

Comparative study on field collected samples of aged silicon rubber composite coatings for high voltage insulators

I.V. Tudose,^{1,4} M. Sucheai,^{1,3,4*} K. Siderakis,^{2,3} E. Thalassinakis,⁵
E. Koudoumas^{1,3}

¹*Center of Materials Technology and Photonics School of Applied Technology, Technological Educational Institute of Crete, 71004 Heraklion, Greece*

²*Center of Energy and Photovoltaic Systems (CEPS), School of Applied Technology, Technological Educational Institute of Crete, 71004 Heraklion, Greece*

³*Electrical Engineering Department, Technological Educational Institute of Crete, Greece*

⁴*“Al.I.Cuza” University of Iasi, 11 Bulevard Carol I, Iasi, 700506, Romania*

⁵*Hellenic Electricity Distribution Network Operator S.A. (HEDNO), Greece*

Abstract: Pollution of high voltage (HV) insulators is a phenomenon with a considerable impact to the performance of transmission and distribution electrical networks. The use of composite materials and especially Silicone Rubber proved to be an efficient improvement, capable of suppressing the problem and diminishing the flashover probability. As a result ceramic insulators in transmission lines are replaced by insulators with composite housing, either HTV Silicone Rubber or LSR. In the case of HV substations however, the replacement of insulators is rather difficult, due to the complexity of the equipment and the

* M. Sucheai, *e-mail*: mirasucheai@staff.teicrete.gr

corresponding financial cost. In this case the application of RTV Silicone Rubber is an equivalent alternative. The ceramic insulators are covered with a 0.5 mm RTV SIR coating which provides the advantages of composite insulators on a ceramic substrate. After installation the possible material lifetime, which is determined by the service conditions and the material formulation, is of primary concern. In Crete, a large scale application exists and coatings that exceed a service period of 10 years are still in operation. The present study focuses on the structural and morphological characterization of field collected composite insulators of various ages so that the degradation degree can be correlated with their service.

Keywords: HV insulators, RTV SIR coatings, aging, characterization.

Introduction

The potential benefits of composite insulators have interested utilities and equipment manufacturers worldwide since polymeric designs were first introduced in the 1960s. Lighter in weight and less susceptible to breakage than glass or porcelain materials, they showed immediate promise for lowering transportation costs, easing installation and reducing maintenance. The savings could be especially dramatic in areas with difficult accessibility. Usually smaller than ceramic insulators, composites can also reduce tower heights and right-of-way space requirements. In particular, polymeric materials have been found to drastically reduce the effects of vandalism on high-voltage insulator. Polymers typically resist mechanical shock much better than ceramics or glass. Materials testing and development for HV insulator applications focused on a number of candidates, including ethylene propylene rubbers (such as EPDM), polyolefins, polyurethanes, polyethylene, epoxies, silicones and PTFE (Teflon).¹ Water repellency has been a fundamental design parameter,

regardless of the material or specific insulator design. Silicone materials of various types have been used in electrical service for over 50 years. In fact, one of the first applications for a silicone was electrical insulation on aircraft in World War II. In the 1970s, Dow Coming developed a room-temperature curing elastomer, designed for spray application to porcelain insulators to reduce insulator maintenance and resist flashovers, particularly in salt fog environments.^{1,2} The product is still used today, allowing utilities to improve the electrical performance of porcelain arrestors without replacing them. Silicone elastomers for high-voltage insulator applications are generally high-consistency rubber compounds. Two types of filler are commonly used: silica is the reinforcement that lends physical strength to the polymer, while alumina trihydrate (ATH) improves arc resistance. Filler treatments, pigments and cure agents may also be part of the formulation in small amounts. The polymer-filler combination is important in silicone insulators. Processing, physical properties and electrical performance are all affected by the molecular weight and structure of the polymer, as well as filler type, size, shape, surface treatment and residual catalyst or contaminants. In determining the optimum formulation for specific applications, device manufacturers and silicone suppliers must determine the best balance of properties, processing characteristics and economic considerations. Silicone has demonstrated better hydrophobicity and lower surface energy than many other organic polymers. The surface properties of silicone are unique, in that it recovers its hydrophobicity between contamination and/or corona episodes, while other materials progressively deteriorate. Corona exposure does temporarily increase the wettability of silicone rubber, a phenomenon associated with an increase in surface oxygen content, but the water-repellency returns after a period of rest. The

material's ability to recover its hydrophobicity is thought to result at least in part from the diffusion of low molecular weight PDMS (polydimethylsiloxane) fluid to the surface.³⁻⁵ Another phenomenon which affects the hydrophobic recovery demonstrated by silicone insulators is surface reorientation. The extreme flexibility of the siloxane chain and the low molecular forces between methyl groups produce a low glass transition temperature and a high free volume of PDMS. These conditions readily permit surface reorientation of silicone rubber, which has the most mobile surface of all common polymers for HV applications. Existing test standards for ceramic insulators have not shown good correlation with actual service experience when applied to composite materials. In particular, it has proven very difficult to develop test conditions that accurately duplicate material degradation which occurs during long-term service. In Crete, Greece a large scale application exists and coatings that exceed a service period of 10 years are still in operation. The present study focuses on the structural and morphological characterization of field collected composite insulators of various ages so that the degradation degree can be correlated with their service.

Experimental

Various field collected samples with different aging conditions and a reference virgin sample of SIR HTV were studied using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FT-IR). SEM and EDX characterization were performed using a JEOL JSM 6362LV electron microscope equipped with an EDAX INCA X-act Oxford Instrument detector. SEM surface characterization was performed in

low vacuum (3-12 Pa) without any sample preparation while EDX characterization and elemental mapping were performed in high vacuum. Elemental mapping of the sample surface was also collected at magnification $\times 10000$ and using large acquisition times (more than 80000 counts) for an accurate definition of surface points. The instrument used for FT-IR characterization was a spectrometer fitted with an ATR module manufactured by Shimadzu.

The characteristics of samples used for the present study are presented in Table 1.

Table 1. Characteristics of samples.

Sample denomination	Characteristics
SIR 1	Reference virgin SIR HTV
SIR 2, 3, 4, 5	Artificially aged SIR HTV
Dg 1, 2, 3, 4 where 1, 2, 3, 4 stands for different spatial positioning onto HV insulator	TR 11, VT PHASE A CONDITION: <i>OLD</i> INST DATE: Estimated 2002
Ge 1, 2, 3, 4 where 1, 2, 3, 4 stands for different spatial positioning onto HV insulator	TR 11, CT PHASE C CONDITION: <i>NEW MATERIAL</i> INST DATE: <i>02/2009</i>
Gz 1, 2, 3, 4 where 1, 2, 3, 4 stands for different spatial positioning onto HV insulator	TR 11, VT PHASE C CONDITION: <i>WASHED AND ADDITION OF NEW MATERIAL COATING (2 LAYERS)</i> INST DATE: <i>02/2009</i>

Results and discussions

Reference sample: Figure 1 presents surface morphology of a virgin SIR HTV sample at two different magnifications and electron acceleration voltages. Higher magnification reveals the filler material distribution in the silicon rubber matrix.

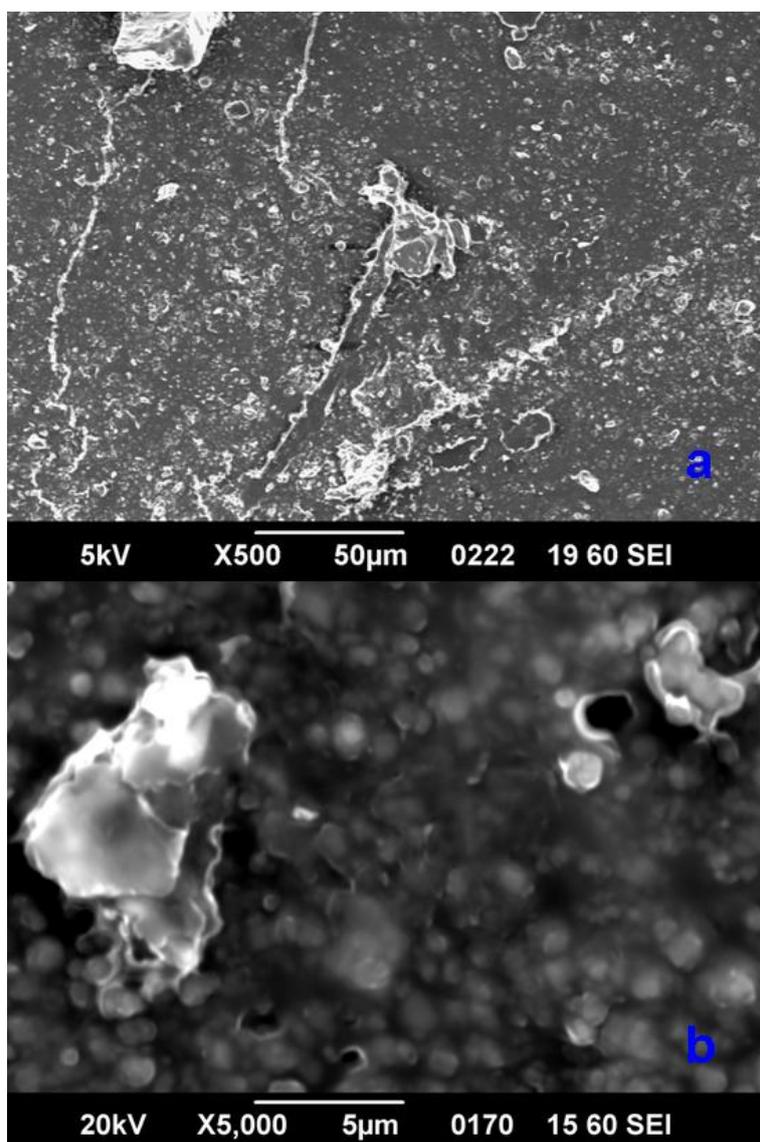


Figure 1. LV-SEM image of reference SIR sample a. general view ($\times 500$ at low acceleration voltage 5kV) b. close up evidencing the filler material ($\times 5000$, 20kV).

Compositional characterization of SIR sample shows the presence of C, Si, Al and O elements in the proportions presented in Figure 2b. A characteristic EDX spectrum corresponding to this sample is presented in Figure 2a.

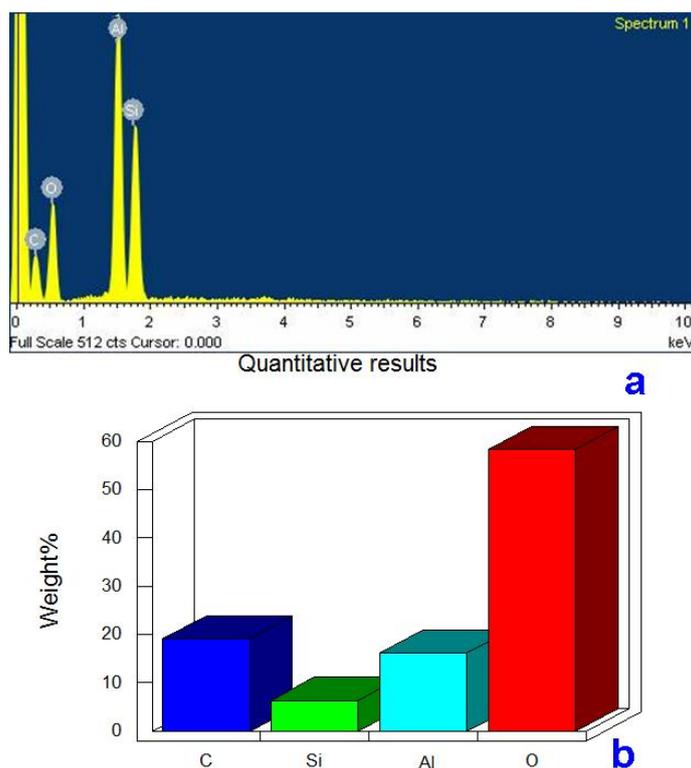


Figure 2. Compositional characterization of SIR sample a. EDX spectrum; b. elemental composition (weight %).

ATR FT-IR characterization was performed for the reference sample and different artificially aged samples since the target of the study is monitoring and degradation control. These are used to set-up a reliable characterization procedure in order to overcome experimental difficulties due to low control of sample thickness when sampling is done in the field from the HV outdoor insulators. The absorbance vs. wavenumber (cm^{-1}) spectra for five reference samples SIR are presented in Figure 3 and Table 2 together with the area of the peaks for Si-O-Si stretching and Si-CH₃ symmetric deformation since these peaks can be correlated with the backbone of the polymer and its hydrophobic properties respectively. It is expected that during degradation processes the polymer will suffer methyl group losses due to oxidation and surface mineralisation and correspondingly the band at 1261.61 cm^{-1} will drop in intensity while the

bands corresponding to backbone stretching (1020.47 and 1091.85 cm^{-1}) will increase in intensity due to cross-linking and surface mineralisation.

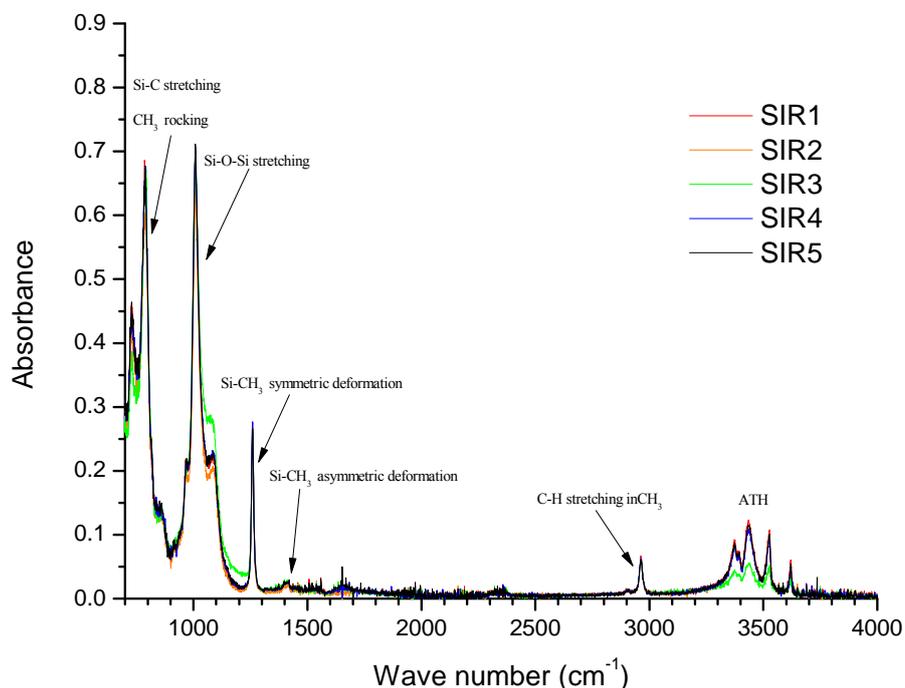


Figure 3. ATR FT-IR spectra corresponding to virgin SIR HTV sample and four artificially aged samples.

Table 2. Corresponding peak areas and area ratios for Si-O-Si and Si-CH₃ bonds from Figure 3.

SIR	Area Si-O-Si peak	Area Si-CH ₃ peak	Ratio CH ₃ /Si-O-Si	Ratio Si-O-Si/CH ₃	SIR
1	53.63308	5.328134	0.0993	10.0660	1.000000
2	49.35862	4.842971	0.0981	10.1918	1.012496
3	62.67803	6.156825	0.0982	10.1803	1.011348
4	54.86732	5.201641	0.0948	10.5481	1.047890
5	55.88716	5.274761	0.0944	10.5952	1.052571

The observed peaks for ATH are in agreement with the EDX analysis results for SIR HTV material composition. The defined ratios indexes are useful for degradation assessment of SIR samples. Normalizing

the ratio Si-O-Si/CH₃ for the samples to the reference sample makes the results easier to compare.

Since the area of the peaks is directly related to the concentration of a group in a given material the ratio of two peaks is equal with the ratio of the absolute quantities of the investigated molecular components. Based on this we can see how a molecular composition changes during degradation. In case the polymer is oxidizing the normalized ratio is expected to grow due to the fact that more Si-O bonds are formed while the methyl groups transform in other products. In case the backbone of the polymer brakes forming lower mass products the Si-O peak will drop thus decreasing the normalized ratio. If a sample has silica as a filling material the results are difficult to interpret since the lower mass molecules are migrating toward the surface modifying the ratio in a random fashion. Based on the above, we may assume that the SIR samples degrade by oxidation.

Field samples:

LV SEM characterization images for the field collected samples magnification $\times 1000$ are presented in Figure 4.

From figure 4 one can conclude that the oldest samples show modified morphology. They have a “dusty” appearance and obvious cracks. Cubic crystalline contaminants are present onto the surface. According to the spatial position onto the insulator body, it seems that position 2 is the less degraded, position 3 is strongly contaminated while position 1 seems the most degraded.

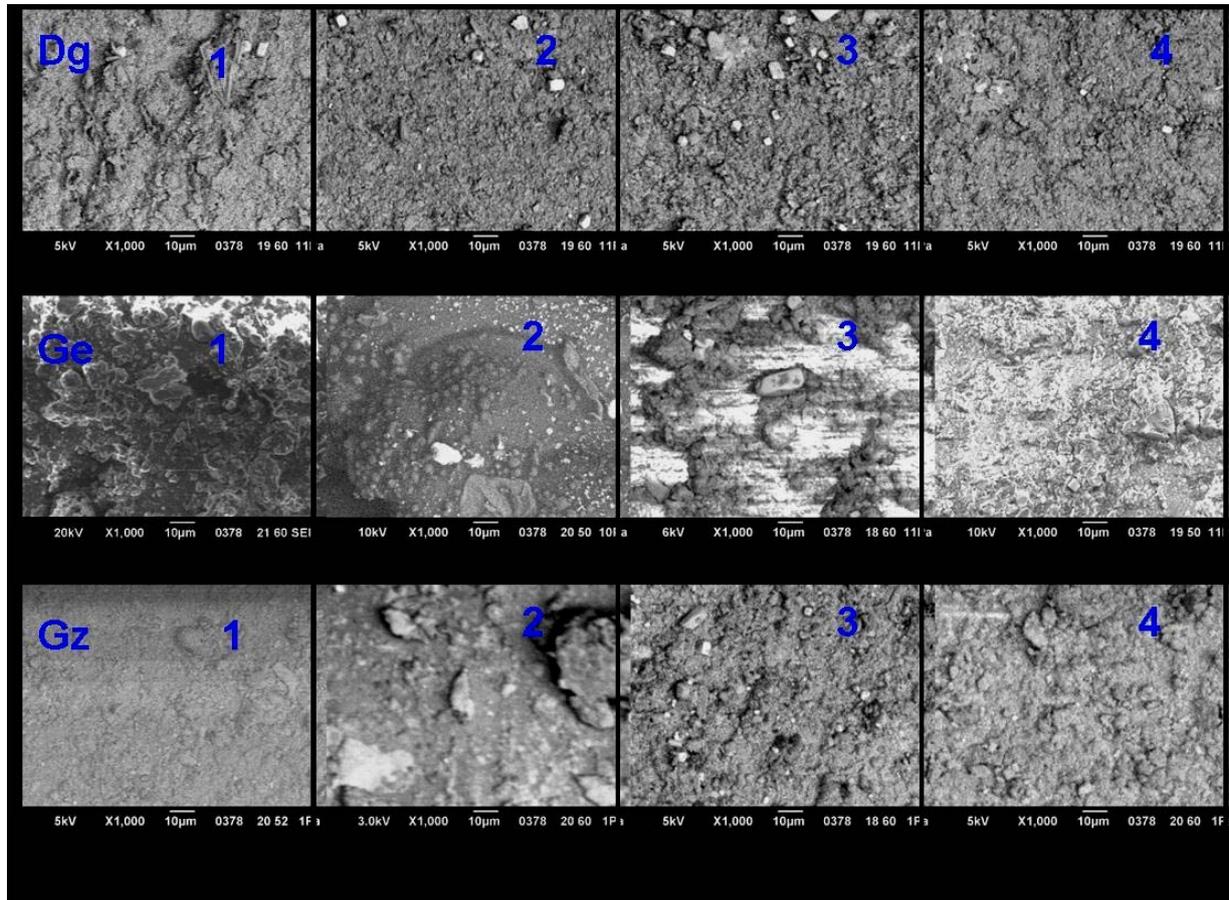


Figure 4. SEM images for the various field samples.

EDX analysis showed a very large variation of carbon content in the samples as well as presence of various contaminants onto surface. The most common contaminants are NaCl (associated with the presence of sea water in the atmosphere), S and metals as K, Ti, Fe, V, Mg, Ca associated with the presence of strong corona discharges. An example of EDX results for the sample Dg1 are shown in Figures 5 and 6.

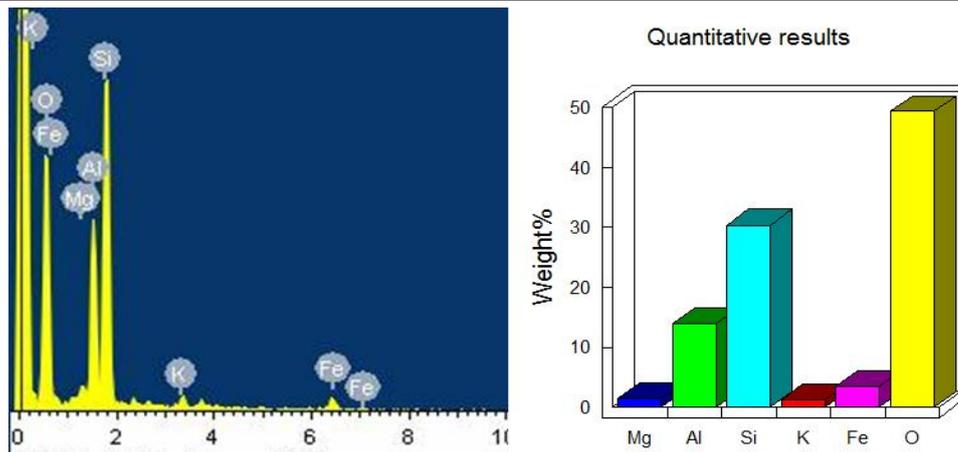


Figure 5. EDX spectrum of Dg1 sample and elemental weight distribution.

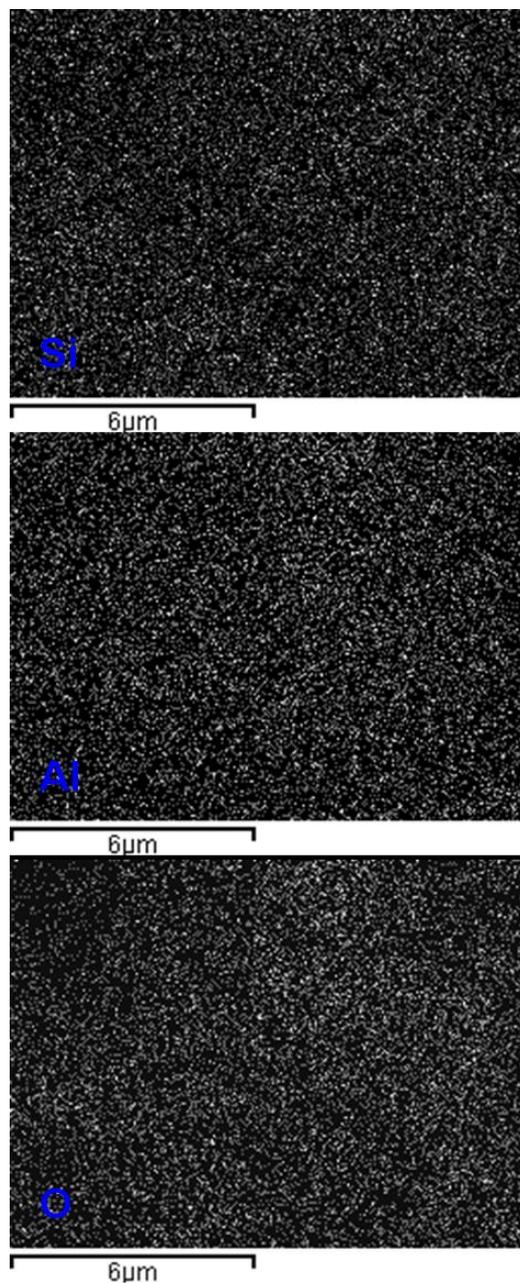


Figure 6. Elemental mapping of O, Si and Al in the analyzed sample.

ATR FT-IR analysis of field aged samples was performed and data processing was done according to the procedure presented for the reference sample using the defined ratio indexes for degradation assessment of SIR samples and normalizing the ratio Si-O-Si/CH₃ for the samples to the reference sample. The results are presented in Table 3.

Table 3. Normalized areas ratios for Si-O-Si and Si-CH₃ bonds from FT-IR spectra for the field aged samples.

Sample	ge1	ge2	ge3	ge4
Si/CH3	14.79	7.95	16.99	13.95
Sample	gz1	gz2	gz3	gz4
Si/CH3	21.29	12.15	16.63	18.72
Sample	dg1	dg2	dg3	dg4
Si/CH3	38.20	23.49	36.33	31.71

The graphical representation of the normalized ratios as a function of spatial position onto the insulator surface is presented in Figure 7.

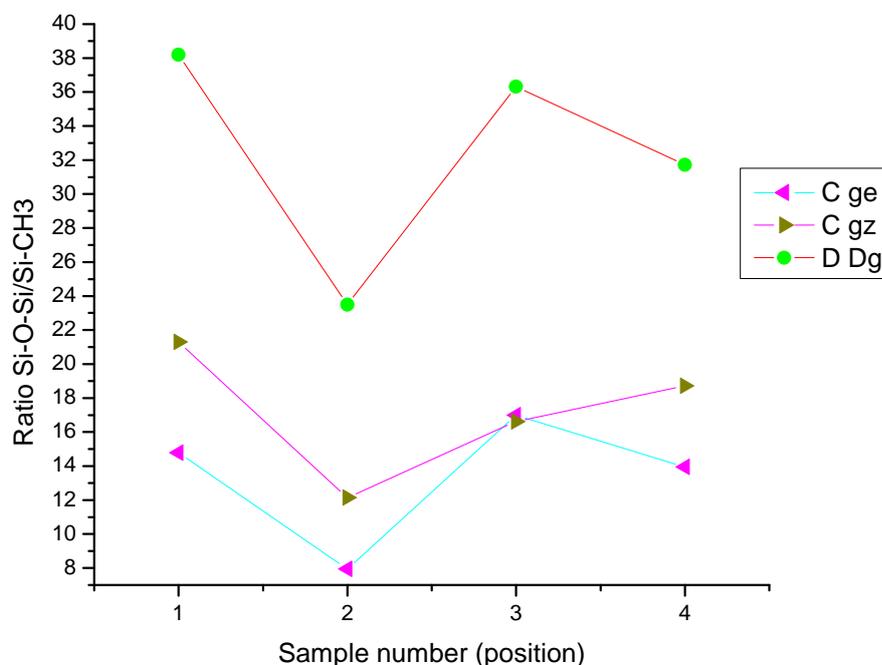


Figure 7. Graphical representations of the normalized areas ratios for Si-O-Si and Si-CH₃ bonds as a function of spatial position.

It is obvious from the above that the variation of normalized areas ratios values fulfils the initial assumptions regarding the normalized areas ratios for Si-O-Si and Si-CH₃ bonds as a measure of SIR HTV degradation and confirms the SEM observations. The oldest and most damaged sample Dg has the largest corresponding report values. Position 2 onto insulator has in all samples series the lowest local value while position 1 corresponds to highest degradation degree.

Conclusions

The present study focused on the structural and morphological characterization of field collected composite insulators of various ages so that the degradation degree can be correlated with their service. For this purpose it was introduced the normalized areas ratios for Si-O-Si and Si-CH₃ bonds as a measure of SIR HTV degradation based on ATR FT-IR measurements. Experimental results proved that this index is a proper parameter for the SIR HTV materials aging description.

Acknowledgements

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