Seeley, A., Fothergill, J., Dissado, L. A., Stevens, G. C., Montanari, G. C. & Laurent, C. (2001). Evaluation of the onset of space charge and electroluminescence as a marker for cross linked polyethylene ageing. Paper presented at the 4th International Conference on Electric Charges in Non Conductive Materials, 2 - 6 July 2001.

CITY UNIVERSITY LONDON

City Research Online

Original citation: Seeley, A., Fothergill, J., Dissado, L. A., Stevens, G. C., Montanari, G. C. & Laurent, C. (2001). Evaluation of the onset of space charge and electroluminescence as a marker for cross linked polyethylene ageing. Paper presented at the 4th International Conference on Electric Charges in Non Conductive Materials, 2 - 6 July 2001.

Permanent City Research Online URL: http://openaccess.city.ac.uk/1354/

EVALUATION OF THE ONSET OF SPACE CHARGE AND ELECTROLUMINESCENCE AS A MARKER FOR CROSS-LINKED POLYETHYLENE AGEING

A.See[1], J.C.Fothergill[1], L.A.Dissado[1], G.C.Stevens[2], G.C.Montanari[3], C.Laurent[4], G.Teyssedre[4]

1=University of Leicester, UK; 2= Polymer Research Center, University of Surrey, UK; 3=University of Bologna, Italy; 4=Université Paul Sabatier, Toulouse, France

Abstract

The aim of the "ARTEMIS" project is to investigate the ageing mechanisms for cross-linked polyethylene under thermo-electrical stress and to identify ageing markers, which can be used to carry out diagnostic procedures. A carefully selected set of techniques which can give cross-correlated information on space charge phenomenology and material degradation were used to investigate specimens peeled from reference and aged cables. The paper shows that ageing induces a change in the density and depth of trapping levels, and an increase in the number and size of mesovoids. Interpretation of these results is discussed in terms of physico-chemical modifications, which can affect trap distribution and microstructure.

1.0 Introduction

In consequence of the liberalisation and privatisation of electrical energy production, transmission and distribution in European countries, projects have been developed to adapt and optimise the technical-economical procedures in the various countries comprising the European Community. The increasing requirement for interconnections and exchanges of significant flows of energy between the countries, coupled with the requirement to maintain low costs, no longer allows significant redundancy in transmission. Several countries have followed the practice in order to maintain quality and reliability. Many European cable networks are approaching their planned "end-of-life" and replacement and/or maintenance plans must be implemented. There is therefore a strong need for diagnostic procedures which may help to evaluate the state of cables.

One of the objectives of the European project "ARTEMIS" is to extract ageing markers on which diagnostic procedures off and on-line can be based. For this reason, the ageing mechanisms affecting cross-linked polyethylene (XLPE) cable insulation subjected to thermo-electrical stress are being investigated through electrical, chemical-physical and micro-structural measurement techniques.

2.0 Experimental techniques and test procedures

2.1 Sample

Cables are being subjected to ageing procedures and examined at predetermined ageing times. Tests are performed both on pieces of cables and on films peeled from them. The ageing and peeling procedures, the thermal treatment at which specimens are subjected before testing, and the lists of techniques employed are described in [1]. Other cables are also investigated.

This communication deals with a comparison that has been made between two identical cables, one being a reference, the other having been aged under thermo-electric stress. The cables had a 1600 mm^2 copper conductor and a 26.6 mm thick XLPE insulation. One of them was aged at different levels of field and temperature (maximum test field=27.5 kV/mm,

withstood for 1 year, maximum temperature 95°C). Films peeled from unaged and aged cables were examined. The electrical measurements were performed under DC field.

2.2 Space charge distribution

Space charge measurements were performed on the 150μm thick cable peelings by the pulsed electro-acoustic (PEA) technique at DC-voltages up to 150 kV/mm. Two different procedures were used to investigate the spatial distribution of the charge and its dynamics under stress. The voltage was applied either as a constant DC voltage (polarisation and depolarisation lasting 10000 s and 2000 s respectively) or a step-wise ramp depending on the desired information.

2.3 Dielectric spectroscopy

Low field dielectric spectroscopy was performed in the frequency range 0.1 mHz to 1 Hz in an attempt to establish the conductivity. If the imaginary component of the complex capacitance is found to be inversely proportional to frequency at low frequencies and the real part remains constant, then it is reasonable to assume that the response is dominated by a conduction process in which the conductance $G = C^{''} \cdot \omega$. The measurements were made using a guarded electrode system by slightly adapting a Keithley 6165 "resistivity adapter" cell. The diameter of the guarded electrode was 50.8 mm. Measurements were made by averaging at least four readings at each frequency, using a 1 V RMS sinusoidal excitation, at temperatures varying from 30°C to 100°C.

2.4 Luminescence techniques

The system for electroluminescence detection has been described in [2]. The first step in the analysis was to investigate the electroluminescence versus field characteristic by using a step-wise ramp test (300s, 4 kV/mm steps from 0 to 120 kV/mm) in the same conditions as for PEA measurements.
 Photoluminescence was used as a diagnostic technique. Two spectra were recorded: (i) the emission spectrum as a function of excitation wavelength and (ii) the excitation spectrum, which is obtained by recording the variation in the amplitude of the main components of the emission spectrum as a function of the excitation wavelength.

2.5 TEM measurements

A practical method for unambiguous determination of mesovoids by transmission electron microscopy (TEM) after a 2-stage replication of the samples has been developed and validated. Two marking methods are employed, both using the directional shadowing in the images, resulting from the metallic replication: (i) imprinting of marks of recognizable size, and (ii) maintaining the shadow direction by using trapezoidal samples. By observing the difference in shadow direction it is possible to distinguish voids from mounds on the surface of the replicas. A statistical analysis may be used to calculate the number of voids per unit volume, the void volumetric fraction and the internal surface area per unit volume of voids. Such an analysis would need to take into account that the surface of the films is a slice through the volume and may therefore slice through the voids at any point. A more accurate technique however takes into account the direction and length of the shadow in the void and

the length of the tail produced during coating. In this way a much more accurate analysis of the size distribution of voids may be made. Details of this technique are (to be???) described in [3].

3.0 Results

3.1 Space charge distribution

The amount of charge involved in the transport and accumulation process is larger for the aged than for the unaged specimen. The charge profiles are compared for unaged and aged in figure 1 after 2 s of depolarisation. It can be seen that more heterocharges have accumulated in the aged sample. A quantitative evaluation of charge stored has been obtained by plotting the total stored charge density: $(x_1 - x_0)^{-1} \int_{x_0}^{x_1} |Q(x,t)| dx$ after 2s of depolarisation for different field values [4]. Figure 2 shows the characteristics for unaged and aged specimens in which the threshold value of field can be estimated at the point where the slope suddenly increases. This threshold value changes from ≈ 15 kV/mm in the unaged specimen to ≈ 10 kV/mm in the aged. The same result is obtained from the conduction current versus field characteristics, plotted according to the space charge limited current, SCLC, approach (not reported here).

3.2 Dielectric spectroscopy

Figure 3 shows the Arrhenius plot of DC conductivity versus temperature for aged and unaged samples. At temperatures below 70°C the measurements were below the noise floor (these are currently being repeated with a higher voltage excitation level). Above these temperatures the features of the complex capacitance versus frequency characteristics (described above) suggested a conductive transport mechanism dominated-especially at high temperatures. The activation energy, Δ, can be derived from the Arrhenius equation: $\sigma = \sigma_\infty \exp\{-\Delta/kT\}$. The activation energies obtained from the Arrhenius plots are 0.88 eV and 1.15 eV for the unaged and aged cable peelings, respectively.

3.3 Luminescence measurements

The electroluminescence (EL) versus field is shown in figure 4 for the two samples. The EL onset is reproducible as reported in details in [5] and is 60 kV/mm for the unaged sample but 75 kV/mm for the aged. The emission of permanent EL under DC conditions has been associated with charge recombination. This occurs when space charge regions of opposite polarities extending from the electrodes overlap to form a bipolar domain. This domain has formed at a higher field in the aged sample. Since electroluminescence also depends on the radiative relaxation probability, photoluminescence has been performed and the luminescence yield has been compared between the two samples. Figure 5 gives the emission and excitation spectra. The analysis of the components of the emission spectrum has been reported elsewhere [6]. What is relevant for this study is the fact that the emission spectra are identical indicating that there were no difference in the chromophores responsible for the photo-stimulated emission. However, the excitation spectra show a decrease of the luminescence yield by a factor 4 in aged samples. Photoluminescence measurements have already been used in ageing diagnosis. A decrease of the luminescence yield would mean an increasing probability of non-radiative de-excitation mechanisms. This may be due to a physical-chemical change near the luminescent species. On the one hand, this measurement gives an indication of a modification of the physico-chemical material properties; on the other hand, it

could also be an explanation for the increasing onset of EL. In order to separate the two factors, the formation of the recombination region has been followed by PEA analysis, using an experimental procedure identical to that adopted in EL experiments.

The space charge profiles have been acquired at the end of each 300 s step. They are shown for a selected set of applied fields in figure 6. For the unaged sample, it can be seen that positive and negative charges have already penetrated deep into the bulk providing the conditions for continuous EL excitation. Further increase of the field enhanced the charge density in the bulk. Note that the net zero charge plane remains in the same position. The situation appears differently for the aged sample. It can be seen that the field at which charges penetrate into the bulk is higher in agreement with a higher field for continuous EL excitation. This means that the higher EL onset observed in aged sample is due to the fact that the excitation conditions are fulfilled at a higher field relative to the unaged specimen, indicating a change in the charge transport parameters.

3.4 TEM observation of voids

It is found that there is a clear increase in the concentration of voids close to the inner screen of the cable and also probably a shift to higher void sizes. No significant change is apparent 4 mm into the insulation. Figure 7 shows the increase of void concentration close to the inner screen. There is a concomitant increase in mesovoid surface area. Typically the mesovoid surface area per cm^3 of insulation near the inner screen is 0.05 mm^2 in the unaged specimens but around 0.15 mm^2 in the aged specimens. This increase in void size suggests that there is an increase in crystallinity elsewhere. The increase in surface of such voids will provide a higher concentration for electron traps.

4.0 Discussion

The results are consistent with the picture of an increase in the density of the deep trapping levels with thermo-electrical ageing. The space charge threshold results show an increase in the overall charge trapped in the aged samples suggesting that more traps have been created in these samples. The dielectric spectroscopy results show a significant increase in activation energy, which may be expected if the charge is hopping between deeper traps in the aged samples. The space charge and EL results show that the negative charges are moving much more slowly in the aged specimens, perhaps indicating that the deeper traps are influencing these carriers more. A higher density of traps in aged sample would also explain the lower luminescence yield through increasing the routes for non-radiative de-excitation. An increase in mesovoid concentration may be responsible for producing these traps.

5.0 Conclusion

The investigations made on specimens peeled from unaged and aged cables bring out some interesting indications regarding the effect of thermo-electrical ageing on cables, in the light of the search for diagnostic tools. The measurements performed on un-aged and aged samples provide information supporting the occurrence of chemical-physical modifications in the tested cables, even if the extent of the modification would suggest that the degradation is not heavy. TEM investigation suggests that microcavities are undergoing a growth process, but the extent of the growth is very limited.

References

[1] L.A. Dissado, J.C. Fothergill, A. See, G.C. Stevens, L. Markey, C. Laurent, G. Teyssedre, U.H. Nilsson, G. Platbrood, G.C. Montanari, "Characterizing HV XLPE cables by electrical, chemical and microstructural measurements on cable peelings: effects of surface roughness, thermal treatment and peeling location", IEEE CEIDP, pp. 136-140, Victoria, Canada, October 2000.

[2] G.Teyssedre, D. Mary, C. Laurent, and C. Mayoux, "Optical Emissions due to Space Charge Effects in Insulating Polymers: an Insight into Electrical Ageing", in "Space Charge in Solid Dielectrics", Edited by J. C. Fothergill and L. A. Dissado, Dielectrics Society, Leicester, Chap. 26, pp. 285-302, 1998.

[3] Gary "Mesovoids detection techniques"

[4] G.C. Montanari, "The electrical degradation threshold of polyethylene investigated by space charge and conduction current measurements", IEEE Trans. on DEI, Vol. 7, n. 3, pp. 309-315, June 2000.

[5] G. Teyssedre, C. Laurent, G.C. Montanari, F. Palmieri, A. See, L. A. Dissado, and J.C. Fothergill, "Charge distribution and electroluminescence in XLPE under DC field", Submitted to J. Phys. D: Appl. Phys.

[6] G. Teyssedre, G. Tardieu and C. Laurent, "Characterization of XLPE Cable Materials by Luminescence Techniques, Submitted to Journal of Materials Science.
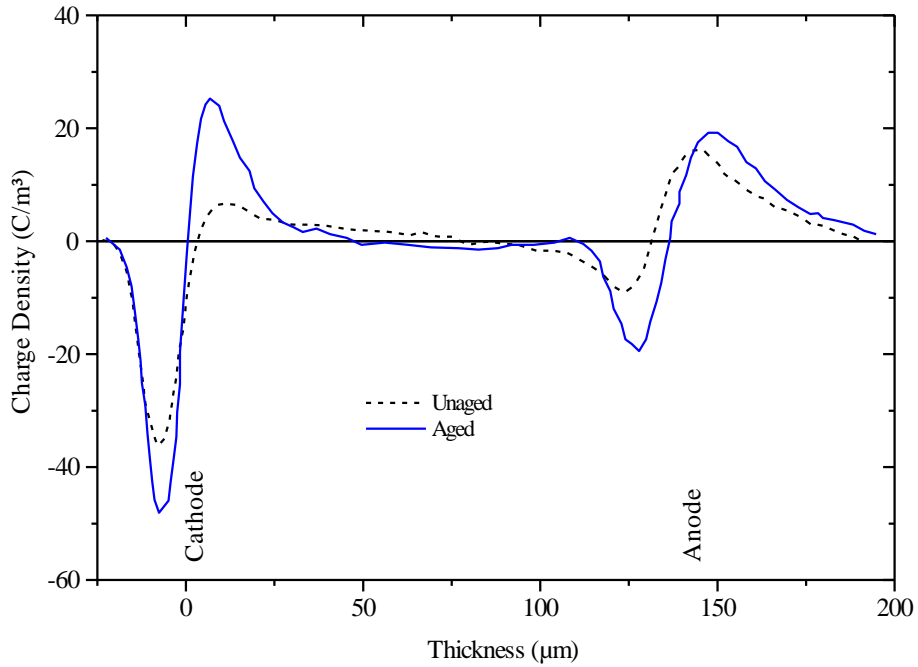
Figure 1 Space charge profiles after 2 s of depolarisation relevant to unaged and aged specimens, poling field 60 kV/mm.
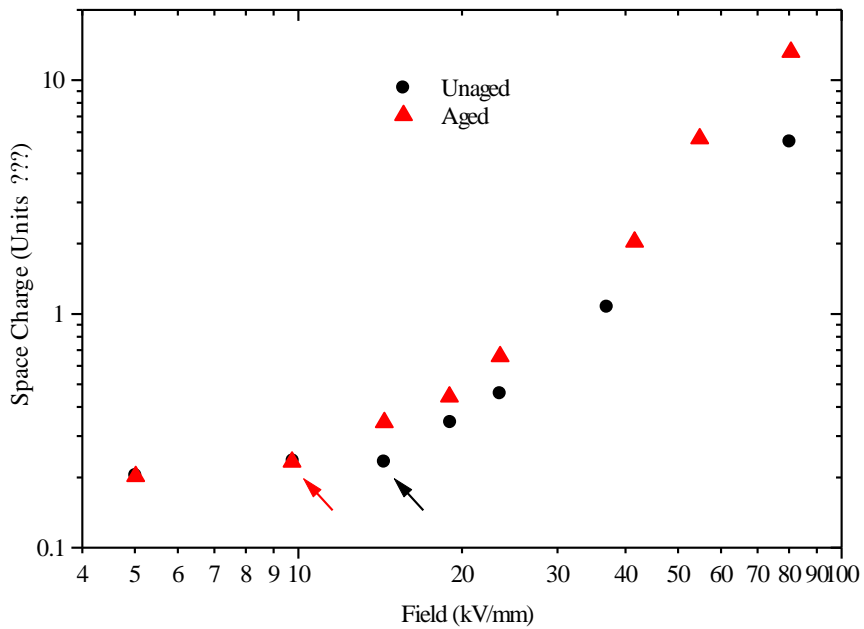

Figure 2 Threshold characteristics (total stored charge density versus poling field) obtained from space charge measurements for unaged and aged specimens. Arrows indicate the estimated thresholds. The units on the vertical axis (??).
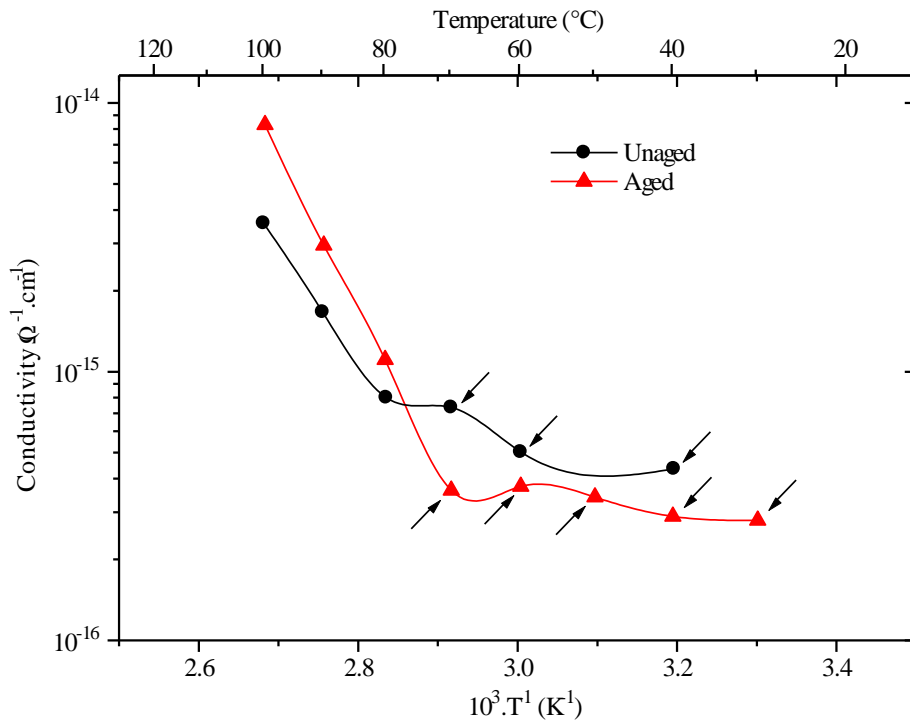
Figure 3 Arrhenius Plot of DC conductivity versus for aged and unaged cable peelings. The data points indicated by arrows are likely to be incorrect as they are below the noise floor.
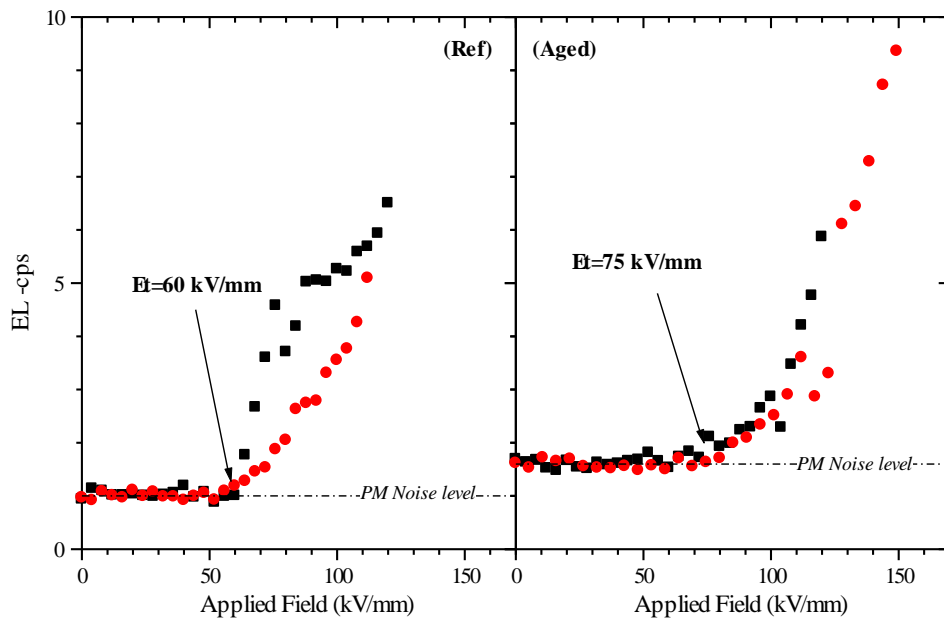

Figure 4 DC threshold for electroluminescence, relevant to unaged and aged specimens.
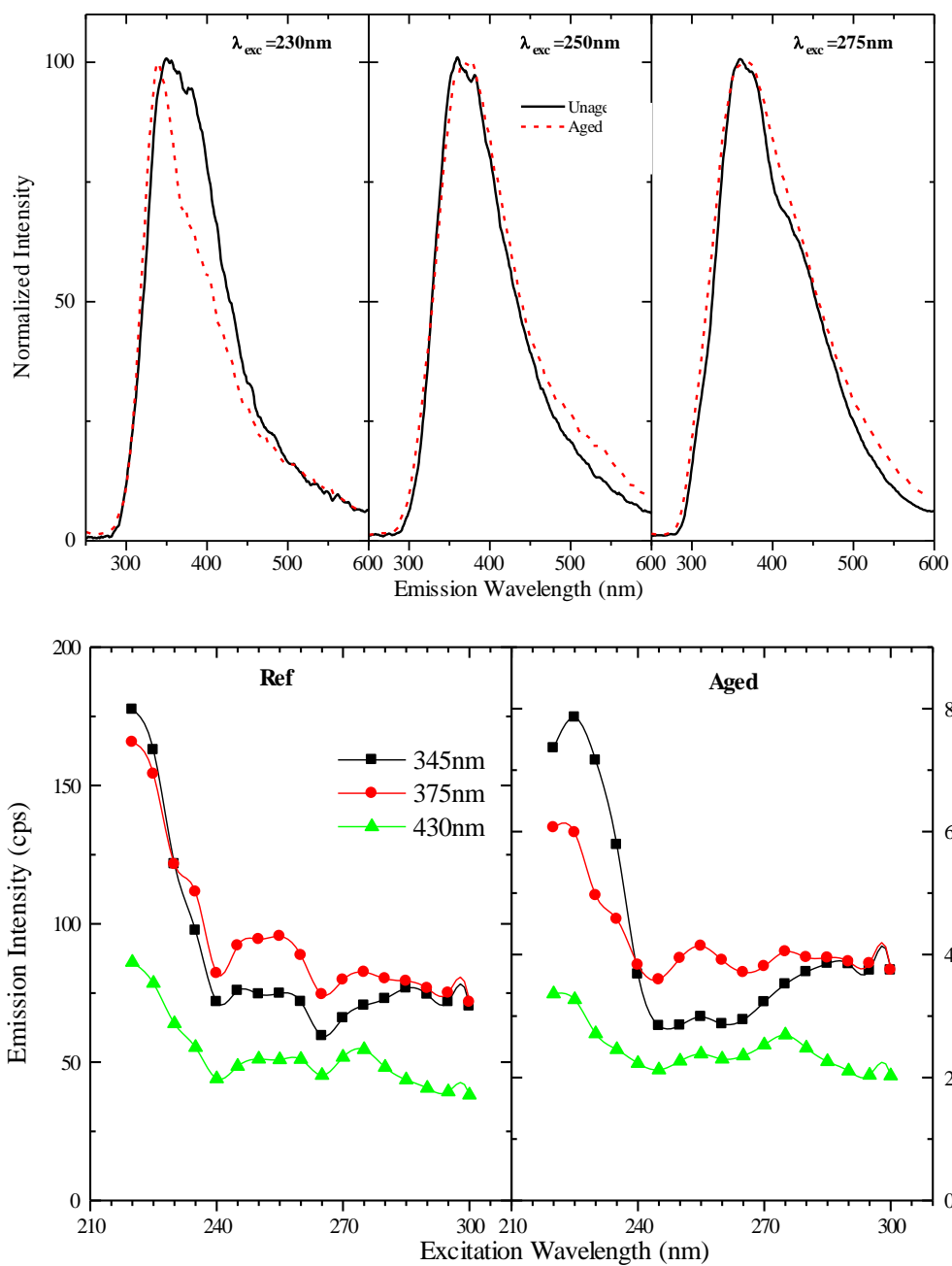
Figure 5 **Top:** Photoluminescence emission spectra for aged and unaged samples at different excitation wavelengths. **Bottom**: Excitation spectra monitored at different emission wavelengths.
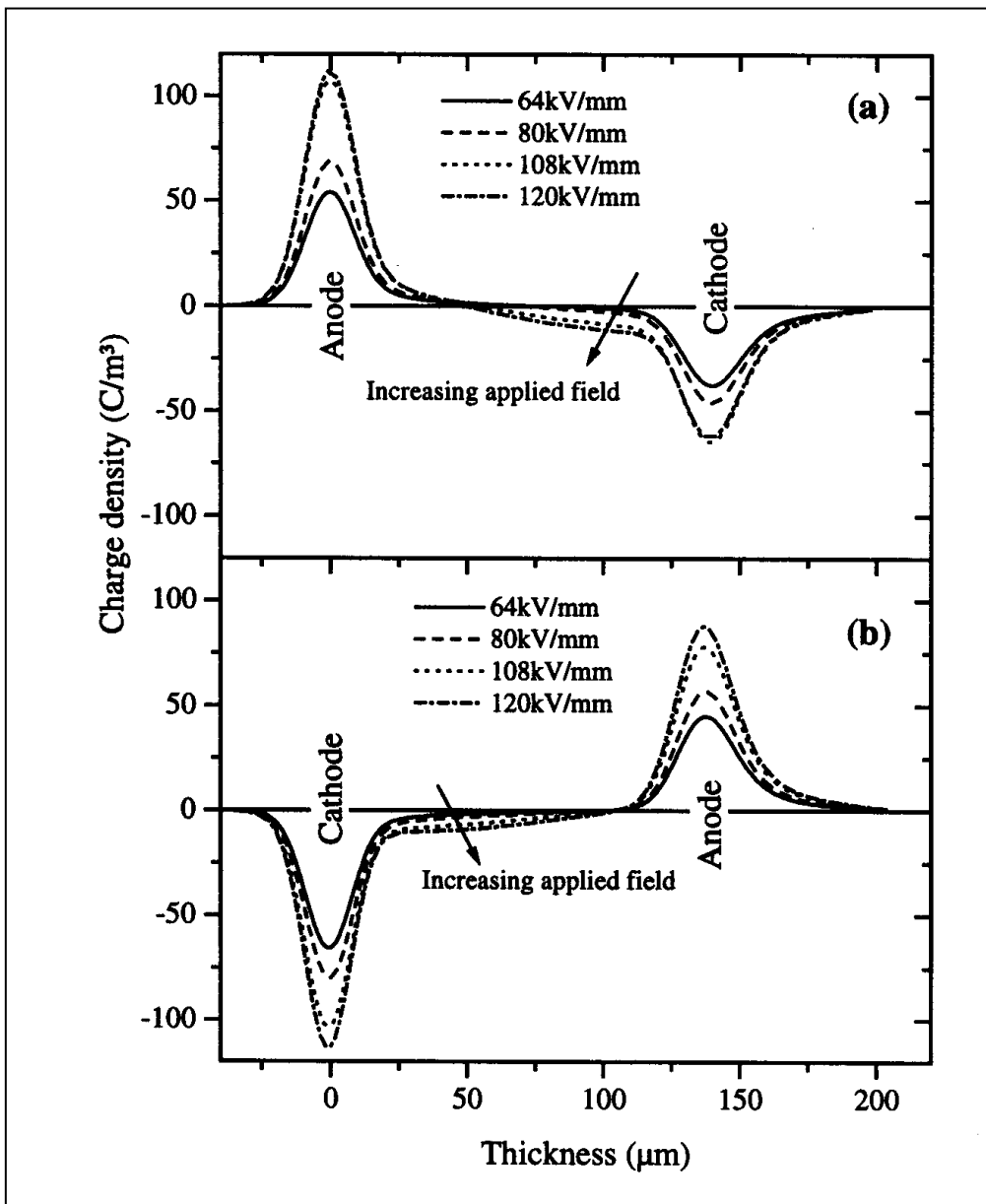
Figure 6 Evolution of the space charge profiles under increasing applied electric field for both the (a) unaged and (b) aged specimens.
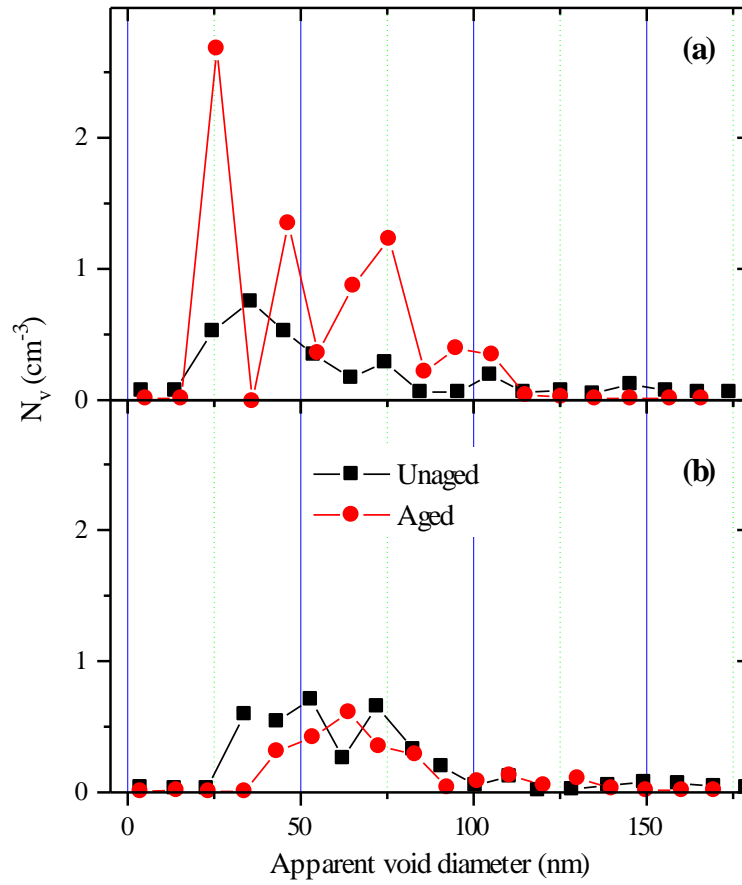
Figure 7 Apparent void concentration in unaged and aged specimens, close to the internal semicon (8A) and at 4 mm from the internal semicon (8B). The data are obtained by TEM made on two-stage replicas.   Gary