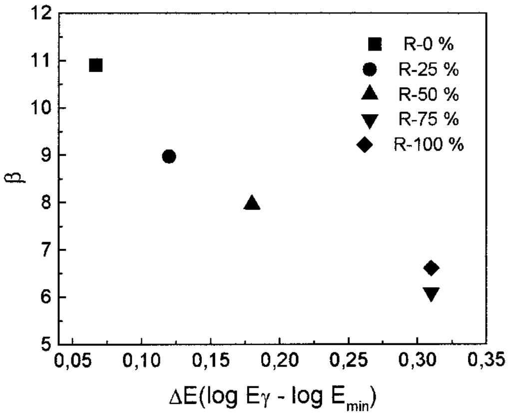

Figure 3 Parameter β as a function of dispersion Δ log E for the formulations R-0%, R-25%, R-50%, R-75%, and R-100%.

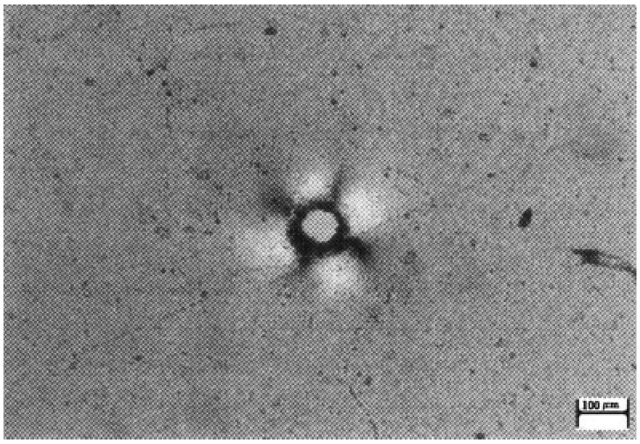

Figure 4 Micrograph showing the punctual rupture for R-25%.

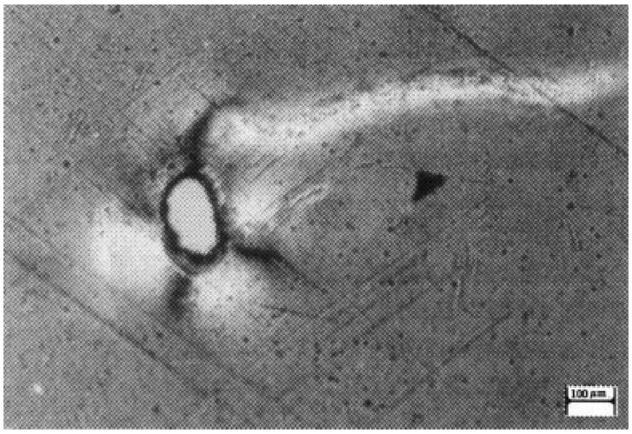

Figure 5 Micrograph showing the pathlike rupture for R-50%.

ration forms, as well as their random occurrences, were also observed in other studies^{5,6} on HDPE with titanium dioxide and carbon black.

CONCLUSIONS

Considering this study, it can be concluded that the incorporation of post-consumer recycled HDPE to the virgin polymer results in 17% decrease in the dielectric strength value. The decrease of the parameter β revealed that for higher concentration of recycled material, there was a smaller dispersion of pigments and fillers and a larger amount of conductive impurities were identified by means of analyses of metallic residues. Still, the values of ΔE indicated a dispersion of the experimental results, mainly for the formulations containing 75 and 100% of recycled material. The lowest experimental $E_{\min}$ values obtained for the 75 and 100% compositions indicate that these formulations display poorer electric performance.

As a concluding remark, formulations containing up to 50% of recycled material may be considered when developing products that require dielectric performance.

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References

1. Ku, C C.; Liepins, R. in Dielectric Breakdown of Polymers; Electrical Properties of Polymers—Chemical Principles; Munich: Hanser Publishers, 1987; pp. 102–199.
2. Ieda, M. IEEE Trans Electron Insul 1980, 15 (3), 206–224.
3. Kolesov, S. N. IEEE Trans Electron Insul 1980, 15 (5), 382–388.
4. Kitagawa, K.; Sawa, G.; Ieda, M. Elect Eng Jpn 1989, 109A (2), 42–51.
5. Ueki, M.; Zanin, M. IEEE Trans Electron Insul 1999, 6 (6), 876–881.
6. Okamoto, T.; Ishida, M.; Hozumi, N. IEEE Trans Electron Insul 1988, 23 (3), 335–344.
7. Ross, R. IEEE Trans Electron Insul 1994, 1, 247–253.
8. Manrich, S.; Herrera, J. C.; Rosalini, A. C.; Acconi, C. U.M. Pat. 7,901,580, 1999.
9. Millstone, Z.; Zhang, H. J. Macromol Sci, Ver Macromol Chem Phys 1995, C35 (4), 555–580.
10. Rabiej, S. Eur Polym J 1991, 27 (9), 947–954.
11. Machado, R. 2002, private communication.
12. Coppard, R. W.; Bowman, J.; Dissado, L. A.; Rowland, S. M.; Rakowski, R. T. J Phys D: Appl Phys 1990, 21, 1554–1561.
13. Bain, L. J. Statistical Analysis of Reliability and Life-Testing Models; Marcel Dekker: New York, 1978; Vol. 24, p. 450.
14. Cruz, S. A. Avaliação da Reciclagem de Polietileno de Alta Densidade Pós-Consumo para Aplicação em Isolamento Elétrico, Master’s Thesis, 2000.
15. Cruz, S. A.; Zanin, M. Polym Degrad Stab 2003, 80, 31–37.
16. Moss, S.; Zweifel, H. Polym Degrad Stab 1989, 25, 217–245.
17. Schawntes, D. Estudo Exploratório do HDPE Utilizando Rigidez Dielétrica e Distribuição de Carga, Master’s Thesis, 2000.