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Electrical Properties of Different Polymeric Materials and their Applications: The Influence of Electric Field

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Abstract

In this chapter, a comprehensive study on the general structure of polymers, their properties and applications has been carried out. In particular, the application of polymers for insulating high-voltage (HV) equipment has been reported, together with the effect of electric field when they are subjected to HV stress. Experimental results related to the effect of partial discharge (PD) on polymeric insulations have been reported and discussed. Practical implications of the results have been discussed, and recommendations are made for future improvement. It is important to obtain new information regarding novel polymeric materials such as nano-polymers that can possibly outperform the currently used ones. It is also vital to investigate the right information for electrical equipment, i.e. by using the appropriate polymer as solid insulation, minimizing the presence of any metallic sharp object and any other conducting path during manufacture in order to avoid any type of internal or external PD.

Keywords: partial discharge, high-voltage, cross-linked polyethylene, polymeric insulation, electric field

1. Introduction

For the last many decades, tremendous increase in the usage of polymers and polymer-based materials can be seen for various applications. One of the important areas is the usage of polymers for electrical applications. Research studies have been focused on the development of polymers with low and high dielectric constant. Polymers having high dielectric constant can be used for applications such as film capacitors, artificial muscle, while the ones with

low dielectric constants are used in the field of capacitors and dielectric materials. Thus, it is important to study the dispersion and compatibility of these fillers with polymers since the inter-facial adhesion will reflect in their performance. This is achieved by studying the electric properties, such as the dielectric constant, loss factor and dissipation factor as functions of temperature and frequency. One major challenge is the preparation of a polymer having good adhesion to substrate, good thermal stability, high glass transition temperature and low moisture absorption suitable as a dielectric material for a high-voltage insulation system. Incorporation of voids into polymers will help to decrease the dielectric properties of polymers. Size and distribution of voids in polymers are very important in the performance of the polymers. Internal (void) and corona partial discharge (PD) are the most common defects that affect the polymeric insulations used for high-voltage insulation system. It is well known that discharge impacting at the void surface deposit conducting layers (e.g. oxalic acid and water) around the void boundary is due to chemical decomposition reactions of the polymer. These conducting charge carriers get trapped on the surface and may change the PD mechanism due to variations in the boundary conditions. In a void, streamer discharges prevail over the first hour of stressing and afterwards these normally change to Townsend discharges as a result of the change in resistivity of the surface due to sustained charge carriers.

This chapter analyses the electrical properties of different polymeric materials and their applications and in particular, investigates the properties of the most commonly used polymers for high-voltage applications. It is intended to present experimental results of the discharge development of voids in polymeric materials over a long high-voltage stressing periods—when the initial deterioration of the insulation material starts developing. The PD patterns and degradation over different void dimensions and arrangements will be reported in order to determine the pattern variations due to the electric field and their effect on the chemistry and composition of the material.

2. Polymer chemistry

A polymer is an organic compound with natural or synthetic preparation and has a high molecular weight due to repetitive structural units. Materials that are not conducting under normal conditions have the ability to store charge, known as dielectrics. The properties of dielectrics of a material in an electrical field are now a wide area of interest for the researchers of physics, chemistry, biology, materials science as well as for electrical engineering. Organic polymers are stable at high temperatures, have the ability to resist radiation, high mechanical, electrical stresses, chemical attacks from the extreme environments [1].

Polymeric materials have a low or high dielectric constant, and it is directly related to the permittivity, which is the ability of materials to polarize under the electrical field. It can be calculated by the permittivity of the dielectric to the permittivity of the vacuum. In a simple way, when the dielectric constant is more, polarization will be more in the electric field. Basically, the dielectric materials are made of inorganic compounds like mica and silicon dioxide. In the early 1960s, the polymers like aromatic [1, 2] and polyvinyl fluoride [2] are used as dielectric materials for capacitors. The presence of highly polarizable groups like aromatic rings, bromine and iodine will increase the dielectric constant of materials. In recent times, high dielectric materials (**Table 1**) and low dielectric materials (**Table 2**) are used for capacitors.

Materials	Dielectric permittivity
BaTiO ₃	1700
PMN-PT (65/35)	3640
PbNb ₂ O ₆	225
PLZT (7/60/40)	2590
SiO ₂	3.9
Al ₂ O ₃	9
Ta ₂ O ₅	22
TiO ₂	80
SrTiO ₃	2000
ZrO ₂	25
HfO ₂	25
HfSiO ₄	11
La ₂ O ₃	30
Y ₂ O ₃	15
α-LaAlO ₃	30
CaCu ₃ Ti ₄ O ₁₂	60,000
La _{1.8} Sr _{0.2} NiO ₄	100,000

Note: PMN-PT (65/35) for 65% lead magnesium niobate and 35% lead titanate. PLZT (7/60/40) for lead lanthanum zirconium titanate.

Table 1. High dielectric materials for capacitors [3].

Materials	Dielectric permittivity
Non-fluorinated aromatic polyimides	3.2–3.6
Fluorinated polyimide	2.6–2.8
Poly(phenyl quinoxaline)	2.8
Poly(arylene ether oxazole)	2.6–2.8
Polyquinoline	2.8
Silsesquioxane	2.8–3.0
Poly(norborene)	2.4
Perfluorocyclobutane polyether	2.4
Fluorinated poly(arylene ether)	2.7
Polynaphthalene	2.2
Poly(tetrafluoroethylene)	1.9
Polystyrene	2.6
Poly(vinylidene fluoride-co-hexafluoropropylene)	12
Poly(ether ketone ketone)	3.5

Table 2. Low dielectric materials for capacitors [3].

2.1. Aromatic dielectric materials

2.1.1. Polyimides

Aromatic polyimides have excellent dielectric properties and are very useful materials at high temperatures and voltage. These materials are chosen as inter-layer dielectrics in thin film microelectronics packaging because it is based on a mature technology and satisfy the requisite properties to maintain the mechanical stresses associated with microelectronic fabrication processes. These also include high thermal stability with glass transition temperature, $T_g > 300^\circ\text{C}$, low dielectric constant, easy processing and good chemical stability. Polyimides are a class of polymers, which are synthesized by using two monomers, a dianhydride and a diamine. The soluble polyamic acid (PAA) intermediates undergo a thermal imidization with the evolution of water to form the insoluble polyimide. The undesirable properties of polyimides, large amounts of moisture absorption and high dielectric constant are eliminated by developing a different polyimide. The polyimide properties can be improved by introducing silicone, a fluorinated flexible bridge monomer with the diamine, dianhydride monomers. The new developed method mingles the voids of air by making nano-foams in the film structure. It is necessary to avoid the voids because this factor is mainly responsible for lowering the dielectric constant of the polyimide-based material, and it is only possible when the dielectric constant is equal to 1.

The formation of polyimides is based upon the PAA [4, 5], and it is formed from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The aromatic polyimides, have a linear, symmetric dimide structure that provides itself a small effective dipole moment for the repeat units and contributes to its low dielectric constant. The polyimide has an ability to absorb moisture that will escalate the polyimide layers, which will significantly increase the dielectric constant.

The general process to reduce the dielectric constant of polyimides is the inclusion of organofluorine components, in the form of pendant perfluoroalkyl groups. The polyamic acid precursor for fluorinated polyimides is commonly based on hexafluorodianhydrideoxydianiline (HFDA-ODA). The inclusion of fluorinated monomers in the polyimide structure is responsible to reduce their moisture absorption and dielectric constant. These polyimides increased susceptibility to chemical attack, making their use in multilayer fabrication. These formulations are commercially available in the polyamic acid form from Amoco under the trade name Ultradel. A slight modification in the polyimide chemical structure was done by using hexafluorodianhydride-aminophenoxy-biphenyl (HFDA-APBP). It is a well-known alternative formulation of an acetylene-terminated polyimide backbone, and it may be used when the polarization of interlayer is an important parameter. The cross-linking between low molecular weight oligomers during the curing through the acetylene end groups resulting in a high temperature, high molecular weight dielectric. It is suggested during the curing, cross-linking of the acetylene groups occurred without evolution of water and achieved excellent planarization by using low molecular-weight oligomers and high solubility resultant oligomers in solvents such as *n*-methyl pyrrolidone (NMP). The polyimide poly(azomethine)s [6], polyimides [7], poly(amideimide)s [8] are soluble in organic solvents

(chloroform, N,N-dimethylacetamide) because they contain pendent pentadecyl chain and these imides are synthesized using 4-pentadecylbenzene-1,3-diamine (PBDA). It is reported that in pyridine and lithium chloride medium, poly(ester-imide)s were derived from 2,2-bis(4-trimellitimidophenoxy)biphenyl, 2,2-bis(4-trimellitimidophenoxy)-1,1-binaphthyl and aromatic dihydroxy compounds [9].

The nano-foam polyimides are synthesized, which have pores of size in nanometres [10] and prepared from thermally labile poly(propylene oxide) (PO) with thermally stable PMDA. The degradation products are diffused from the films when the produced foam is affected by thermolysis that pull out the pore size and shape from the initial polymer morphology. The dielectric constant of the polymer can be reduced by introducing air into the pores. The challenge of polymer scientists is to introduce the polyimides into thin film in a multilayer process. The polyimides are characterized using different sophisticated instruments such as infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction and thermogravimetric analysis (TGA).

2.1.2. Polynitriles

The nitrile polymer is composed of three monomers, namely acrylonitrile, butadiene and carboxylic acid. The properties of the polymer depend on the composition and attachment of monomers. The monomers are contributing individual ability to control the overall properties of the polymers. The presence of large occupying groups in the structure will increase the adhesion behaviour, stability and low dielectric constant. The presence of the monomer acrylonitrile and its polar nature will show reluctance to diffuse in many solvents, chemicals such as fats, hydrocarbon oils. The butadiene monomer improved flexibility, softness of the polymer and it is responsible for increasing elastic quality during vulcanization process with sulphur and accelerators. Polynitrile aromatics are prepared via palladium-catalyzed cyanation of aryl bromides with potassium hexacyanoferrate (II) [11] and plasma-polymerized 4-biphenylcarbonitrile (PPBPCN) thin films [12].

2.2. Silicon containing dielectric material

Silicones containing polymers are made up of the siloxane unit means alternating chain of silicon and oxygen atoms, combined with carbon and hydrogen. The materials have excellent heat resistant properties, and they are used as insulators, lubricants, adhesives and sealants in electrical, thermal, and pharmaceutical industries. The polymer properties in terms of resistance to oxidation can be modified by incorporating silicone compounds such as clays, silicates, silica, polyhydrogen silsesquioxanes (PHSSQ), and polymethylsilsesquioxane (PMSSQ) covalently bonded with the polymer matrix [13–15]. It was found out that solid polymer dielectrics have low thermal conductivity. So it is necessary to improve their conductivity without disturbing other electrical properties. So the studies suggested, introducing fillers that work as an insulator (silicon dioxide, SiO₂) increased the compatibility as well as adhesion behaviour of the polymer. Under electric stress, the polymers that contain silicon oxide or silicon carbide are more resistant to partial discharge, because the erosion depth reduced as compared to polymers without fillers [16–19].

2.3. Epoxy resins

Flexible thermosetting resins are known as polyepoxides and are formed by copolymerization of an epoxide with another compound having two hydroxyl groups. Epoxy resin was first discovered by Pierre Castan, a Swiss chemist in the year 1938. The epoxy resin can be used in different fields such as electrical, electronics, paints, coating, engineering and aerospace because it has excellent properties of chemical resistance, mechanical strength, electrical insulation as well as excellent bonding with various curing substances [20, 21].

Epoxy resins can be used to clean the switches and prevent shorts in a various circuits, transistors and printed circuit boards with the help of their insulation properties. The epoxy resins are used in sophisticated electronics to increase the thermal resistance, capability to self-extinguish in case of emergency and physical flexibility. Epoxy-resin systems are thermosets, so it may be used in rotating machines, ground wall of generator, insulators and transformers [17, 22–24]. At elevated temperatures, epoxy resins are cross-linked through the polymerization reaction. The higher glass transition temperatures and strength of the resin system after curing increased more at higher temperature than room temperature [25]. The epoxy-silica composite is most popular resin due to its different properties such as enhanced partial discharge resistance [26, 27], higher volume resistivity [28], lowered thermal expansion [27], improved electrical breakdown property [27, 29], reduced erosion depth [27, 30], enhanced mechanical properties [27] and improved thermal conductivity [31]. The long-term break down degradation process of epoxy resin is improved by increasing treeing time to breakdown and incorporating small amount of zinc oxide or aluminium oxide nanoparticles [32–34]. Under constant AC voltage (10 kV to 1 kHz), the resin breakdown time will be double after addition of small amount of organically modified layered silicates than the base resin at 20°C and it will be six times at 80°C. At 145°C, the composite had breakdown time more than 20,000 min and the base epoxy resin had breakdown time of 280 min [18].

The epoxy resins are cross-linked with carboxyl or anhydride groups to make excellent resistance property, and the product is very useful as a coating in industry. The outstanding physical and chemical properties can be achieved by combination of glycidyl ether functional bisphenol A resins and carboxyl terminated polyester [35] but glyceryl ester functional acrylic polymers used 1, 12 dodecanedioic acid as a cross linker for powder-coating system [36]. The epoxy group reacted with the carboxyl group without a catalyst but the reaction rate can increase in the presence of a catalyst.

3. Polymers used in high-voltage applications

Basically, polymeric materials can be found naturally or synthetically thanks to chemical processes conducted in laboratories. Paper, wood, wax, leather, cellulose and rubber are examples of natural polymers; while the phenol formaldehyde commonly known as Bakelite is a good example of a polymer synthesized in laboratory. In several applications, simple polymers with some additives can be used for power cables, transformers, insulators and rotating machines [37, 38]. In general, the polymer used in high-voltage applications can be divided into three

categories, according to their properties, such as thermal characteristics, physical and chemical structures, mechanical and electrical behaviours, among others (see **Table 3**) [37–40]:

1. Thermoplastic polymers are defined as plastics that soften and become supple on heating and solidify back on cooling [27]. The heating and cooling cycle within certain temperature limits can be applied to these materials several times without affecting their properties and without the need of any earlier chemical processing [41]. The synthetic thermoplastic polymers mostly used in insulation systems of electric machines and equipment are: polyethylene (PE), polyvinylchloride (PVC), polypropylene (PP) and polyamide (PA). Likewise, depending on their transition temperature characteristics, this type of polymers can be divided into two large classes: amorphous and crystalline [42].

Polyethylenes are the most common commodity polymers that have found applications in household items, packaging, electric insulations, medical applications, automotive applications, containers, etc. Polymerization of the ethylene monomer gives linear or branched polyethylene that is mainly thermoplastic in nature depending on the manufacturing conditions. These conventional thermoplastic polyethylene plastics can be subjected to cross-linking to become a thermoset polyethylene called cross-linked polyethylene (XLPE or XPE) with different or improved properties. Thus, XLPE is linear or branched polyethylene that has long chains inter-connected to form three-dimensional network structures that improved density, chemical resistance and reduced the flow of the polymer. The polyethylene (PE) is cross-linked by chemical processes (peroxide, silane) and radiation energy (electron beam). The main advantage of the radiation process to chemical processes is that there is no requirement of any other chemicals to be used with the original polymer compound.

2. Thermoset polymers are materials cured by heat or chemical reaction and become infusible and insoluble. This process, leading to the formation of a network structure, is also

Type	Material	Application
Thermoplastics	Polyethylene (PE)	Cables
	Polyvinylchloride (PVC), polypropylene (PP), polyamide (PA)	Transformers
Thermosets	Epoxy impregnant:	Rotating machines
	Polyester-resin	
	Phenol-resin	
	Silicon-resin	
Elastomers	Epoxy resins	Polymer insulators
	Silicone	
	Ethylene propylene rubber (EPR)	
	Ethylene propylene diene monomer (EPDM)	

Table 3. Types of polymeric insulation.

known as setting of the polymer [43]. The main characteristic of these materials is that they have a permanent irreversible polymerization, this occurs, because they have a cross-linked molecular structure and are formed in two polymerization stages. The first stage is formation of a polymer with linear chains. The second stage is the final cross-linked structure [41–43]. The thermal, mechanical and electrical properties of the thermoset polymers may vary considerably depending on their application. After the cross-linking stage, the material does not soften on reheating; instead it becomes thermally more stable compared to thermoplastic materials. From a practical point of view, polyester-resin, phenol-resin, silicon-resin and epoxy resins (widely used in rotating machines) can be considered as examples of cross-linked polymer resins [27].

3. **Elastomer polymers** are flexible polymers that comprise a low cross-link density and generally have a low Young's modulus and high-failure strain compared to other materials. Among the main elastomers, polymers commonly used in electrical applications are silicone, ethylene propylene rubber (EPR) and ethylene propylene diene monomer (EPDM). The elastomers such as silicone, EPR and EPDM are major elemental materials for polymer insulators [37–40].

Thermoplastic, thermoset and elastomer polymers can be used for several types of ageing mechanisms when they are used as insulation systems of electrical assets and subjected to electrical field.

4. Ageing in polymer insulation systems

The ageing process present in the insulation systems of an electric machine or equipment can be defined as the irreversible changes of their intrinsic properties due to action by one or several degradation mechanisms or factors [44]. These mechanisms are imposed by the operation, environment or test that influences the performance of the insulation material. In this sense, the polymer materials used in the insulation systems can be subjected to various kinds of stresses, even, under normal operating conditions. According to the literature, these mechanisms or degradation factors can be classified as thermal, electrical, ambient and mechanical (see **Figure 1**) [45–47].

Over time, all these ageing mechanisms tend to degrade the material and taking it to the final loss of its insulating properties and therefore the total breakdown of the material. The ageing caused by only one mechanism is denoted as single factor. When there are several mechanisms, either simultaneously or sequentially applied, it is called as a multi-factor stress. Below, each of these degradation mechanisms that may influence the lifetime of a polymeric material is described [48–50].

1. *Electrical stress*: The presence of non-uniform fields in polymeric insulation is a necessary condition for dielectric ageing under normal voltage and over-voltage conditions. When high-voltage is applied space charge is formed inside of the dielectric material. The space charge distorts the electric field distribution in the insulation and even in inter-facial regions for the case of composite insulation systems. This phenomenon occurs due to the

Figure 1. Degradation mechanisms or factors.

presence of air and other gases in the form of vacuoles within the polymeric material. All these factors facilitate the presence of a series of chemical changes thanks to an electronic and ionic bombardment of high energy that breaks chemical bonds and erodes isolation when subjected to continuous electrical stresses [38, 40].

2. *Thermal stress:* Can be considered another important stress factor in polymer insulation systems, since the increased temperature and heat cycles accelerate most of their degradation processes such as oxidation, hydrolysis, chemical attack and mechanical creep. Hot spots may arise due to ohmic losses in conductors, these tend to dissipate through the surrounding insulation. Finally, as a result of the thermal stress, the material can be degraded until it significantly lose its mechanical properties [38, 47].
3. *Environmental stress:* Can be identified as one the main reasons of failure in polymeric insulations. Among the main factors of environmental stress, the authors would like to highlight: sunlight, gamma ray and X-ray radiation, salt and dust contamination, acid rainfall, and even pressure. Thanks to these factors, many polymers commonly used as insulation on different equipment and electric machines begin to accelerate their ageing processes due to the occurrence of phenomena such as tracking, treeing, cracking, decomposition, pitting, dry-band arcing, erosion or oxidation, among others [48].
4. *Mechanical stress:* For most of the electrical equipment, mainly electric machines, the mechanical stress can appear in the form of compression, tension, bending, vibration and impact. All these factors act directly on the insulation, leading in many cases to fissures in the bulk of the material or at interfaces between materials of the insulation system.

Consequently, the insulation system begins to weaken product of these new spaces of lower dielectric strength, leading the insulation to failure. Likewise, other mechanisms of ageing can start acting simultaneously [49].

All above types of stresses can activate a typical and dangerous mechanism that can degrade the polymeric insulation material that is partial breakdown discharges.

5. Partial discharges: description and physical fundamentals

As mentioned in the previous sections, polymeric insulation systems associated with electrical machines and insulated wires may suffer unexpected failures associated with continuous stresses such as mechanical, thermal, electrical and environmental ones [44–46]. These stresses, after a while, tend to age and degrade the insulation system, leading to the permanent loss of their insulating properties and therefore to a possible breakdown.

In the pre-failure stage, it is possible to detect ionization processes of low energy, i.e. in small vacuoles trapped within the material or on the surface of a contaminated dielectric, wherein highly divergent electric fields are present. These processes are so-called partial discharges (PD) and can be considered as an important indicator of the overall condition of the insulation system [50, 51].

A partial discharge is a phenomenon of dielectric breakdown (low energy), limited to a region of the insulating medium between two conductors that are under different potentials [52]. The discharge location is due to an increase of electric field in a region that is relatively small compared to the overall dimensions of the insulating medium, or by the presence of a medium of lower dielectric strength in the insulation system. In some cases, both circumstances may occur simultaneously. This region must be completely or partially in the gaseous phase and may correspond, for example, to solid insulation occlusions, bubbles formed by vaporization of a liquid or gases surrounding conductive tips with small bending radius. Therefore, gases such as air, H_2 , O_2 , CO_2 , etc. can be considered as enabling environments where PD may be originated [52].

According to the above, it can be considered that the partial discharge phenomenon is based on disruption processes of a gaseous dielectric, whose theories are much consolidated [53, 54]. From its study, it can be concluded that there is PD activity in an insulation system if there are two conditions happening simultaneously:

1. Presence of a sufficiently high-electric field: necessary to ensure an electrical breakdown in the area with lower dielectric strength or volume portion containing the gas. This condition also strongly depends on the pressure at which the gas is subjected, defined by the Panchen's Law [53, 54].
2. Free electrons available: necessary to ionize other neutral molecules with its acceleration in order to create new electron-ion positive pairs resulting in an avalanche process within the electric field.

In **Figure 2**, the applied voltage (U_a) to the whole insulation system and applied voltage in the area of greatest divergence of the electric field (U_c) and lower dielectric strength are represented. When the U_c voltage reaches the ignition voltage U_i^+ , also called as partial discharge inception voltage (PDIV) in the electrically weaker volume, a discharge occurs, and immediately, U_c voltage drops sharply to a value (U_e) called extinction voltage discharge (DEV), thereby forming a transient current. After discharge, the gas in the cavity is subjected to progressively increasing voltage that increases trying to follow it. The increased voltage causes another discharge when it again reaches the level of the ignition voltage U_i^+ [55].

This process is repeated continuously in the positive and negative half cycle, generating through the insulation a current pulse whose behaviour is classified as stochastic. This character of partial discharges lies in the nature of initiation and evolution of the discharge. As it is seen above, both processes are strongly determined by quantum or mechanical-statistical aspects (appearance of free electrons, kinetic energy of electrons in collisions, etc.), so that, PD measurement should always be considered the probabilistic nature of the phenomenon [56].

According to this behaviour, PD activity will produce displacement of short duration currents (0.1–10 ns) in the insulation. These current pulses can be measured by the suitable detection circuits and generally are acquired and displayed superimposed on the applied voltage in so-called phase-resolved partial discharge (PRPD) patterns [55, 57].

As it is mentioned above, PD measurement allows detection of defects in insulation systems generated by multiple ageing agents. Moreover, apart from being a result of other mechanisms of degradation, PD activity will be an additional ageing process itself, since they can

Figure 2. Partial discharges in a cavity subjected to alternating voltage.

continuously provoke [58]: (1) chemical attack generated by chemical reactions between oxygen, ozone and free radicals on the surface of the imperfection; (2) physical attack on the material due to electronic and ionic high-energy bombardment, which breaks chemical bonds and erodes the insulation system; (3) deterioration of imperfection surface caused by ultra violet (UV) radiation and (4) additional heating of the dielectric and power losses.

The combination of these ageing effects can accelerate the breakdown of the insulation system of any electrical asset (high-voltage cables, power transformers, rotating machines, etc.). Therefore, PD activity detection, tracking, identification of the source type, and its evolution over time are of great importance to establish the insulation condition of electrical equipment and to be able to apply an optimum maintenance.

5.1. Types of partial discharge

Basically, the PD phenomenon can be divided into three basic categories according to their origin: internal, surface and corona [59]. However, the vast experience developed in PD measurement in many types of high-voltage equipment allows detecting, with higher accuracy, other concrete defects. The PD type identification is important because not all PD sources are necessarily harmful to the electrical equipment, as will be seen later.

5.1.1. Internal PD

Internal PD may occur in vacuoles with low dielectric strength, encrusted foreign particles, metal bumps and internal cracks in the material or in the nearby border to one of the electrodes (see **Figure 4a**). The origin of such PD depends on the defect geometry, the ageing of the material due to the different stresses to which it may be subjected (mechanical, thermal and electrical), the electric stress strength in the cavities of the material due to difference between permittivity of the two media (insulation and imperfection), and free electrons from previously destroyed chemical bonds or by ionizing radiation [59].

The number of discharges per cycle is generally affected by the appearance of space charge in the bulk material, which explains that their appearance is highly probable for the phase in which the slope of the applied voltage is maximum (see **Figure 3**). In **Figure 4a**, it is shown the physical process of internal PD. It is observed that when the DIV is exceeded, it is probably that an ionization occurs in imperfection (depending on the presence of a free electron), causing the appearance of new charge carriers (electrons and ions) resulting from the breakdown of bonds of neutral gas molecules. Therefore, after a PD starts, the charges appearing distributed within the cavity depending on their polarity generating clusters of space charge on its walls. This space charge causes an induced electric field inside the insulation (E_q), which overlaps the electric field generated by the applied voltage (E_i). Initially, the induced field opposes the applied field, reducing the total applied field. However, in polymers subjected to alternating voltages, the applied electric field changes its direction in each cycle, which may cause the total field ($E_t = E_i + E_q$) at the instant of polarity change saw intensified, as the field induced by the accumulated charge can maintain its polarity until it returns to redistribute after another PD. This effect of the induced field can be mitigated by eliminating the space

Figure 3. PD produced in a cavity of a dielectric result of the superposition of the electric field induced by charge E_q and electric field applied by the alternating voltage E_i .

Figure 4. PD example with corresponding PRPD pattern (a) internal PD, (b) surface PD and (c) corona PD.

charge of the vacuole walls due to increased conductivity of the same or by a repetition rate of discharge too low [60, 61].

In general, the presence of internal PD sources can be considered as critical to the insulation system, because its activity is concentrated in smaller and weak points of the material. Besides, in the case of having a persistent activity they can erode the material surrounding the vacuole to completely destroy it. For these reasons, it is necessary to well identify their main electrical characteristics as the voltage ignition in polymer's cavities.

5.1.2. Surface PD

Surface PD occurs at the interfaces between dielectric materials or between the conductive element and the insulation when any type of contamination exists on the material surface (rain, snow, moisture, pollution, salinity, etc.). This is because the presence of tangential electric field components of large intensity can originate discharges that are extended beyond their origin point along the surface of the insulation in order to follow a path to the electrode with a lower potential. In practice these types of discharge are presented in cable terminals, coil heads rotary machines, contaminated insulators and bushings, among other sources. Various examples of configurations that give rise to this type of shock observed in **Figure 4b**. Although this type of discharges can be harmful, their detection could help to locate the source and mitigate its presence, for example, cleaning the contaminated surface or by applying a layer of silicone (hydrophobic material) insulator.

These types of partial discharges occur in phases with higher applied voltage and present, as internal PD, great variability in the detected magnitude (are events conditioned by the state of the insulating surfaces, which can changing), being more likely, discharges with lower magnitude, see **Figure 4b**.

5.1.3. Corona PD

As it is shown in **Figure 4c**, corona PD occur around a sharp conductive material or with a small radius of curvature subjected to a strong electric field within dielectric liquid or gas [59]. The inhomogeneity caused by high-electric field gradients make that in the vicinity of the tip will produce the ionization of the surrounding gas, and therefore, a local insulation breakdown in the area of high-electric field strength.

In volume material farthest from the sharp electrode, the electric field is reduced and ionization is extinguished. This phenomenon is typical in transmission lines, provoking in them energy losses, radiofrequency interferences, even audible, and degradation of polymeric insulator by the appearance of nitric acid [62]. In some cases, these discharges can be caused in loose threads in high-voltage connections, which are not an immediate threat for the electrical assets. Finally, if corona PD sources cause is detected, it can be easily removed.

In order to determine the electric-field effect on polymer insulation systems, next section shown experimental results for PD measurements in insulated underground cables.

6. Partial discharges in polymeric insulation: underground cables

Cross-linked polyethylene (XLPE) is commonly applied as the insulation material for high-voltage underground cables. XLPE possesses excellent dielectric properties and can withstand high-voltages up to 380 kV. As stated previously, one major PD defect in the HV insulation is the void. It is necessary to understand possible internal PD activity over time in order to ascertain whether different void PD patterns vary in uniqueness and characteristics. It is also important to understand different void degradation characteristics and how they affect the lifeline of the HV apparatus. Discharges in voids are known to have unpredictable behaviour [4]. Discharges and PD amplitude in a void can sometimes increase or decrease and in some cases even disappear. Discharges impacting at the void surface depositing conducting layers (e.g. oxalic acid and water) around the void boundary due to chemical decomposition reactions of the polymer. These conducting charge carriers get trapped in the surface and may change the PD mechanism due to variations in the boundary conditions. In a void, streamer discharges prevail over the first hour of stressing and afterwards these normally change to Townsend discharges as a result of the change in resistivity of the surface due to sustained charge carriers [5].

A number of research investigations have analysed PD activity within voids in polymeric insulation systems [5, 63, 64], but few have analysed voids in polyethylene-terephthalate (PET) insulations [4, 65]. PET is a thermoplastic polymer resin belonging to the polyester family. It has mechanical strength and an excellent moisture- and water-protective system. In this section, experimental results void developments in PET will be reported. Specifically, experimental results involving dielectric bounded an electrode-bounded cavity in PET over a 7-h stressing stage will be reported. This is important in order to understand the deterioration mechanism of PET over hours of degradation. In conducting the experiments and to ensure that the experimental set-up is discharge-free prior to the samples with voids being investigated, PET layers without any voids were primarily stressed to confirm discharge free environments for PET layers.

6.1. Dielectric bounded cavity

For the dielectric-bounded void, experiments were conducted using a set of samples containing dielectric-bounded void in PET. Up to nine PET layers are created for each experiment and the void is located within the centre of the PET layers (see **Figure 5**). The inception voltage was approximately 2.82 kV and all measurements were taken at approximately 3.6 kV. PD data was captured over 50 and 250 power cycles from the start up to 7 h continuous stressing.

Figure 6 shows typical ϕ - q - n (phase-amplitude-number) patterns for the dielectric-bounded void at 1 h and 7 h periods captured over 50 and 250 cycles, respectively. It can be observed that discharges are centred between 20° and 110° in the positive half cycle and between 150° and 270° in the negative half cycle. Also, it appears there is no significant maximum amplitude change between the 1 h and 7 h captures for both the 50 and 250 cycle captures in

Figure 5. Sample set-up showing a dielectric bounded void at the middle of the PET layers.

Figure 6. Series of φ - q - n plots for dielectric bounded void captured at (a) 1 h, 50 and 250 cycles, (b) 7 h, 50 and 250 cycles.

the dielectric-bounded void (see example **Figure 7a** and **b**). This indicates that the void is still at the initial degradation period and probably the insulated cable has enough lifetimes to be in service.

Figure 7. Electrode bounded void.

6.2. Electrode bounded void

Discharges from an electrode-bounded void are studied by placing a 10 mm diameter void layer to the top-most PET layer adjacent to the HV electrode (see **Figure 7**). This is to ensure that the void has an electrode surface at one side and PET surface on the opposite side. Similar to the dielectric-bounded void experiments, nine PET layers are used, including the one possessing the cavity. For all the experiments, a voltage of 3.6 kV is applied and ϕ - q - n patterns captured at 15-min intervals over a period of 7 h.

Examples of the ϕ - q - n patterns are shown in **Figure 8**. In comparison to dielectric-bounded voids considered in the previous section, asymmetry between the discharges in the positive and negative half cycles is visible in the electrode-bounded cavity consistent with the general literature [66]. Gulski's conclusions are based on a 20-min test but in this work discharge patterns are captured up to what appears to be initial stages of deterioration of the void (i.e. over a 7-h period). The asymmetry between the two half-power cycles can be explained as follows. Gulski [66] suggested that during the positive half-power cycle, the residual charge on the dielectric surface produces a high number of instigating electrons, while in the negative half-power cycle, the initiating electron may be released from the electrode surface itself or from background radiation.

7. Conclusion

This chapter presents a comprehensive study on the general structure of polymers, their properties and applications. Particular interest is on the application of polymers as insulating materials for high-voltage apparatus such as transformers, electrical machines and underground cables. The effect of electric field distribution on polymeric insulations subjected to partial discharges have been reported and analysed. Epoxy resin and XLPE polymers are the widely applied for high-voltage applications though it is necessary to estimate and understand their lifetime. Internal partial discharges in polymer voids can create a discontinuity of electric field in the insulation system and a continued activity can lead to total breakdown of the high-voltage insulation. Therefore, it is important to understand and obtain new information regarding novel polymeric materials such as nano-polymers that can possibly outperform currently used ones.

Figure 8. Series of φ - q - n plots for electrode bounded void captured at (a) 1 h and (b) 7 h.

For practitioners in the field, it is necessary to design correct information system for electrical equipment, i.e. by using the appropriate polymer for solid insulation, avoiding metallic sharp components and any other conducting path in order to prevent any type of external PD, such as surface and corona. Breakdowns of polymers and other kinds of insulation systems can be warned by measuring and identifying PD activity, mainly internal PD sources by using condition-monitoring techniques.

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