

HYDROPHOBICITY OF SILICONE RUBBER USED FOR OUTDOOR INSULATION (AN OVERVIEW)

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Abstract. Among the new insulating materials widely used in high voltage outdoor insulation systems, silicon rubber materials also called polymeric materials are very important; during last 20 years they have been applied for manufacturing outdoor insulators. These materials are organic in nature; therefore they are prone to decomposition under different environmental conditions; the most important among these conditions for consideration of w.r.t. of high voltage electrical insulation is the hydrophobicity.

Hydrophobicity is treated as the resistance to formation of conducting water tracks that increase leakage current, chances of flashover, and other deterioration effects. The superior contaminant performances of polymer outdoor insulating materials are regarded as the contribution of their hydrophobic surfaces. In other words, it is the formation of water beads on surface, which resist the flow of water in continuous conducting track.

Hydrophobicity theory, its importance for polymeric silicon rubber insulators, methods of hydrophobicity measurements - especially by leakage current, low molecular weight component chains responsible for hydrophobicity recovery, chemistry of hydrophobicity loss and recovery, hydrophobicity recovery related with temperature, humidity, UV radiation, corona, electric field and dry band arcing are overviewed in this paper.

1.WHAT IS HYDROPHOBICITY?

Hydrophobicity of any material is its resistance to flow of water on its surface. A material is highly hydrophobic if it resists to flowing water dropped on it and is least hydrophobic if dropped water flows in form of tracks on its surface. The hydrophobic surface is water repellent, in contrast with a hydrophilic surface that is easily wetted.

Hydrophobicity of a material can be described using the contact angle on the material surface (θ_c) that liquid drop makes when it comes into the contact with a solid surface; this angle is a measure of the surface wettability. The material which is easily wettable allows water to touch a large surface area and hence makes a contact angle of less than 90° ; hydrophobic material allows less water surface contact and thus makes a contact angle greater than 90° as shown in Fig. 1.

The contact angle gives information about surface energies, surface roughness, and surface heterogeneity. Contact angle is also a measure of the surface contamination. The surface hydrophobicity of insulation material is often quantitatively evaluated by the value of contact angle formed between water droplet and material surface, which is direct representation of the tension between interfaces of water and the material atoms [1]. The shape of the liquid droplet depends on the type of the solid material and physical and chemical state of its surface.

It is clear from Fig. 1 that the smaller is the contact angle, the more wettable is the surface and vice versa. Surfaces are assumed to be hydrophilic when the contact angle is less than 35° ; for contact angles greater than 90° , the surface is assumed to be hydrophobic and the surfaces char-

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acterized by the contact angles from 35° to 90° are partially wettable.

It should be also noted that the term “hydrophobicity” represents resistance to water, however, it is generally used to represent resistance to any liquid.

2. IMPORTANCE OF HYDROPHOBICITY FOR POLYMERIC INSULATORS

The most obvious drawback of hydrophobicity reduction in electrical insulators are an increase in surface leakage current activity and, as a result, the increased dryness of the surface. This fact is known as a major insulation performance factor for ceramic insulators, but for polymeric or non-ceramic insulators hydrophobicity loss or reduction causes other serious effects, which will be discussed below.

Hydrophobicity affects the polymeric silicon rubber materials/insulators in two ways. Firstly, the loss of hydrophobicity causes reduction in electrical insulation and pollution withstands performance. Secondly, it also prominently influences the aging process of SIR insulators [1]. For polymeric insulators operating in polluted condition, hydrophobicity can be determined by two types of measurements: static hydrophobicity measurement and dynamic hydrophobicity measurement.

Static hydrophobicity means hydrophobicity of raw material or hydrophobicity of material under normal constant magnitude of stresses. The dynamic hydrophobicity measurement involves monitoring of hydrophobicity transfer, loss, and recovery; mechanisms involved in parameters causing these factors are not clear up to now. Therefore, quantitative measures to improve the design, selection, and maintenance of operating Silicon Rubber insulators are not successful till now.

Many investigations are systematically attempting to study the actual hydrophobicity status of SIR insulators in various polluted areas [2,3]; all of them have the aim to provide guidance to power companies for the usage and maintenance of composite insulators in contaminated areas.

Results from various testing sites show that all insulators still preserve very good hydrophobicity properties even after ten years operation in some heavily polluted areas. It is interesting that a clear correlation exists between the deterioration of hydrophobicity and the local strengthening of electric field. Basing on some new findings in the field, detailed laboratory research on hydrophobicity

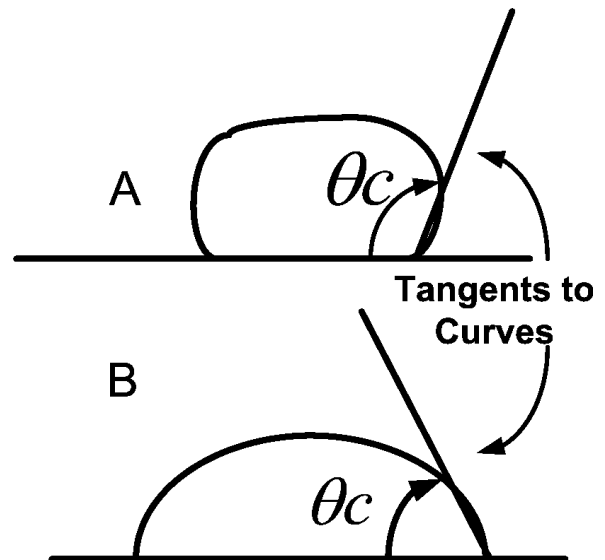


Fig. 1. The shape of a liquid Droplet on a (A) Hydrophobic surface and (B) Less Hydrophobic surface.

transfer, recovery, and loss properties have been conducted concurrently [4-7].

The aging test continuing in artificial, normal outdoor, and heavily polluted environment of Pakistan also includes measurement of hydrophobicity using STRI classification and leakage current measurement techniques. Three years aging performed in extremely polluted field of Pakistan have shown various results of hydrophobicity ranging from HC1 to HC7 [8]. Some of these results are shown in Fig. 2, one can see one plate of rubber material showing extreme hydrophobicity loss (HC6 to HC7) and another plate of the same material which maintained good hydrophobicity under the same conditions. This figure is showing the surface of insulating material under water spraying for hydrophobicity classification as discussed in Section 3 below.

The results reported from Pakistan also verify the fact that the larger is the surface area, the more probable are chances of hydrophobicity loss. So, this fact supports the conventional approach used by insulator manufacturers dealing with the insulators geometry - insulators are always of round shape, and hence cylindrical surface has least surface to volume ratio.

Fig. 2 also provides a clear way to understand what happens with a leakage current activity over the surface of a material with high loss of hydrophobicity during a rain. The water tracks shown in

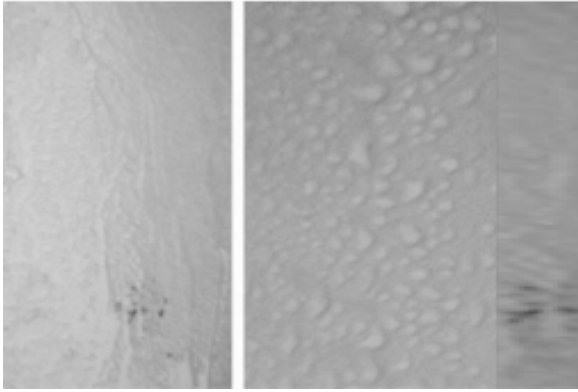


Fig. 2. The hydrophobicity of two different silicon rubber plates tested in field environment of Pakistan. (A) Extreme Loss of hydrophobicity (HC 7). (B) Good Hydrophobicity (HC 2).

Fig. 2a provide a clear continuous path for current under rain conditions; obviously, this may easily lead to flashover causing major degradation.

The surface of unaged (unexposed to environment) composite (Silicon rubber) insulators shows a hydrophobic behavior. In pure state, the various material groups such as RTV, HTV, EPDM, *etc.*, vary slightly with surface roughness, hydrophobicity or axial molding line.

The hydrophobicity of silicon rubber exposed to environmental conditions and/or partial discharges is reduced. An excellent advantage of SIR consists in its high resistance retaining its hydrophobicity even after the removal of harsh conditions. In other words, hydrophobicity will be recovered in case of temporary reduction or loss in it. These dynamic processes are more or less summarized by the term “recovery”; they are discussed in detail in the following sections.

3. METHODS OF HYDROPHOBICITY MEASUREMENT

There are a lot of methods to measure hydrophobicity; some widely used methods will be discussed in this section.

3.1. STRI hydrophobicity classification

It is a simple procedure to obtain manually a collective measure of the hydrophobic properties of insulating surfaces in outdoor environment.

For practical purposes, the degree of the water repellency of an insulator surface may be divided into seven hydrophobicity classes (HCs) according to the STRI classification guide [9,10]. HC1 is the most water repellent class whereas HC7 refers to completely hydrophilic surfaces. The intermediate classes are defined by receding angles of the majority of the droplets and the size of wetted areas in each case.

One of the manual methods to detect the hydrophobicity class in outdoor environment can be described as follows. First, the surface to be studied (50-100 cm²) is sprayed with water. The obtained drop pattern is observed and attributed to one of the seven hydrophobicity classes. As a help, the examiner has a set of reference images of typical wetting patterns representing each HC class [2,7,11].

The disadvantage of this method is that the measure is dependent on human judgment. Digital image analysis can be used to solve this problem. In such a procedure, computer software interprets the image, taken by a high-resolution digital camera, such examination increases the accuracy of the measurement. Aged samples or artificial methods like sand blasting, which reduces hydrophobicity of a sample to HC7 in a short time, can be used to deploy and calibrate the software for this method; the images of these samples are imported in software to calibrate image analysis for the first time.

Note that samples during the spraying for hydrophobicity test should be kept at inclinations between 10 and 35° from the horizontal plane. These inclinations should be chosen since they represent well typical inclinations of insulator surfaces in actual service. In order to make measurements comparable, all directions and distances between camera, illumination levels, and sample position should be also fixed; taking a large number of photographs for each HC is considered to be a good practice here. Reliability of software image analysis increases if the images are stored and reviewed at least twice at different times.

Tokoro *et al.* [12] have also applied image analysis to study hydrophobic properties of SIR, they used a high-speed camera equipped with a high magnification lens to observe behavior of water drops on small areas (1.5 x 1.5 mm). Small drops were chosen because the gravity influence becomes low compared to the effect of surface free energy; hence, the problems associated with inclination variations could be reduced. SIR samples were immersed in distilled water for different times

Table 1. Change in receding contact angle measurement of different surfaces. Three readings are taken for each sample to get an average value.

Material	Virgin	Receding Contact angle measurement			
		1st	2nd	3rd	Average
HTV SIR Plate	960	930	880	940	91.60
HTV SIR Reinforced Rod	1080	930	910	1010	9500
RTV SIR Plate	1120	1060	104	990	1030
Epoxy	1040	920	900	930	91.60

to reduce hydrophobic properties. Images taken after the samples had been exposed to mist of different solutions were analyzed with respect to size and shape distributions of the observed droplets. Observation showed that more smaller and circular drops are formed on hydrophobic surfaces as compared to hydrophilic surfaces [12,13].

3.2. Sessile drop technique

The hydrophobicity of silicone rubber materials is also measured by measuring contact angles between the material and water drops on its surface. The most commonly used method is the so-called sessile drop technique.

In this technique, a water drop is placed on the surface using a syringe. The static contact angle is then measured manually using a goniometer or in an image taken by a camera fitted to a microscope or computer using some image analysis software like MATLAB, etc. Addition of more water drops on an already sprayed surface results in an increase of contact angle finally causing the drop to advance over the surface. This angle is called advancing contact angle. Similarly, the angle at which the drop starts to recede during water removal, is called receding contact angle. The difference between these two angles depends on parameters like: surface roughness, surface heterogeneity, contact time of surface and water, and drop volume.

There is correlation between tropical weather of natural environment and the contact angle. The pollution accumulated on the surface result in the rapid increase in the contact angle due to the higher surface roughness. The samples having lower surface pollution provide lower contact angle. On the contrary, some of the samples exposed with shielding showed slightly increase in their contact angles.

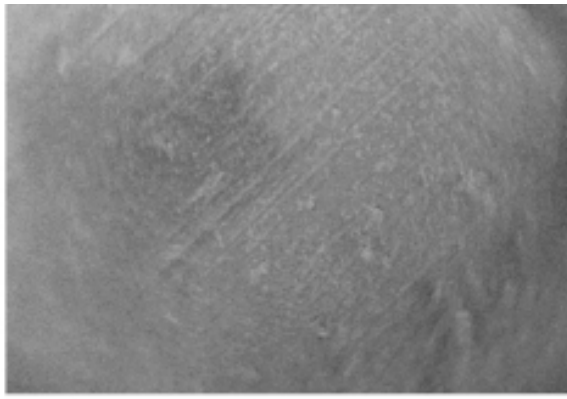
These phenomena indicated that the natural pollutants strongly affect variations in the contact angle of silicone rubber.

The sessile drop method is applicable in laboratory environment only since it requires good illumination and optimal view of single drops on flat horizontal samples. This drawback in the methods for estimating hydrophobicity of insulators in the field conditions led to popularity of STRI hydrophobicity classification method.

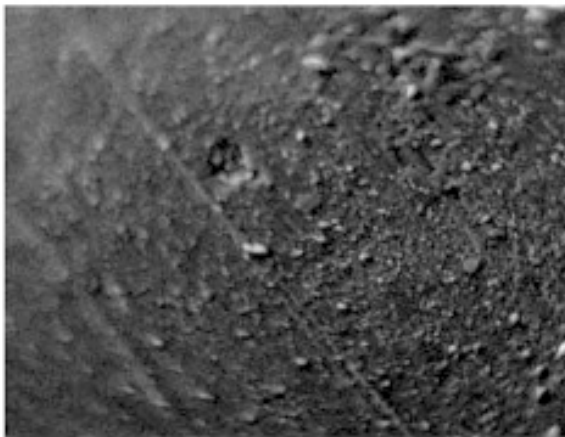
The receding contact angles measurements of different polymer materials before and after being dripped in artificial acid rain in a lab aging chamber at UET Taxila, Pakistan are shown in Table 1. The value of contact angle for virgin sample is also mentioned for each material type. It can be seen from the table that the contact angles decrease with soaking time in the solution of acid rain. It is clear that the surface hydrophobicity of insulator also becomes worse with decrease in contact angle receding.

3.3. ESDD, NSDD, and TSDD measurements

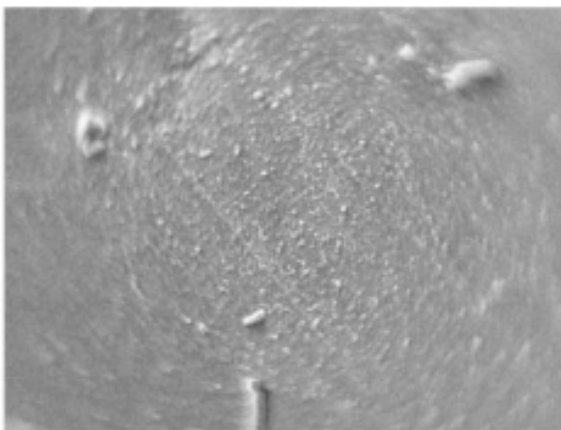
In this method, a salt deposited on a small area of insulator ($\sim 2 \text{ cm}^2$) is removed; the weight of an insulator is measured before and after salt removing using a microgram sensitive electronic balance. After that the ratio of weight of total salt removed to the insulator area from which it is removed is calculated; this ratio dimension is called Total Salt Deposit Density (TSDD) and its dimension is mg/cm^2 . Chemical analysis of these salt removed is done to detect the content of non-soluble salt in it. This defines two more indices: Equivalent Salt Deposit Density ESDD (proportional to soluble salt amount) and Non Soluble Salt Deposit Density NSDD.



A) Virgin sample



B) 36 days aged



C) 65 days aged

Fig. 3. The SEM images of silicon rubber plate aged in industrial environment of Pakistan.

The amount and type of dust/dirt deposited on surface of an insulator can be quantified using ESDD and NSDD contamination indices, e.g. one can identify that some cracking, chalking, or erosion had happened.

Typical values of ESDD measured under very light contamination conditions may be like 0.003 - 0.006 mg/cm². Severe pollution levels correspond to ESDD larger than 0.4 mg/cm².

3.4. Scanning electron microscopy (SEM)

SEM technique was introduced about 40 years ago; it gives us a magnified micro-image of a surface of analyzed material. It resembles to that of viewing an object by electron microscope. An electron beam produced in SEM is accelerated and focused to strike the material surface. When the beam strikes the sample, its electrons divide into four groups. Stopped Electrons are the electrons which stop upon striking specimen and transfer their energy to the electrons of material. This energy transfer excites the material electrons giving rise to the subsequent energy loss in a form of luminance. Absorbed Electrons are the electrons absorbed by a material; they eject the electrons of material out of it producing X-rays. Deflected or Secondary Electrons are continuing their motion, Reflected or Back Scattered Electrons are directed back towards the electron beam source. All these electrons are detected by various methods; correspondingly, an image is produced that depicts the details of material surface shape and roughness.

SEM information on surface roughness and micro cracks responsible for hydrophobicity loss is fairly important for hydrophobicity analysis; examples of the SEM images of virgin and aged samples of silicon rubber plate aged in natural outdoor industrial environment of Pakistan are shown in Fig. 3.

The use of SEM is justified by the fact that surface hydrophobicity of materials has direct relation to the surface appearance (smoothness and contaminant extent [14]) in addition to the inherence of materials, i.e. the binding energy and surface energy.

3.5. Other methods to monitor hydrophobicity changes

The effect of hydrophobicity can be quantified by many other methods such as sensitive optical measurements of surface utilizing Kerr effect, by Hydrophobic Interaction Chromatography (HIC), by

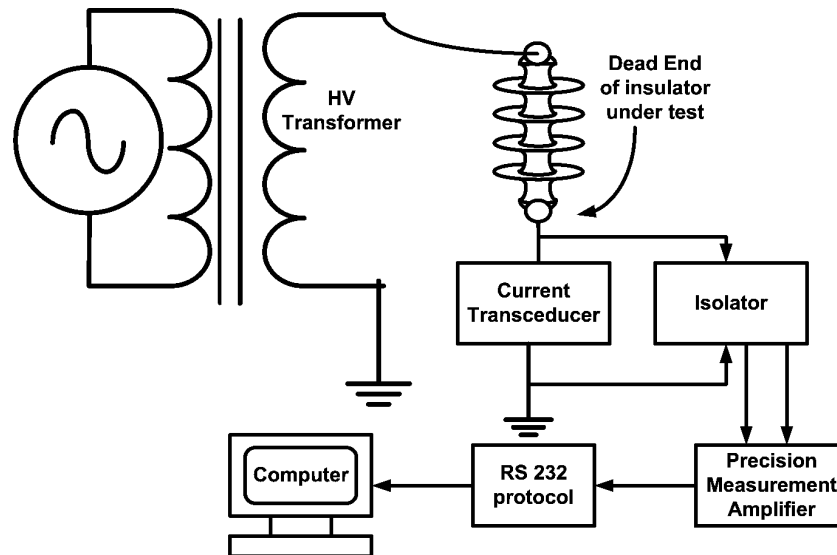


Fig. 4. A typical leakage current monitor system.

salt aggregation test (SAT), by electrical values such as leakage current (discussed in Section 4 below), flashover voltage measurement (also called cross over voltages COV), water immersion tests, *etc.*

3.6. Instructions for hydrophobicity measurements

Hydrophobicity measurements of any surface done by Sessile drop or STRI methods should be done immediately after the samples are removed from a field. However, if the by leakage current or COV methods are applied using a laboratory chamber or special purpose test station in outdoor environment, measurements can be done directly on surface and no delay time is involved. These requirements are due to very dynamic nature of silicon rubber surface; it starts to recover surface hydrophobicity immediately when the stress is removed. Therefore, the delay in the measurement leads to false results or unreliable good performance predictions [15].

4. HYDROPHOBICITY MONITORING USING LEAKAGE CURRENT ACTIVITY

The most popular method for continuous unattended monitoring of hydrophobicity changes under energized conditions in field or lab aging is the

use of leakage current method. There are three reasons for this.

1. Leakage current is directly proportional to hydrophobicity loss. The more is the hydrophobicity loss, the more the leakage current becomes, see e.g. [5,6,16,17].
2. It as parameter that follows change in hydrophobicity properties very dynamically; for this reason, the error involved in other methods due to delay in measurements are reduced. The method of leakage current monitoring is costly as compared to STRI Classification but very cheap as compared to SEM, Kerr effect measurement, *etc.*
3. In contrast to sessile drop or STRI methods, there is no necessity in complex image processing software or programming for image matching. However, the leakage current measurement just needs the computer to record leakage current values after a certain time intervals.

Many methods for leakage current measurement to monitor hydrophobicity loss have been reported in literature. The most easy and typical approach is to deploy a current transducer coupled with insulator at dead end and to measure the voltage across it by a precision amplifier; these values can be recorded them manually after a few days period or by a computer after any desired interval. The computer measurement involves conversion of analog volt reading to digital and then to RS232 format; this can be easily done by cheap hardware.

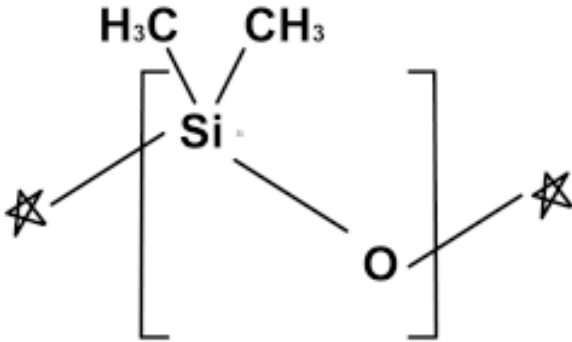


Fig. 5. Chemical structure of PDMS (Poly Di-Methyl Siloxane), the Low Molecular Weight Component of silicon rubber.

The data are imported in computer software by reading its ports and saving it in some file continuously. A typical issue which arises is the interval between two readings stored. For example, if the reading after every five seconds is stored, it results a huge record file for a month; obviously, this file can be stored, but its analysis and utilization is almost impossible. So, a very common practice adopted by many researchers all over the world is to save a reading only if it exceeds a certain level (say 10 micro ampere or so) [18]. This will result only those readings where some change has occurred due to some change in surface properties of an insulator; this is known as monitoring of current according to change in value. A typical setup of such apparatus is shown in Fig. 4.

5. HYDROPHOBICITY AND LMW

5.1. Hydrophobicity transfer property

The hydrophobicity of a material is a property shown by Low Molecular Weight components (LMW) at the outer surface of that material. The more is the LMW on the surface of a material, the larger is its hydrophobicity and vice versa. The loss of hydrophobicity is due to the loss of low molecular weight components from the surface which are removed either by excessive wetting conditions along with the application of electrical field, or by dry band arcing due to carbon tracking on surface, or by acidic rain.

These Low molecular weight components can be inherently present in many materials and their amount can be enhanced in a material artificially

by adding another material to them; e.g. Alumina trihydrate can be added in silicon rubber insulators to increase their LMW content in the bulk.

The presence of large amount of LMW in material still does not ensure that material possesses high hydrophobicity. For a material to preserve good hydrophobicity, it should have ability to transfer the LMW components from the inner bulk to surface as soon as their concentration on the surface reduces due to hydrophobicity loss.

Cured silicone rubber has a stabilized cross structure. Under ideal conditions, silicone rubber cannot be solved by solvents and does not melt even under very high temperatures. It is found that in silicon rubbers there always exist some low molecular weight components which can be pulled out from inner bulk of material to surface by deploying proper solvents. If, somehow, water is converted into such a proper solvent, then rain and wetting will cause recovery of surface hydrophobicity of an insulator. However, there is always a movement of low molecular weight chains within the material without application of any external solvent due to natural diffusion process. As a considerable amount of LMW have been removed from surface, a transfer of LMW from inner side to surface starts due to this diffusion process and tends to recover LMW content on surface and, hence, hydrophobicity.

5.2. Overall effect of fillers

An important result is that materials added as impurities or fillers in other silicon rubbers have very important influence on the performance of SIR insulators since they provide an increase in concentration of dynamic LMW components. It is found that the increasing of ATH filler type in HTV is very important to the anti-tracking properties.

It has also been found that adding too much filler can increase the influence of absorbed water on the dielectric properties and may lessen the hydrophobicity quality. The RTV1 and HTV2 samples may be an alternative as insulator material for outdoor application under tropical climate because they have good dielectric performance and hydrophobicity than the other samples

5.3. Transfer of hydrophobicity to deposited pollution layers

A very important property regarding insulating behavior of SIR insulators is the transfer of hydrophobicity into pollution layers, which cover the surface and become hydrophobic after a certain time.

Comprehensive investigations have been performed to understand the dynamic behavior of recovery and transfer of hydrophobicity after exposure to different stresses in many regions of world; the reported results can be found in [13,19-24].

In spite of extreme harsh conditions, the hydrophobicity loss of a silicon rubber insulator is temporary to a large extent; this is due to the fact that small quantities of highly mobile low-molecular-weight chains exist in the bulk of silicone rubber even if the loss of these components from surface is observed. The FTIR absorption peak near the wave number 1258~1259 shows that it is a repeated chain of PDMS (Poly Di-Methyl Siloxane) as shown in Fig. 5, which is assumed to be major LMW responsible for silicon rubber hydrophobicity characteristics [25].

Hydrophilic pollutants deposited on the surface of silicone rubber gradually vary its hydrophobicity because of the transfer of LMW components from inside or from surface of original rubber to the pollutant layer due to their extreme dynamic nature balancing their concentration throughout the material. This overall effect is known as hydrophobicity transfer; CH_3 radicals are mainly responsible for this effect. This fact was verified by FTIR measurements – the analyses of liquid extracting from the hydrophobic pollutants showed that the FTIR spectrum in this case is quite similar to that detected for LMW [26].

Washing of insulators to remove pollutants in order to retain hydrophobicity is not easy. An alternative approach, spraying of LMW components on deposited pollution layer works very well; two positive mechanisms here are: first, it reduces the amount of LMW transferred from the bulk of insulator to pollution layer preserving its long life and, second, it accelerates the process in which pollutants gain hydrophobicity.

5.4. Hydrophobicity recovery times

The speed of hydrophobicity recovery is directly proportional to the amount of LMW left inside the bulk of silicon rubber insular. The reason is obviously the law of diffusion, which states that the diffusion rate is directly proportional to the concentration gradient. It is found that if the main part of LMW in the silicone rubber is extracted to surface from time to time, the speed of hydrophobicity transfer process prominently decreases. The more the LMW is extracted, the lower the speed is.

Tests on surface hydrophobicity were made for many different types of silicone rubber insulators

under artificial lab environment and extremely polluted natural environment at UET Taxila, Pakistan. It was found that after the removal from the test chambers and/or field many samples, which were initially completely wettable, recovered their non-wettability in almost 30 to 48 hours. This behavior with varying duration of recovery time from 24 to 60 hours has been also reported by many authors [27-29]. These authors claim that this behavior is due to the mobility of the silicone chains and, also, to the presence of mobile low molecular weight silicones in the material.

This data helps to explain why silicone rubber has excellent life behavior during the 15 years exposure in severe seacoast climates despite poor performance shown in accelerated laboratory tests. In service, the specimen dries and renews its water repellent surface usually long before the next rainstorm. Whenever the fog or rain begins, the salty contaminated surface is water repellent. It may become wettable again, but by that time, the salt has been removed. Further test programs may reveal other polymeric materials which behave similarly, decreasing their contact angle, while the other samples start to recover its hydrophobicity.

Washing by rain lowers the ability to recover the hydrophobicity. This is due to the removal of LMW in the pollution layer gained by hydrophobicity transfer property. This fact can be verified by long duration tests under the influence of natural tropical stresses.

The UV radiation and the increasing temperature may accelerate the diffusion process of LMW to the pollution layer.

5.5. Essential factors in evaluation of hydrophobicity

There are three major factors necessary to consider for the evaluation of hydrophobicity loss of polymeric insulators:

- Electrical discharges (partial arc, corona);
- Adsorption of pollution layers;
- UV radiation;

Each factor will be discussed in details below.

5.5.1. Electrical discharges

The discharges over the surface in wet conditions cause the major loss of hydrophobicity of silicon insulators. There is a contradiction between high energy or corona discharge and low energy water-induced discharges. In case of silicon rubber insulators, the water-induced discharges occur more frequently than corona discharge under normal

humidity and thus become an important long-term aging factor. So more attention should be given to study water-induced discharges and their effect. Discharges, which are locally stabilized, can lead to a fast loss of hydrophobicity and recovery time becomes large - from hundred to thousands hours [26].

An essential criterion is often the change of the contact angle in relation with the intensity and duration of the stress. A high sensitiveness for more detailed material ranking and process understanding can be achieved by using the receding contact angle measurement [30]. There is some indication [31] that only the receding angle gives a direct correlation to a leakage current, which flows over a surface with a humid pollution layer. The relation is that the higher the receding angle, the smaller the leakage current.

5.5.2. Pollution adsorption

Pollution layers, as they deposit on the surfaces of insulators, reduce the hydrophobicity to an extent depending on the chemical structure of the pollution. This fact is even used for pollution tests of composite insulators. It has also been observed that microbiological attack or a growth of mold under humid conditions can reduce the hydrophobic behavior.

LMW in the bulk of silicone rubber tends to adsorb on much higher surface energy; the adsorption process of LMW is therefore the essence of the hydrophilic to hydrophobic change of deposited pollutants on the surface. Adsorption of materials with some surface energy is the inherent necessity of the energy minimization in the system. The larger difference of surface energy exists, the more prominent adsorption process occurs.

Actually, in wetting condition, the adsorption layer of LMW always cannot completely bypass the influence of pollutants. In addition, before the pollutants deposits on the surface of silicone rubber, it has already reached an energy-balance status by adsorbing water molecules in the environment, which will necessarily lessen or delay the adsorption of LMW to pollution layer.

For inorganic salts deposited on surface, LMW adsorption is nearly stopped because of the strong affinity of these salts with water, which completely obviates the possibility of hydrophobicity recovery. This statement and the results reported in [19,22,30] support the fact that hydrophobicity transfer process is mostly dependent on the chemical properties of pollutants and, more specifically, their affinity with water. However, inorganic pollut-

ants cannot gain hydrophobicity even after a long rest time if they don't have any dynamic LMW chains.

5.5.3. Effect of UV radiation

Service experience and laboratory tests under the effect of UV radiation are different on Silicon rubber and EPDM insulators. It has been observed that silicon rubber insulators maintain almost the same level of hydrophobicity if exposed to stress of UV radiation alone, while already aged samples exposed to UV radiation improve their hydrophobicity. The effect is so clear that, in many cases, the sides of insulators not exposed to sun (like bottom of sheds and cores) even showed less hydrophobicity compared to those directly exposed to sun. The reason for this could be the acceleration of diffusion process of LMW inside the bulk of SIR insulators by the energy contained in UV radiation.

But the effect of UV radiation observed in EPDM insulators is quite opposite to that observed in SIR insulators. Different experiments, in which the only UV radiation was applied on aged samples, have shown that EPDM rubber insulators were more hydrophobic on the undersides and very hydrophilic on the upper side of the sheds. This fact directly dictates degradation of hydrophobicity by UV in the areas of insulators directly exposed to sun. One reason justifying this could be that exposure of wet and contaminated surfaces to UV radiations results in reorientation of the hydrophobic methyl groups; so, in case of EPDM, the surface loses its hydrophobicity. Structural changes of the material affect the hydrophobic properties and, thereby, the electrical performance of an insulator.

However, in spite of all the above facts, it has been reported that hydrophobic properties of SIR and EPDM insulators are maintained even after several years in service at many locations [16]. From many sites, reported classes of hydrophobicity for assembled insulator lie in HC 1 to HC 4 according to STRI guide.

Last year a very high hydrophobicity loss ranging from HC 1 to HC 7 was reported on test samples installed under polluted industrial environment in Pakistan [8]. However, this maximum loss HC 7 observed was for the sample of plate of SIR specially designed for experimental purposes and having much larger surface area than any largest shed of insulator. This has been already mentioned above that large contact area of a surface results in more hydrophobicity loss.

6. CHEMISTRY OF HYDROPHOBICITY

Transfer of LMW from inside bulk of SIR material to its surface can be thought of as combined effect of surface energy, filler type, pollution layer chemistry, thickness of pollution layer deposited, extent of electric field and energized to relaxed time ratio [15]. It has not been possible yet to formulate all or even a few of these effects in one strict relation, however a lot of work is in progress on evaluating equations representing transfer of LMW under three or four of these combined effects for two or three combined effects. However, two major factors, surface energy and pollution layer chemistry are considered reasonably represent LMW transfer phenomena. The affinity of the pollution on the surface to increased leakage current and arcing is not completely suppressed by diffusion of a few or a thin layer of LMW from inside to surface, particularly in the case of thick pollution and increased humidity. So to estimate what will be transfer speed, whether or not the pollution layer deposited on the surface of silicone rubber will obtain sufficient hydrophobicity, and what will be the value of maximum final hydrophobicity achieved, we have to consider following factors.

6.1. Material dependency

- 1) Physical and chemical properties of rubbers
 - Persistence of mobile LMW
 - Material allowance for diffusion activity
- 2) Physical and chemical properties of pollutants

6.1.1 Persistence of mobile LMW

There should be enough amount of LMW in total bulk to continue process of their diffusion for many years to maintain LMW concentration at surface. According to many laboratory tests, most of the commercial silicone rubbers available today for making composite insulators have enough LMW to sustain excellent property of hydrophobicity transfer. The artificial increase of LMW through adding low molecule silicone oil into the raw silicone rubber cannot remarkably improve the hydrophobicity property. However, effect of adding fillers like alumina trihydrate has been observed positive [2].

6.1.2. Material allowance for diffusion activity

There should be enough flexibility in silicon rubber material to allow a continuous activity of LMW diffusion. This flexibility depends upon content, cross

linking, and weight distribution of molecules in the raw silicone rubber. There is still large space left for the optimization of hydrophobicity performance through the good balance between these factors. The accurate control of the above two factors requires the deep knowledge in the corresponding fields of chemical engineering and should be done with regard to recommendations of different researchers in this field.

6.1.3. Physical and chemical properties of pollutants

If the two factors stated above are positively present, it means that insulator is ready to give LMW to pollution layer when it will be deposited, but the important thing is - will pollution also allow exchange of LMW from the bulk of insulator material? This solely depends on chemical and physical properties of pollution layer deposited. Pollution layer chemical properties and physical morphology can never be predicted nor artificially controlled, since it have to come from atmosphere and could be anything. However, it can be anticipated in advance by choosing more insulation redundancy and extra cautions are necessary during the selection and maintenance. For SIR insulators, areas near alkali plants and the sea shores seem more severe due to higher content of salt and possibly less hydrophobicity.

6.2. Reason for LMW diffusion

The cause responsible for LMW diffusion is based on the fact that all systems try to minimize their total internal energy. This means that all atoms/molecules should be involved in as many intermolecular interactions as possible to achieve same level of energy throughout their distribution in that material. The possibility for successful intermolecular interactions at surfaces and some interfaces is heavily reduced to about half because no molecule can leave the material so this causes energy imbalance at surface or interfaces.

If a material is solid, this type of energy interface is called surface free energy. For liquids, it is called surface tension; both these terms tell how much uncanceled energy is present on the surface or interface. An example of this can be illustrated by the binary and completely mixable system of water and glycol; it has been shown for it that the concentration of glycol is much higher in the surface layer compared with the bulk [6] in order to decrease the surface tension.

In general, sufficient flexibility for intermolecular diffusion is present even for solid materials; the constituent with the lowest intermolecular forces will be enriched at the surface. Further, if one applies a liquid droplet on a solid surface, the surface tension will show repulsion to liquid spreading or we can say surface will show good hydrophobicity [7].

Almost all types of non-polar organic materials have a free surface energy half or less as compared to liquid water; therefore, water will not spread on such surfaces. This low surface energy, for the same reason, also leads to low adhesion to solid particles, such as those brought by field pollution.

The inherent hydrophobicity recovery property of SIR insulators is one of the main reasons for using them in high voltage outdoor insulation applications. In a highly mobile system as SIR, arising from the high flexibility of the backbone, the matter with the lowest intermolecular forces will be enriched at interfaces against air in order to lower the total energy of the system. Different environmental stresses, like electric discharges, the deposition of pollutants, the influence of water, etc., can lead to a loss of the material water-repellent property, but PDMS also has ability to repeatedly recover this property.

6.3. Chemistry of hydrophobicity loss and recovery

The loss of hydrophobicity is caused by three types of chemical changes that can happen.

1. Oxidation of surface.
2. Build up of pollution layers.
3. Reorientation of methyl group chains.


The oxidation of silicon rubber insulators is just like oxidation of any surface in air by oxygen; the process is accelerated by dry band arcing on surface or corona discharges. Build up of pollution layer is obviously from environment. Chain reorientation occurs when immersed in water (for example continuous rain and persistent high humidity conditions) and results in increase of contact angle of SIR.

The recovery of hydrophobicity can be done by forcing the following three types of chemical changes achieved either artificially or naturally.

1. Reorientation of methyl and oxidized groups.
2. Condensation of silanol groups.
3. Diffusion of PDMS.

For a clean surface, the reorientation of the polymer methyl groups can occur; it recovers hy-

drophobic properties and this is a fast process. Hydrophilic silanol groups are formed during oxidation of PDMS; two such silanol groups can form siloxane cross links by means of a condensation reaction resulting in improvement of hydrophobicity. However, surface pollution stops the processes of chain reorientation or silanol condensation in case of SIR used for outdoor insulators. But still, due to encapsulation, the transfer of oligomeric compounds to both damaged and pollution layers continues; this fact balances much of hydrophobicity loss. This process is much slower, but it still complies with real life experience because hydrophobicity loss in real life is not as fast as it is usually simulated in lab aging chambers.

The factors which limit the recovery rate by controlling diffusion are formation and cracking of a heavy oxidized silica-like layer [3,32]. The silica-like layer is hydrophilic; it is much denser than the virgin SIR and, thus, acts as a diffusion barrier. The oxidized layer is brittle; when the mechanical stresses become too high, cracks in deposited layer appear which break the barrier settled by it previously [13,32]. This process enables a faster diffusion and, thus, a faster recovery. The mechanical forces might originate from external stresses, such as handling. As a consequence, the recovery rate of hydrophobicity  Thickness of Pollution layer Deposited

Diffusion of PDMS is controlled, but it has been observed that samples in which the original oligomers were extracted prior to corona treatment, also recovered according to diffusion mechanisms [3,33]; this implies that oligomers can be regenerated from the cross linked matrix under certain conditions. Diffusion and pollution encapsulation rates have also been found to be higher for low molar mass cyclic oligomers compared to linear and larger cyclic ones [34,35]. This is due to the fact that they are more compact compared with the linear ones. For larger cyclics, trapping due to entanglement hinders the diffusion [3].

The problem is - will oligomers be formed during service due to depolymerization or not. If not, then the ability to recover will, at last, end when initial reservoir of oligomers is exhausted. The examination of SIR insulators installed in different locations do not show a decrease in extractable oligomeric content [24,36]. This indicates that depolymerization might have happened. It has also been verified by mass spectroscopy that the mass

distribution of oligomeric PDMS does change with time, showing an increase in the very shortest chains [27], thus supporting the idea of the regeneration of oligomers by depolymerization of the cross linked PDMS matrix.

Hydrophobic activity largely depends on polarity of solvent (water here) also. Materials with A-polar molecules are almost resistant to interact with water molecules and, hence, water molecules near the A-polar molecules in a material orient themselves to maximize hydrogen bonding between them.

When two A-polar molecules come near each other, these water molecules are squeezed out making the material hydrophobic. Van der Waals interactions have been assumed to initiate such interactions.

7. RELATIONSHIP BETWEEN DIFFERENT FACTORS AND HYDROPHOBICITY RECOVERY

7.1. Temperature and hydrophobicity recovery

The temperature has a great influence on the hydrophobicity [37]. The hydrophobicity is a physical performance of solid that has low surface free energy, which can be considerably affected by the temperature. The surface free energy decreases with the increase of temperature. The change of surface free energy of SIR with the temperature is a main reason for the presence of temperature-dependent hydrophobicity. The process is distinctly affected by the temperature. The speed and quantity of LMW transfer determine the positive and negative factors of SIR hydrophobicity transfer at different temperature, respectively. Either the hydrophobicity recovery or the hydrophobicity transfer after corona treatment can be significantly affected by temperature.

A lot of work has been already done and in progress now on high temperature stability and the depolymerization of PDMS [28,32]. The thermal degradation of polymeric housings is based on local heating. Local heating can be achieved by standing discharges on the surface. The temperature within such channels might very well exceed the required temperature for fast depolymerization of even pure PDMS liquids. Basically, thermal decomposition in a non-oxidizing atmosphere leads to depolymerization.

Depolymerization of PDMS, that has been expected from many results, might be done thermally

at high temperatures. But it is a well known fact that depolymerization happens above 350 °C; so, we need ionic catalysts to cause it below 350 °C. There is no way to achieve depolymerization below 150 °C, since this is too low temperature to break a bond chemically; the only alternative way is the hydrolysis. It is concluded that ionic nature of the siloxane backbone makes the PDMS susceptible to hydrolysis [29]. Water is capable to break the siloxane bond, especially at moderate acidic or basic pH values [12]. The hydrolysis involves equilibrium with molecular water, where the siloxane bond can break to hydroxyl and re-condense [2].

Methyl terminated PDMS is thermally more stable compared with hydroxyl terminated ones. In the absence of ionic impurities, hydroxyl terminated chains decompose mainly by back-biting, whereas methyl terminated ones decompose only by random chain scission. When thermal aging takes place in an oxygen-containing atmosphere, the removal of methyl groups followed by the formation of siloxane cross links will dominate over the depolymerization process and finally leads to the formation of a silica-like structure.

The hydrophobicity recovery characteristic of thermally aged sample was evaluated for hydrophilic film coating [31]. It was found that the hydrophobicity of the thermally aged sample recovers to values equally the same to that of virgin up to 10 h. However, the recovery speed of the thermally aged sample became slow above 10 h. During the evaluation of dissolved LMW in the thermally aged sample, the sample broke because of the reduction of mechanical strength induced by thermal ageing and the penetration of n-hexane into the sample. However, the reduction of mobile LMW was clearly found. The weight of the thermally aged sample decreased by 0.1% of the total weight in 0.03 h while the weight of the virgin sample decreased by 0.1% in 0.004 h. Thus, the aggravation of the hydrophobicity recovery characteristic by thermal leads to the conclusion that depletion of mobile LMW occurs with temperature increasing.

7.2. Humidity and hydrophobicity

The reported HC classes mentioned in Section 5.4 have been determined for the samples removed in summer season, since it is expected that hydrophobicity loss would be severe in summer due to rain and excessive heat factors. But a contradiction arises when the samples removed near the end of winter and autumn season showed more hydrophobicity loss than those removed in the end

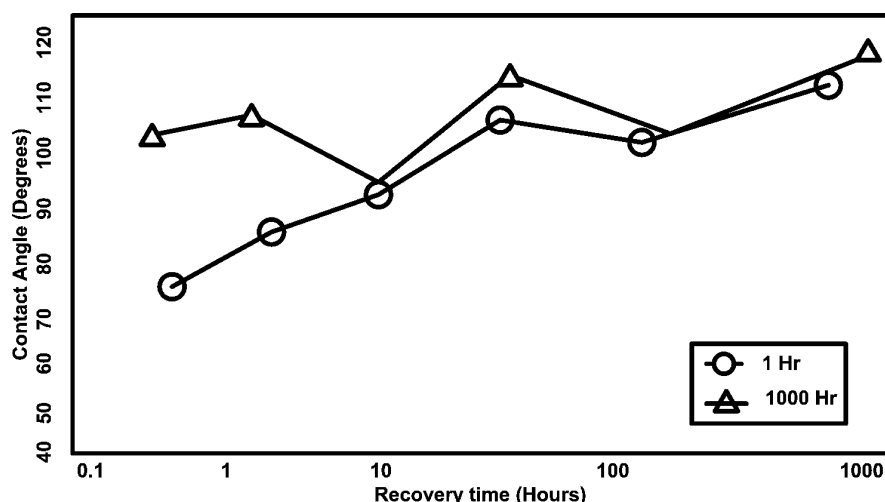


Fig. 6. Relationship between hydrophobicity recovery and corona exposure duration.

of summer. The reason could be the increased level of humidity leading to wet and less sunny environmental conditions prevailing during these periods of the year [38].

In general, we cannot give any exact statement about loss of hydrophobicity from above discussion with respect to nay season; but the conclusion that is more realistic is that the loss of hydrophobicity due to prolonged wet atmosphere is greater than those caused by rains. Hydrophobicity loss is also increased with water immersions or absorption [39].

7.3. Dry band arching and hydrophobicity recovery

For silicones, it is known that heat generated from dry band arcing causes hydrolysis, scission and cross-linking of Si-O bonds. This gives rise to decreased CH₃ groups and increased levels of oxygen in the siloxane bonds [40]. As a result of such increased oxygen levels, high interaction forces between the polymer and water deposited on its surface are formed. This process is called oxidation and leads to easy wetting of surface. To resist this process, antioxidants are usually added; they slow down process of chain scission. Many polymeric materials show considerable improvement in stability against oxidative deterioration by addition of antioxidants; but a unique behavior is shown by PDMS, whose resistance to oxidative degradation is independent of antioxidants added [41].

However, recently a research was started in Sweden, in which antioxidants were added to

samples of PDMS cured model materials, which showed improvement in oxidative stability. But this type of improvement based on additions of antioxidants may introduce a false prediction about degradation time because once the antioxidant is consumed, the material degrades rapidly degrades.

It is well known that oxidation is an irreversible process, unless drastic physical chemical modifications (e.g. rubbing of the oxidized surface to remove the affected area) are made. Under these circumstances, even the deposition and removal of water drops could hardly be considered as a factor contributing to eliminate any oxidized area from the sample surface.

The stability of PDMS without adding antioxidants is due to ionic character of the siloxane bond. The oxygen atom acts as an electron drain which increases the stability in the Si-CH₃ bonds, and makes the methyl group slightly polarized [3]. In HTV SIR, there are a number of possible reactions which can lead to changes in the polymer network, for instance, siloxane bond interchange and hydrolysis of siloxane bonds [23].

7.4. Corona and hydrophobicity recovery [31].

The variation of contact angle, representing a hydrophobic transfer, was observed after the exposure of corona to three different samples [31]

- A. Virgin sample;
- B. Already aged sample and exposed to corona for one hour;

C. Already aged sample and exposed to corona for 250 hours.

The virgin sample (without a subjection of corona stress) was also evaluated as a standard for further measurement. Only a small difference in the recovery rate between the virgin and the 1 h corona exposed samples was observed. The contact angle for both these samples reached 90° in 3 h and 100° in 20 h. However, the contact angle of the 250 h aged samples exposed to corona showed very quick 0.1-30 h recovery time. The relation between contact angle and recovery time is shown in Fig. 6.

To investigate why long corona stress resulted in speed up of hydrophobicity recovery, the LMW dissolution properties of all samples were obtained in n-hexane solution and a large weight loss was observed. This indicates that a heavy loss of LMW has occurred which is possible only if LMW present in these samples were highly mobile.

The weight loss in virgin sample was 1% after 3 hours. The weight loss observed in aged sample exposed to corona for one hour before dissolution in n-hexane was same as that of virgin sample. However, the amount of dissolved LMW of from the samples exposed to corona for 250 hours was much more than first two samples. Its weight decreased by 1% in 0.1 h. The obvious result is that corona exposure increases the amount of mobile LMW in the material. This could be possibly due to the fact that corona increases the free surface energy of material accelerating the natural diffusion process within the material. It is also clear from these results that short duration exposure of corona does not produce a significant change in the hydrophobic transfer and LMW aspects [31].

7.5. UV radiation and hydrophobicity recovery [31]

The two types of reactions have been found to occur in silicon rubbers by UV radiations

A. Photo oxidative attacks on side groups of the PDMS;

B. Cleavage Plane breaking of bonds.

However, it is well known that these two reactions can be initiated only if UV light with a wavelength shorter than 290 nm is applied [32]. Both these reactions lead to the formation of hydroxyl groups. The formation of hydroxyl groups lead to depolymerization reactions.

UV-radiation of long wavelengths mainly produce organic cross links, as the photons cut bonds between hydrogen and carbon in the methyl group.

On shorter wavelengths the atmospheric oxygen becomes peroxide taking energy from UV photons. The peroxide reacts with methyl groups to eventually form Si-OH groups, which upon condensation give siloxane bridges.

The hydrophobicity recovery characteristic of the rectangular shape sample previously subjected to UV-rays for 1000 h were evaluated [31]. Only the one side of sample was irradiated. The hydrophobicity loss was created by coating sample with a thin hydrophilic film and exposing to corona for few hours.

It was found that the recovery speed of the side of sample exposed to UV for 1000 h was lower where as other side of sample recovered quickly. The contact angle of the sample exposed for 1000 h took 1000 h to reach 90° while that of the virgin took 3 h. So it is safe to state that hydrophobicity recovery becomes worse due to the prolonged UV exposure. To investigate further, the influence of UV-rays on LMW transfer mechanism was monitored from dissolution properties in n-hexane solution. It was observed that the dissolution amount of LMW of the UV exposed sample was much smaller than that of the virgin. It is hence proved that decrease in the hydrophobicity recovery speed due to UV-rays is true and it is related with the reduction of mobile LMW [41].

7.6. Electric field, surface charge accumulation and hydrophobicity recovery

Hydrophobicity status of Silicon Rubber insulators in service shows that a good direct proportionality exists between the hydrophobicity distribution and the electric field distribution. It means that more electric field will appear around the areas with more hydrophobicity degradation expected [41]. The obvious reason is the presence of low resistance path in hydrophobicity degraded parts of an insulator. In many sites the distribution of hydrophobicity has been found non-uniform over the surface of insulator as predicted by electric field method mentioned above. The non-uniform distribution dominates the prominent increase in leakage current that leads to dry band discharges. The areas where non-uniformity is observed mostly are the rim of sheds and intersection between bottom shed and adjacent shank. In general, hydrophobicity degradation is maximum at hot end and decreases linearly till middle shed and then remains approximately constant up to bottom shed and again shows a different value between bottom shed and shank.

A strong relationship between the presence of static charge on surface and the loss of hydrophobicity has been observed [42]. Hydrophobicity recovery took place after decaying of surface charge. This directly leads to fact that water repellency can be recovered if a period of no electrical activity takes place. This result has also been previously reported for ceramic insulators. Insulator surface static charge accumulation results from either polarization process or electrical activity [39] (corona and dry band arcing). Therefore, the charge accumulation on polymeric insulator surfaces should also be considered as a factor limiting the hydrophobicity recovery of Silicon rubber insulators in addition to other mechanisms discussed above. Many electric field calculation methods have been presented in the text, a simple method can be seen in [43].

7.7. Acidic rain and hydrophobicity

The unstable Nitric and Nitrous oxide compounds in air under rain conditions lead to formation of nitric acid which makes the rain acidic. The obvious effect of acid rain on the silicon insulating materials is erosion. Insulating materials work under the electrical stress which speeds up the erosion and aging caused by acid rain [41].

The acid anhydride present in acidic rain attacks the unsaturated macro molecules in the bulk of silicon and breaks them into small molecules or free terminal molecules (called Radicals) which have tendency to react at free ends and may attach to water molecules in air; so they become hydrophilic [44].

SEM images show clear erosion effect of acid rain on the materials, see Fig. 3. The smooth surface of materials has become rough [8] leading to reduction in hydrophobicity. The reduction of surface hydrophobicity leads to the increase in discharge current on insulator surface, especially in rain conditions. The heat of discharge is transferred to the material; further, it accelerates the tracking degradation of materials. Rupture of chemical structure, formation of micro cracks and pits on the surface layer of material decrease the binding energy and surface energy; this gives rise to reduction of thermal withstand capability of surface layer which aggravates all other degradation effects [45].

8. CONCLUSION

Pollution performance of polymer insulators is closely related with their hydrophobicity property.

Pollution severity levels also play an important role. UV radiation and temperature contribute strongly to hydrophobicity transfer speed and gain of LMW by pollution layer. Heavy acidic rains reduce the speed of recovery of the hydrophobicity because of the breaking of LMW (by acid action) on surface or on pollution layer that has gained LMW.

The pollutants effect on changing the contact angle of silicon rubber surface is very noticeable. It has been observed that more pollution on the surface results in an increase of the contact angle and also in the surface roughness. In general, lower surface of sheds accumulates more pollutants than upper surface, and therefore, exhibits poor hydrophobicity.

It is confirmed by many authors [2,21,31,33,39] that hydrophobicity status has not any prominent relationship with the years of service. It only corresponds to the particular environment where it is investigated.

The sum of results achieved from experiments on hydrophobicity is that water droplets induced discharges are main reason for the hydrophobicity degradation of Silicon Rubber insulators in service [5,19]. To achieve good performance of these insulators, electric field distribution should be equalized in all sections over the surface of insulator especially near the end-fittings. This can be done by increasing overall surface leakage distance or in other words decreasing the KV/ Cm stress over the surface. A suitable level is to keep it a maximum of 5-6 KV/cm.

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