# Thermal aging studies and lifetime prediction of commercial filled Ethylene Propylene Rubber (EPR) cable insulation

by

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

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## DEDICATION

This thesis is affectionately dedicated to my mother, Radheika and my grandfather, Raman Thatha for inspiring me to reach for the stars.

# TABLE OF CONTENTS

LIST O	F TABLES	vi
LIST O	F FIGURES	vii
ACKNO	DWLEDGMENTS	ix
ABSTR	ACT	xi
СНАРТ	TER 1. GENERAL INTRODUCTION	1
1.1	Chapter Overview	1
1.2	Motivation - The Big Picture	1
1.3	Dissertation Overview	$\overline{2}$
1.4	Background and Literature Review	3
	1.4.1 Cable function and failure	3
	1.4.2 Cable insulation and jacket materials	5
	1.4.3 An introduction to Ethylene Propylene Rubber (EPR)	6
	1.4.4 Thermal degradation in cable insulation	8
1.5	Hypothesis	12
1.6	Approach	12
1.0	Research Objectives	13
1.1	References	13
1.0		
CHAPT	TER 2. MATERIALS AND CHARACTERIZATION METHODS	17
2.1	Chapter Overview	17
2.2	Materials	17
	2.2.1 Ethylene Propylene Rubber (EPR) insulation	17
	2.2.2 Jacketed EPR/CPE power cable	18
2.3	Characterization Methods	19
	2.3.1 Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS).	19
	2.3.2 Thermogravimetric Analysis (TGA)	21
	2.3.3 Differential Scanning Calorimetry (DSC)	22
	2.3.4 Dielectric Spectroscopy (DS)	23
	2.3.5 Dielectric Breakdown (DB)	26
	2.3.6 Elongation at Break (EaB) tensile test	27
2.4	Preliminary Characterization Studies on EPR	28
	2.4.1 Evaluation of composition and morphology by SEM/EDS analysis	28
	2.4.2 Investigation of electrical properties	30
2.5	Accelerated Isothermal Aging	33

	2.5.1 Aging temperature and methodology	33
	2.5.2 Time-Temperature (t-T) superposition studies	35
2.6	Conclusion	38
2.7	References	39
CHAPT	FER 3. KINETIC MODELING OF THERMAL MODELING OF THERMAL DEGRA-	
DA	FION IN ETHYLENE PROPYLENE RUBBER (EPR)	41
3.1	Abstract	41
3.2	Introduction	42
3.3	Materials and Sample Preparation	43
3.4	Methods	43
3.5	Results and Discussion	44
	3.5.1 Thermal degradation in EPR	44
	3.5.2 Kinetic modeling	46
3.6	Conclusion	50
3.7	References	51
0.1		01
CHAP	FER 4. A KINETIC MODEL FOR DIELECTRIC BREAKDOWN IN THERMALLY	
AG	ED ETHYLENE PROPYLENE RUBBER (EPR)	54
4.1	Abstract	54
4.2	Introduction	54
4.3	Materials and Methods	56
	4.3.1 Materials and sample preparation	56
	4.3.2 Characterization methods	57
4.4	Theoretical Development	58
	4.4.1 Formation of a conducting submicrocrack	58
	4.4.2 Submicrocrack propagation and dielectric breakdown	60
4.5	Results and Discussion	62
	4.5.1 Relative permittivity of EPR as a function of aging	62
	4.5.2 Measured dielectric breakdown strength of EPR	63
	4.5.3 U and $\gamma$ as empirical functions of permittivity	66
	4.5.4 Dielectric breakdown strength prediction at various temperatures	67
4.6	Conclusion	69
4.7	References	70
CHAP'	FER 5. CHARACTERIZING THERMAL DEGRADATION IN ETHYLENE PROPY-	
LEN	VE RUBBER (EPR) INSULATION AGED ALONGSIDE CHLORINATED POLYETHY-	
LEN	NE (CPE) JACKET IN POWER CABLES	71
5.1	Abstract	71
5.2	Introduction	72
5.3	Materials and Methods	74
	5.3.1 Sample preparation	74
	5.3.2 Characterization methods	75
5.4	Results and Discussion	77
	5.4.1 Optical Microscopy - interaction layer growth	77
	5.4.2 SEM/EDS Analysis - changes in elemental composition	78

	5.4.3	TGA/MS Analysis - characterizing thermal degradation behavior 81
5.5	Conch	usion $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $87$
5.6	Refere	nces
СНАРТ	TER 6.	MEASURING DISSIPATION FACTOR OF THERMALLY AGED EPR/CPE
JAC	KETE	D CABLES USING INTERDIGITAL CAPACITIVE SENSORS 91
6.1	Abstra	act
6.2	Introd	uction $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $$
6.3	Mater	ials and Methods
	6.3.1	Materials
	6.3.2	Accelerated aging and sample preparation
	6.3.3	Methods
6.4	Result	s and Discussion $\ldots \ldots $
	6.4.1	Measured dissipation factor (D)
	6.4.2	Comparison of dissipation factor and indenter modulus
6.5	Conch	1sion $102$
6.6	Refere	$nces \ldots \ldots$
СНАРТ	TER 7.	GENERAL CONCLUSION
7.1	Propo	sed Directions for Future Work
	· 1.	

# LIST OF TABLES

## Page

Table 1.1	Properties of XLPE and EPR	6
Table 2.1	Overview of EPR and CPE characteristics	18
Table 2.2	Aging temperatures and time points	34
Table 2.3	Extrapolated Aging Lifetimes of EPR	38
Table 3.1	Parameters for kinetic model fit to TGA data	50

# LIST OF FIGURES

## Page

Figure 1.1	Cable insulation and jacket materials in NPPs	5
Figure 1.2	DSC scans for four EPR in an inert atmosphere	10
Figure 1.3	Carbonyl Absorbance in EPR as a function of Thermal Aging $\ . \ . \ . \ .$	11
Figure 2.1	Frequency dependence of real and imaginary permittivity	25
Figure 2.2	BSE image of EPR at $1500 \times$ magnification $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	28
Figure 2.3	Elemental dot maps acquired by EDS analysis of EPR $\ .\ .\ .\ .$	29
Figure 2.4	Frequency dependence of real and imaginary permittivity of EPR $\ldots$ .	30
Figure 2.5	Dielectric Breakdown Strength of EPR at three voltage ramp rates $\ldots$ .	32
Figure 2.6	Weibull distribution of EPR dielectric breakdown strength	33
Figure 2.7	Picture of EPR samples placed in the over	35
Figure 2.8	Normalized Imaginary Permittivity versus Aging Time	36
Figure 2.9	Superimposed normalized imaginary permittivity versus shifted aging time .	37
Figure 2.10	Arrhenius plot of shift factor versus inverse temperature	38
Figure 3.1	TGA and DTG curves of EPR at four heating rates	44
Figure 3.2	DTG and QMID curves of EPR at four heating rates	45
Figure 3.3	Fridman plot and CFML lines	48
Figure 3.4	Fridman plot and CFML lines	49
Figure 3.5	Activation energies obtained from isoconversional analysis	50
Figure 3.6	Steps of EPR thermal degradation reaction	51

Figure 3.7	Kinetic model prediction of mass loss	52
Figure 4.1	Relative permittivity of EPR at 50 Hz	63
Figure 4.2	Breakdown Strength of unaged EPR	64
Figure 4.3	Breakdown Strength of EPR aged at 160 $^{\circ}\mathrm{C}$	65
Figure 4.4	$U$ and $\gamma$ of EPR versus real permittivity $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	66
Figure 4.5	Dielectric breakdown strength as a function of real permittivity $\ldots$ .	68
Figure 4.6	Predicted Breakdown Strength versus EPR aging time	69
Figure 5.1	Thermally aged EPR/CPE cable samples	74
Figure 5.2	EPR/CPE cable segments aged 7 to 63 days	75
Figure 5.3	Optical macrograph of EPR/CPE cable segments	77
Figure 5.4	Schematic of unaged and aged cable segment layers	78
Figure 5.5	Layer thicknesses of cable segments plotted as a function of aging time	79
Figure 5.6	EDS Analysis on aged EPR/CPE cable segments	80
Figure 5.7	TGA and DTG curves of CPE and EPR	82
Figure 5.8	QMID curves of evolved gases for CPE	90
Figure 6.1	Fringing electric field of and IDC on a cable jacket	93
Figure 6.2	Thermally aged EPR/CPE cable samples with jacket removed	95
Figure 6.3	Interdigital Capacitive Electrode (IDC)	96
Figure 6.4	Dissipation Factor of CPE versus frequency	98
Figure 6.5	Dissipation Factor of CPE versus aging time at 10 kHz	99
Figure 6.6	Dissipation Factor of EPR versus frequency	100
Figure 6.7	Dissipation Factor of EPR versus aging time at 10 kHz	102
Figure 6.8	Dissipation Factor and Indenter Modulus of CPE versus frequency	103

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## ABSTRACT

There are over 600 miles of power cable installed in a typical nuclear power plant. Degradation due to thermal and radiation damage of cable insulation has been identified as one of the key factors that contribute to the loss of performance and ultimate failure of the cable. A critical aspect of cable health monitoring is to understand the nature of degradation and develop aging models to predict the service lifetime of the insulation. In this work, thermal degradation in a commercial grade of ethylene propylene rubber (EPR), a cable insulation material used extensively in nuclear power plants, is assessed under accelerated aging conditions. Characterization of thermally aged EPR is performed by assessing macroscopic changes in thermal, electrical and mechanical properties as a function of aging time and temperature. Two kinetic models are developed to estimate the remaining useful life of EPR based on measured changes in thermal and electrical properties, respectively. Finally, the degradation characteristics of EPR aged alongside a chlorinated polyethylene (CPE) jacket in a medium voltage power cable are examined and changes in electrical properties as a function of thermal aging are investigated by an interdigital capacitive electrode (IDC).

## CHAPTER 1. GENERAL INTRODUCTION

This thesis is devoted to the study of thermal degradation in ethylene propylene rubber in an oxidative environment to support the development of condition monitoring techniques for cable aging assessment in nuclear power plants.

## 1.1 Chapter Overview

This chapter introduces the big picture context for this study in Section 1.2. The organization of this dissertation with a brief mention of the topics addressed in each chapter is presented in Section 1.3. This is followed by a background overview and literature review (Section 1.4) outlining the key materials and processes that set the foundation for this work. The research hypothesis is stated in Section 1.5, followed by a brief description of the approach in Section 1.6. Finally, the major research objectives are outlined in Section 1.7.

#### **1.2** Motivation - The Big Picture

Most of the currently operating nuclear power plants (NPPs) in the United States are 40 to 60 years old and preparing for subsequent license renewal by the Nuclear Regulatory Commission (NRC), to extend their operating period by another 20 years [1]. With nuclear power being the single largest source ( $\sim$ 70%) of non-greenhouse-gas-emitting electrical energy in the United States, it is important to ensure safe, reliable and cost-efficient operation of the existing NPPs to meet the growing demand for domestic electricity [2]. This requirement for continued safe operation of NPPs under normal and accident conditions is a prime motivator for the development of scientific methods and technologies that measure, characterize, and predict long term degradation of inservice material components in NPPs.

In this context, for several decades of operation during the original licensing period, electric cables servicing NPPs have been considered reliable components requiring little to no maintenance. However, over the past 10 to 15 years, there have been increasing reports of cable failures, primarily in adverse operating environments [3]. A typical NPP contains over 600 miles worth of installed power, instrumentation and control cables, which are intrinsically important for safe and reliable operation [4] [5]. As NPPs move to extend their operating life by several more decades, cable aging management has emerged as one of the key factors considered by the NRC for granting license extensions [6].

Cable failure is primarily attributed to the degeneration of its protective electrical insulation and jacket materials leading to exposure of the conductor within [7]. Short circuits, electrical fires, and power loss are potential consequences of such cable failure. Thermosetting polymeric rubber compounds with superior chemical stability, dielectric and mechanical strength, and weather resistance are typically employed as insulation and jacket materials for these cables. However, on long-term exposure to radiation and elevated temperatures in NPPs, these materials undergo thermo-oxidative degradation and aging, which leads to loss of cable performance and failure or severe damage [8] [9]. Furthermore, long cable runs may pass through several different operating environments across the plant, and localized hot spots of harsh temperature and radiation conditions may lead to rapid degradation in parts of the cable, concluding in catastrophic failure [10].

As cables are ubiquitous in NPPs and power several safety-related systems, their reduced reliability with age is a major concern. These safety concerns accompanying license renewals have fueled the need to develop precise cable monitoring, characterization and lifetime prediction techniques that describe the aging processes that occur in cable insulation and jacket materials, and reliably estimate their remaining useful life (RUL) for sustained safe generation of nuclear power [11].

### 1.3 Dissertation Overview

This dissertation is organized into seven chapters. Chapter 1 is the general introduction, and sets the context of this work. A literature review citing prior studies and a background overview of key concepts is presented. Further, the hypothesis and research objectives for this work are outlined in this chapter. The chosen commercial formulation of ethylene propylene rubber (EPR) insulation material and characterization methods employed for this study are detailed in Chapter 2, along with preliminary information about material characteristics and a description of the accelerated isothermal aging process. Thermal aging and lifetime prediction studies on the EPR insulation material are reported in Chapters 3 and 4. Chapter 3 describes a kinetic study of thermal degradation in EPR by thermogravimetry. In Chapter 4, a lifetime prediction model for isothermally aged EPR is presented based on changes in real relative permittivity and dielectric breakdown strength. After evaluating EPR insulation independently, in Chapters 5 and 6 the discussion moves to understanding and tracking EPR degradation in the presence of a less thermally stable chlorinated polyethylene (CPE) jacket employed in a medium voltage power cable. The chemical changes accompanying EPR degradation on thermal aging in an EPR/CPE cable is explored in Chapter 5. The macroscopic changes in electrical and mechanical properties of CPE jacket and EPR insulation on thermal aging of the EPR/CPE cable is presented Chapter 6. Finally, the dissertation wraps up with the general conclusion (Chapter 7) wherein the key outcomes and future directions for this work are delivered.

## 1.4 Background and Literature Review

#### **1.4.1** Cable function and failure

The configuration of a typical cable for low- and medium-voltage applications includes a central conductor (of copper or aluminium strands) covered by a polymer- or silicon- or rubber-based electrical insulation layer, which may or may not be protected by a surrounding jacket. Commonly, electrical shielding layers are also applied between these three components [12].

Cables in NPPs are broadly categorized into three major types; instrumentation, control and power cables, based on the function that they serve. Instrumentation cables are smaller (<#14AWG conductor), carry low voltage (<50 V) and are primarily responsible for carrying analog and digital signals that provide system status information from sensors across the plant such as temperature, pressure and vibration detectors [13]. Control cables also use conductors in a similar size range as instrumentation cables, but are typically constructed as multi-conductor cables. They carry a higher voltage, of around 120 to 240 V, and transmit signals to start, stop or change the operating state of a system [14]. Lastly, power cables are configured as single conductor or three-conductor cables that are typically larger than #10 AWG. Their major function is to power electrical load centers such as motors, batteries, heaters, etc, and have operating voltages categorized as low-voltage (0.25 to 2 kV), medium-voltage (2 to 35 kV) and high-voltage (>35 kV) [15] [6].

In the simplest terms, the primary function of a cable is to carry electricity (with minimal losses) from point A (the source) to point B (the electrically powered system). Now if, for some reason, the cable is unable to deliver electricity reliably to point B, it has "failed" to perform its intended function.

As mentioned earlier, cables installed in nuclear power plants experience a large variety of environmental and operational stressors under normal and accident conditions. These stresses include ionizing radiation, temperature, humidity, electrical and mechanical stress (bending, pressing and vibrations) [16]. Of the stressors listed, temperature and radiation are the two types that are most commonly experienced by cables under normal operating conditions in NPPs [6] [17]. Cable failure on long-term exposure to these conditions is the primary concern for NPPs looking to extend life for up to 80 years.

One of the primary failure modes in NPP cables is brought about by the degradation of the external insulation and jacket layers which sheath the conductor that carries electricity. The purpose of the insulation is to minimize leakage of current so that electricity is delivered with little to no loss of energy. It also serves as a physical barrier protecting the conductor from environmental stressors. Some cables are additionally equipped with an outer jacket layer which improves cable toughness and protects both the insulation and the conductor within from external physical or chemical damage. When exposed to adverse environments, the deterioration of the insulation and jacket materials may alter their physical and chemical attributes, lowering their ability to perform their required functions effectively. On prolonged exposure, the onset of severe damage may lead to



Figure 1.1 Percentages of materials used used as insulation and jacket for cables employed in NPPs. [19]

several problems including cracking that results in exposure of the conductor, or leakage of current on partial or complete dielectric breakdown of the insulator, or electrical arcing resulting in loss of power, short circuits and even fires.

#### 1.4.2 Cable insulation and jacket materials

Figure 1.1 illustrates the most predominantly used cable insulation and jacket polymers across 106 U.S. NPPs, as reported by the Electric Power Research Institute (EPRI) in 1994 [18]. Cross-linked Polyethylene (XLPE) and Ethylene Propylene Rubber/Ethylene Propylene Diene Methylene (EPR/EPDM) polymers were determined to be the most prevalent materials in use for cable insulation at 89% and 73% abundance respectively. The usage of other materials in NPPs was found to be significantly lower than of the above-mentioned polymers. Notable jacket materials in use in NPPs include Chloro-sulfonated Polyethylene (CSPE) at ~ 25% and Polyvinyl Chloride (PVC) and Neoprene at under 10% usage each [19].

Property	XLPE	EPR
Ethylene Content (wt.%)	$\sim 100$	45 - 75
Crystallinity (%)	30 - 55	0 - 50 (usually amorphous)
Density $(g/cm^3)$	0.9 - 0.93	0.85 to $1.4$
Dielectric Constant	2.3 - 2.5	2.5 - 3.5
Dissipation Factor at 23 $^{\circ}\mathrm{C}$ and 1 kHz	${\sim}10^{-4}$	$\sim 10^{-3}$
Dielectric Strength (kV/mm) at 40 $^{\circ}\mathrm{C}$	65 - 75	35 - 55
Dielectric Strength (kV/mm) at 90 $^{\circ}\mathrm{C}$	40 - 45	35 - 55
Nominal Temperature Range (°C)	-40 to 130	-60 to 150
Glass Transition Temperature, $T_g$ (°C)	-130 to -80	-60
Melting Temperature, $T_m$ (°C)	110  to  125	30 to 60
Thermal Conductivity (w/m°C) at 90 °C	0.27	0.27 - 0.35
Elongation at Break (%)	350 - 500	250 - 600
Tensile Strength (MPa)	19 - 20	9 - 21
Modulus of Elasticity (MPa)	120	5 - 14

Table 1.1Comparison of typical properties of XLPE- and EPR-based insulation materials[19][20][23][21].

XLPE and EPR/EPDM polymers are applied as insulators for low-, medium- and high-voltage cables employed in NPPs owing to their superlative electrical insulating properties. The typical properties of XLPE and EPR insulators are enlisted in Table 1.1. The electrical properties of the two insulators are seen to be comparable, with XLPE displaying relatively superior dielectric strength and dissipation factor at lower temperatures. However, EPR shows higher heat resistance and corona resistance, making it a competitive choice for higher voltage and higher temperature applications than XLPE [20]. Additionally, while EPR shows excellent moisture resistance, XLPE is known to be more oil resistant. Most physical and electrical properties of both materials are temperature sensitive, with XLPE exhibiting higher temperature sensitivity than EPR [21] [22].

#### 1.4.3 An introduction to Ethylene Propylene Rubber (EPR)

The cable insulation material studied in this work is an ethylene propylene rubber (EPR) compound. As discussed in the previous section, formulations of EPR are extensively employed as cable insulation materials in operational NPPs, second only to cross-linked polyethylene (XLPE) compounds.

Primarily known to be a non-polar, random co-polymer of ethylene and propylene monomeric units, EPR is characterized with a saturated backbone [24] [25]. The combination of ethylene and propylene monomers to form an alternating amorphous EPR polymer chain is illustrated below:

$$\begin{array}{ccc} & & & & & & & & \\ H_2C = CH_2 & + & CH_3 - C = CH_2 \xrightarrow{\text{polymerization}} & -\left(CH_2 - CH_2 - CH_2 - CH_2\right)_n \\ & & & \\ Ethylene & & Propylene & EPR \end{array}$$

This simple alternating sequence of EPR bears a striking resemblance to that of Natural Rubber (*cis* 1,4 polyisoprene) given by,

$$-\left(CH_2 - CH = C - CH_2\right)_n$$
  
Natural Rubber

The difference between the two structures lies in the saturation of the EPR polymer backbone. As a consequence of this saturation, the sulfur curing agents commonly employed for rubber vulcanization are not successful in curing EPR. Instead, curing is achieved by free radicals created by peroxide cures with or without additional co-agents to form the EPR thermoset polymer [25]. The excellent heat and oxidation resistance exhibited by EPR may be attributed to the saturation of its monomer. Unsaturation (C=C double bonds) may be introduced in EPR by copolymerizing ethylene and propylene with a third nonconjugated diene monomeric unit to form an EPDM (ethylene propylene dielene methylene) rubber, which is a type of EPR. The unsaturation is EPDM is present in the side groups, while the backbone remains saturated. This allows for sulfur crosslinking, while still retaining the chemical inertness attributed to the saturated backbone. Most common diene monomers, used at typically at 3 to 7 wt.% to prepare EPDM rubbers include, dicyclopentadiene (DCPD), ethylene norbornene (ENB) and 1,4 hexadiene (1,4 HD) [26].

For electrical applications, peroxide-cured EPR is preferred over sulfur-cured EPDM because superior electrical properties are realized in the former [27]. In the presence of a Ziegler-Natta catalyst, long chains of EPR are formed from ethylene and propylene starting reactants. The arrangement of the ethylene and propylene units is random, resulting in a polymer which is neither alternating nor very blocky [25][27]. Crystallinity in a polymer is caused by the ordered arrangement of identical repeating units (atoms or groups of atoms). In EPR, crystallinity is imparted by the ethylene groups, specifically when adjacent polymer chains in EPR form crystallites of ordered ethylene groups. Polypropylene units, on the other hand, do not form blocks of sufficient length to form crystalline regions within the polymer [28]. The degree of crystallinity in EPR is limited, however, because the blocks of repeating ethylene units are usually too short to impart significant crystallinity. Consequently, EPR is primarily an amorphous polymer. As seen in Table 1.1, commercially manufactured EPR insulation contains 45 to 75% by weight of ethylene. Crystallinity is observed only for compositions containing >60 wt.% ethylene.

#### 1.4.4 Thermal degradation in cable insulation

The degradation of cable insulation has been identified as a prime factor that may limit the ability of an NPP to operate beyond its initial design life. Although EPR is seen to exhibit excellent chemical and thermal stability, EPR-insulated cables that experience prolonged exposure to elevated temperature conditions are susceptible to thermally activated degradation processes [29]. Therefore, studies that investigate the thermal degradation processes in EPR are critical to aging management of cables employed in NPPs. Cable insulation degradation studies are usually conducted under accelerated aging conditions (higher temperature and shorter aging times), based on which extrapolations are made to determine degradation at NPP operating conditions (lower temperature and longer aging times).

A common approach to predicting cable insulation lifetime is the Arrhenius methodology, in which the underlying assumption is that the dominant degradation mechanism occurring in the polymer is temperature independent. However, a vast majority of recent research shows that this technique often overestimates polymer lifetimes at lower temperatures because of the complex reaction mechanisms involved in the degradation process. The major factors that determine the nature of polymer degradation include transition temperatures, diffusion limited oxidation effects, solubility and volatility of inclusions, among others. Of the popular cable insulation polymers, XLPE is observed to exhibit non-Arrhenius behavior owing to the different degradation mechanisms occurring above and below its melting temperature [30] [31] [32]. The melting point of XLPE lies in the 110 to 125 °C temperature range, owing to its high crystallinity, which ranges between 50 and 100% by weight. The degree of crystallinity in the polymer changes as the temperature approaches the melting point as the crystallites slowly disappear. In the case of XLPE, the temperature and the morphology of the polymer are interrelated, which must be accounted for in accelerated thermal studies. When it comes to EPR, the story is a little different. As discussed in the previous section. EPR materials typically vary from rubbery to semi-crystalline based on their ethylene content (more ethylene implies greater crystallinity). The rubbery nature of EPR varies greatly for different commercially manufactured compounds. One way to identify the crystallinity and melting point in EPR is by Differential Scanning Calorimetry (DSC) [33]. Melting is an endothermic process, and an increase in heat flow to the sample is observed in a DSC scan when the crystalline regions melt. This is clearly seen in Figure 1.2, which shows the DSC scans for four different commercially produced compounds of EPR [34]. While the two formulations manufactured by the Anaconda company show little to no crystallinity, Okonite and Eaton manufacture EPR compounds which show some crystallinity (indicating higher ethylene content). Based on these studies, it is seen that the activation energy for degradation in the Anaconda materials may likely be constant at low and high temperatures, suggesting possible Arrhenius behavior of these formulations of EPR. However, for the Eaton and Okonite materials, there is a possibility that the activation energy for degradation is different above and below the melting temperatures owing to the change in the degree of crystallinity of the polymer.

The fundamental reason why the degree of crystallinity plays a crucial role in the degradation mechanisms observed in polymers is the mobility of free radicals. In the amorphous regions of the polymer, the free radicals are fairly mobile and are able to participate in various thermooxidative reactions. In the crystalline region, however, the free radicals are fixed and immobile at low temperatures. When the crystalline regions melt, trapped free radicals are released and are available to participate in the degradation reactions.

Thermo-oxidative degradation in polymers involves changes at the molecular level. For EPR, such degradation mainly involves two competing processes –



Figure 1.2 Differential Scanning Calorimetry (DSC) scans for four different commercial formulations of EPR [34]

- chain scission leading to formation of chain fragments with lower molecular weight, opposed by
- inter-chain crosslinking, which forms branched systems with increased molecular mass [24]
  [35].

This complex thermal aging behavior of EPR contributes to its susceptibility to thermo-oxidative damage even in the absence of gamma radiation. After the curing process during EPR manufacture, the peroxide curing agents remain in the polymer compound. At elevated temperatures, the activation energy of the curing process may be realized, which in turn may lead to further cross linking of the polymer chains. Conversely, the polymer chains may acquire sufficient energy to undergo cleavage (chain scission) to create smaller fragments. Whether the polymer undergoes cross-linking or chain scisson on exposure to elevated temperatures depends on which of the two competing



Figure 1.3 Increasing carbonyl absorbance at 1730 cm<sup>-1</sup> in EPR as a function of thermal aging at 115, 130 and 145 °C [36]

mechanisms is dominant. When chain scission is dominant, EPR degrades. The occurrence of both processes is dependent on temperature and oxygen availability.

A convenient method to detect oxidation of EPR as a function of thermal degradation is to track the carbonyl group formation exhibited by the 1730 cm<sup>-1</sup> Fourier transform Infrared (FTIR) spectroscopy absorption band [36]. In Figure 1.3, the change in carbonyl absorbance intensity for EPR aged under accelerated aging at isothermal temperatures of 115, 130 and 145 °C is presented. At all three temperatures, carbonyl intensity remains constant for a certain induction period after which a rapid increase is observed. This behavior may be attributed to the presence of stabilizing agents within the EPR formulation. Once the effectiveness of the stabilizer is lost, rapid oxidation of the compound takes place, which is reflected in the increase in carbonyl index. Similar results were obtained for different commercial formulations of EPR [4].

Stabilizers and antioxidants are added to EPR in 1 to 2 phr (parts per hundred rubber) quantities to minimize oxidative degradation at elevated temperatures. Several mechanisms have been proposed for the role of the antioxidant during the thermal degradation process. Primarily, the mechanism may be by the depression of free radical formation when the polymer chain is thermally activated, or by the termination of existing free radicals.

## 1.5 Hypothesis

In response to long-term exposure to elevated temperatures, EPR-based insulators undergo thermal degradation as a result of microscopic changes in morphology and chemistry. It is hypothesized that

- (i) similar long-term aging effects can be realized under accelerated aging conditions, and
- (ii) the changes in the underlying chemistry and structure of the insulation will, in turn, cause a change in its macroscopic electrical, thermal and mechanical properties, and
- (iii) by measuring these changes as a function of aging time, analytical aging models may be developed that can effectively predict the remaining useful life of thermally aged productiongrade EPR.

## 1.6 Approach

Accelerated aging of EPR is carried out at chosen isothermal temperatures to access the thermal degradation mechanisms over a span of elevated temperatures for varying aging times. Measurable thermal, electrical and mechanical property changes that serve as key indicators for thermal degradation are obtained by various characterization techniques. Some of these measurements serve as input parameters to kinetic rate-of-degradation-based predictive aging models for EPR lifetime. Further, degradation in an EPR-insulated commercial power cable fortified with an external CPE jacket is evaluated by examining changes in composition and microstructure, as well as macroscopic electrical and mechanical properties.

## 1.7 Research Objectives

In this section, the four main objectives for this research are laid out, and the chapter(s) that describe the work done to realize each objective is (are) also specified.

The following objectives are proposed in support of the aforementioned hypothesis:

- 1. Accelerated isothermal aging of production-grade EPR from high-temperature/short aging time spans to low-temperature/long aging time spans to generate thermal degradation data over a range of temperatures (Chapter 2).
- 2. Characterization of thermally-aged, production-grade EPR by measuring macroscopic changes in thermal, electrical and mechanical properties as a function of thermal aging time and temperature (Chapters 3, 4, 5 and 6).
- 3. Development of kinetic predictive aging models that estimate the remaining useful life (RUL) of production-grade EPR based on measured changes in its thermal and electrical properties (Chapters 3 and 4).
- 4. Thermal aging studies on a commercial, jacketed EPR/CPE cable to understand microscopic and macroscopic changes in the EPR insulation when aged in the presence of an external CPE jacket (Chapters 5 and 6).

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## CHAPTER 2. MATERIALS AND CHARACTERIZATION METHODS

#### 2.1 Chapter Overview

The primary focus of this study is to evaluate thermal aging in a production-grade EPR-based cable insulation to support condition monitoring and predict the remaining useful life of power cables employed in NPPs. For this purpose, accelerated isothermal aging studies were performed on a chosen formulation of production-grade EPR. Further, to evaluate thermal aging characteristics of EPR in a jacketed cable configuration, thermal degradation studies were conducted on a commercial medium-voltage power cable. In this chapter, the commercially manufactured EPR-based insulation chosen for this study is introduced in Section 2.2.1 and the jacketed cable evaluated is described in Section 2.2.2. The characterization methods employed in this study are detailed in Section 2.3, and the results of preliminary characterization studies on the unaged EPR compound are reported in Section 2.4. This is followed by an explanation of the accelerated isothermal aging process in Section 2.5. Finally, a summary of key information from the chapter and concluding remarks are given in Section 2.6.

#### 2.2 Materials

## 2.2.1 Ethylene Propylene Rubber (EPR) insulation

The chosen material for study is production-grade pink EPR insulation with the trade-name Okoguard<sup>®</sup> directly obtained in the form of press-cured plaques  $(220 \times 220 \times 1.6 \text{ mm}^3)$  from the manufacturer, the Okonite Company. The Okoguard<sup>®</sup> insulation is an EPR-based thermosetting compound having a distinctive pink color. With excellent dielectric and mechanical strength, this insulation finds application in both jacketed and non-jacketed medium voltage cables installed in NPPs. Cables insulated by Okoguard<sup>®</sup> are typically employed for service in the 5 to 69 kV

Characteristic	EPR	CPE
Elongation at Break (%)	$289\pm7$	$343 \pm 9$
Inorganic Filler Content (wt.%)	$49\pm2$	$37 \pm 1$
Glass Transition Temperature, $T_g$ (°C)	-55	
Melting Temperature, $T_{m}$ (°C) (wt.%)	$390\pm2$	$275\pm3$
Real Relative Permittivity at 1 kHz	2.85	6.25
Dielectric Strength at 0.5 kV/s ramp rate (kV/mm) $$	22.7	

Table 2.1 Overview of key characteristics of Okoguard<sup>®</sup> EPR and Okolon<sup>®</sup> CPE

operating voltage range. From here on in this document, 'EPR' will be used to refer specifically to the Okoguard<sup>®</sup> EPR formulation described above.

#### 2.2.2 Jacketed EPR/CPE power cable

A single core, non-shielded 2.4 kV power cable supplied by The Okonite Company with the trade name Okoguard<sup>®</sup>-Okolon<sup>®</sup> TS-CPE Type MV-90 and an outer diameter of 22.4 mm was chosen for this study. In this cable configuration, the conductor diameter is approximately 9.2 mm, and is formed by annealed, compact stranded copper. The approximate thickness of the non-bonded CPE-based jacket (Okolon<sup>®</sup> TS-CPE) is 2 mm and that of the EPR-based insulation (Okoguard<sup>®</sup>) layer is 3.5 mm. The cable also comprises a layer of a black semiconducting EPR screen (reinforced with carbon black) lining the interface between the EPR insulation and the copper conductor, which has an approximate thickness 0.5 mm. The semiconducting screen is included to minimize sites for partial discharge at the insulation-conductor interface. From here on in this document, 'CPE' will be used to refer specifically to the Okolon<sup>®</sup> TS-CPE formulation described above.

Table 2.1 provides an overview of the characteristics of the EPR and CPE formulations described above as measured in this study. The experimental methods implemented to characterize the materials are described in Section 2.3.

## 2.3 Characterization Methods

A variety of characterization tests were conducted in this work to support one or more of the following objectives:

- 1. To assess the composition and features of the materials investigated.
- 2. To understand the relationship between macroscopic property changes and microscopic degradation mechanisms occurring within the material on thermal aging.
- 3. To obtain input parameters required for the development of analytical models that predict thermal aging lifetime.

An overview of the characterization methods employed for materials testing are described below. For each method, the operating principle and research purpose are explained. The specifications for the instruments used and the sample preparation for testing are described in detail in the following chapters for each study, as relevant.

#### 2.3.1 Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)

Working Principle: When a focused beam of accelerated electrons strikes the surface of a sample, the electrons interact with the near-surface area of the sample in a variety of ways. As in the case of visible light, the incident electrons (also known as primary electrons) may be reflected, transmitted or absorbed by the sample. Furthermore, the electrons may interact with the atoms present in the sample of which the most prevalent interactions may be categorized as elastic or inelastic scattering. In elastic scattering, there is minimal loss of energy and no change in wavelength of the primary electron. Where as, inelastic scattering causes loss of energy of the incident electron. Based on the type of interaction, different signals are emitted from the sample, including (but not limited to) backscattered electrons, secondary electrons, characteristic x-rays, and auger electrons. Based on the type of signal analyzed, different information about the sample may be obtained.

#### • Surface imaging using a Scanning Electron Microscope (SEM):

In an SEM, secondary electrons and backscattered electrons are routinely exploited to create an image of the sample. Secondary electrons (SEs) are emitted as a result of inelastic scattering, wherein the incident electrons knock out the loosely bound outer (valence) electrons of the sample atoms. On the other hand, backscattered electrons (BSEs) are a consequence of elastic scattering of the primary electrons, which occurs when there is a head-on collision between the electron and the nucleus of the sample atoms. In both cases, if the emitted electrons have energy higher than the surface energy of the sample, they escape from the sample and are captured by a detector. While secondary electrons are used to image sample morphology and topography, backscattered electrons illustrate contrasts in composition in multiphase samples.

#### • Elemental analysis by Energy Dispersive Spectroscopy (EDS):

EDS analysis is a standard technique employed to identify and quantify the elemental composition a small volume of the sample. When primary electrons from the incident beam bombard and eject electrons from the inner shells of the sample atoms, vacancies are created in the inner shells. The presence of these vacancies is energetically unfavorable and electrons from higher energy levels quickly transition to fill the vacancy by emitting their excess energy in the form of X-ray photons. The emitted X-rays have sharply defined energies associated with the difference between the atomic energy levels of the sample atoms, making them a unique characteristic of each element. Consequently, a "fingerprint" spectrum of the constituent elements in a sample can be obtained by comparison with reference spectra. Both qualitative and quantitative EDS analysis of elemental composition may be performed. An SEM fitted with an energy dispersive detector may be utilized to identify the elemental composition of the sample by analyzing the characteristic X-rays emitted from the sample.

**Research Purpose:** SEM/EDS analysis was performed to characterize the elemental composition of the EPR compound and identify the inorganic fillers present in the formulation. Further, cable segments were evaluated to assess qualitative changes in composition and microstructure of the EPR insulation on thermal aging alongside the CPE jacket.

## 2.3.2 Thermogravimetric Analysis (TGA)

Working Principle: Thermogravimetry (TG) involves continuously monitoring the change in the mass of a sample as a function of temperature and time in a controlled atmosphere. The temperature program may be isothermal (constant temperature), non-isothermal (constant heating rate) or a combination of both. The mechanism and the kinetics of the thermal degradation process in a given atmosphere primarily determine the shape of the TG mass change curve as a function of temperature (or time).

Typically, a TGA consists of a sample pan or crucible supported by a precision balance to measure changes in sample mass. The apparatus resides inside a furnace where the sample is either heated or cooled for the test. The mass of the sample is continuously monitored throughout the experiment as a function of temperature and time. The sample environment is controlled by the constant flow of a sample purge gas. Depending on the desired sample characterization, the purge gas is chosen to be an inert or a reactive gas.

Thermogravimetric analysis provides insight into the thermal degradation characteristics of a sample. The technique is typically used to quantify thermal and oxidative stability. Moreover, by analyzing the data obtained from a TG experiment inferences can be made about the composition of a sample.

## • TGA coupled with evolved gas Mass Spectrometry (TGA/MS):

Advanced studies of materials decomposition mechanisms and kinetics can be performed by characterizing the gases evolved as degradation products during a TGA experiment. TG analyzers can be configured to operate with a compatible Mass Spectrometer (MS) for qualitative and/or quantitative analysis of evolved gases, where the gases exiting the sample are directly transferred from the TGA furnace to the MS analyzer. In the mass spectrometer, the evolved gases are ionized by bombardment with electrons and then accelerated towards a detector by an applied electromagnetic field. A mass spectrometer may operate either in a positive ion mode or a negative ion mode, based on which the gases are ionized to form positive or negative ions respectively. The ions formed are sorted according to mass and charge by two processes, acceleration and deflection. When accelerated by an applied electric field, the charged ions will travel at different velocities towards the detector depending on their mass (lower the mass, higher the velocity). Further, the magnetic field deflects the ions to varying degrees, once again, depending on the mass of the ions (lower the mass, greater the deflection) and the charge on the ion (higher the charge, greater the deflection). An output spectrum of relative ion intensity as a function of mass to charge ratio (m/z) is obtained for the evolved gases from the sample. The atoms or molecules in the evolved gases can be identified by comparison with known reference spectra. Interpretation of mass spectra of evolved gases is subjective to knowledge of the sample being analyzed and the nature of the TGA test being performed.

**Research Purpose:** TGA/MS analysis was conducted to evaluate the thermo-oxidative degradation mechanism of EPR, gain insight into its composition and quantify the inorganic filler content. Thermal degradation kinetics of EPR were also studied to develop a predictive model to determine EPR lifetime under isothermal conditions. The influence of the CPE jacket on thermal aging characteristics of EPR insulation was also investigated by this method.

#### 2.3.3 Differential Scanning Calorimetry (DSC)

Working Principle: The heat capacity for a given mass of any substance is defined as the amount of heat required to be provided to produce a unit change in its temperature. For the purpose of materials characterization, physical and chemical changes occurring in a material as a function of temperature may be captured by measuring changes in its heat capacity. Differential scanning calorimetry is a thermoanalytical technique that measures changes in the heat capacity of a material as a function of temperature in a controlled environment. In this method, a known mass

of a sample is heated or cooled according to a defined temperature program, and the changes in heat flow are tracked to obtain a measure of changes in the heat capacity of the sample. Typically, changes in heat flow to the sample are measured relative to the heat flow to a reference sample being tested simultaneously under identical conditions. The fundamental principle underlying this measurement technique is that, when a sample undergoes a physical or chemical change, more or less heat will need to flow to the sample than the reference in order to maintain both at the same temperature. If the change that the sample undergoes is the result of an exothermic process, less heat must flow to the sample, while for an endothermic process, more heat must flow to the sample. The resulting output of the experiment is a measure of the heat flux as a function of temperature (or time).

For the purpose of polymer characterization, DSC analysis is a standard technique employed to measure sample characteristics such as the glass transition and melting temperatures, percent crystallinity, thermal and oxidative stability, percent cure and purity. Similar to TGA analysis, the data obtained from a DSC experiment may be interpreted to gain insight into the compositional make up of the sample.

**Research Purpose:** Thermal properties of EPR, including glass transition temperature  $(T_g)$  and melting temperature  $(T_m)$  were acquired by DSC analysis.

#### 2.3.4 Dielectric Spectroscopy (DS)

Working Principle: Dielectrics do not easily allow the free flow of charge carriers through them. Instead, they are able to store electrical energy in the form of an electric field. The complex permittivity of a dielectric is a measure of the electrical storage (real permittivity,  $\epsilon'$ ) and loss modulus (imaginary permittivity,  $\epsilon''$ ) of the material. A measure of the complex permittivity of a dielectric quantifies the intrinsic electrical properties of the material that govern its response to an applied electric field. Consider a dielectric placed between the electrodes of a parallel plate capacitor. When a vector electric field,  $\vec{E}$  is applied across the dielectric, the material becomes polarized. Polarization mechanisms may be i) electronic (distortion of electron cloud of an atom), ii) ionic (slight displacement of charges from average equilibrium positions within an ionic crystal), iii) dipolar (orientation of permanent or induced dipoles in the applied field direction) and iv) space charge (accumulation of charge at the interface of two regions within the material). Regardless of mechanism, the result of polarization is the partial or complete alignment of the polarized species in a direction opposite to that of the applied field. This decreases the effective electric field between the electrodes of the capacitor resulting in storage of greater amount of charge between the parallel plates. The higher the polarizability of a dielectric, the greater is its ability to sustain an electric field. Energy losses may occur if the material allows for even small amounts of free flow of charge carriers. The complex permittivity of a dielectric provides information on its ability to store electrical energy ( $\epsilon'$ ), as well as its tendency to dissipate energy ( $\epsilon''$ ) on interaction with an external electric field.

Relative complex permittivity of a material  $(\epsilon_r)$  is given by,

$$\epsilon_r = \frac{\epsilon}{\epsilon_o} = \epsilon_r' - j\epsilon_r''.$$

Where,  $\epsilon_o$  is the electric permittivity of free space,  $8.854 \times 10^{-12}$  F/m,  $\epsilon$  is the absolute complex permittivity of the dielectric, and  $\epsilon_r'$  and  $\epsilon_r''$  are the relative real and imaginary permittivities of the dielectric medium respectively.

#### 2.3.4.1 Frequency dependence of complex permittivity:

The dependence of the relative complex permittivity on the frequency of the applied electric field may be attributed to the polarization mechanisms that occur within the dielectric. The contributions of the different polarization mechanisms to the frequency response of a dielectric depend on the size and mobility of the polarized species. When a dielectric is placed in an alternating electric field, the dipoles attempt to maintain alignment with the applied field as the polarity of the electrodes are reversed back and forth. This process requires a finite amount of time determined by the polarization mechanism. The frequency at which the dielectric loss factor is at a maximum for a given polarization mechanism is the relaxation frequency. At frequencies above the relaxation frequency, the dipoles will no longer be able to keep up with the changing electric field and no



Figure 2.1 Schematic representation of frequency dependence of real and imaginary permittivity for a hypothetical material having interfacial, dipolar, ionic and electronic polarization mechanisms [1].

longer contribute to the polarization of the dielectric. Figure 2.1 illustrates the frequency dependence of real and imaginary permittivities for a hypothetical dielectric in which all four polarization mechanisms (interfacial, dipolar, ionic and electronic) are present.

Broadband dielectric spectroscopy (BDS) provides insight into the insulating properties of a dielectric and the underlying mechanisms that govern the electrical response of the material. It is a highly effective technique to investigate dielectric properties of insulation materials. Typically, a flat sample is placed between the electrodes of a parallel plate capacitor and a frequency sweep of applied electric field is carried out to obtain the frequency-dependent dielectric response.

**Research Purpose:** DS measurements were conducted on EPR and CPE to evaluate electrical properties of the insulation and jacket. Further, dielectric response of EPR was investigated as a function of thermal aging to characterize insulation performance. Changes in relative real permittivity of EPR were evaluated and employed as inputs to a model to predict the remaining useful life of EPR as an effective cable insulator. Dielectric spectroscopy studies were also performed on
jacketed cables using interdigital capacitive electrodes (IDCs) to investigate changes in complex permittivity of EPR and CPE when thermally aged in the intact cable geometry.

## 2.3.5 Dielectric Breakdown (DB)

Working Principle: As mentioned in section 2.3.4, free flow of charge carriers is not easily allowed by a dielectric material. However, when a high enough voltage is applied across an electrically insulating material, a conducting pathway is burnt through it. This process is known as electrical breakdown or failure of the dielectric. Typically in an insulator, the band gap between the valence and conduction bands in so large that the electrons do not have sufficient energy to cross over. However, when a sufficiently large electric field is applied across the dielectric, the valence electrons gain enough energy to cross the band gap and move into the conduction band, resulting in the flow of current. The voltage of the applied field at which breakdown occurs is known as the breakdown voltage  $(V_b)$  of the dielectric. Electrical breakdown strength  $(E_{db})$  of a material is defined as the highest electric field intensity it can withstand prior to undergoing electrical breakdown, and is given by,

$$E_{db} = V_b/d \tag{2.1}$$

where, d is the sample thickness.

Good insulators are characterized by high dielectric strength. For cable insulation materials, high dielectric strength is a highly desirable characteristic. Macroscopic electrical breakdown is the result of complex physical and chemical changes occurring within the material microstructure. Consequently, changes in chemical composition and microstructure strongly influence the dielectric breakdown characteristics of an insulator. Further, the breakdown strength for identical samples of a material is not a definite value, but is rather scattered over a range of values owing to imperfections and heterogeneity in the material. Therefore, dielectric breakdown strength of a material is better represented as a distribution over a range of values.

Breakdown studies are standardized tests conducted to evaluate the electrical strength of dielectrics. Typically a sample is placed between a high voltage and a low voltage electrode and the applied electric field is increased at a constant ramp rate until current flow is detected. The voltage at which current flow occurs is recorded as the measured breakdown voltage of the sample, from which the dielectric strength is calculated using equation 2.1.

**Research Purpose:** The dielectric strength of EPR insulation was measured for a variety of applied voltage ramp rates to assess its performance as an insulator for medium voltage cable applications. Changes in dielectric strength were tracked as a function of aging to develop a kinetic model that predicts electrical breakdown in EPR as a function of thermal aging at various temperatures.

#### 2.3.6 Elongation at Break (EaB) tensile test

Working Principle: Elongation at break is a measure of material ductility, or its ability to be extended. If a given test specimen (having initial length, L) subject to a uniaxial tensile load applied at a constant stress rate  $\dot{\sigma}$ , undergoes breakage after elongation by  $\Delta L$ , the elongation at break EaB is given as,

$$EaB = \left(\frac{\Delta L}{L}\right) \times 100$$

The measurement quantifies the ability of a material to undergo significant deformation prior to mechanical failure. Materials with higher elongation at break are said to exhibit higher ductility. Materials with low ductility are typically brittle and undergo fracture prior to significant deformation. The macroscopic deformation and mechanical failure of a material is strongly dependent on its chemical make up and physical properties.

EaB testing is a destructive technique which requires permanent deformation and fracture of the test specimen. It is a widely accepted standard measure in the industry for quantitative assessment of the mechanical properties of rubber compounds.

**Research Purpose:** Changes in mechanical properties and thermal lifetime of EPR aged at various isothermal temperatures was evaluated by EaB studies. Further, EaB measurements were compared and contrasted with electrical property changes to evaluate the effectiveness of mechanical and electrical condition monitoring techniques to track EPR aging.



Figure 2.2 Backscattered Electron (BSE) image of EPR at 1500× magnification as imaged via SEM. The white rectangular inset marks the region of the sample selected for EDS analysis.

#### 2.4 Preliminary Characterization Studies on EPR

The key results of preliminary studies conducted to evaluate EPR composition and dielectric properties are presented below. It must be noted that the EPR insulation studied in this work is a production-grade compound with a proprietary formulation. The objective of characterization studies presented in this section is to gain a working knowledge of the main constituents of the system and its dielectric properties as an insulator.

#### 2.4.1 Evaluation of composition and morphology by SEM/EDS analysis

SEM imaging of EPR was carried out to assess the morphology and identify the nature and size of the inorganic fillers included in the compound. Figure 2.2 is a back scattered electron image of the ion-milled surface of EPR. The surface of the sample was coated with iridium to minimize charging due to the incident electron beam. The SEM image shows that an enormous quantity of reinforcing fillers are present in EPR. The particle size of the fillers varies over a wide range roughly between 80 nm to about 20  $\mu$ m. As with size, the geometry of the added fillers is also seen to have



Figure 2.3 Elemental dot maps acquired for Carbon (C), Oxygen (O), Titanium (Ti), Aluminum (Al), Silicon (Si), Zinc (Zn) and Lead (Pb) species by EDS analysis of EPR at 3000× magnification.

vast irregularities. The white box within Figure 2.2 highlights the region of the sample where EDS analysis was performed. Gray-scale elemental dot maps of the species identified by EDS (excluding iridium) in this region are shown in Figure 2.3. In each individual dot map, the white and black spots respectively indicate regions in which a particular element is present or absent.

EPR being a polymer, carbon is unsurprisingly the most prevalent elemental species identified by EDS analysis. The fillers are seen to be evenly distributed within the EPR polymer matrix. Aluminum (Al), silicon (Si), titanium (Ti), zinc (Zn) and lead (Pb) species are identified to be the key constituents of the inclusions added to the matrix. The overlap of the regions in which oxygen



Figure 2.4 Real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of complex permittivity of EPR as a function of frequency of applied AC field.

and the metallic species are detected indicate that the fillers are metal oxides. The overlap of the regions in which Al and Si are detected along with oxygen suggest that they are both present in the same filler mineral containing oxides of aluminum and silicon. This mineral filler may be a form of kaolin clay, which finds widespread use as a reinforcing filler for rubber, to impart high mechanical strength and insulating ability as well as to improve weathering resistance. Another possibility is that the oxide identified is that of Al, whose surface has been treated with a silane coupling agent to improve its compatibility with the polymer [2]. The Al- and Si- based filler is the most abundant inorganic inclusion in the EPR compound. Oxides of Zn, Ti and Pb are present in lower quantities, and are known to be widely used to enhance the mechanical and electrical shielding properties of rubber.

#### 2.4.2 Investigation of electrical properties

## 2.4.2.1 Broadband Dielectric Spectroscopy (DS)

Figure 2.4 shows real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of complex permittivity of EPR measured as a function of the frequency of the applied electric field, ranging from  $10^{-2}$  to  $10^5$  Hz. Real relative permittivity decreases from approximately 2.92 at  $10^{-2}$  Hz to 2.83 at  $10^5$  Hz. This gradual decrease in  $\epsilon'$  corresponds to the beginning of a broad relaxation over the wide frequency range (seven decades) measured. In the frequency range studied, the most prevalent polarization mechanisms are interfacial (space charge) and orientational (dipolar). At low frequencies,  $(10^{-2}-10^{0} \text{ Hz})$ , there is enough time for charge build-up at heterogeneous interfaces within the compound leading to the space charge polarization mechanism.

Imaginary permittivity shows a rapid decrease from about 0.03 at  $10^{-2}$  to 0.009 at  $10^{0}$  Hz corresponding to the latter portion of a loss peak suggesting the loss of a contributing polarization mechanism below this frequency range. This polarization mechanism is most likely interfacial in nature. Between  $10^{0}$  and  $10^{3}$  Hz,  $\epsilon''$  is fairly constant at 0.007, after which it begins to increase slowly to reach 0.01 at  $10^{5}$  Hz indicating the occurrence of a subsequent loss peak at higher frequencies. In this range, orientational mechanisms are most likely to be prevalent. EPR is essentially a non-polar polymer with limited contributions to dipolar mechanisms, which can explain the low value of real permittivity in this region. Furthermore, over the entire range of frequencies measured, EPR exhibits low loss modulus ( $\epsilon''$ ), a characteristic of a good insulator.

## 2.4.2.2 Evaluation of Dielectric Breakdown (DB)

The dielectric strength quantifies the maximum applied field intensity the insulation can withstand prior to electrical breakdown. The dielectric breakdown strength of EPR was calculated from measured breakdown voltage ( $V_b$ ) at three constant applied voltage ramp rates (0.5, 2 and 5 kV/s). The results of 20 measurements per applied voltage ramp rate are displayed as a box and whiskers plot in Figure 2.5. There is an overall increase in dielectric strength with increasing ramp rate. The values of average measured breakdown strength for EPR at 0.5, 2 and 5kV/s ramp rates are 22.7, 24.9 and 26.5 kV/mm respectively. Given the random distribution of electrically weak points, the dielectric breakdown strength of an insulation material is best represented as a distribution rather than as an absolute value [3]. The cumulative distribution function (CDF) for a two-parameter Weibull Distribution is given by

$$F(E;\alpha,\beta) = 1 - \exp\left[-\left(\frac{E}{\alpha}\right)^{\beta}\right]$$
(2.2)



Figure 2.5 Box-and-whisker plot of dielectric breakdown strength  $(E_{db})$  of EPR measured at three constant applied voltage ramp rates (0.5, 2 and 5 kV/s).

where, F is the probability of failure at an electric field up to E, the measured breakdown strength.  $\alpha$  and  $\beta$  are the scale and shape parameters respectively. Here, two-parameter statistical Weibull distribution is applied to analyze the dielectric breakdown strength of EPR at three applied voltage ramp rates. The failure probability (occurrence CDF) is plotted as a function of logarithmic dielectric strength in Figure 2.6. The symbols represent the measured dielectric breakdown strengths and the solid lines represent a least squares linear fit to the measured data. With higher applied voltage ramp rate, the linear fits to the measured data shift towards higher measured dielectric strength and decrease in slope, which indicates greater dispersion in dielectric strength values. Dielectric strength measured at 0.5 kV/s shows the least spread while that measured at 5 kV/s shows the maximum spread.



Figure 2.6 Two-parameter Weibull distribution failure probability (occurence CDF) plotted as a function of the natural logarithm of dielectric breakdown strength  $(E_{db})$ .  $E_{db}$  data was acquired at three constant applied voltage ramp rates (0.5, 2 and 5 kV/s).

# 2.5 Accelerated Isothermal Aging

## 2.5.1 Aging temperature and methodology

Accelerated thermal aging is commonly performed on insulation polymers to induce thermal degradation that is representative of long-term aging of the material at NPP service temperatures. It is critical that the choice of accelerated aging conditions is such that the activated degradation mechanisms in the material are representative of what is observed under operating conditions.

To arrive at the best choice of temperature range for accelerated aging, the following considerations were taken into account. The onset of thermal degradation in EPR as measured by thermogravimetric analysis (Section 5.4.3) was determined to be around  $249 \pm 5$  °C. As mechanisms of thermal degradation properties are expected to change dramatically in this temperature range, it is sensible to choose accelerated aging temperatures that are lower than the onset temperature for thermo-oxidative degradation. Another factor to consider is the temperature rating that

Temperature °C	Full Aging Time (days)	Aging time points (days)
140	70	0, 7, 14, 21, 28, 35, 42, 49, 56, 63, and 70
150	35	0, 7, 14, 21, 28, and 35
155	21	0, 8, 11, 15, 19, and 21
160	14	0, 2, 5, 7, 9, 11, 12, 13, and 14
165	10	0, 3, 5, 6, 8, and 10

Table 2.2 Accelerated aging temperature and aging time points for EPR flat mats

Okoguard<sup>®</sup> insulated cables are qualified to operate at. According to standard qualification tests, Okoguard<sup>®</sup> EPR cables are rated for continuous operation at 90 °C and for emergency operation at 130 °C [4][5]. In a typical nuclear power plant ambient temperature conditions range from 30 to 40 °C, and hot spot areas may even reach elevated temperatures of 100 °C. Consequently, depending on the location of the installed cable, the operating temperature that it is exposed to may be quite different. Based on these considerations and on supporting evidence from prior aging studies that relate measurable property changes in Okoguard<sup>®</sup> EPR to the aging condition induced by thermal stress, accelerated isothermal aging temperatures between 120 and 170 °C were identified as being suitable for this study.

EPR samples were thermally aged in a ThermoFisher Scientific Heratherm<sup>TM</sup> Advanced Protocol OGH-180 mechanical air circulating oven in order to maximize air circulation and ensure a fresh supply of oxygen during the thermal aging process. Oven temperature was monitored using two thermocouples placed close to the samples during aging. The flat extruded mats were cut into squares or dogbones of desired size prior to aging, and suspended from a rack as shown in Figure 2.7. EPR flat mats were isothermally aged at 140, 150, 155, 160 and 165 °C to generate sample sets representative of lifetime aging at each temperature. For each aging temperature, the samples were placed inside the oven all at once, and removed removed sequentially to develop a set of samples with increasing aging time points up to EPR lifetime. The chosen aging temperatures along with the aging time points and the full aging time are presented in Table 2.2. Jacketed EPR/CPE cables were aged at 140 °C for up to 63 days in a similar manner, the specifics of which are discussed in section 5.3.



Figure 2.7 Image of EPR squares and dogbones hanging from a rack inside an air-circulating oven prior to thermal aging.

# 2.5.2 Time-Temperature (t-T) superposition studies

Time-temperature superposition analyses were carried out to verify that the degradation reactions in this temperature range are only accelerated and otherwise mechanistically unchanged under accelerated aging conditions. The governing principle of time-temperature (t-T) superposition analyses is that if raising the accelerated aging temperature increases the speed of the degradation process without changing the underlying reactions, the degradation curves at two different aging temperatures will be related by a constant multiplicative factor known as the shift factor ( $a_T$ ). This means that the shape of the curve for different aging temperatures should be similar when plotted as a function of aging time.

Time-temperature superposition analysis was conducted on the change in the imaginary permittivity ( $\epsilon''$ ) of EPR as a function of aging time. Loss modulus of EPR was found to be an excellent tracker for EPR aging and lifetime because of which, imaginary permittivity was the chosen measure of EPR degradation for t-T superposition studies [6]. Further,  $\epsilon''$  is a measure of the lossy



Figure 2.8 Plot of normalized imaginary permittivity measured at 1 kHz frequency as a function of aging time for EPR aged at 150, 155, 160, and 165 °C.

nature of the dielectric, which is a direct indicator of insulation performance, i.e., the higher the dielectric loss, the poorer the insulation.

Figure 2.8 is a plot of the normalized imaginary permittivity  $(\epsilon_n'')$  measured at 1 kHz frequency as a function of aging time for EPR isothermally aged at 150, 155, 160 and 165 °C. Normalized values for  $\epsilon''$  were calculated by the following relationship,

$$\epsilon_n'' = \frac{\epsilon'' - \epsilon_{min}''}{\epsilon_{max}'' - \epsilon_{min}''}$$

where,  $\epsilon''$  is the measured value of imaginary permittivity, and  $\epsilon''_{min}$  and  $\epsilon''_{max}$  are the minimum and maximum values of imaginary permittivity measured for samples aged at a given temperature.

With 150 °C as the chosen reference temperature, the multiplicative shift factor  $a_T$  needed, for each higher-temperature data set, to shift the measurement data for the best superposition of results was calculated. The best superposition was identified as the one in which standard deviation of the transposed data points from the reference data set was minimum. The multiplicative shift factor that achieves the best superposition of results was calculated to be 1.64, 2.55 and 3.50 for results measured at 155, 160 and 165 °C respectively. The multiplicative factor for 150 °C is 1,



Figure 2.9 Superimposed normalized imaginary permittivity presented as a function of shifted aging time for samples aged at 150, 155, 160 and 165 °C.

by definition. The superimposed result is presented as a function of shifted aging time in Figure 2.9. The excellent superposition of the data strongly supports the hypothesis that the chemical reaction mechanism governing thermo-oxidative degradation in EPR is dominant over this range of accelerated aging temperatures. Figure 2.10 is an Arrhenius plot of the multiplicative factors  $a_T$  plotted as a function of inverse Kelvin temperature. The results demonstrate a linear Arrhenius behavior to which a straight line was fitted using least squares methods.

Using this plot, extrapolations can be made to lower temperatures to evaluate EPR lifetime. For instance, by extrapolating the result to 140 °C, the shift factor obtained is ~ 0.43, which implies that EPR lifetime is ~ 2.32 times greater than that determined at 150 °C. Consequently, if we define "failure" as the aging time point when normalized imaginary permittivity ( $\epsilon_n''$ ) exceeds 0.2, the lifetime determined at 150 °C would be around 30 days. By extrapolation, the lifetime of EPR at 140 °C would be around 70 days. Experimental data measuring loss modulus of EPR aged at 140 °C show that lifetime aging occurs around 70 days. Extrapolated EPR lifetimes for operating temperatures that a cable may experience during service in a nuclear power plant are illustrated Table 2.3.



Figure 2.10 Arrhenius plot for shift factors for EPR versus inverse Kelvin temperature.

	Temperature (°C) Predicted lifetime (years)					
	may experience during service in a nuclear power plant.					
Table 2.3	Aging lifetimes of EPR predicted at various temperatures that a typical c	able				

Temperature (°C)	Predicted lifetime (years)		
140	0.18		
130	0.46		
90	32		
60	>1,000		
40	>30,000		

# 2.6 Conclusion

In this chapter, the materials chosen for this study and the characterization methods employed to evaluate material characteristics are described. Additionally, the results of preliminary characterization studies on EPR are included upon which the results of future chapters will be built. Finally, the accelerated isothermal aging process is detailed. The key takeaways from this chapter are listed below:

• A production-grade EPR formulation (trade name Okoguard<sup>®</sup>) is the chosen insulation material under investigation.

- In addition to Okoguard<sup>®</sup> EPR, a non-shielded medium voltage jacketed cable insulated with the same formulation of EPR and a thermosetting CPE jacket (trade name Okolon<sup>®</sup>) is evaluated in this work.
- Analytical techniques employed for materials characterization include Scanning Electron Microscopy/ Energy Dispersive Spectroscopy (SEM/EDS), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Dielectric Spectroscopy (DS), Dielectric Breakdown (DB) testing and Elongation at Break (EaB) testing.
- The working principle and the research purpose have been given for each characterization method implemented.
- Preliminary results of SEM/EDS analysis, DS and DB have been discussed to gain insight into the compositional and dielectric characteristics of EPR.
- The accelerated aging process to induce thermal degradation representative of long-term aging during service has been discussed and a time-temperature superposition analysis of the chosen accelerated aging temperatures was performed to demonstrate that degradation mechanisms are consistent throughout the chosen range.

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# CHAPTER 3. KINETIC MODELING OF THERMAL MODELING OF THERMAL DEGRADATION IN ETHYLENE PROPYLENE RUBBER (EPR)

1

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## 3.1 Abstract

Thermosetting elastomers with excellent dielectric and mechanical strength are typically employed as insulation materials for power cables installed in nuclear power plants (NPPs). Thermooxidative degradation of the insulation on exposure to elevated temperatures has been identified as one of the major factors leading to the loss of performance and ultimate failure of cables in NPPs. Ethylene propylene rubber (EPR) is a thermosetting polymer widely employed for insulating applications, in a variety of formulations. In this work, thermo-oxidative degradation mechanism and kinetics in a production-grade EPR compound has been characterized by thermogravimetric analysis (TGA) coupled with an evolved gas mass spectrometry (MS). A kinetic model based on TGA results was developed using isoconversional methods. Furthermore, MS characterization of the gases evolved during the TGA experiment was used to provide insight into the heating-rate dependent degradation processes occurring in EPR.

#### 3.2 Introduction

The insulation of cables installed in nuclear power plants (NPPs) slowly degrades over decades of prolonged exposure to harsh operating environments such as elevated temperatures and radiation. Insulation aging leads to gradual loss of cable performance and ultimate failure which, depending on the severity of damage, may result in short circuits, power loss, fires or explosions. Consequently, the service lifetime of a cable is primarily determined by the thermal stability of its polymeric insulation. Various formulations of ethylene propylene rubber (EPR) find widespread use as an insulators for medium- and high-voltage NPP cables owing to their high dielectric strength, chemical stability, mechanical strength and ozone resistance. Thermal degradation in the EPR polymer has been extensively studied and documented in literature [1] [2] [3] [4]. However, kinetic models based on thermal degradation, which can predict the high-temperature degradation of EPR-based insulators would be extremely beneficial for cable aging management in NPPs, especially for evaluation of EPR aging in hot spot areas.

In this context, thermogravimetry (TG) is one of the most common techniques used to analyze thermal degradation in polymers. TG provides a measure of the degree of polymer degradation or mass loss as a function of time and temperature. TG tests capturing the degradation of a polymer at different heating rates generate a data set which can be analyzed through the use of isoconversional techniques to obtain degradation kinetic parameters, such as activation energy, for various reaction models [5].

In this study, the thermo-oxidative degradation characteristics of a production-grade EPR compound were evaluated by thermogravimetric analysis (TGA) [6]. Mass spectroscopy analysis was performed to identify the gases evolved during the complex degradation process observed for EPR. For kinetic model development, first, isoconversional kinetics were employed to obtain initial values of kinetic parameters. This data, along with TG data was analyzed to develop an advanced kinetic model based on the mechanisms identified. A mathematical model representing high-temperature thermo-oxidative degradation was developed with a strong fit to the experimental TG data.

#### **3.3** Materials and Sample Preparation

The chosen material for study is a production-grade pink EPR-based insulation with the tradename Okoguard (R) directly obtained in the form of press-cured plaques  $(220 \times 220 \times 1.6 \text{ mm}^3)$  from the manufacturer, the Okonite Company. The samples were stored in a desiccator to minimize undesired exposure to humidity. Five flat circular samples of approximately 9.0  $\pm$  0.1 mg mass were stamped out from the larger EPR square plaque using a circular punch of 1 mm diameter, ensuring consistent size and weight.

#### 3.4 Methods

Thermogravimetric analysis (TGA) along with evolved gas analysis was performed in an air atmosphere to evaluate thermo-oxidative degradation in EPR. A Netzsch STA449 F1 Jupiter ( $\mathbb{R}$ ) analyzer coupled with a Netzsch QMS 403 D Aëolos Quadro mass spectrometer was employed to study thermal degradation behavior and analyze the evolved gases (degradation products) respectively. The chosen crucible type was alumina with a hole in the lid to allow for evolved gases to escape. Each sample was placed in a crucible and carefully weighed, and the experiment was run in the controlled environment of the TGA furnace from 40 °C to 1000 °C in an air atmosphere (80% N<sub>2</sub>/20% O<sub>2</sub>) at one of four constant heating rates: 5, 10, 30 and 50 °C/min. The purge gas and protective gas lines were also air, and the flow rate for both was set to 20 mL/min. In order to correct for buoyancy effect, prior to every sample run, a baseline test at the same heating rate was run on an empty alumina crucible. Furthermore, each sample was run with a four-point temperature calibration, as well as a sensitivity calibration, both set at the same ramp rate as the sample being characterized.



Figure 3.1 (a) TGA Mass Loss traces and (b) DTG curves of EPR for four different heating rates

## 3.5 Results and Discussion

#### 3.5.1 Thermal degradation in EPR

TGA/MS analysis was carried out at four different heating rates to evaluate the thermal decomposition kinetics of EPR. The resulting mass loss data and corresponding first derivative thermogravimetric (DTG) curves are presented as a function of temperature in Figures 3.1(a) and (b) respectively. At all measured heating rates, EPR is observed to be thermally stable (no mass loss) up to around 280 °C. Additionally, the onset of degradation increases slightly with increasing heating rate. The first degradation step occurs between 280 to 390 °C. Across all four heating rates, the primary degradation step (step 2) corresponding to maximum mass loss is rapid and proceeds from approximately 390 to 500 °C. This is followed by a secondary shoulder step, which proceeds from approximately 500 to 550 °C. Through this process, complete degradation of the polymeric component and organic inclusions of the EPR compound occurs, leaving behind a white powdery residue of inorganic fillers constituting 47 - 49 wt. % of the sample in the crucible after combustion up to 800 °C. The temperature derivative of mass loss provides insight into the mechanism of degradation. For any given heating rate the number of peaks in the derivative curve indicates the



Figure 3.2 Temperature derivative curves for mass loss of EPR and quasi multiple ion detection (QMID) curves obtained by mass spectroscopy of evolved gases during EPR degradation at (a) 5 K/min, (b) 10 K//min, (c) 25 K/min and (d) 50 K/min temperature ramp rates.

minimum number of steps involved in degradation reaction. The purpose of varying the heating rates is to separate and isolate the individual reaction steps. As seen in Figure 3.1, at higher heating rates, the individual reaction steps are more distinct and provide for better understanding of degradation kinetics. The results show that a minimum of three reaction steps are observed for EPR at a heating rate of 50  $^{\circ}$ C/min.

Analysis of the composition of evolved gases to assess the major gaseous products for the degradation reaction in EPR was conducted by mass spectroscopy. Figures 3.2(a), (b), (c) and (d), represent the the quasi multiple ion detection (QMID) curves for the evolution of CO<sub>2</sub> and H<sub>2</sub>O

plotted alongside the DTG curve as a function of temperature for thermo-oxidative degradation of EPR at 5, 10, 25 and 50 °C/min. The largest intensity peaks in MS data correspond to the most predominant thermo-oxidative degradation reaction products. Two high intensity peaks are observed in the mass spectra; one at 44 m/z corresponding to carbon-dioxide ( $CO_2$ ) and one at 18 m/z corresponding to water vapor (H<sub>2</sub>O). Both evolved gases are recognized to be the common by-products of hydrocarbon combustion. The peak intensities of  $H_2O$  and  $CO_2$  correspond to the main degradation steps identified previously. A comparison of the peaks of the QMID and DTG curves illustrates the evolved gases for each of the degradation steps observed for EPR. The first step occurs between 290 and 390  $^\circ$  where a small spike in  $\rm CO_2$  and  $\rm H_2O$  is also observed. This may be attributed to the combustion of low molecular weight components and small molecules (including oils, plasticizers, etc.) present in the polymer. Following this, the primary thermo-oxidative degradation of the polymer occurs between 390 and 500 °C. In this temperature range a large intensity spike in CO<sub>2</sub> and H<sub>2</sub>O indicates that the polymer undergoes near-complete combustion in this step. The final degradation step occurs between 500 and 550 °C. Here, a  $CO_2$  peak is detected, however a  $H_2O$  peak is fairly small. The occurrence of this step is primarily seen in the thermal degradation in silane-cured EPR, in which highly crosslinked and cyclized networks are formed that degrade at a slightly higher temperature than the bulk polymer [1] [4]. These characteristics indicate that the EPR formulation examined in this study is likely silane-cured.

#### 3.5.2 Kinetic modeling

#### **3.5.2.1** Isoconversional model-free analysis

To extract information about the degradation kinetics from the results of the TG analysis, first Friedman and Ozawa-Flynn-Wall (OFW) analyses were performed. The degree of degradation, represented by the fractional mass loss,  $(\alpha)$  is given by:

$$\alpha = \frac{w_o - w}{w_o - w_f},\tag{3.1}$$

where, w is the weight of the sample at time t, and  $w_o$  and  $w_f$  are the initial and final values of the mass loss event of interest. From Equation 3.1, it is seen that the value of  $\alpha$  varies from 0 (no mass loss) to 1 (complete mass loss). Generally, it is assumed that the rate of degradation (or conversion) is proportional to the concentration of reacted material during polymer degradation [7]. The rate of degradation may be expressed as,

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = K(T)f(\alpha), \qquad (3.2)$$

where,  $\beta$  is the applied heating rate, K(T) is the temperature-dependent rate constant, and  $f(\alpha)$  is the degradation reaction model.

The rate constant K(T) is obtained from the Arrhenius equation:

$$K(T) = A \exp\left(-E/RT\right) \tag{3.3}$$

where, R is the universal gas constant, E is the activation energy, and A is a pre-exponential factor. Both Friedman and OFW approaches use modifications of the rate equation (3.2) to isolate and extract kinetic parameters for the degradation process, such as E and A, without the need to know the governing reaction model,  $f(\alpha)$ , for the process. To achieve this, a particular mass loss fraction is isolated from each heating trace, and the corresponding points are then fitted with a straight line. The points connected by the straight line are isoconversional, i.e., they all correspond to the same fractional mass loss (or same conversion). To develop a full kinetic model, the initial values of activation energy and pre-exponential factor are first obtained by Friedman and OFW analyses. The Friedman method is a differential isoconversional approach based on the following equation,

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln\{Af(\alpha)\} - \frac{E}{RT},\tag{3.4}$$

from which, activation energies over a wide range of fractional mass loss may be obtained from the slope of isoconversional lines on a plot of  $\ln \left(\beta \frac{d\alpha}{dT}\right)$  against  $\frac{1}{T}$ .

On the other hand, the OFW approach is an integral isoconversional method for which the equation can be obtained by using Doyle's approximation to give the following expression,

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT},$$
(3.5)



Figure 3.3 Friedman plot from data shown in Figure 3.1. Solid black lines represent CFML from 0.2, 0.4, 0.6 and 0.8

from which activation energy may be obtained from the slope of the line fitted to the points corresponding to constant  $\alpha$  on a plot of  $\ln \beta$  versus  $\frac{1}{T}$ .

Using either approach, activation energy may be obtained for each isolated mass loss fraction from the slope of the constant fractional mass loss (CFML) lines. Moreover, an estimate for preexponential factor, A may be obtained from the vertical axis intercept of these lines, but necessarily requires an assumption for the  $f(\alpha)$  reaction type.

The Friedman and OFW plots obtained for EPR degradation are shown in Figures 3.3 and 3.4, respectively. From the curvature of the plot, a multi-step reaction is evident. For each heating rate, the reaction peaks are separate, which indicates the probability that the reaction(s) occurring during degradation may be dependent on heating rate. Furthermore, the reaction type can be determined by comparing the slope of the CFML lines with the with slope of the mass loss trace. The slope of the CFML line is steeper than that of the mass loss curve, indicating a retarded reaction, possibly a diffusion-limited deceleration function [8]. Friedman analysis was used to calculate the activation energy from the slopes of the CFML lines as shown in Figure 3.5. The non-constant activation energy seen for increasing fractional mass loss further confirms the multi-



Figure 3.4 OFW plot from data shown in Figure 3.1. Solid black lines represent CFML over a range of isolated fractional mass loss values between 0.2 to 0.8

step process of degradation. As the reaction begins, the activation energy is around 450 kJ/mol, after which, at around 0.25 mass fraction, it shifts to 375 kJ/mol. Activation energies calculated by OFW analysis are also shown in Figure 3.5. A comparison of the values of E by both methods provides some perspective on the type of degradation step to model for the reactions involved. Degradation steps involving competitive reactions show variations between the activation energies obtained from the two approaches [6].

#### 3.5.2.2 Kinetic model development

The DTG peaks and the isoconversional analysis show that there are a minimum of three steps with a combination of competitive and consecutive steps. A model of three parts was developed according to the schematic representation shown in Figure 3.6. In the first part, the conversion from reactant A to reactant B proceeds along two different paths, 1 and 2. The second part is a single-path (3) reaction from reactant B to reactant C, and the third part is the reaction proceeding along two paths (4 and 5) from C to D. It is necessary to include two different paths for the third step because the TGA results show that there is a heat-rate dependent step for the last 10% of



Figure 3.5 Activation energy calculated from the CFML lines from the Friedman and OFW plots.

-	Step Number	E (kJ/mol)	Log(A)	Reaction Order	Log(K)
-	1	448.2	7.86	0.59	1.21
	2	452.3	8.21	0.64	1.17
	3	346.7	6.65	0.47	0.04
	4	58.46	-2.72	2.44	1.79
	5	10.99	-3.17	0.87	1.54

Table 3.1 Parameters for kinetic model fits to production-grade EPR shown in Figure 3.7

mass loss. Linear regression was applied to determine the optimal fit to the data and obtain kinetic parameters by applying a multivariate version of the Borchardt and Daniels method. The results of fit of the developed kinetic model to the mass loss data is illustrated in Figure 3.7. The obtained values for the fit parameters are listen in Table 3.1.

## 3.6 Conclusion

In this work, kinetic reaction models were employed to analyze the degradation of productiongrade EPR in an air environment. Thermogravimetric analysis was conducted on EPR at four different heating rates. The evolved gases from the TGA degradation reaction were analyzed to



Figure 3.6 Schematic of the kinetic model used to describe the degradation of EPR.

gain insight into the degradation mechanisms involved. Isoconversional methods namely Friedman and Ozawa-Flynn-Wall (OFW) were utilized to isolate fractional mass loss to calculate initial kinetic parameters from TGA mass loss data. Through the combined use of DTG and isoconversional analysis, a multi-step reaction model was chosen to represent thermal degradation in EPR. The development of such kinetic models from TG experiments provides useful insight into the high-temperature thermal degradation characteristics of insulation polymers. Particularly, the estimation of the kinetic parameters for the fractional mass loss reaction steps may be extrapolated to make predictions of thermal degradation lifetimes for EPR under isothermal temperature profiles typically experienced by the cables in NPPs [9][6].

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# CHAPTER 4. A KINETIC MODEL FOR DIELECTRIC BREAKDOWN IN THERMALLY AGED ETHYLENE PROPYLENE RUBBER (EPR)

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## 4.1 Abstract

In this paper, a kinetic rate-dependent model is developed for electrical breakdown in polymers as a function of the submicroscopic crack damage. The model is developed as an electrical analog of the rate dependent kinetic theory for mechanical fracture in polymers. The model is applied to predict the dielectric breakdown strength of ethylene propylene rubber (EPR) for constant applied electric field ramp rate. Further, empirical relationships between dielectric breakdown strength and relative permittivity as a function of thermal aging are obtained. Dielectric breakdown strength is calculated as a function of changing permittivity of EPR. The model is able to make correct predictions within error limits for dielectric breakdown strength of EPR as a function of thermal aging and permittivity changes.

## 4.2 Introduction

Electrical breakdown or failure of a dielectric material occurs when a conducting pathway is burnt through it on the application of a large electrical stress field [1]. Dielectric breakdown of an insulator is a complex physico-chemical process and typically requires a very high applied electric field across the material. On application of a sufficient electric field, the electrons in the insulator gain enough energy to move across the bandgap from the valence band to the conduction band, allowing electric current to flow. This leads to permanent material damage and is undesirable in insulators. The ability of a dielectric to perform as an insulator is quantified by its dielectric strength, which is the highest electric field intensity that the material can withstand prior to macroscopic electrical breakdown [2]. The mathematical expression for dielectric breakdown strength ( $E_{db}$ ) is

given by,

$$E_{db} = V_b/d,$$

where,  $V_b$  is the breakdown voltage and d is the electrode separation, which is equivalent to the thickness of the sample being tested.

The phenomenon of dielectric breakdown is considered to be the electrical equivalent of fracture in an elastic solid[3]. Linear dielectric breakdown electrostatics theories evaluate the spontaneous macroscopic dielectric breakdown brought about by the propagation of a conducting crack within in the dielectric medium on application of a uniform external electric field. Defect-initiated dielectric breakdown occurs when existing defects or cracks within the material grow to form a conducting pathway on the application of an electrical stress until they reach a critical value after which breakdown will occur spontaneously [4] [5]. Similar to defect-initiated mechanical fracture, breakdown begins at the submicroscopic level and the critical field at which spontaneous electric failure occurs is a function of the permittivity (or electric modulus), crack length and breakdown surface energy [3].

A rate dependent kinetic model that describes mechanical fracture in polymers under a uniaxial applied stress was put forth by Hansen and Baker-Jarvis in 1990 [6]. The model defines a crack damage state variable to quantify the material damage at the submicroscopic scale prior to macro-scopic fracture. The first part of this article discusses the theoretical development of an analogous kinetic model for rate dependent dielectric breakdown in polymers as a result of the propagation of conducting submicroscopic damage on application of an external unaxial electric field.

In the second part of the paper, the model is applied to evaluate dielectric breakdown in industrial-grade ethylene propylene rubber (EPR). Compound formulations of ethylene propylene rubber (EPR) find widespread use as electrical insulation for medium- and high- voltage cables. because of their superior dielectric and mechanical properties, and chemical stability. However, when employed in high stress environments such as nuclear power plants, the cables are exposed to elevated temperatures and ionizing radiation which cause significant physical and chemical degradation in the insulation polymer [7] [8]. Thermal and radiation aging of EPR insulation may result in cable failure, leakage of current, malfunction in the circuitry and, in extreme cases, fires and explosions. Knowledge of dielectric breakdown strength as a function of EPR aging can provide valuable and reliable insight into insulation performance and the lifetime of the cable. However, measurements of dielectric breakdown strength are inherently destructive and are unsuitable for condition monitoring when the insulator is in service. Alternatively, broadband dielectric spectroscopy is a non-destructive measurement of the complex permittivity (storage and loss moduli) of the insulator. In this paper, an empirical relationship between the real part of permittivity and dielectric breakdown strength is established to obtain dielectric breakdown strength from direct measurements of EPR permittivity.

## 4.3 Materials and Methods

#### 4.3.1 Materials and sample preparation

Pressed mats of pink EPR-based cable insulation material (trade name Okoguard<sup>®</sup>) manufactured and obtained directly from The Okonite Company, were chosen for this study. EPR mats were cut into 26 squares, each with dimensions of approximately  $51 \times 51 \times 1.6 \text{ mm}^3$ .

To induce insulation aging representative of long-term thermo-oxidative degradation under elevated temperatures, accelerated isothermal aging was carried out at select high temperatures in a ThermoFisher Scientific Heratherm<sup>TM</sup> Advanced Protocol OGH-180 mechanical air circulating oven. The EPR squares were suspended from a rack in the oven and isothermally aged at one of three chosen temperatures, i.e., 160, 150 and 140 °C. Sixteen samples were aged at 160 °C for 2, 5, 7,

9, 11, 12, 13, and 14 days, with two squares per aging time point. Five samples were aged at 150 °C for 7, 14, 21, 28 and 35 days each. Finally, ten samples were aged at 140 °C for 7, 14, 21, 28, 35, 42, 49, 56, 63 and 70 days each. At each temperature, all the samples were hung from a rack inside and placed in the oven together and removed one by one after the desired aging duration was achieved.

## 4.3.2 Characterization methods

#### 4.3.2.1 Dielectric Spectroscopy

Permittivity measurements were conducted using a Novocontrol Alpha-A series dielectric impedance analyzer. The sample cell employs two 28.7 mm electrodes, which together form a parallel plate capacitor. The sample is placed in between the electrodes to measure capacitance. Sample thickness was measured using a Fowler Ultra Digital Mark IV micrometer with systematic uncertainty of 1  $\mu$ m. Ten thickness measurements were made per sample and the average and standard deviation were computed. Mean sample thickness was manually entered into the Novocontrol WinDETA software to compute real permittivity of the sample from measured capacitance. Unaged EPR and aged EPR samples were tested for permittivity at 50 Hz frequency. The frequency was chosen to correspond with the frequency at which the dielectric breakdown strength tests were conducted. Three measurement trials were made per sample. The average and standard deviation were reported. All measurements were carried out at room temperature.

#### 4.3.2.2 Dielectric Breakdown Test

Dielectric breakdown strength of the EPR insulation was measured using a Dielectric Rigidity 6135.054 instrument designed in accordance with ASTM D-149 and D-876 standards. The testing apparatus consists of an oil-insulated transformer and a shut-proof resistant testing chamber which contains a bath for insulating liquid medium and a mobile electrode support of 6.34 mm diameter. The instrument is capable of supplying up to 60kV of AC voltage. Envirotemp®FR3®fluid was employed as the insulating and cooling medium. The high voltage electrode is a tungsten rod of 0.5

mm diameter with a hemispherical tip also having a diameter of 0.5 mm. The low voltage electrode is brass with a flat surface and a diameter of 5 mm. Frequency of the applied field was 50 Hz and the breakdown current threshold was set at 10 mA. The EPR sample was mounted in between the two electrodes and re-positioned for every trial. Sample thickness was measured for each trial in order to compute dielectric breakdown strength. The breakdown voltage was measured for three applied voltage ramp rates, 0.5, 2 and 5 kV/s, for EPR samples aged at 160 °C. The samples aged at 150 and 140 °C were tested only at a ramp rate of 0.5 kV/s. For a given ramp rate, 20 trials were conducted per sample and the average calculated to obtain the dielectric breakdown strength. All measurements were carried out at room temperature.

## 4.4 Theoretical Development

#### 4.4.1 Formation of a conducting submicrocrack

The theoretical analysis begins at the submicroscopic level. In a polymer, thermal fluctuations lead to the formation of dilatons, or micro-fluctuations that result in rupture of atomic bonds in weak regions. This results in the formation of localized high-field intensity regions consisting of free charge carriers and leads to the formation of submicroscopic conducting microcracks within the polymer. On the application of an external uniaxial field, the intensity of the local fields increases and a number of such conducting cracks propagate and coalesce to form macroscopic cracks. When the length of the conducting pathway reaches a critical value, rapid electrical failure occurs.

Consider a uniaxial electric field (or voltage stress) of magnitude, E, applied across an isotropic linear polymer with dielectric constant  $\epsilon$ . To model the dielectric breakdown process under the applied field, consider a submicroscopic conductive crack of length c within a region of the polymer confined by an effective potential well. Initially, the potential energy barrier of the well walls is U. On the application of the external field, E, the electrically-charged particles experience a high Coulombic force,  $F_c$ , in the direction of the applied field which modifies the potential barrier by  $\Delta V$  such that,

$$-\frac{\Delta V}{\Delta x} = F_c \text{ or }$$

$$-\Delta V = F_c \Delta x = -2\gamma\sigma. \tag{4.1}$$

Where,  $\gamma$  is an intrinsic property (material co-efficient) of the polymer. A potential difference arises across the potential well such that the potential barrier inhibiting the crack propagation in the field direction is reduced in height by  $\gamma E$  and the potential barrier inhibiting the charge mobility in the reverse direction is increased by the same amount, such that,

in the field direction, 
$$U^{(-)} = U - \gamma E$$
, (4.2a)

and in the reverse direction, 
$$U^{(+)} = U + \gamma E.$$
 (4.2b)

The probability that the conducting crack will extend in a given direction is determined by the probability that the local breakdown reaction energy exceeds the height of the potential well in that direction. This is obtained by integrating the probability density of the charged particles over energy values greater than the potential barrier. From classical statistical physics, the probability of a thermally activated carrier to transition across the energy barrier in time dt is given by,

$$P(transition) = \nu_o \exp\left(\frac{-E_A}{kT}\right) dt.$$
(4.3)

Where,

$$\nu_o = \omega/2\pi \approx 10^{13} s^{-1}$$

is the characteristic frequency of the atoms oscillating in a solid and  $E_A$  is the activation energy (or energy barrier) for the transition, which is given by equation 4.2a (along field direction) and 4.2b (along reverse direction). This probability of carrier transition across the wall in time dt is given by the product of probability of the carrier to have energy greater than the height of the potential well and the frequency of oscillation of the particle (or in other words, the frequency of collision with the potential wall per unit time).

The rate constants for the forward and reverse conducting submicrocrack propagation reactions are given by the probability of overcoming the potential barrier per unit time as,

$$K_b = \frac{\omega}{2\pi} \exp\left[\frac{-(U - \gamma E)}{k_b T}\right] \text{(breakdown)}$$
(4.4)

$$K_b = \frac{\omega}{2\pi} \exp\left[\frac{-(U+\gamma E)}{k_b T}\right] (\text{reformation})$$
(4.5)

In positive applied field, bond rupture (and subsequent charge conduction) is largely favored over bond reformation. In the following development, the bond reformation term is neglected. In this context, U may be considered as the activation energy for dielectric breakdown to occur.

## 4.4.2 Submicrocrack propagation and dielectric breakdown

The excitation and rupture of atomic bonds by thermal fluctuations and the subsequent propagation of material damage illustrates the kinetic nature of the dielectric breakdown in a polymer. It is seen that under a mechanical load, the concentration of submicrocracks within a polymer is a function of the deformation and independent of the mechanical loading conditions. If we assume that this holds true under electrical loading conditions as well, the concentration of conducting submicrocracks within the polymer may be used as a quantifiable scalar parameter to characterize crack damage resulting in electrical failure. The following development is the electrical analog to that described by Hansen and Baker Jarvis for mechanical fracture in polymers.

For a material with variable electrical stress histories, the differential equation describing the rate of change of the concentration of conducting submicrocracks with time may be given by:

$$\frac{dN}{dt} = (N_o - N)K_b, N(0) = 0$$
(4.6)

Where,  $N_o$  is the number of potentially weak regions withing the material at time t = 0 and N is the submicrocrack concentration at any given time, t.  $K_b$  is the rate of submicrocrack growth as a result of bond breakdown. The initial condition, N(0) = 0 represents a perfect material i.e., one that has not undergone any prior damage.

A normalized crack damage state variable, n(t) may be introduced to quantify the extent of material damage as follows,

$$n(t) = \frac{N(t)}{N_b},\tag{4.7}$$

Where,  $N_b$  is the submicroscopic concentration at breakdown. Then, n = 0 corresponds to the condition where there is no crack damage in the material, while n = 1 corresponds to formation of a macrocrack resulting in dielectric breakdown. A value in between the two implies that the conducting crack has propagated through the material, but has not resulted in macroscopic failure.

The differential rate equation for submicrocrack growth may be expressed in terms of the crack damage state variable as follows:

$$\frac{dn}{dt} = -K_b n + n_o K_b, \ n(0) = 0 \tag{4.8}$$

Where,

 $n_o = N_o/N_b.$ 

The general solution for equation 4.8 is obtained as:

$$n(t) = \int_0^t n_o k_b(\xi) \exp\left(-\int_{\xi}^t K_b(\beta) \, d\beta\right) \, d\xi, \tag{4.9}$$

The value of  $n_o$  was determined to be 1.58 from equation 4.9 and the fundamental equation of the kinetic theory of fracture.

#### 4.4.2.1 Dielectric breakdown strength for constant applied field ramp rate

Under a constant applied field ramp rate condition, dielectric breakdown strength is given by,

$$E_{db} = \dot{E}t, \, \dot{E} = \text{constant.}$$
 (4.10)

The solution for the crack damage state variable is given by,

$$n(t) = 1.58 \left\{ 1 - \exp\left[-\frac{kT}{\tau_o \gamma \dot{E}} \exp\left(\frac{-U - \gamma \dot{E}t}{kT}\right) - \exp\left(\frac{-U}{kT}\right)\right] \right\}.$$
(4.11)

To solve for failure time, t equation 4.11 is evaluated for n = 1 (macroscopic failure), which gives:

$$t = \frac{kT}{\gamma \dot{E}} \left\{ \ln \left[ \frac{\tau_o \gamma \dot{E}}{kT} + \exp(-U/kT) \right] + (U/kT) \right\}.$$
(4.12)
At realizable temperatures, the value of  $\exp(-U/kT)$  is negligible. From equation 4.12 and equation 4.10, we obtain an expression for the dielectric breakdown strength of the material as:

$$\sigma = \frac{kT}{\gamma} \left[ \ln \dot{E} + \ln \left( \frac{\tau_o \gamma}{kT} \right) + (U/kT) \right].$$
(4.13)

Equation 4.13 represents the mathematical expression for the dielectric breakdown strength of a polymer for a constant applied field ramp rate. According to the equation, the dielectric breakdown strength of the material varies linearly as a function of the natural logarithm of the applied field ramp rate. The slope of the line is given by  $kT/\gamma$ , while the y-intercept is given by

$$\frac{kT}{\gamma} \left[ \ln \left( \frac{\tau_o \gamma}{kT} \right) + (U/kT) \right].$$

## 4.5 Results and Discussion

## 4.5.1 Relative permittivity of EPR as a function of aging

Figure 4.1 displays the results of the real permittivity measured at 50 Hz on EPR aged 160, 150 and 140 °C. Relative permittivity of unaged EPR is 2.85, and is observed to increase with aging time. While a cubic polynomial was identified to be the best fit curve to represent the change in permittivity of EPR aged at 160 °C, a Padé(1,1) approximant was employed to represent permittivity changes at 140 and 150 °C. At 160 °C rapid increase in permittivity is observed from 0 to 2 days, which is followed by a steady increase from 2 to 11 days after which a rapid increase in permittivity is seen up to 13 days. An overall steady increase in EPR permittivity is seen for up to 28 days and 63 days in samples aged at 150 and 140 °C respectively. This is followed by a sudden and rapid increase in permittivity in the most heavily aged samples for both aging temperatures. Permittivity changes in EPR as a function of thermal aging are indicative of intrinsic changes in the dielectric behavior as a consequence of changes in the chemistry and microstructure brought about by thermal degradation. The degradation processes are accelerated at higher temperatures, which leads to rapid changes in permittivity at shorter aging times. Chain fragmentation and cross-linking are identified as two competing degradation processes that occur in EPR on thermal aging. While an increase in permittivity is observed on chain fragmentation, a decrease is observed on crosslinking [7]. At lower temperatures (140 and 150 °C), initially, both processes are prevalent, with the chain fragmentation being slightly more dominant, which leads to a gentle overall increase in permittivity. At higher aging times, when cross-linking can no longer occur, chain fragmentation takes over entirely and a rapid increase in permittivity is observed which also corresponds to the rapid degradation in the material. At higher temperatures (160 °C) chain fragmentation is observed to be the dominant degradation process right from the start, with little competition from cross-linking. This leads to rapid increase in permittivity corresponding to material degradation at shorter aging times. Permittivity changes quantify the macroscopic dielectric behavior of EPR as a function of microscopic chemical changes on thermal aging.



Figure 4.1 Relative permittivity of EPR measured at 50 Hz as a function of aging time, at three different aging temperatures.

## 4.5.2 Measured dielectric breakdown strength of EPR

To verify that the model is in fact a robust representation of electrical breakdown in EPR, dielectric breakdown studies were conducted on unaged EPR at four constant applied voltage ramp rates (0.5, 1, 2 and 5 kV/s). The model predicts a linear relationship between the measured

dielectric strength of the polymer as a function of the natural logarithm of the applied field ramp rate. The field ramp rate was calculated as the ratio of the applied constant voltage ramp rate,  $\dot{V}$ (in kV/s) and the electrode separation, d (in mm) for each sample. Dielectric breakdown strength of unaged EPR is shown as a function of the natural logarithm of the applied field ramp rate in figure 4.2. As expected, average dielectric breakdown strength of EPR is found to increase linearly as a function of the logarithm of applied field ramp rate. The slope and y-intercept of the straight line fitted to the data were used to calculate the U and  $\gamma$  values for unaged EPR, which were found to be  $1.82 \times 10^{-19}$  kV and  $2.41 \times 10^{-21}$  mm<sup>2</sup> respectively.



Figure 4.2 Dielectric Breakdown Strength  $E_{db}$  of unaged EPR as a function of applied electric field ramp rate

To evaluate how U and  $\gamma$  change as EPR undergoes thermal aging, dielectric breakdown measurements were conducted at three chosen applied voltage ramp rates (0.5, 2 and 5 kV/s) for the samples aged 0, 2, 5, 7, 9, 11, and 13 days at 160 °C. It was noted that the samples showed slight variations in thickness ( $\sim 0.05 \text{ mm}$ ) from one another because of which the electrode separation (d) also varied slightly. As a result, for a given applied voltage ramp rate ( $\dot{V}$ ), small differences in the applied field ramp rate ( $\dot{V}/d$ ) were observed between the samples. Figure 4.3 shows the average measured dielectric breakdown strength of EPR as a function of applied field ramp rate for unaged and aged samples. For any given applied field ramp rate, dielectric breakdown strength is observed to decrease with increasing aging time. Lower breakdown strength indicates that the material undergoes electrical breakdown (allows flow of charge) at a lower applied field. Lower dielectric strength corresponds to poorer insulation properties. The results show that as EPR thermally degrades, its performance as an insulator is also lowered.



Figure 4.3 Dielectric breakdown strength of EPR aged at 160  $^{\circ}\mathrm{C}$  as a function of applied field ramp rate

For any given aging time, EPR shows a strong linear relationship between the dielectric breakdown strength and the logarithm of the applied field ramp rate. However, the slope and y-intercept

of the fitted line is different for the different aging times, which implies that the activation energy (U) of the breakdown process and the material co-efficient  $(\gamma)$  of EPR change as a function of thermal aging. Similar to unaged EPR, U and  $\gamma$  were calculated for each aged sample from the slope and y-intercept of the fitted straight line. The changes in U and  $\gamma$  as a function of thermal aging is expected because the intrinsic dielectric properties of the material are different (as captured by the permittivity). Appendix 1A lists the calculated U and  $\gamma$  values for the unaged and aged EPR samples.



#### 4.5.3 U and $\gamma$ as empirical functions of permittivity

Figure 4.4 Calculated U and  $\gamma$  of EPR aged at 160 °C as a function of real relative permittivity

We know that the lifetime of EPR differs for different aging temperatures. So, it is more meaningful to express U and  $\gamma$  as functions of an intrinsic dielectric property of EPR rather than its aging time. If U and  $\gamma$  are expressed as a functions of the changing permittivity of EPR, the breakdown strength of EPR can be estimated from a direct measurement of EPR permittivity. An empirical relationship between the change in U and  $\gamma$  as a function of the real permittivity was established for the samples aged at 160 °C as shown in Figure 4.4. Both U and  $\gamma$  are best represented as quadratic functions of EPR permittivity. The coefficients of both equations are given in Appendix 1B.

#### 4.5.4 Dielectric breakdown strength prediction at various temperatures

Figure 4.5 shows the measured and predicted dielectric breakdown strength of EPR as a function of measured permittivity for samples aged at 140, 150 and 160 °C. Dielectric breakdown strength predictions were made employing the input parameters U and  $\gamma$  as empirical quadratic functions of EPR permittivity. The unaged sample (0 days) with permittivity 2.85 exhibits the highest breakdown strength of  $\sim$ 22.6 kV/mm. As EPR permittivity increases, the predicted dielectric breakdown strength decreases for all aging temperatures. This further illustrates that given the mechanism of aging is only accelerated but otherwise consistent across the range of temperatures evaluated, EPR of a certain permittivity is seen to have a corresponding breakdown strength independent of aging temperature. Consequently, measurement of permittivity may be used to track insulation aging and to estimate the dielectric breakdown strength independent of thermal history.

In figure 4.6, the measured and predicted dielectric breakdown strength of EPR is presented as a function of aging time for the three chosen temperatures. Fitted permittivity values were used to evaluate the dielectric breakdown strength of EPR. The empirical functions relating Uand  $\gamma$  with permittivity were established for the samples aged at 160 °C. It is understood that the activation energy (U) and the material coefficient ( $\gamma$ ) quantify the spontaneous macroscopic dielectric breakdown as a function of intrinsic conducting microcrack propagation. As discussed earlier, if the same mechanisms of thermal breakdown prevail in the given temperature range, it can be further argued that the empirical relationships of U and  $\gamma$  with permittivity will be independent of aging temperature. The predicted dielectric breakdown strength of EPR at all three temperatures



Figure 4.5 Dielectric breakdown strength as a function of real permittivity

was calculated by applying the quadratic functions of U and  $\gamma$  obtained from dielectric breakdown measurements conducted on the samples aged at 160 °C. At the lower aging temperatures of 140 and 150 °C, breakdown strength of EPR decreases gradually over a longer aging time period before the onset of a sudden rapid decline at 63 and 28 days respectively. At 160 °C, breakdown strength rapidly declines over a short time period of 14 days. Dielectric breakdown strength is observed to decrease as a function of aging time for all three temperatures with the unaged sample exhibiting the highest breakdown strength and the most heavily aged sample exhibiting the lowest breakdown strength.



Figure 4.6 Measured and predicted dielectric breakdown strength of EPR aged at 140, 150 and 160 °C as a function of aging time at three different aging temperatures

## 4.6 Conclusion

In this article, a kinetic model based on the formation and growth of conducting microcracks under an applied electric field has been presented as an electrical analog to crack propagation under mechanical loading. Crack propagation is shown to result in charge conduction in the dielectric which, upon reaching a critical value, results in catastrophic electrical failure of the material. Furthermore, expressions for the dielectric breakdown strength and the time to dielectric breakdown were derived for a constant applied field ramp rate. The model was applied to calculate the dielectric breakdown strength of ethylene propylene rubber at different applied field ramp rates. EPR showed a linear increase in dielectric breakdown strength as a function of the natural logarithm of the applied field ramp rate, as predicted by the model. Moreover, changes in real permittivity of EPR were measured as a function of aging time for three aging temperatures (140, 150 and 160 °C). Real permittivity was found to increase as a function of aging time. Empirical relationships were established for the activation energy for dielectric breakdown (U) and the material coefficient ( $\gamma$ ) as functions of measured real permittivity. Using these empirical relationships, dielectric breakdown strength of EPR at multiple aging times at varying temperatures was predicted using the kinetic model. This work shows that dielectric breakdown strength of EPR, which is a direct measure of insulation performance, may be calculated from permittivity measurements. As permittivity measurements are made non-destructively, such a model is valuable to evaluate insulation performance based on data obtained from non-destructive dielectric spectroscopy tests for cable insulation condition monitoring.

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# CHAPTER 5. CHARACTERIZING THERMAL DEGRADATION IN ETHYLENE PROPYLENE RUBBER (EPR) INSULATION AGED ALONGSIDE CHLORINATED POLYETHYLENE (CPE) JACKET IN POWER CABLES

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## 5.1 Abstract

The primary cause for cable aging in nuclear power plants (NPPs) has been identified to be the degradation of the polymeric insulation and jacket layers on long-term exposure to heat, ionizing radiation and moisture. As NPPs seek to extend operating life by another 20 to 40 years, aging management of cables is critical for continued safe operation. For a given operating environment, degradation mechanisms in different types of cable insulation and jacket polymers depend greatly on their composition. Cross-contamination processes that may occur when the jacket and insulation age in close proximity may significantly alter thermal degradation mechanisms in the materials and result in unexpected catastrophic cable failure. In this work, the cross-contamination processes in a commercial power cable with a chlorinated polyethylene (CPE) jacket employed alongside ethylene propylene rubber (EPR) insulation for medium-voltage applications were investigated. The changes occurring in the composition of EPR when aged alongside CPE was studied under accelerated thermal aging conditions. Optical microscopy testing showed the formation and growth of two interaction layers at the EPR-CPE polymer interface. SEM/EDS analysis performed to

evaluate elemental composition showed that Cl and Sb species migrated from the CPE jacket into the EPR insulation. The effect of cross-contamination between the two layers on thermal degradation characteristics of EPR was examined by thermogravimetric analysis (TGA). Significant changes were observed in the high-temperature thermal degradation behavior of EPR when aged in the presence of CPE indicating compositional changes and lower thermal stability. Microscopic chemical changes identified in the EPR insulation formulation as a consequence of thermal aging alongside CPE may be the underlying cause for severe loss of macroscopic thermal stability and electrical performance of EPR which, in turn, would result in shorter cable service lifetimes.

## 5.2 Introduction

Cables employed in nuclear power plants (NPPs) degrade on prolonged exposure to harsh operating environments such as elevated temperature, ionizing radiation, and elevated humidity [1][2]. This process, known as cable aging, is predominantly caused by changes in electrical, mechanical, and chemical properties of the cable jacket and insulation layers. Over time, material properties deteriorate, lowering both cable performance and service lifetime [3][4]. Consequences of unexpected cable failure on aging include fires, power loss, service interruptions and, ultimately, plant shutdown. As NPPs pursue license renewals to extend their operating lifetime by another 20 to 40 years, aging management of cables is essential for continued safe and economical operation [5].

For a given operating environment in an NPP, cable degradation behavior is primarily determined by the composition of insulation and jacket materials. Typical material formulations include a base polymer with added organic and inorganic inclusions; stabilizers, plasticizers, fire retardants and antioxidants. For low voltage (LV) and medium voltage (MV) applications, ethylene propylene rubber (EPR) and cross-linked polyethylene (XLPE) compounds find widespread use as insulators [6]. Formulations of chlorosulphonated polyethylene (CSPE), chlorinated polyethylene (CPE) and neoprene compounds are jacket materials commonly employed alongside the aforementioned insulators [7]. In regards to both the base polymer and the added inclusions, insulation and jacket materials often differ significantly in composition based on their respective functions in the cable. The aging characteristics and remaining useful life (RUL) of the cable are directly influenced by how the jacket and insulation polymer compounds degrade.

In cables configured with the jacket and insulation adjacent to one another (bonded or nonbonded), the two layers age in close proximity. Depending on layer composition, cross-infection or contamination processes are likely to occur, which makes the overall thermo-oxidative degradation of the cable different and more complex as compared to the individual layers [8]. To this effect, major research efforts have been made to study thermal- and radiation-induced aging in EPR/CSPE and EPR/Neoprene cables [9][10][11][12][13]. These prior studies on EPR/CSPE cables show that the external CSPE jacket exhibits lower tolerance to elevated temperatures than the underlying EPR insulation. When EPR ages in a rapidly deteriorating CSPE environment, its degradation is accelerated. Shrinking, cracking and unexpected failure of the EPR insulation under Loss of Coolant Accident (LOCA) conditions were observed for the cables in which EPR and CSPE were adjacent to one another. Consequently, the expected durability of some EPR/CSPE jacketed cables was questioned in a notice issued by the Nuclear Regulatory Commission (NRC) [14]. While cautionary steps have been exercised in the implementation and evaluation of EPR/CSPE cables. degradation studies on similarly designed, widely used EPR-insulated cables fitted with CPE jackets are very limited [3][15]. Given the similarities in compounding properties and high temperature performance of CPE and CSPE [16][17], it is hypothesized that cross-infection processes may be prevalent in EPR/CPE cables in which the two layers are in direct contact.

This work aims to address the above-mentioned research gap by investigating the thermooxidative degradation in EPR/CPE cables and identifying the chemical changes occurring in the layers as a function of accelerated thermal aging. A medium-voltage cable comprising a non-fireretardant EPR insulation extruded with a non-bonded, fire-retardant CPE jacket was chosen for this study. This paper explains the results of optical microscopy, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and thermogravimetric analysis with evolved gas mass spectroscopy (TGA/MS) characterization tests to evaluate changes in composition on aging. A discussion of i) the growth of interaction layers between EPR and CPE, ii) the key interacting species



Figure 5.1 Cable samples aged from 0 to 63 days at 140 °C with. The ends of the samples are sealed by Aluminum foil held in place by o-rings.

identified to cause cross-infection, and iii) the resulting influence on insulation degradation behavior is presented.

The arrangement of the paper is as follows; the materials used and experimental methods for accelerated aging and characterization tests are described in Section 5.3. The results and a discussion of key inferences drawn from each test are detailed in Section 5.4. Finally, Section 5.5 includes the major conclusions of the study.

## 5.3 Materials and Methods

## 5.3.1 Sample preparation

A single core, non-shielded 2.4 kV power cable supplied by The Okonite Company with the trade name Okoguard<sup>®</sup>-Okolon<sup>®</sup> TS-CPE Type MV-90 and an outer diameter of 22.4 mm was chosen for this study. In this cable configuration, the conductor diameter is approximately 9.2 mm and is formed by annealed, compact stranded copper. The approximate thickness of the non-bonded CPE-based jacket (Okolon<sup>®</sup> TS-CPE) is 2 mm and that of the EPR-based insulation (Okoguard<sup>®</sup>) layer is 3.5 mm. From here on in this article, 'CPE' and 'EPR' will be used to refer to the Okolon<sup>®</sup> TS-CPE and Okoguard<sup>®</sup> formulations described above, respectively. The cable also incorporates a layer of semiconducting EPR (SC EPR) reinforced with carbon black lining the interface between the EPR insulation and the copper conductor, which has an approximate thickness 0.5 mm.

The cable was cut into ten sections, each 100 mm in length. To induce thermal degradation representative of long-term thermo-oxidative aging that the cable may experience in service,



Figure 5.2 Thermally aged cable segments (aged 7 to 63 days at 140  $^{\circ}$ C) cut from cross–sectional discs as seen through the navigation camera of a scanning electron microscope.

isothermal accelerated aging was performed by placing the cable sections in a ThermoFisher Scientific Heratherm<sup>TM</sup> Advanced Protocol OGH-180 mechanical air circulating oven. The ends of the cable sections were sealed with aluminum foil held in place by rubber O-rings and these samples were aged isothermally in the oven at 140 °C for up to 63 days. A sample was removed from the oven every seven days, resulting in a sample set (shown in Figure 5.1) comprising 10 samples aged 0, 7, 14, 21, 28, 35, 42, 49, 56, and 63 days. Thin cross-sectional discs of around 2 mm thickness were sliced from each of the aged samples. Each disc was cut into segments for characterization studies as shown in Figure 5.2.

## 5.3.2 Characterization methods

## 5.3.2.1 Optical Microscopy

An Olympus SZX12 Stereomicroscope was used to conduct optical imaging of the thermally aged cable cross sections. The focal length of the microscope lens and the imaging magnification was kept constant at  $20\times$  for each of the samples to ensure consistent length scales for each image. The images were analyzed using the ImageJ1 processing software, to measure the thicknesses of

the jacket and insulation layers. The thickness of each layer was measured along the radius of the sample and is reported as an average of 20 measurements per layer, per sample.

## 5.3.2.2 Scanning Electron Microscopy/Energy Dispersive Spectrometry

Cross-sectional cable samples were imaged using a FEI Quanta-FEG 250 field emission SEM operated at 10 kV. Additionally, qualitative elemental analysis on the microscopic scale was carried out with an accompanying Oxford Aztec energy-dispersive spectrometer (EDS). The accelerating voltage was set at 15 kV to obtain EDS spectra and elemental maps. To prevent charging when exposed to the electron beam, each sample surface was coated with a thin layer of iridium of around 5 nm thickness. Back-scattered electron imaging (at  $60 \times$  magnification) and elemental analysis were carried out by scanning along a radial line of each of the cross-sectional cable samples, moving the electron beam from the interior (insulation layer) to the exterior (jacket layer). Qualitative EDS spectra were obtained at multiple locations in both EPR and CPE layers along the radial line scanned on the sample.

#### 5.3.2.3 Thermogravimetric Analysis with Evolved Gas Mass Spectrometry

To investigate thermal degradation behavior, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed simultaneously on a given sample using a Netzsch STA449 F1 Jupiter<sup>®</sup> analyzer. Additionally, the instrument was coupled with a Netzsch QMS 403 D Aëolos Quadro mass spectrometer to analyze the gases evolved during TGA/DSC experiments. Insulation and jacket samples of approximately 5–7 mg mass were excised from desired locations on the segments (discussed in Section 5.4.3) using a razor blade. Each sample was placed in an alumina crucible, with a hole in the lid to allow for evolved gases to escape, and the test was run from 40 °C to 800 °C at a heating rate of 10 °C/min. A baseline test at the same heating rate was run on an empty alumina crucible prior to sample analysis in order to correct for the buoyancy effect. Furthermore, each sample was run with a four-point temperature calibration, as well as a



Figure 5.3 Optical macrograph of EPR/CPE cables aged 0, 35 and 63 days at 140 °C.

sensitivity calibration, both set for a ramp rate of 10 °C/min. All sample, baseline, and calibration runs were performed under an air atmosphere.

## 5.4 Results and Discussion

## 5.4.1 Optical Microscopy - interaction layer growth

An optical macrograph of the cable samples for three chosen representative aging time points, 0, 35, and 63 days, is displayed in Figure 5.3. At the interface between the CPE jacket and EPR insulation, an intermediate interaction region forms and grows in thickness with increasing aging time. Additionally, it can be seen that the interaction region is located primarily within EPR and comprises two different layers. Figure 5.4 is a schematic representation of the unaged and aged cable segments, which includes the nomenclature used to reference each individual layer of the cable segment in this paper. The CPE jacket, EPR insulation, and semiconducting EPR layers are numbered 1, 2 and 3 respectively. The interaction layers are labeled 2a and 2b as modifications of the EPR insulation layer.



Figure 5.4 Schematic representation of (a) unaged and (b) aged cable segments with layer nomenclature.

From optical micrographs obtained for the aged cable samples, the thickness of each of the layers was measured and plotted as a function of aging time (Figure 5.5). The measurements show an overall increase in the thickness of both 2a and 2b interaction layers from 0 to 63 days. For up to 28 days, there is a rapid increase in interaction layer thickness, after which the rate of growth decreases, tending towards a plateau by 63 days aging time. While the thicknesses of CPE and SC-EPR remain fairly constant with increasing aging time that of EPR decreases rapidly as the cable ages. The rapid increase in the growth of the interaction layers and the corresponding decrease in thickness of layer 2 indicate that EPR undergoes significant changes as a result of interaction with CPE on thermal aging. The chemical species responsible for the formation and growth of the interaction layers are identified and discussed in Section 5.4.2.

## 5.4.2 SEM/EDS Analysis - changes in elemental composition

To gain insight into the chemical changes driving layer growth, qualitative elemental analysis was performed independently on every layer of the unaged and aged cable segments. The EDS peaks are observed at specific energies that correspond to characteristic X-rays emitted from individual elemental species present within a given region of the sample being studied. Consequently, the EDS spectra obtained over a range of energies provide insight into the chemical composition of the examined region. The EDS spectra obtained for each individual layer of the cable segments were



8

3 - SC EPR

3.5

3.0

(a)



Figure 5.5 Layer thicknesses of cable segments plotted as a function of aging time.

carefully evaluated to identify the key interacting species in the thermal aging process. Qualitative characterization was performed by this method, first on the unaged sample, then on the aged samples. The results obtained by this analysis are summarized below using the unaged cable and select intermediate (35 d) and heavily (63 d) aged samples as reference time points of cable lifetime.

Qualitative EDS on the unaged and aged cable samples revealed two primary interacting inorganic chemical species between CPE and EPR; chlorine (Cl) and antimony (Sb). The EDS peaks observed at 2.621 keV (K $\alpha_1$ ) and 2.812 keV (K $\beta_1$ ) correspond to X-ray energies of Cl and are shown for each individual layer of the cable segments aged for 0, 35, and 63 days in Figure 5.6(a). The sample schematic insets included in Figure 5.6(a) illustrate the position of the electron beam when each EDS spectrum was obtained. Starting at 0 days, large peaks of Cl species are identified within the CPE jacket as expected, but are absent in EPR. This shows that chlorine is not a part of the EPR formulation and is found only within the CPE jacket in a new cable. On thermal



Figure 5.6 EDS spectra for (a) chlorine (at 2.621 and 2.812 keV) and (b) antimony (at 3.604 and 3.842 keV) in each layer of cable samples aged 0, 35 and 63 days at 140 °C.

aging for up to 35 days, the interaction region is formed within EPR, and chlorine peaks are now identified within the so-called interaction layers, 2a and 2b. This process continues for up to 63 days. However, it must be noted that Cl is detected only within layers 1, 2a, and 2b, and not within EPR. This indicates that Cl is confined within the interaction region. As Cl is incorporated within the insulation on thermal aging, EPR is modified to form interaction layers 2a and 2b, which grow in thickness as a function of aging time.

Figure 5.6(b) follows the peaks of the second interacting species, Sb, across the layers of the cable segments aged 0, 35 and 63 days respectively with the electron beam position depicted by the sample schematic included in each plot. Sb peaks, identified at 3.604 keV (L $\alpha_1$ ) and 3.842 keV

 $(L\beta_1)$ , are observed only in the jacket layer (1) and not in the insulation layer (2) of the unaged cable sample. Consequently, as in the previous case, the chemical composition of new EPR does not include Sb. It is noted that alongside the Sb peak at 3.604 keV, the CPE-based compound also includes Ca, detected at 3.692 keV. On studying the EDS spectra of the sample aged 35 days, it can be observed that the Sb peaks are no longer found within CPE, and are instead evident only within interaction layer 2b. Similarly, at 63 days, Sb peaks are only detected in 2b, and not observed in any other layer of the sample. These results demonstrate that the Sb contained within the cable system migrates, in entirety, from CPE into EPR on aging, and can be identified to be present exclusively within 2b. The presence of Sb within layer 2b, along with differences in Cl content, is what distinguishes its elemental composition from that of layer 2a. Additionally, it is noted that while the Sb peak is no longer observed within CPE on aging, the Ca peak is retained within CPE throughout the aging process confirming that Ca is not involved in the interaction between the jacket and insulation. To summarize, elemental compositional changes occurring in EPR within the interaction region were identified to occur due to the migration of Cl and Sb species from the CPE jacket (1) into the EPR insulation (2). While Cl was identified in both interaction layers, 2a and 2b, Sb was found only in layer 2b.

## 5.4.3 TGA/MS Analysis - characterizing thermal degradation behavior

#### 5.4.3.1 Overview of thermal degradation characteristics of EPR and CPE

Changes in thermal behavior of the cable materials as a result of jacket-insulation interaction were assessed by TGA/MS performed on each layer of the cable segments. Differences in mass loss and evolved gases in the cable layers as a function of aging time were closely investigated and are described below for 0 days and 63 days as representative aging time points. The results of the degradation experiments and the evolved gas analysis are observed to be fairly complex for the two polymers. Figures 5.7(a) and (b) show, respectively, the TGA mass loss traces and corresponding temperature derivatives measured on CPE aged for 0 and 63 days. Three primary degradation steps are observed in unaged CPE. The first occurs between 250 and 350 °C, the second from



Figure 5.7 (a) TGA mass loss traces and (b) DTG curves of CPE aged 0 and 63 days at 140 °C. (c) TGA mass loss traces and (b) DTG curves of EPR aged 0 and 63 days at 140 °C.

400 to 500 °C and the third from 525 to 600 °C. White powdery inorganic residue constituting 36.6 wt. % of the unaged CPE sample remained in the crucible after complete combustion of the organic component up to 800 °C. At 63 days, the onset of degradation is observed at around 90 °C, which is much lower than that observed for unaged CPE, indicating a loss in thermal stability with aging. The three primary degradation steps identified for unaged CPE are still prevalent for the aged sample across the same temperature ranges. A powdery residue of the inorganic inclusions constituting 37.5 wt. % of the sample remained in the crucible after the test was completed. This residual mass is the same as that obtained for the unaged sample within uncertainty limits of  $\pm 5$  wt.% indicating no significant changes in inorganic filler content on thermal aging. By examining

the temperature derivative of mass loss, inferences can be made on mechanism of degradation. Typically, the number of peaks in the DTG curve indicates the minimum number of reaction steps involved in thermal degradation. It is apparent from the DTG curves of both unaged and aged CPE that several steps are involved in the complex degradation process of the compound. The temperature derivative curves of CPE aged 0 and 63 days differ slightly in shape, indicating possible changes in the underlying physical and/or chemical properties of CPE on aging, resulting in the observed differences in thermal degradation mechanisms.

Mass loss and derivative curves are respectively shown in Figures 5.7(c) and (d) for EPR (2), 2a and 2b layers. Thermal degradation onset in unaged EPR occurs between 290 and 390 °C, after which the largest degradation step occurs from 400 to 500  $^{\circ}$ C, followed by a smaller step from 500 to 530 °C. As seen in CPE, a fluffy white inorganic residue which was 46.8 wt. % of the unaged sample remained in the crucible on completion of the TGA analysis. An assessment of the EPR, 2a and 2b layers of the 63 days aged sample indicate that the high-temperature degradation behavior of EPR changes as a function of aging time and position. The wt.% of inorganic residue that remained in the crucible for each of the EPR sample tested was fairly constant, lying within the range of 45.7 to 50.1%. The primary differences in shape between the 0 and 63 days samples are seen in the third degradation step, between 490 and 550 °C. The magnitude of this degradation step increases in the following order; 0 days (2), 63 days (2), 63 days (2b) and finally 63 days (2a). The observable changes in this degradation step suggest that the degradation mechanisms prevalent in each layer of aged EPR may be a consequence of the changes in its underlying chemistry. Further differences in degradation mechanisms are illustrated by the shape and the peaks of the derivative mass loss traces for EPR. Two peaks are observed for 63 days (2b), whereas one sharp peak is present for 0 days (2), 63 days (2), 63 days (2a) layers in their respective DTG curves. This suggests a two-step degradation pathway in 2b, while a single step pathway is prevalent in 2 and 2a. However, the degradation onset temperature (at around 280 °C) remains fairly unchanged for aged and unaged samples, which exhibits the excellent low-temperature thermal stability of the polymer. This type of thermal degradation behavior is typically observed in silane- and peroxide-cured EPR [18]. The bond energy of an Si-O-Si linkage is around 779 kJ/mol, which is higher than that of the C-C single bond (628 kJ/mol), which results in higher stability of EPR against thermo-oxidative degradation. Moreover, silane crosslinking inhibits chain fragmentation by scission, which is a major contributing process involved in EPR thermal degradation.

Further information about the degradation mechanisms may be gathered from evolved gas MS data obtained during the TGA process. Figure 5.8 is a representative plot of the QMID (quasi multiple ion detection) curves of the most pertinent evolved gas species in the degradation process in EPR and CPE shown alongside the corresponding DTG traces. The largest peaks in MS data typically represent the most predominant molecules evolved during the degradation process. For both EPR and CPE (0 and 63 days aged), two molecules, water (H<sub>2</sub>O) at 18 m/z and carbon-dioxide (CO<sub>2</sub>) at 44 m/z, have the most prevalent peaks. Both are common by-products of hydrocarbon combustion reactions, and are seen to peak during most of the main degradation steps. These are the primary thermo-oxidative degradation products for all the layers of EPR and CPE as seen in Figure 5.8 (a) through (f).

#### 5.4.3.2 Evaluation of thermal degradation mechanisms

TGA/MS is a powerful tool to gain insight into the chemical composition of elastomeric rubbers, and their key thermal degradation pathways. Based on the results described in Sections 5.4.2 and 5.4.3.1 important inferences can be made about the impact of the thermal aging process on the degradation of the jacket and insulation compounds.

The results show that thermal degradation in both EPR and CPE is a very complex multistep process taking place over a wide range of temperatures. Degradation by dehydrochlorination mechanisms have been observed to occur as the first degradation step in CPE polymers of varying crystallinity between 180 and 400 °C [19] [20] [21]. The chlorine content of CPE is the main factor that contributes to the nature of the dehydrochlorination step. Unaged CPE loses about 20.1% of its mass during the first degradation step (260 to 380 °C), which provides an estimate of the chlorine content present in the polymer by weight. For CPE aged 63 days, the mass loss occurring in this step decreases to 13.8%. The near 6 wt. % decrease in Cl content in CPE may be attributed to two factors, i) migration of Cl from CPE into EPR (as shown by EDS analysis in Section 5.4.2) and ii) dehydrochlorination of CPE during the thermal aging process. Typically in CPE, the higher the chlorine content in the sample, the faster is the rate of dehydrochlorination [22]. The steeper slope of the dehydrochlorination step in unaged CPE as compared to aged CPE shows that dehydrochlorination occurs at a faster rate, and further verifies the loss of chlorine from the CPE compound during thermal aging. On examining the QMID curves of the evolved gases during this degradation step between 200 and 400 °C for unaged CPE, it is observed that only trace amounts of hydrogen chloride (HCl) are evolved in this temperature range. Additionally, between 550 and 600 °C, a small spike in intensity of HCl is observed. The low rate of HCl gas evolution is a consequence of the combined effect of several additives that are incorporated in the CPE compound. While the inclusion of  $CaCO_3$  is observed to retard the beginning of HCl evolution, the effect of Sb<sub>2</sub>O<sub>3</sub> is similar to that of other metal salts included in PVC and CPE, wherein the inclusion reacts with the evolved HCl to form a metal chloride [23] [24]. The metal chlorides may be left behind as ash following complete decomposition of the polymer. No HCl peaks were observed in the MS spectra for aged CPE and EPR. Further studies are required to thoroughly explain the complex mechanisms involved in the dehydrochlorination step.

On the other hand, prior to combustion of the main polymer occurring between 400 and 490  $^{\circ}$ C, a small mass loss peak is observed in unaged and aged EPR (from 300 to 400  $^{\circ}$ C), defining the first degradation step. The evolution of CO<sub>2</sub> and H<sub>2</sub>O along with this step may be explained as the degradation products of the combustion of small organic molecules within the polymer, including plasticizers, stabilizers and antioxidants. The main degradation step corresponding to polymer combustion (step 2) for both CPE and EPR occurs in the 400 to 490  $^{\circ}$ C temperature range. The DTG peak in this region is accompanied by peaks in CO<sub>2</sub> and H<sub>2</sub>O, which, as mentioned before, correspond to the two most common hydrocarbon combustion products. This step remains fairly unchanged on thermal aging for both CPE and EPR.

The third major degradation step in both CPE and EPR occurs between 490 and 550  $^\circ\mathrm{C}.$ Primarily only  $CO_2$  is synthesized during this reaction step, from which it can be inferred that the primary decomposing material in this temperature range, is carbon. In CPE, the carbon content is likely due to the presence of carbon black reinforcing filler in the compound which undergoes combustion after the polymer matrix degradation is complete. In unaged EPR, the mass loss in this degradation step is fairly small ( $\sim 5\%$ ), and the degradation step is shaped more like a small shoulder to the preceding step. This is a common feature of thermal degradation in silane- and peroxide-cured EPR, in which highly crosslinked and cyclized networks are formed that degrade at a slightly higher temperature than the bulk polymer [18] [25]. However, this quantity increases to about  $\sim 10\%$  when aged for up to 63 days. Moreover, in interaction layers 2b and 2a, mass losses of around 10% and 15% are recorded, respectively. One possible explanation for this increase is higher interchain cross-linking as a consequence of increased polarity introduced in EPR on the migration of Cl from the jacket. Another possible explanation for the increase in the wt. % of the carbon component contributing to the mass loss in this step is that some of the carbon black present in the form of colloidal particles in the jacket has moved into the insulation through the complex cross-contamination processes that take place during thermal aging. Carbon black combustion is typically observed in the temperature range of 450 to 600  $^{\circ}$ C depending on the surface area of the particles included [26] [27]. Particles having higher surface area (i.e., smaller particles) undergo combustion at lower temperatures. The blackening of EPR in the interaction region with the CPE jacket (Figures 5.2 and 5.3), also points towards the possible migration of carbon black from the jacket to the insulation by physical or chemical processes. A combination of increased cross-linking and carbon black migration may also be a possibility. Further thermogravimetric studies performed on both materials, first in an inert environment and then an oxidative environment will be required for a quantitative assessment of carbon black content in the individual layers.

## 5.5 Conclusion

Through this work it is shown that cross-contamination processes on thermal aging are prevalent in EPR/CPE cables in which the two layers are in direct contact. The thermal aging processes in a jacketed EPR/CPE medium voltage cable were evaluated by optical microscopy, SEM/EDS and thermogravimetric analysis. The formation and growth of two intermediate interaction layers within EPR at the EPR-CPE interface was observed as a function of accelerated thermal aging at 140 °C. The rate of growth of the thickness of the two interaction layers in EPR decreased with increasing aging time. By SEM/EDS analysis, two elemental species, Chlorine (Cl) and Antimony (Sb) were identified to migrate from the CPE jacket into the EPR insulation. While Cl was found to be present in both interaction layers, 2a and 2b, Sb was identified only in 2b (the layer farther away from the EPR-CPE interface). The complex thermal degradation characteristics of EPR and CPE were evaluated. While CPE showed lower thermal stability than EPR, cross-contamination processes occurring between the two polymers on thermal aging resulted in observable changes in the high-temperature thermal degradation characteristics of EPR. Based on this study, it is apparent that observable chemical interactions take place between the CPE jacket and the EPR insulation during accelerated thermal aging. Changes in EPR composition as a result of interaction with CPE may play a crucial role in its insulating performance. Further studies are required to understand the mechanistic pathways of degradation and the resulting effects on macroscopic properties of EPR.

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Figure 5.8 QMID Curves for relevant evolved gases along with DTG curves of (a) 0 days and (b) 63 days aged CPE.

## CHAPTER 6. MEASURING DISSIPATION FACTOR OF THERMALLY AGED EPR/CPE JACKETED CABLES USING INTERDIGITAL CAPACITIVE SENSORS

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## 6.1 Abstract

Thermal degradation of cable insulation and jacket layers on exposure to elevated temperatures in nuclear power plants (NPPs) leads to poor cable performance and ultimate failure. In order to make accurate predictions of cable lifetime while in service, effective non-destructive measurements of cable health are essential. In this work, changes in dissipation factor (D) as a function of thermal aging in a jacketed cable are investigated using an interdigital capacitive (IDC) sensor. A single core non-shielded medium voltage power cable with ethylene propylene rubber (EPR)-based insulation and chlorinated polyethylene (CPE)-based jacket was chosen for this study. The cable was thermally aged at 140 °C in an air-circulating oven for seven time periods between 0 and 35 days. Broadband dielectric spectroscopy measurements were performed in the frequency range 1 kHz to 1 MHz an IDC with copper electrodes printed on a flexible substrate and connected to a precision LCR meter. Measurements of indenter modulus were performed on the cable jacket to evaluate mechanical property changes as a function of thermal aging. These were compared with changes in dissipation factor. Similar increasing trends were observed for measured changes in indenter modulus and dissipation factor as a function of aging time. Capacitive measurement of D using an IDC shows promise, therefore, as a non-destructive indicator of electrical performance of thermally aged cables.

## 6.2 Introduction

A typical low- or medium-voltage cable employed in nuclear power plants (NPPs) includes a central conductor formed by strands of copper or aluminum, which is covered by a polymeric electrical insulator and an external protective jacket layer. Shielding layers are also applied between the three components of the cable [1]. During service in NPPs, cables suffer from degradation due to various environmental conditions such as heat, ionizing radiation, and elevated humidity [2]. Cable jacket and insulation degradation has been identified as one of the primary factors that may limit cable operation beyond their initial design life [3]. Over extended operating periods, the polymeric insulation and jacket materials may ultimately fail, no longer properly insulating the cable, which and may lead to several problems including current-arcing, short circuits, and associated loss and fires [4]. In this context, there is a pressing need to assess cable insulation integrity, especially for the purpose of monitoring cable lifetime during service in the NPP.

A direct measure that quantifies the capability of an insulator to perform its intended electrical function is the dielectric breakdown strength [5] [6]. The technique is, however, destructive, making it unsuitable for condition monitoring (CM) applications. Alternative nondestructive testing (NDT) techniques are required for a simple and quick evaluation of the cable performance during operation. Numerous NDT techniques including radiography, ultrasonics, and eddy current measurements, have been developed and applied to characterize the structural integrity and performance of a broad range of materials.

However, cable insulation polymers do not always respond well to some types of interrogation, such as those using electrical currents [7]. A technique with the potential to address the limitations in investigating cable insulation and jacket materials is the use of a capacitive sensor [8] [9] [10] [11]. Cable insulation polymers are most typically low permittivity dielectrics whose electrical



Figure 6.1 A schematic representation of a fringing electric field of an IDC on a cable jacket [12]

properties are sensitive to temperature changes. Therefore, the cable performance may be interpreted from low-voltage capacitance measurements of the insulation and jacket layers. Further, the technique is fairly quick and cost effective, making it potentially suitable for long-term cable monitoring. Additionally, capacitive sensors may be designed in various shapes and configurations to suit measurement requirements.

The simplest configuration of a capacitor is the parallel-plate capacitor, which requires electrodes on either side of the flat sample being evaluated. Such an electrode configuration is not suited for inspecting cylindrical cables. On the other hand, A single-sided capacitive sensing element, wherein both electrodes are positioned side-by-side, would find practical use in cable testing to investigate the available portion of the cable surface. In the region between the two electrodes of opposing polarity, a fringing electric field is generated as shown in 6.1. A single-sided capacitor constructed by the periodic arrangement of several electrodes of opposite polarity is commonly called an interdigital capacitive sensor (IDC). Such an arrangement of electrodes boosts signal strength for better measurements. An arbitrary yet important measure of electric field strength at the subsurface of the material being investigated is the penetration depth, which can be tuned by changing the separation between adjacent electrodes (Chen and Bowler, 2013). In this study, an interdigital sensor was employed to examine cable jacket degradation as a function of accelerated thermal aging to evaluate the potential of IDCs for condition monitoring applications. A single-core, medium voltage cable with an ethylene propylene rubber insulation and a chlorinated polyethylene jacket was thermally aged at 140 °C for up to 35 days. Capacitive measurements were conducted on both the insulator and the jacket. Further, the changes in the measured dissipation factor of the jacket as a function of aging time were compared and contrasted with corresponding changes in indenter modulus.

#### 6.3 Materials and Methods

## 6.3.1 Materials

A single-core, non-shielded 2.4 kV power cable supplied by The Okonite Company with the trade name Okoguard<sup>®</sup>-Okolon<sup>®</sup> TS-CPE Type MV-90 and an outer diameter of 22.4 mm was chosen for this study. In this cable configuration, the conductor diameter is approximately 9.2 mm and is formed by annealed, compact stranded copper. The approximate thickness of the non-bonded CPE-based jacket (Okolon<sup>®</sup> TS-CPE) is 2 mm and that of the EPR-based insulation (Okoguard<sup>®</sup>) layer is 3.5 mm. From here on in this article, 'CPE' and 'EPR' will be used to refer to the Okolon<sup>®</sup> TS-CPE and Okoguard<sup>®</sup> formulations described above, respectively. The cable also incorporates a layer of semiconducting EPR (SC EPR) reinforced with carbon black lining the interface between the EPR insulation and the copper conductor, which has an approximate thickness 0.5 mm.

#### 6.3.2 Accelerated aging and sample preparation

The cable was cut into ten sections, each about 200 mm in length. To induce thermal degradation representative of long-term thermo-oxidative aging that the cable may experience in service, isothermal accelerated aging was performed by placing the cable sections in a ThermoFisher Scientific Heratherm<sup>TM</sup> Advanced Protocol OGH-180 mechanical air circulating oven. The ends of the cable sections were sealed with aluminum foil held in place by rubber O-rings and these samples were aged isothermally aged in the oven at 140 °C for up to 35 days. A sample was removed from



Figure 6.2 EPR/CPE cable samples aged 0 to 35 days at 140 °C after post-aging removal of the jacket from one half of each sample.

the oven every seven days, resulting in a sample set comprising 6 samples aged 0, 7, 14, 21, 28, and 35 days.

After aging, two shallow incisions were made on each sample using a sharp razor blade. The first was made around the circumference at the halfway point of the cable ( $\sim 100 \text{ mm}$ ) and the second along the length of half of the cable from the end to the halfway point. Placing the blade along the longitudinal incision, the jacket on half the cable sample was carefully peeled off to expose the underlying insulation. The resulting samples are shown in Figure 6.2.

## 6.3.3 Methods

## 6.3.3.1 Dielectric Spectroscopy (DS)

Broadband dissipation factor (D) was measured for the CPE jacket and the exposed EPR insulation independently using an intrdigital capacitive electrode printed by American Standard Circuits, Inc. The electrode was etched from a 17.8  $\mu$ m thick bare copper cladding deposited on a low dielectric loss and low moisture adsorbent polymer substrate of 0.2 mm thickness to form a flat and flexible sensor (Figure 6.3). The width (w) of each digit (or finger) is 0.1 mm, the

95



Figure 6.3 Interdigital Capacitive Electrode (n = 9, w = 0.1 mm, g = 0.1 mm, L = 38.1 mm) used for broadband dielectric spectroscopy measurements on EPR/CPE cable.

separation (or gap, g) between each digit is 0.1 mm to ensure good penetration of the electric field during testing, the overlapping length (L) of each digit is 38.1 mm and the total number of digits (n) is nine. Agilent<sup>®</sup> E4980A Precision LCR Meter with a two-point probe fixture was used to perform DS measurements. The IDC was wrapped around the surface of the cable and taped onto the sample to minimize air gaps such that the digits of the IDC were entirely in contact with the cable surface and the two contact pads of the IDC were exposed. The two-point probe was placed on the contact pads of the IDC to make dielectric spectroscopy measurements on the cable. A frequency sweep from 1 kHz to 1 MHz was made, and dissipation factor was measured across the entire range. Dissipation factor was reported as the average of three measurements, each taken at a different location on the material being tested (CPE or EPR).

Complex capacitance  $(C^*)$  was measured for EPR and CPE, in which C is the real part and D is the imaginary part given by the equation,

$$C^* = C(1 - jD) \tag{6.1}$$

where, C and D are functions of the applied frequency, f. While C quantifies the storage modulus of the dielectric, D is a measure of the loss modulus of the dielectric. For a parallel plate capacitor, D is expressed as the ratio of the imaginary permittivity to the real permittivity of the dielectric. Consequently, it is a combined measure of both the dissipating and storage capabilities of the dielectric.

#### 6.3.3.2 Indenter Modulus (IM)

Indenter Modulus measurements were carried out on the jacketed portion of the thermally aged EPR/CPE cable segments using an Ogden Environmental & Energy Services Indenter Polymer Aging Monitor 2 (IPAM2). The maximum applied probe force was 9 N, while the maximum probe speed was 5 mm/s. Measurements were made at five equidistant points along the length of the jacketed cable by using a probe to press against the surface of the sample. The indenter modulus of the sample is reported as the average of the five measured values.

## 6.4 Results and Discussion

## 6.4.1 Measured dissipation factor (D)

## 6.4.1.1 Chlorinated Polyethylene (CPE)

Dissipation factor is a quantity that represents the ratio of the electrically lossy behavior of a polymer to its electrical energy storage behavior. An increase in its value indicates an increase in the mechanisms that contribute to loss of electrical energy within the material. Figure 6.4 is a plot of the frequency dependence of CPE dissipation factor as measured by an IDC for cables aged 0 to 35 days at 140 °C. Several features of this plot provide valuable insight into the changes in the dielectric response of CPE as a function of aging time and frequency. Unaged (0 days) CPE shows a very slight increase in dissipation factor from around 0.035 at 1 kHz to 0.052 at 1 MHz frequency. A similar frequency dependence is observed for samples aged 7 and 14 days for which dissipation factor shows little to no increase as a function of frequency. This dielectric response of CPE in the applied frequency range changes significantly for the samples aged 21, 28 and 35 days. Between 1 - 100 kHz, the latter portion of a relaxation peak occurring at lower frequencies can be observed for the samples aged from 21 to 35 days. The polarization mechanism contribution in this frequency range may be attributed to the local movements of C – Cl dipoles of the vinyl chloride groups present in CPE, which are known to undergo a  $\beta$  relaxation process [13] [14].


Figure 6.4 Dissipation factor (D) of the CPE jacket of cables aged from 0 to 35 days in seven-day increments, at 140 °C measured as a function of frequency from 1 kHz to 1 MHz by an IDC.

Another view of the change in CPE dissipation factor as a function of aging time at a chosen frequency of 10 kHz may be obtained from Figure 6.5. A monotonic increase in CPE is observed as a function of aging time. The increase in D is initially gradual, up to 21 days of aging, after which a rapid rise in D is observed up to 35 days. The enhancement of the dipole orientation relaxation process in the 1 to 100 kHz frequency range as a function of aging time may be explained by the loss of the included plasticizer on thermal degradation [15]. Prior to compounding, CPE is a high glass transition polymer with a strong polarity caused by the dipole moment (~1.5 debye) of the C-Cl bond, which leads to strong dipole interactions between the polymer chains. During compounding, when a thermodynamically soluble polar plasticizer is incorporated into the polymer, the dipole attraction is significantly reduced, and CPE behaves more like a rubbery polymer [16]. At low aging times, the plasticizer is present within the rubber and the dipole interactions are suppressed. However, over time, on thermal aging at elevated temperatures, the increasing loss of plasticizer by diffusion or evaporation allows for strong dipole-dipole interactions between the



Figure 6.5 Dissipation factor (D) of CPE measured at 10 kHz and plotted as a function of aging time.

polymer chains, which can be measured as changes in dissipation factor. Moreover, another key inclusion that has been identified to influence the electrical properties of rubbers on thermal aging, is carbon black (CB) [17] [18]. An increase in CPE conductivity on thermal aging has been observed when reinforced with even low carbon black loading (< 20 phr). This is primarily attributed to the aggregation of CB particles during the thermal degradation process, leading to the creation of a conducting pathway within the polymer compound. Conduction mechanisms within a polymer are a major cause for loss of electrical energy, therefore resulting in an increase in its measured dissipation factor.

### 6.4.1.2 Ethylene Propylene Rubber (EPR)

To understand the macroscopic changes in electrical properties of the underlying EPR insulation, direct measurements of EPR dissipation factor using an IDC were made on the portion of the cable from which the CPE jacket was stripped off after aging, Figure 6.2. The measured values of Das a function of applied AC frequency for cables aged 0 to 35 days are presented in Figure 6.6. Irregularities in the measured values of D below 2 kHz for all data sets is an artefact of the D values



Figure 6.6 Dissipation factor (D) measured on the EPR insulation of cables aged 0 to 35 days at 140 °C measured as a function of frequency from 1 kHz to 1 MHz by an IDC.

being close to the lower limit of the measurable range of the LCR meter, and do not represent the dielectric response of EPR. In the discussion of EPR dissipation factor below, only the measured values between 2 kHz and 1 MHz are considered. Unaged EPR is observed to have a dissipation factor ranging from 0.006 at 20 kHz to 0.009 at 1 MHz. Across all aging times from 0 to 28 days, EPR dissipation factor is observed to remain fairly frequency independent between 20 kHz and 200 kHz. In the 200 kHz to 1 MHz range, a very slight increase in dissipation factor is observed, which may represent the start of a relaxation peak occurring at higher frequencies beyond the tested range. The sample aged 35 days deviates slightly from this trend between 2 kHz and 100 kHz, where D decreases from around 0.04 to 0.02. This feature may be the latter part of a very broad relaxation occurring in EPR.

The dependence of dissipation factor (measured at 10 kHz) on aging time for EPR is displayed in Figure 6.7. Initially, between 0 and 7 days, there is an increase in EPR dissipation factor from 0.006 to 0.013. From 7 to 28 days, dissipation factor is fairly constant, ranging between 0.012 and 0.013. Finally, at 35 days, dissipation factor increases to around 0.03. The large uncertainty in the measurement of D for EPR aged 28 days is primarily due to improper contact between the IDC and the sample because of surface irregularities caused by imperfect removal of the CPE jacket. The change in dissipation factor of EPR from 0 to 35 days is around one order of magnitude. This kind of increase is not typically seen in EPR insulation of similar formulation. Parallel plate capacitor measurements on Okoguard<sup>®</sup> EPR extruded flat mats aged from 0 to 70 days at 140 °C have shown that D changes from around 0.003 (at 0 days) to 0.004 (at 70 days) [13]. When aged independently, EPR exhibits excellent thermal stability and electrical insulating performance. However, when aged in the presence of CPE, EPR undergoes significant changes in morphology and chemistry which result in poorer thermal and electrical properties. A detailed study of the microscopic compositional changes and thermal degradation mechanisms of the EPR/CPE cables tested in this study are presented in Chapter 5. Based on this evaluation, the major contributor to chemical changes in EPR was identified to be the migration of chlorine and carbon black from the CPE jacket into the EPR insulation. Although present in fairly small quantities, chlorine

introduces polarity to the EPR compound while carbon black may also contribute to changes in electrical behavior [19] [20] [18].

#### 6.4.2 Comparison of dissipation factor and indenter modulus

Dissipation factor provides a direct measure of the electrical condition of a given material. This is particularly useful when investigating thermal degradation in power cables, because direct inferences of the condition of the cable can be made non-destructively. During online condition monitoring of jacketed cables, the insulation is hidden and direct measurements can only be made on the external jacket. To examine the performance of dissipation factor measured by an IDC, in tracking changes in the cable as a function of aging, a comparative assessment was made with a commonly employed condition monitoring technique, Indenter Modulus (IM) measurements. Figure 6.8 shows the dissipation factor (D) at 10 kHz as measured by an IDC and the Indenter Modulus (IM) for the CPE jacket of cables aged from 0 to 35 days at 140 °C. Both D and IM increase mono-



Figure 6.7 Dissipation factor (D) of EPR measured at 10 kHz and plotted as a function of aging time.

tonically with number of days aging. The increase in indenter modulus indicates significant loss of elasticity and increase in embrittlement of CPE. This is expected, as a consequence of dehydrochlorination pathways of thermal degradation, the loss of plasticizer and the increase in crystallinity of CPE on thermal aging. The increase in D indicates that the CPE jacket is becoming more lossy with increasing aging time. Further, this increase in D by almost two orders of magnitude, as aging time increases from 0 to 35 days, makes it a highly sensitive measure of the degradation condition of the jacket. Such a scale allows for the designation of a distinct threshold value of measured D above which the cable can be regarded as having reached the end of its useful life, which is of tremendous potential in non-destructive condition monitoring of NPP cables.

## 6.5 Conclusion

The dissipation factor of a jacketed EPR/CPE cable was measured using an interdigital capacitive electrode (IDC) to evaluate the changes in electrical properties as a consequence of accelerated thermal aging. The cable was aged at 140 °C for 0, 7, 14, 21, 28 and 35 days. The jacket was stripped from half of the sample, for each aging time point, in order to evaluate the changes in



Figure 6.8 Dissipation factor (D) measured at 10 kHz using an IDC and Indenter Modulus (IM) of the CPE jacket of cables aged 0 to 35 days at 140 °C.

dissipation factor of the underlying EPR insulation. Dissipation factor measured at 10 kHz was found to increase by nearly two orders of magnitude for CPE, and by a little less than an order of magnitude for EPR on thermal aging from 0 to 35 days. The dissipation factor measured on CPE was compared with its indenter modulus. Both parameters showed a significant increase with aging time. Capacitive testing of cables using IDCs therefore shows promise for long-term cable monitoring applications.

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## CHAPTER 7. GENERAL CONCLUSION

As nuclear power plants (NPPs) work towards extending their operating life for another 20 to 40 years, cable aging management is an intrinsic requirement for continued safe and reliable operation. As cable failure reports in NPPs are on the rise, researchers are taking a closer look at the primary cause for cable failure; insulation degradation. Some of the most extensively employed insulators for power cables servicing NPPs are compound formulations of ethylene propylene rubber (EPR). The goal of this work was to identify the key indicators of thermal degradation in a commercially manufactured EPR insulation, based on accelerated aging studies to support online condition monitoring and lifetime prediction of EPR-insulated power cables installed in nuclear power plants (NPPs). In this concluding chapter, the major research outcomes are described in accordance with the original hypothesis and research objectives outlined in Chapter 1.

Cables installed in NPPs often operate under elevated temperatures consistently for several decades. Thermo-oxidative degeneration of the cable insulation in such operating environments alters its physical and chemical properties as well as its electrical insulating ability, which, in turn, contribute to loss of performance and ultimate failure of the cable. In Chapter 1 it was hypothesized that similar long-term aging effects can be realized under accelerated aging conditions. Accelerated aging of EPR was achieved under isothermal conditions at several chosen temperatures. Time-temperature superposition studies conducted on the aged samples verified consistent degradation mechanisms across the chosen temperature range and predicted EPR lifetimes at NPP operating conditions as detailed in Chapter 2.

Next, the changes in the macroscopic thermal and electrical insulation characteristics were evaluated by several techniques. Thermogravimetric studies were conducted at various heating rates, and a kinetic model developed using isoconversional methods was put forth in Chapter 3 to describe thermal degradation in EPR and predict EPR lifetime under isothermal conditions. In Chapter 4 an in-depth investigation of changes in dielectric breakdown strength and real relative permittivity on thermal aging was explored, and a rate-dependent kinetic theory for defect-initiated dielectric breakdown was developed for EPR. The two models presented in chapters 3 and 4 were individually used to make predictions of EPR lifetime based on thermal degradation kinetics and electrical property changes and the results were compared and contrasted with measurements made on samples aged under accelerated conditions. The strong agreement between the predicted and measured values supports the hypothesis that models developed on the basis of tracking changes in thermal and electrical properties in EPR can effectively predict EPR thermal aging lifetime.

Isothermal accelerated aging and subsequent characterization of degradation-induced changes in composition and morphology of an EPR-insulated and CPE-jacketed power cable is described in Chapter 5. It was observed that the degradation characteristics of EPR were significantly altered on degradation alongside the CPE jacket. Migration of carbon black, Cl and Sb from the CPE to the EPR insulation was observed, resulting in observable changes in composition and degradation behavior of the insulation. The macroscopic effects of the interaction between the jacket and insulation were assessed in Chapter 6. Dissipation factor of the jacket and insulation was measured as a function of frequency using an interdigital capacitive electrode. It was observed that dissipation factor measured at 10 kHz was found to increase by a large amount for both CPE and EPR as a function of increasing aging time. Through the studies conducted and described in Chapters 3 to 6, it was shown that the changes in the underlying chemistry of the EPR insulation does cause a change in its macroscopic electrical, thermal and mechanical properties, which plays a significant role in determining the lifetime of the insulated cable.

#### 7.1 Proposed Directions for Future Work

 There are several stressors that a cable may be simultaneously exposed to during service in an NPP. Ionizing radiation, elevated humidity, and other operating stressors along with elevated temperature play an important role in determining cable lifetime. The models developed in this study are limited to thermally-induced failure modes. Further development of lifetime prediction models based on the other influential stressors is important to ensure an all-round assessment of cable lifetime. Simultaneous application of multiple models based on different failure modes may provide a dynamic approach to cable lifetime prediction, which will be extremely beneficial for the nuclear power industry.

- 2. Evaluation of the influence of a less thermally stable jacket on the degradation behavior of the insulation is another major consideration for successful estimation of cable lifetime. This study presents a qualitative assessment of the interactions observed between a CPE jacket and an EPR insulation layer protecting a medium voltage power cable. Further work investigating the underlying reaction mechanisms and activation energy of the process is required to develop a deeper understanding of degradation-induced insulation-jacket interactions.
- 3. Dielectric spectroscopy using interdigital capacitive electrodes shows promise as a potential method for online condition monitoring of power cables in NPPs. Subsequent studies on extracting the insulation permittivity based on finite elemental analysis of IDC measurements made on the cable jacket are required for further development of the technique.