1-1-2006

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Effect of Heat and Saline Water on the Hydrophobic Behavior of EPDM Insulator

by

Behdad Elahipanah

A Thesis
Submitted to the Faculty of Graduate Studies and Research through the Department of Electrical and Computer Engineering in Partial Fulfilment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

Windsor, Ontario, Canada
2006

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Abstract

This is a study of the aging characteristics and the mechanisms responsible for the loss and recovery of hydrophobicity in EPDM insulator, under stress conditions of heat, water salinity and the time length of aging.

Aging characteristics of EPDM insulator were determined under combined stresses of thermal, and immersion in saline solution as a function of time, by measuring the static contact angle of water droplets on the surface of insulator specimens and variations in the weight of specimens. EPDM specimens were aged by placing in stationary air and in water with different salinity levels, 5×10⁻³, 1, 10 and 100 mS/cm, at 0, 25, 50, 75 and 98 °C, for up to 6000 h.

The effect of two cleaning methods on the contact angle of water on the surface of EPDM specimens was also studied. In the first cleaning method the surface of the specimens was cleaned with a constant spray of distilled water for about 2 minutes. In the other method, the specimens were washed and cleaned in distilled water with an ultra soft toothbrush.

The surface of EPDM was studied to investigate the effect of heat and water salinity during the aging process. ATR-FTIR spectroscopy, SEM and EDS were employed to study the physical and chemical changes on the surface.

The surface free energy and its relation to hydrophobicity was investigated. The surface energies of EPDM were determined by measuring the contact angles of water and methylene iodide during the aging process.

The recovery of hydrophobicity of EPDM specimens was investigated after removing them from the stress conditions and keeping them in stationary air at room temperature for up to 4000 h. The contact angle of water and the variations of the weight of the specimens were measured intermittently during the recovery process.
LMW fluid content of EPDM specimens was extracted by immersing them in analytical hexane. The composition of the extracted LMW fluid was investigated by the application of several identification techniques, including GC-MS, IR spectroscopy and NMR spectroscopy. It was shown that the extracted LMW fluid contained dioctyl adipate, an ester of octanol and adipic acid. Effect of heat in regeneration of the LMW fluid was also investigated.

It is suggested that in EPDM, generation of the LMW fluid in the bulk and its migration to the surface and to the top of the contamination layer maintains the hydrophobicity of the insulator in wet and contaminated conditions.
To my beloved parents

for their never-ending support and inspiration
Acknowledgements

I would like to extend my sincere gratefulness to my supervisor, Dr. R. Hackam, for his guidance, encouragement and support throughout this work. It has been the greatest privilege to be his student.

I wish to thank the members of the Master’s committee, Dr. R. Lashkari and Professor P. Alexander, for their invaluable suggestions and guidance.

I would also like to thank the Natural Science and Engineering Research Council of Canada for providing the funds for this project and Research Assistantship.

Also thanks to ENWIN Utilities Ltd., Windsor, Ontario, for supplying the EPDM insulators for this study.

I wish to thank Dr. J. Green, Ms. S. Amiralaeei and Mr. N. Pieczonka of the Department of Chemistry and Biochemistry for their time and technical assistance in performing GC-MS, NMR and IR spectroscopy and Mr. J. Robinson of the Department of Mechanical, Materials and Automotive Engineering for conducting SEM-EDS analysis. It would not have been possible to complete this work without their valuable assistance.

I appreciate the help and support from Mr. D. Tersigni and Mr. F. Cicchello, the Technical Assistants, and Ms. S. Marchand and Ms. A. Turner, the Administrative Assistants of the Department of Electrical and Computer Engineering and also the University of Windsor’s Technical Support Center.
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Nomenclature

EPDM  ethylene propylene diene monomer
LMW  low molecular weight
MI  methylene iodide
IR  infrared
FTIR  Fourier transform infrared
ATR-FTIR  attenuated total reflectance Fourier transform infrared
SEM  scanning electron microscopy
EDS  energy dispersive spectrometry
GC  gas chromatography
MS  mass spectrometry
NMR  nuclear magnetic resonance
ATH  aluminum trihydrate
STDV, s  standard deviation
FID  flame ionization detector
NIST  National Institute of Standards and Technology
CAS  Chemical Abstracts Service
DTGS  deuterated triglycine sulfate
DOA  dioctyl adipate
\( \theta \) contact angle of liquid droplet on solid surface (°)

\( \theta_{water} \) contact angle of droplet of water on solid surface (°)

\( \theta_{MI} \) contact angle of droplet of MI on solid surface (°)

\( n \) population of sample

\( \mu \) confidence interval

\( \bar{u} \) mean of sample

\( s \) standard deviation

\( \gamma \) surface free energy per unit area (J/m²)

\( \gamma_l \) surface free energy of liquid (J/m²)

\( \gamma_{ld} \) dispersive component of surface free energy of liquid (J/m²)

\( \gamma_{lh} \) polar component of surface free energy of liquid (J/m²)

\( \gamma_s \) surface free energy of solid (J/m²)

\( \gamma_{sd} \) dispersive component of surface free energy of solid (J/m²)

\( \gamma_{sh} \) polar component of surface free energy of solid (J/m²)

\( \gamma_{sl} \) interfacial energy of liquid and solid (J/m²)

\( W_{sl} \) energy of adhesion of liquid on the surface of solid (J/m²)
1. General Introduction

1.1 Organic Insulators

Some forms of polymeric (organic) insulators have been in use in power systems for more than seventy years. Special formulations of these non-ceramic insulators are being increasingly used worldwide due to their advantages over traditional ceramic and glass insulators [1, 2, 15, 16].

These advantages include light weight, low surface energy, higher mechanical strength to weight ratio, resistance to vandalism, better performance in the presence of heavy pollution in wet condition, and comparable or better withstand voltage than ceramic insulators. On the other hand, they have some disadvantages; they are subjected to chemical changes on the surface due to exposure to ultraviolet radiation in air and from dry band arcing. They also suffer from erosion and tracking in the presence of contamination and humidity which eventually lead to failure of polymer insulators [1, 3–14].

Several polymeric compositions and materials have been used in organic insulators. These include high-temperature vulcanized (HTV) and room temperature vulcanized (RTV) silicone rubber (SIR), ethylene propylene rubber (EPR), ethylene propylene monomer (EPM), ethylene propylene diene monomer (EPDM), ethylene vinyl acetate (EVA), cycloaliphatic and aromatic epoxy resins, high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), polyurethane (PUR), etc [1, 2, 15].

1.1.1 Ethylene Propylene Diene Monomer (EPDM)

Details on the chemical structure and properties of EPDM have been reported previously [17, 18]. EPDM rubber, one of the polymeric materials widely used in outdoor insulations, is a chemically cross-linked elastomer with good electrical insulating properties and excellent flexibility at high and low temperatures. It has good insulation and high dielectric strength, as well as excellent abrasion resistance and mechanical...
properties. It is also recognized for its resistance to weathering and high temperatures. EPDM can withstand the abuse of all types of weather including sunlight, ozone and oxidants [8, 15, 17, 18].

One of the most important properties of EPDM is its inherent low surface energy which prevents the formation of continuous water filming on the surface in wet and contaminated conditions. This reduces the development of the leakage current and flashover. The hydrophobicity of the surface is maintained by diffusion of the low molecular weight (LMW) fluid from the bulk to the surface [14, 18, 37–39, 65].

1.2 Scope of This Work

Polymeric materials in composite insulators are used in different climate conditions (temperature, humidity and low pressure) and are exposed to contaminants (such as high salinity near coastal areas and industrial and agricultural pollutions). Additionally, because the advanced types of polymeric insulators are relatively new, their expected lifetime and aging characteristics are not well known and are of interest to the users and manufacturers of insulators [1].

Although there are several national and international organizations attempting to develop standards, guidelines and tests for composite polymer insulators or insulating materials [19–25], currently there are not well defined specifications for accelerated life testing of insulators [1]. Most existing laboratory tests for this purpose are basically useful for ranking of the compounded materials. Only tests in actual performance in power transmission lines and in outdoor substations could produce realistic results on outdoor service performance [1, 8–10, 27].

Some studies have been done on the effect of salinity and temperature on the hydrophobicity of EPDM [1]. This research is an extended laboratory study of the aging characteristics and the mechanisms responsible for the loss and recovery of hydrophobicity in EPDM insulator, under stress conditions (heat, water salinity and the duration of aging). The following studies have been done:
• Aging characteristics of EPDM insulator were determined under combined stresses of thermal, and immersion in saline solution as a function of time, by measuring the static contact angle of water droplets on the surface of insulator specimens and variations in the weight of the specimens (Chapter 2).

• Studies were supplemented with other appropriate analysis methods, such as application of different washing methods, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), to find an explanation for the aging mechanism (Chapter 3).

• Surface energies of EPDM insulator were determined during the aging process (Chapter 4).

• Recovery of hydrophobicity was investigated as a function of time (Chapter 5).

• Low molecular weight (LMW) fluid content of EPDM insulator and its effect on maintaining the hydrophobicity at high temperatures was studied and further supplementary measurement techniques, such as gas chromatography-mass spectrometry (GC-MS), infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy were carried out to support the findings (Chapter 6).

• Microsoft Excel has been used interactively throughout this work to store and manipulate collected data, perform analyses and produce the graphs and charts. Also, MATLAB was used to solve the surface energies equations and obtain their graphical interrelation.

1.3 Experiment Planning
In the following research, in all sets of experiments and measurements where the behavior of the measured parameters were not predictable physically, mathematically or from the literature, a prototype experiment was usually performed, where possible, prior to the main experiments. The results of the prototype experiments were used for planning the
main experiments. In cases where the results were predictable, the experiments were planned from the beginning.
2. Aging Characteristics of EPDM Insulator

2.1 Introduction

Hydrophobicity is the tendency of the surface of a material to repel water and therefore not to let water to spread over it. It is one of the most important properties of EPDM insulator which is due to its inherent low surface energy. This prevents water from spreading on the surface of the insulator in wet conditions which in turn reduces the development of leakage current and flashover of the insulator and results in a better performance in outdoor service [1].

We are interested in the aging characteristics of insulator materials because aging in outdoor service, as a result of weathering in the presence of severe contamination and sustained moisture, degrades the surface of the insulator due to tracking and erosion which leads to loss of hydrophobicity, developing leakage current and eventually, failure of the insulator.

Hydrophobicity is best determined by measuring the static contact angle of a droplet of distilled water on the surface of the insulator [3–5, 36, 42, 47, 48]. The relationship between hydrophobicity and the contact angle is described in detail in Chapter 4.

The contact angle of a liquid droplet on a solid surface is the angle between the tangent to the droplet at the point where the three phases (solid, gas, liquid) meet, and the horizontal surface of the solid, shown in the figure as $\theta$. The higher the static contact angle of the droplet of distilled water on the surface of the insulator, the more hydrophobic is the insulator.

In the following experiments EPDM specimens were aged by placing them in stationary air and in water with different salinity levels at different temperatures for up to 6000 h.
The contact angle of the droplet of water on the surface of specimens and changes in the weight of the specimens were intermittently measured during the aging process.

2.2 Experimental Procedure

2.2.1 Preparation

EPDM specimens were cut into 1cm×1cm×(0.5–0.8)cm pieces from the sheds of a new 46 kV outdoor insulator. To remove any previous contamination from the surface of the specimens, they were washed in a Branson B–220 ultrasonic cleaner with 5% acetic acid diluted with water (with the ratio of 1 to 10) for two minutes, rinsed with distilled water and dried at room temperature.

Five different temperatures, 0, 25 (room temperature), 50, 75 and 98 °C, and four different salinity levels 5×10⁻³ (lowest possible, distilled water), 1, 10, 100 (saturated) mS/cm and also stationary air were used to age the specimens.

To ensure constant heat for a long period three VWRbrand 1350GM microprocessor-controlled gravity convection ovens were utilized and set to 50, 75 and 98 °C. A refrigerator was used for 0 °C.

Saline solutions were prepared by adding table salt (NaCl) to distilled water at room temperature until the desired conductivity was reached. A Horiba ES–12 digital conductivity meter was used to measure the conductivity. Distilled water was taken from a Barnstead NANOpure DIamond UV water purification system.

2.2.2 Measurement of the Contact Angle and Weight

To ensure the reproducibility of the results and also for use in other experiments, three specimens were used for each set of salinity-temperature totaling 25×3 specimens. The weight and the contact angle of all the virgin specimens were measured, as follows, prior to being aged. The specimens then were put in sealed glass containers at all combinations of heat-salinity reported above, for up to 6000 h. The weight of the specimens and the
contact angle of water on the surface were measured intermittently during the aging process.

Prior to each reading, specimens were taken out of the containers, washed and dried at room temperature for less than ten minutes.

Different washing methods have been tried to establish their effect on the measurement of the contact angle. The effect of different cleaning methods on the contact angle of some polymeric insulators has been previously reported in [58]. In the current study, in the early stages of the aging process specimens were only washed in the ultrasonic cleaner with distilled water for two minutes. Later in the process, the specimens were occasionally washed and cleaned with an ultra soft toothbrush while immersed in shallow distilled water. The brush was used to ensure the removal of any contamination or salt deposits off the surface of specimens. Washing the surface of the specimens with brush has been previously reported to be the most effective cleaning method [58]. Usually a reading after the specimen had been washed in ultrasonic cleaner was subsequently (within few hours) followed by another reading after being brushed, as explained above, to show the immediate effect of complete removal of contaminations, especially when the specimens had been aged for a while without being washed. Further investigation on the effect of washing methods on the measurement of the contact angle is reported in Chapter 3.

After the specimens had been washed and dried prior to the measurement of the contact angle, they were weighed with a Sartorius BP 110 S balance with a precision of 0.1 mg.

The contact angle was determined by averaging of at least five different readings for each specimen. For each reading a droplet of distilled water was placed on the surface of the specimen by a small syringe and a goniometer was used to read the contact angle with an accuracy of 1°. This method of reading the contact angle using a goniometer has been referred to, in the literature, as “direct observation method”, “sessile drop method” and “tangent method” and has been reported to be a reliable technique [3].
It has previously been shown in the literature that the contact angle of water on the surface of a solid varies with a few parameters including the temperature of the droplet and the time lapsed after placement of the droplet on the surface. Other parameters such as salinity and size of the droplet, up to 50 µl, have shown negligible effects on the contact angle [33, 43, 49–51]. In this work, to keep the consistency of the measurements, droplets of distilled water with a size of about 5 µl have been used and the readings took place within 10 s. Room temperature and humidity were also measured to be 25±3 °C and 60±10%, respectively, during the experiments.

Variations in the weight and the contact angle were closely monitored throughout the measurements to identify sudden large changes in the values which might indicate reading errors. That means as soon as an unexpected change was observed in a reading, another reading would be taken immediately to ensure the reproducibility of the result.

2.2.3 Accuracy of the Measurements

A statistical measure, confidence interval, has been used to show the accuracy of the direct observation method using the goniometer for measuring the contact angle. The definition of the confidence interval and a brief explanation on how to calculate it can be found in Appendix A.

In our case, a sample of 30 readings of the contact angle of distilled water on the surface of a washed virgin EPDM specimen has been collected as shown in Figure 2.1. All the readings were collected in less than one hour to keep them consistent.

Table 2.1 shows basic statistical measures as well as the calculated 95% confidence interval for samples 1 and 2, consisting of all 30 readings and the first five readings, respectively, of the sampling shown in Figure 2.1.

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>min</th>
<th>max</th>
<th>mode</th>
<th>Median</th>
<th>mean (µ)</th>
<th>STDV (σ)</th>
<th>t</th>
<th>µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>30</td>
<td>93</td>
<td>105</td>
<td>98</td>
<td>98</td>
<td>2.9</td>
<td>2.04</td>
<td>98±1</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>5</td>
<td>94</td>
<td>102</td>
<td>–</td>
<td>98</td>
<td>3.19</td>
<td>2.78</td>
<td>98±4</td>
<td></td>
</tr>
</tbody>
</table>
In Table 2.1, \( n \) represents the sample size of; \( \text{min} \) and \( \text{max} \) are the lowest and the highest measured values of the contact angle in the sample, respectively; mode, median, and mean are the basic statistical measures; STDV stands for the standard deviation of the data; \( t \) is a statistical value which depends on the number of readings, \( n \), and the required confidence (usually 95%) and is looked up from a table (Appendix A) and \( \mu \) is the “true” value or the confidence interval.

The above-calculated confidence intervals imply, by definition, that in the case of 5 readings for example, the probability of the next readings to fall between 98-4 and 98+4 is more than 95%, which is good enough for our purpose. It is important to note that the confidence interval does not show anything about the distribution of the actual collected data samples.

![Data sample of 30 readings of contact angle of droplet of distilled water on the surface of a virgin EPDM specimen.](image)

*Figure 2.1.* Data sample of 30 readings of contact angle of droplet of distilled water on the surface of a virgin EPDM specimen.
2.3 Results

2.3.1 Variations in the Contact Angle

Figures 2.2–2.6 show the time variation of the contact angle of distilled water on the surface of EPDM specimens being aged in 5×10⁻³, 1, 10 and 100 mS/cm saline solutions and also in stationary air, at five different temperatures of 0, 25, 50, 75 and 98 °C. One specific specimen was chosen for each condition from the 3 specimens in each salinity-temperature stress condition.

The contact angle of all virgin specimens prior to being aged was 95±3°.

2.3.1.1 Specimens in air at all temperatures

Specimens kept in air at all temperatures maintained almost constant contact angles at their original values during the aging process. Few high variations in the original virgin contact angle were observed, two of which at 0 °C (Figure 2.2) and 98 °C (Figure 2.6) were as high as 120° at some point, but returned to the normal contact angle after being washed. The specimens in air were not usually washed except for the few above mentioned cases.

2.3.1.2 Specimens in water (all salinity levels) at 0 °C

The contact angle of the specimens in water with different salinity levels, at 0 °C (Figure 2.2) also remained almost constant at their original value throughout the aging process.

2.3.1.3 Specimens in water (all salinity levels) at 25 °C and higher

For specimens that were kept in water at temperatures of 25 °C and above (Figures 2.3–2.6), the contact angle was observed to follow different patterns depending on the salinity level of water and the aging temperature.

During the first 1000–2000 h of the aging process, the contact angle decreased gradually in the beginning, and then, either remained constant at low values in the cases of 25 °C (Figure 2.3) and 50 °C (Figure 2.4), or returned to its original value between 90 and 100° and even higher in the cases of 75 °C (Figure 2.5) and 98 °C (Figure 2.6). In addition,
specimens at higher temperatures, e.g., 75 and 98 °C, had wider ranges of variation of the contact angle, i.e., they reached lower values of contact angle, even as low as 40°, but also returned to higher values, as high as 140°. At these early stages of the aging process specimens were only washed with distilled water in the ultrasonic cleaner, after being removed from their stress conditions prior to the measurement of the contact angle.

In order to find an explanation for the above mentioned variations, more effective washing methods were applied to see the effect of removal of any possible contamination or deposits from the surface of the specimens, on the contact angle. For this purpose, specimens were occasionally washed and cleaned with an ultra soft toothbrush while immersed in shallow distilled water. Usually a reading of the contact angle after being washed in ultrasonic cleaner was subsequently (within few hours) followed by another reading after being brushed, especially when the specimens had been aged for a while without being washed.

From Figures 2.2–2.6, It can be seen that whenever the specimens had not been cleaned with brush for a long period of time, as in the early stages of the aging process, the contact angle increased gradually in the cases of higher temperatures (75 and 98 °C) and decreased in the cases of lower temperatures (25 and 50 °C). It was also observed that, in all cases, the contact angle would maintain its original value again, immediately after using the brush to clean the specimens.

A possible explanation for this behavior could be as follows: in the case of lower temperatures (25 and 50 °C), salt from the saline solution and other contaminations leaching from the specimens deposit on the surface of specimens during a long period of immersion, and yield low contact angles. In this case, the higher the salinity level, the lower the contact angle. Effectively cleaning the surface of specimens, of course, removes the deposit from the surface and results in normal values of contact angles.

In the case of higher temperatures (75 and 98 °C), however, another mechanism is in effect which suppresses the effect of contamination and yields higher contact angles even in high salinity levels. This mechanism has previously been suggested, for some
polymeric insulators, as the generation and diffusion of the low molecular weight (LMW) fluid and its migration from the bulk of the insulator material to the surface and even on top of the contamination layer [14, 18, 37–39, 65], resulting in more hydrophobic characteristics. This mechanism will be discussed in details in Chapter 6. In this case, the higher the temperature, the higher the contact angle is observed to be. Effective cleaning, again, recovers the contact angle to its original value by removing both the contamination and the diffused LMW fluid from the surface of the specimens. This will be discussed in the next chapter.
Figure 2.2. Time variation of the contact angle of distilled water on the surface of EPDM specimens during aging in different salinities and in air at 0 °C.
Figure 2.3. Time variation of the contact angle of distilled water on the surface of EPDM specimens during aging in different salinities and in air at 25 °C.
Figure 2.4. Time variation of the contact angle of distilled water on the surface of EPDM specimens during aging in different salinities and in air at 50 °C.
Figure 2.5. Time variation of the contact angle of distilled water on the surface of EPDM specimens during aging in different salinities and in air at 75 °C.
Figure 2.6. Time variation of the contact angle of distilled water on the surface of EPDM specimens during aging in different salinities and in air at 98 °C.
2.3.2 Changes in Weight during Aging under Heat and Salinity Stresses

Figures 2.7–2.11 show the time variation of the percentage of weight gain for the same set of specimens and the same aging conditions, as in Figures 2.2–2.6.

With a close look at these figures, it can be seen that for the specimens kept in air at 0, 25, 50 and 75 °C (Figures 2.7–2.10), the changes in weight is almost negligible, although it shows a very slight decrease over time (less than 1%). At 98 °C (Figure 2.11), however, the decrease in weight is more considerable and is as high as 2.61% at the end of the aging process.

In addition, for specimens kept in air at temperatures higher than room temperature, e.g., 50, 75 and 98 °C, the decrease in weight seems to be occurring at a faster rate in the first few hours, which could be because of instant evaporation of water content of specimens due to the higher temperature of the specimens.

For specimens immersed in water, on the other hand, the changes in weight are completely different than in air. Almost at all salinity levels and temperatures, the weight starts to increase at a fast rate in the initial hours of immersion, due to instant water uptake in specimens, and then slows down for the rest of the process. The total increase in weight could get as high as 6.05% for the specimen at 5 μS/cm and 98 °C (Figure 2.11).

The total increase in the weight of specimens immersed in water varies with the stress conditions, i.e., temperature and salinity level of water. In general, for a constant salinity level, the higher the temperature, the higher is the increase in weight. In contrast, for a constant temperature, the higher the salinity level of water, the lower the percentage of increase in weight of specimens would be. However, there are a few exceptions to this rule. For example, specimens in 100 mS/cm saline solution seem to be losing weight at the higher temperatures, e.g., 75 and 98 °C, in the long run, although they gain weight in the beginning few hundred hours. A possible explanation for this behavior could be as follows; these specimens cannot absorb much water due to the high salinity level and
saturated condition of the solution and at the same time lose some of their LMW fluid content as a result of the high temperature. A more detailed study of this behavior is reported in the following chapters.

Table 2.2 is a summary of the final changes in the weight of EPDM specimens during the aging process, as explained above.

<table>
<thead>
<tr>
<th>% of weight gain (+) and weight loss (-) after aging</th>
<th>Aging salinity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0.005 1 10 100</td>
<td>Air 0.76 1.03 0.71 0.33 036</td>
</tr>
<tr>
<td>25 0.04 1.73 2.03 -0.35 0.15 1.33 1.33 0.45</td>
<td></td>
</tr>
<tr>
<td>50 0.33 2.3 1.86 1.33 0.45 3.03 2.02 1.02 -0.73</td>
<td></td>
</tr>
<tr>
<td>75 0.68 3.03 2.02 1.02 -0.73 9.61 6.05 5.72 3.32 -3.84</td>
<td></td>
</tr>
<tr>
<td>98 2.61</td>
<td></td>
</tr>
</tbody>
</table>

A similar study on the effect of immersion for 14 months in a saline solution of 70 μS/cm on the loss of LMW fluid in RTV-SIR was reported in [43, 46].
Figure 2.7. Time variation of percentage of weight gain of EPDM specimens during aging in different salinities and in air at 0 °C.
Figure 2.8. Time variation of percentage of weight gain of EPDM specimens during aging in different salinities and in air at 25 °C.
Figure 2.9. Time variation of percentage of weight gain of EPDM specimens during aging in different salinities and in air at 50 °C.
Figure 2.10. Time variation of percentage of weight gain of EPDM specimens during aging in different salinities and in air at 75 °C.
Figure 2.11. Time variation of percentage of weight gain of EPDM specimens during aging in different salinities and in air at 98 °C.
3. Supplementary Experiments

3.1 Introduction

As reported in the previous chapter, the contact angle of a droplet of water on the surface of EPDM specimens, used as a measure of hydrophobicity of the insulator, aged in water with various salinity levels, at different temperatures, was found to be a function of both the salinity level and the temperature. The contact angle also varied with the cleaning method applied to the specimens. At lower temperatures (25 and 50 °C), deposition of salt and contamination from the saline solution on the surface of specimens after a long period of immersion was attributed to the decrease in the contact angle. However, at higher temperatures (75 and 98 °C) generation and diffusion of the low molecular weight (LMW) fluid in the bulk of the insulator material and its migration to the surface and even to the top of the contamination layer has been suggested to be responsible for the increase in the contact angle of specimens.

This chapter is an in-depth investigation to determine the mechanisms of aging of EPDM insulator. The studies performed consist of the effect of different washing methods on the contact angle of specimens aged at various temperatures and salinity levels, the application of surface analysis such as scanning electron microscopy (SEM) with X-ray microanalysis and Fourier transform infrared (FTIR) spectroscopy in finding the aging characteristics of EPDM.

3.2 Experiments

3.2.1 Effect of Cleaning the Surface of the Specimens on the Contact Angle

The effect of different cleaning methods on the contact angle of RTV silicone rubber has been previously reported in [58]. In this research two of the previously reported washing methods were used in a test sequence to study their effect on the measured contact angle of the EPDM specimens during the aging process.
3.2.1.1 Experimental Procedure and Washing Methods

A selection of 8 specimens from those aged in Chapter 1 was used to study the effect of cleaning the surface of the specimens on the contact angle. The selected specimens were aged for about 6000 h at the time of this experiment. The selection is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>50</td>
<td>75</td>
<td>75</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>Salinity level (mS/cm)</td>
<td>0.005</td>
<td>10</td>
<td>0.005</td>
<td>10</td>
<td>1</td>
<td>100</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

A 6-step sequence of measurements A to F of contact angle combined with two different washing methods was employed for all selected specimens as follows.

In the first cleaning method the surface of the specimens were cleaned with a constant spray of distilled water for about 2 minutes. In the other method, the specimens were washed and cleaned with an ultra soft toothbrush while immersed in shallow distilled water. The brush was used to ensure the removal of any contamination, salt deposit or diffused fluid layer off the surface of the specimens. Washing the surface of the specimens with brush has been previously reported to be the most effective cleaning method [58].

A typical sequence started with removing the specimen from the saline solution and measuring the contact angle of water on its surface after letting the specimen dry in stationary air for about two minutes without being cleaned (step A). The specimen was then left in stationary air at room temperature for ten minutes after which the second measurement of the contact angle took place (step B). Another measurement followed right after the second one and after washing the specimen with a spray of distilled water for 2 minutes and drying it at room temperature for additional two minutes (step C). The next measurement occurred right after step C, after cleaning the surface of the specimen with a soft brush, while immerged it in distilled water, and then drying it at room temperature for about two minutes (step D). Afterwards, the specimen was aged again, in
the same condition as before, for 12 h, after which it was washed once more with a spray of distilled water for two minutes, dried at room temperature for two minutes and its contact angle was measured (step E). In the last step, which followed immediately, the specimen was cleaned with the brush and distilled water, dried for two minutes and its contact angle was measured (step F). The last two steps (E and F) were meant to examine the reproducibility of the measurements, for both cleaning methods. Table 3.2 is a summary of the steps and the applied cleaning methods.

Table 3.2. Contact angle measurement sequence used to study the effect of different methods of cleaning the surface of specimens, during the aging process. RT, room temperature.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Washing method</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>measured after removal from saline solution; dried in RT</td>
<td>no cleaning</td>
</tr>
<tr>
<td>B</td>
<td>measured after being left in stationary air at RT for 10 min.</td>
<td>no cleaning</td>
</tr>
<tr>
<td>C</td>
<td>measured right after step B</td>
<td>washed with water</td>
</tr>
<tr>
<td>D</td>
<td>measured right after step C</td>
<td>brushed</td>
</tr>
<tr>
<td>E</td>
<td>measured after removal from saline solution, well after step D; dried in RT</td>
<td>washed with water</td>
</tr>
<tr>
<td>F</td>
<td>measured right after step E</td>
<td>brushed</td>
</tr>
</tbody>
</table>

Each contact angle was determined by averaging of at least five readings at different locations in each specimen. For each reading, a droplet of water was placed on the surface of the specimen by a small syringe. A goniometer was used to read the contact angle with an accuracy of 1°. This method of reading the contact angle was described in Chapter 2. To keep the consistency of the measurements, droplets of water with a size of about 5 μl have been used and the readings took place within 10 s. Room temperature and humidity were also measured to be 25±3 °C and 60±10%, respectively, during the experiments.
3.2.1.2 Results

Figures 3.1 and 3.2 show the contact angle in each step of the measurement sequence described in Table 3.2, for samples in Table 3.1. Samples 1–4 are the specimens aged at lower temperatures of 25 and 50 °C and samples 5–8 are aged at higher temperatures of 75 and 98 °C.

From Figure 3.1 it can be seen that the contact angle of all four specimens, which aged at 25 and 50 °C and various salinity levels, changed in similar patterns during the measurement sequence, i.e., there was a slight increase in the contact angles, after washing the specimens with a spray of distilled water in step C, compared to their contact angles after removal from aging conditions in step A with no cleaning. The use of brush for the first time to clean the specimens in step D increased the contact angle significantly, in all cases, from an average of 65 to 80°. The second time the brush was used in step F, after another aging period, again resulted in an increase of contact angle, compared to the spray-wash in step E. It is also interesting to note that the contact angles in steps D and F, where brush was used to clean the specimens, are almost identical and their average (87°) is the closest, among the average contact angles in other steps, to the contact angle of the virgin EPDM specimen (95±3°); whereas the average of the contact angles in two steps C and E, where the specimens were cleaned with water spray, are 70 and 80°, respectively, and are both lower than the original contact angle of the virgin specimen (95±3°). This suggests that using the brush removes the contamination and salt deposit from the saline solution off the surface of the specimens and recovers the contact angle to near its original value.

By looking at Figure 3.2, which is the same as Figure 3.1 but for 75 and 98 °C aging temperatures, it is understood that although changes in the contact angle are not following exactly similar patterns, whenever brush is used to clean the specimens, the contact angle merges to the average value of 98°, which is again close to the original value of 95±3°, regardless of the aging temperature and salinity level. However, unlike what was seen in Figure 3.1 for lower aging temperatures, in this case when the water spray cleaning method is used, specially for the first time in step C, the contact angle is higher or at least
very close to the contact angle in the next step after cleaning with brush. This again suggests that brushing effectively removes the deposits, which in the case of higher aging temperatures is the LMW fluid from the bulk of the insulator material that has increased the hydrophobicity of the surface, from the surface of the specimens.

These results are in agreement with what has been reported in [58] on the effectiveness of cleaning the specimens with brush. In addition, they support the explanation about variations in the contact angle of the specimens aged in various salinity levels and temperatures due to application of different washing methods in Chapter 2.
Figure 3.1. Contact angle with the application of different cleaning methods in a measurement sequence with 6 steps, A–F, as described in Table 3.2, for specimens aged in: 1, 0.005 mS/cm at 25 °C; 2, 10 mS/cm at 25 °C; 3, 0.005 mS/cm at 50 °C; 4, 10 mS/cm at 50 °C (Table 3.1).

Applied cleaning method:
A: no cleaning, upon removal from solution
B: no cleaning, after 10 min. in air at room temperature
C: water spray
D: brush
E: water spray
F: brush
Contact angle with the application of different cleaning methods in a measurement sequence with 6 steps, A–F, as described in Table 3.2, for specimens aged in: 5, 1 mS/cm at 75 °C; 6, 100 mS/cm at 75 °C; 7, 1 mS/cm at 98 °C; 8, 100 mS/cm at 98 °C (Table 3.1).

Applied cleaning method:
A: no cleaning, upon removal from solution
B: no cleaning, after 10 min. in air at room temperature
C: water spray
D: brush
E: water spray
F: brush
3.2.2 SEM/EDS

3.2.2.1 Experimental Procedure

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) are techniques which permit the observation and characterization of organic and inorganic materials and surfaces. Utilization of these techniques to study the hydrophobicity of the organic insulators was previously reported in [28, 31, 35, 41].

Three EPDM specimens from those used for the aging process in Chapter 2 were used for SEM/EDS analysis and were compared to a virgin specimen. Specimens were chosen from various salinity levels at 75 °C after aging for about 6000 h. Table 3.3 lists the selected specimens.

<table>
<thead>
<tr>
<th>ID</th>
<th>Temperature (°C)</th>
<th>Salinity (mS/cm)</th>
<th>Aged for (h)</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>25</td>
<td>air</td>
<td>virgin</td>
<td>none</td>
</tr>
<tr>
<td>II</td>
<td>75</td>
<td>0.005</td>
<td>&gt;6000</td>
<td>no cleaning</td>
</tr>
<tr>
<td>III</td>
<td>75</td>
<td>10</td>
<td>&gt;6000</td>
<td>brushed</td>
</tr>
<tr>
<td>IV</td>
<td>75</td>
<td>100</td>
<td>&gt;6000</td>
<td>no cleaning</td>
</tr>
</tbody>
</table>

One of the aged specimens was cleaned with brush and distilled water prior to the analysis to make possible the simultaneous study of the effect of cleaning and aging on the surface of the specimens. The other two specimens were simply dried in stationary air at room temperature after removal from the aging conditions prior to the analysis. All four specimens including a virgin sample were then mounted, coated with a thin layer of gold and introduced to the vacuum chamber of the microscope.

A Joel JSM-5800 LV scanning microscope was used for secondary electron imaging to closely examine the physical changes on the surface of the specimens, with accelerating voltage 5 kV under conventional vacuum. The composition of the elements on the surface of the specimens was also determined with the attachment of a Kevex Super Quantum x-ray detector with an accelerating voltage 15 kV and a penetration depth of a few microns.
3.2.2.2 Results

Figures 3.3–3.6 show the SEM images of the surface of different EPDM specimens introduced above. From these images it is clearly observed that the surface roughness of the specimens increases with increasing aging salinity level. In the last image with the highest salinity level of 100 mS/cm the surface has completely lost its original shape. However, it seems that the use of brush to clean the specimen in Figure 3.5, even at a relatively high salinity level of 10 mS/cm, has effectively recovered the surface to its original status.

Figures 3.7–3.10 show the energy-dispersive spectra of the same specimens as above. Figure 3.11 is the same spectrum as in Figure 3.10, but from a different area on the surface of the same specimen. Significant elements that have been detected on the surface of all specimens are Al, Si and Ca. There are also some other elements with negligible intensity counts compared to those mentioned, which are not important for the purpose of this study. There are also Au peaks in all spectra which are coming from the gold coating that was used to provide proper grounding for the specimens.

From Figure 3.7 it can be seen that the virgin specimen does not have any significant element on its surface; whereas in aged specimens, Figures 3.8–3.10, more intensity of Al, Si and Ca is detected. In addition, it is observed that the intensity of Al and Si varies with the salinity level and applied washing method, e.g., the intensity of Al is dominant in Figure 3.9 where the specimen was cleaned with brush, compared to the specimen with the high salinity level of 100 mS/cm in Figure 3.11, which has high intensity of Si and no Al. The Al originates from the aluminum trihydrate (ATH) filler which is added to the base polymer during the manufacture of the insulator to enhance its resistance to tracking and erosion as well as to improve its mechanical performance and to reduce flammability [14, 15, 19, 26, 29, 40]. The specimen aged in distilled water in Figure 3.8 also shows relatively higher intensity of Al than Si. These results imply that the intensity counts of Al decreased with the aging salinity level and returned to its higher values with the use of effective washing methods as it exposes the original surface.
Figure 3.3. SEM image of the surface of a virgin EPDM specimen (specimen I, Table 3.3); top: 100x, bottom: 1000x.
Figure 3.4. SEM image of the surface of the EPDM specimen aged in distilled water at 75 °C for about 6000 h and dried in stationary air at room temperature prior to the imagery (specimen II, Table 3.3); top: 100×, bottom: 1000×.
Figure 3.5. SEM image of the surface of the EPDM specimen aged in 10 mS/cm saline solution at 75 °C for about 6000 h and cleaned with brush in distilled water prior to the imagery (specimen III, Table 3.3); top: 100×, bottom: 1000×.
Figure 3.6. SEM image of the surface of the EPDM specimen aged in 100 mS/cm saline solution at 75 °C for about 6000 h and dried in stationary air at room temperature prior to the imagery (specimen IV, Table 3.3); top: 100x, bottom: 1000x.
Figure 3.8. Energy-dispersive spectrum of the EPDM specimen aged in distilled water at 75 °C for about 6000 h and dried in stationary air at room temperature prior to the spectroscopy (specimen II, Table 3.3); range: 20 keV.
Figure 3.9. Energy-dispersive spectrum of the EPDM specimen aged in 10 mS/cm saline solution at 75 °C for about 6000 h and cleaned with a brush in distilled water prior to the spectroscopy (specimen III, Table 3.3); range: 20 keV.
Figure 3.10. Energy-dispersive spectrum of the EPDM specimen aged in 100 mS/cm saline solution at 75 °C for about 6000 h and dried in stationary air at room temperature prior to the spectroscopy (specimen IV, Table 3.3); range: 20 keV.
Figure 3.11. Same as Figure 3.10, but with the incident electron beam focused on the bright spots (as pictured in the SEM image of the specimen in Figure 3.6) on the surface of the same specimen.
3.2.3 ATR-FTIR Spectroscopy

3.2.3.1 Experimental Procedure

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to investigate the composition of the surface of the samples. Utilization of these techniques to study the hydrophobicity of the organic insulators was previously reported in [30, 32, 33].

Four EPDM specimens from those used for the aging process in Chapter 2 were used for ATR-FTIR analysis and were compared to a virgin specimen. Specimens were chosen from various salinity levels and temperatures after aging for about 6000 h. Table 3.4 lists the selected specimens. One of the aged specimens (specimen V) was cleaned with brush and distilled water prior to the analysis to make possible the simultaneous study of the effect of cleaning and aging on the surface of the specimens. Other three specimens were simply dried in stationary air at room temperature after removal from the aging conditions prior to the analysis. Table 3.4 also lists the contact angle of water on the surface of specimens after preparation and prior to conducting the IR spectroscopy.

<table>
<thead>
<tr>
<th>ID</th>
<th>Temperature (°C)</th>
<th>Salinity (mS/cm)</th>
<th>Aged for (h)</th>
<th>Preparation</th>
<th>$\theta_{\text{water}}$ (degrees) after preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>25 air</td>
<td></td>
<td>virgin</td>
<td>none</td>
<td>95</td>
</tr>
<tr>
<td>II</td>
<td>50 0.005</td>
<td>&gt; 6000</td>
<td>no cleaning</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>98 0.005</td>
<td>&gt; 6000</td>
<td>no cleaning</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>75 1</td>
<td>&gt; 6000</td>
<td>no cleaning</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>75 1</td>
<td>&gt; 6000</td>
<td>brushed</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

A Bruker Equinox 55 Fourier transform infrared spectrometer, equipped with ZnSe ATR crystal and a DTGS detector was used to record the spectra. Each spectrum was taken with a resolution of 4 cm$^{-1}$. Before recording the spectra of the specimens, the test was run once with no specimens to obtain the background spectrum to be subtracted from the main spectra later. The specimens then were tested one at a time, and twice each, to
ensure the reproducibility of the results. The crystal was cleaned with methanol before testing each specimen.

3.2.3.2 Results

Figures 3.12–3.16 are the ATR-FTIR spectra of the selected aged EPDM specimens compared to a virgin specimen and also to each other.

Wavenumber in these figures is a wave property inversely related to wavelength. It is the spatial analogue of frequency. Application of a Fourier transformation on data in the time domain yields a frequency spectrum; applied on data in the spatial domain (data as a function of position) yields a spectrum as a function of wavenumber. The unit of this quantity is cm\(^{-1}\), pronounced as *reciprocal centimeter*.

In the spectra the peaks of interest, which can be seen in the virgin specimen as well as all aged specimens, of course with different absorbance levels, are as follows:

- 2918 and 2849 cm\(^{-1}\) due to C–H stretching bond in CH\(_2\) and CH\(_3\) units
- 1738 cm\(^{-1}\) due to C=O stretching in COOR (esters)
- 1500–1600 cm\(^{-1}\) due to C=C stretching
- 1400–1500 cm\(^{-1}\) due to CH\(_2\) and CH\(_3\) bending
- Broad peaks around 3500 cm\(^{-1}\) and 1015 cm\(^{-1}\) due to OH stretching in the ATH filler

Among all the above-mentioned bonds, polar ones, such as C=O, contribute to the hydrophobic behavior of the EPDM insulator even during the aging process. In addition, changes in the absorbance level of C=O stretching bonds in different specimens, may be interpreted as regeneration of polar groups during the aging process, due to diffusion of the LMW fluid, which results in the maintenance of the hydrophobic properties of the insulator. There are also significant changes in the absorbance level of OH stretching bonds among the specimens, which could be related to the changes in the composition of ATH particles due to various aging conditions and different washing methods. These
findings about the diffusion of the LMW fluid are consistent with the results reported in the literature, [14, 18, 37–39, 65], and also with our findings in Sections 3.2.1 and 3.2.2 above.
Figure 3.12. Comparison between the IR spectra of I, a virgin EPDM specimen, and II, the specimen aged in distilled water at 50 °C for about 6000 h. The aged specimen was removed from stress condition and dried in stationary air at RT prior to the measurement. The contact angle of water right before these measurements was 95 and 80° for I and II, respectively.
Figure 3.13. Comparison between the IR spectra of I, a virgin EPDM specimen, and III, the specimen aged in distilled water at 98 °C for about 6000 h. The aged specimen was removed from stress condition and dried in stationary air at RT prior to the measurement. The contact angle of water right before these measurements was 95 and 130° for I and III, respectively.
Figure 3.14. Comparison between the IR spectra of I, a virgin EPDM specimen, and IV, the specimen aged in 1 mS/cm saline solution at 75 °C for about 6000 h. The aged specimen was removed from stress condition and dried in stationary air at RT prior to the measurement. The contact angle of water right before these measurements was 95 and 140° for I and IV, respectively.
Figure 3.15. Comparison between the IR spectra of I, a virgin EPDM specimen, and V, the specimen aged in 1 mS/cm saline solution at 75 °C for about 6000 h. The aged specimen was removed from stress condition, cleaned with brush and distilled water and dried in stationary air at RT prior to the measurement. The contact angle of water right before these measurements was 95 and 100° for I and V, respectively.
Figure 3.16. Comparison between the IR spectra of two EPDM specimens aged in the same stress conditions (1mS/cm saline solution at 75 °C) for about 6000 h. Before the measurement, the specimens were removed from the stress condition. IV was dried without cleaning; V was cleaned with brush and distilled water and dried in stationary air at RT. The contact angle of water right before these measurements was 140 and 100° for IV and V, respectively.
3.3 Suggested Aging Mechanism

Considering the suggestions in Chapter 2 and also our findings from the supplementary experiments in this chapter so far, the tentative aging mechanism is as follows.

In case of lower temperatures (≤ 50 °C), salt and other contaminations from the saline solution deposit on the surface of the specimens during a long period of immersion, and yield low contact angles. In this case, the higher the salinity level, the lower the contact angle. In the case of higher temperatures (≤ 75 °C), however, generation and diffusion of the low molecular weight (LMW) fluid from the bulk of the insulator material to the surface and migrating to the top of the contamination layer, results in more hydrophobic characteristics. In this case, the higher the temperature, the higher the contact angle is observed to be. Effective cleaning removes both the contamination and the diffused LMW fluid from the surface of the specimens deposit or contamination from the surface of the specimens and recovers the contact angle to its original value.

However, final decision about the aging mechanism in EPDM including the composition of the LMW fluid and diffusion and regeneration of this fluid from the bulk to the surface of the specimens during the aging process requires further investigations with the application of more analytical techniques. Such investigations and their results will follow in Chapter 6.
4. Surface Free Energies

4.1 Introduction

In Chapter 2, hydrophobicity was introduced as one of the most important properties of polymeric insulators, enhancing their performance in wet conditions in outdoor service, by preventing water from spreading over the surface of the insulator. In that chapter, the static contact angle of a droplet of distilled water on the surface of the insulator was used as an indication of hydrophobicity of EPDM insulator during the aging process.

Hydrophobicity of a substance is determined by its surface free energy. The lower the surface energy of a material, the more hydrophobic is that material, and vice versa. Fluorocarbons, hydrocarbons and silicones are examples of materials with low surface energies. They possess good hydrophobic properties and are mostly used in high-voltage insulators. Glass and porcelains, on the other hand, have high-energy surfaces and therefore are not considered as hydrophobic materials.

Surface free energy, and therefore the hydrophobicity of insulators, is subjected to change as a result of some changes in the composition of their surface, for instance, changes during the aging process. Therefore, studying the surface energy of an insulator during the aging process may lead to important information about the nature of the changes in the composition of the insulator, which helps to understand the aging mechanism.

In this chapter, first, the concept of surface free energy will be introduced to explain the relationship between the contact angle of water on the surface of the insulator and its hydrophobicity, and then it is used to supplement the study of the aging process of EPDM insulator.
4.2 Surface Free Energies

4.2.1 Definition

Surface free energy, or surface tension, is defined as the work required to increase the area of the substance by one unit. Surface free energy per unit area, \( \gamma \) (J/m\(^2\)), can be divided into a dispersive component, caused by London dispersion forces, with suffix \( d \), and a polar component, due to hydrogen bonding forces, with suffix \( h \); and can be written for a liquid as [3–5]:

\[
\gamma_l = \gamma_{ld} + \gamma_{lh}.
\]

(4.1)

and for a solid as:

\[
\gamma_s = \gamma_{sd} + \gamma_{sh}.
\]

(4.2)

For a solid, \( \gamma_{sd} \) and \( \gamma_{sh} \) are responsible for hydrophobicity and hydrophilicity (the tendency of a molecule to be dissolved in water; opposite of hydrophobicity), respectively.

Equation (4.2) implies that changes in the surface energy and hence the hydrophobicity of an insulator can be a result of changes in any or both of its components, \( \gamma_{sd} \) and \( \gamma_{sh} \). This fact will be used later in the chapter to suggest the aging mechanism in EPDM insulator.

4.2.2 Surface Free Energies and the Contact Angle

The state of a drop of liquid on the surface of a solid is described by the contact angle \( \theta \), the angle between the surface and the tangent to the surface of the liquid at the point of contact. This angle ranges in value from zero, if the liquid completely wets the surface, to 180°, if the liquid does not wet the surface at all and remains as a drop.

Thomas Young in 1805 was the first to equate the three surface tension vectors in equilibrium at the three-phase point of contact. He wrote the equation which is usually associated with his
name, the Young’s equation [3–5, 53]:

$$\gamma_i = \gamma_{sl} + \gamma_l \cos \theta,$$  \hspace{1cm} (4.3)

where $\gamma_s$, $\gamma_l$ and $\gamma_{sl}$, all in J/m$^2$, are the surface free energies of the solid, liquid and the interfacial energy of liquid and solid, respectively.

The interfacial energy of liquid and solid, $\gamma_{sl}$, also relates to the energy of adhesion on the surface, $W_{sl}$ (J/m$^2$), with Dupre’s equation [59]:

$$\gamma_{sl} = \gamma_s + \gamma_l - W_{sl}.$$ \hspace{1cm} (4.4)

Combining (4.3) and (4.4) gives:

$$W_{sl} = \gamma_l (1 + \cos \theta).$$ \hspace{1cm} (4.5)

### 4.2.3 Calculating the Surface Free Energies

Although (4.3) is a theoretically significant equation, it is of little practical value taken on its own in calculating $\gamma_s$. However, there are several approaches for determining the surface energy of solid substrates based on (4.3). Some of these approaches include the “critical surface tension (Zisman)” method, “geometric mean (Fowkes)” method, “harmonic mean (Wu)” method and “acid-base (Van Oss)” method. In the current study the harmonic mean approximation has been used to calculate the surface free energies of EPDM insulator specimens as follows.

#### 4.2.3.1 Harmonic Mean Approximation

This method utilizes the harmonic mean approximation, suggested by Wu in [3]:

$$\gamma_{sl} = \gamma_s + \gamma_l - \frac{4\gamma_{sl}\gamma_{sh}}{\gamma_{sh} + \gamma_{lh}} - \frac{4\gamma_{sh}\gamma_{lb}}{\gamma_{sh} + \gamma_{lb}},$$ \hspace{1cm} (4.6)

where all parameters are as defined in (4.1)–(4.3). This equation combined with the Young’s equation in (4.3) gives:
(1 + \cos \theta) \gamma_i = \frac{4 \gamma_{sd} \gamma_{id}}{\gamma_{sd} + \gamma_{id}} + \frac{4 \gamma_{sh} \gamma_{ih}}{\gamma_{sh} + \gamma_{ih}}. \quad \text{(4.7)}

Rewriting (4.7) for two known liquids, water and methylene iodide (MI) gives:

\[
\begin{align*}
(1 + \cos \theta_W) \gamma_{W,i} &= \frac{4 \gamma_{sd} \gamma_{id}}{\gamma_{sd} + \gamma_{id}} + \frac{4 \gamma_{sh} \gamma_{ih}}{\gamma_{sh} + \gamma_{ih}} \\
(1 + \cos \theta_{MI}) \gamma_{MI,i} &= \frac{4 \gamma_{sd} \gamma_{id_{MI}}}{\gamma_{sd} + \gamma_{id_{MI}}} + \frac{4 \gamma_{sh} \gamma_{ih_{MI}}}{\gamma_{sh} + \gamma_{ih_{MI}}}
\end{align*}
\] \quad \text{(4.8)}

This system of equations with two variables \(\gamma_{sd}\) and \(\gamma_{sh}\) can now be solved with any pair of measured \(\theta_W, \theta_{MI}\) as the input parameters and \(\gamma_{id}, \gamma_{ih}\) and \(\gamma_i\) as known values from literature [3], as given in Table 1.1.

\textit{Table 4.1. Literature values of \(\gamma_{sh}, \gamma_{ih}\) and \(\gamma_i\) for water and methylene iodide [3].}

<table>
<thead>
<tr>
<th>Surface energies (mJ/m\textsuperscript{2})</th>
<th>(\gamma_{sd})</th>
<th>(\gamma_{ih})</th>
<th>(\gamma_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>22.1</td>
<td>50.7</td>
<td>72.8</td>
</tr>
<tr>
<td>MI</td>
<td>44.1</td>
<td>6.7</td>
<td>50.8</td>
</tr>
</tbody>
</table>

From (4.2), simply adding the just calculated \(\gamma_{sd}\) and \(\gamma_{sh}\) gives the value of the surface free energy, \(\gamma_s\).

\textbf{4.2.3.2 Parametric Solution and Analysis}

A MATLAB program (Appendix C) is used to solve the system of two nonlinear equations (4.8) with two variables \(\gamma_{sd}\) and \(\gamma_{sh}\) for all physically possible values of \(\theta_W, \theta_{MI}\) as parameters. It should be noticed that, in some cases these solutions do not necessarily have a physical realization and are merely used for the mathematical analysis of the surface free energies.

Figures 4.1–4.9 (top) show the two possible sets of solutions for the system variables, \(\gamma_{sd}\) and \(\gamma_{sh}\), and their sum, \(\gamma_s\), for \(0 \leq \theta_{\text{water}} \leq 150^\circ\) and some selected realistic values of \(\theta_{MI}\) between 40 and 80°. As it can be seen from the figures, solution 2 always contains
negative values for surface energies which is not physically realizable and hence is not an acceptable solution.

Figures 4.1—4.9 (bottom) show solution 1 curves in a single graph, for a realistic range of $50^\circ \leq \theta_{\text{water}} \leq 120^\circ$ and the same set of selected values of $\theta_{\text{MI}}$. From these figures it is realized that, with use of the harmonic mean approximation, at a given $\theta_{\text{MI}}$, as $\theta_{\text{water}}$ increases, $\gamma_{\text{sh}}$ decreases approaching to zero. This means that, mathematically, for any given $\theta_{\text{MI}}$ there is always an upper limit for $\theta_{\text{water}}$ in order to have nonnegative surface energies. These upper limits are marked with a vertical line in each figure. Table 4.2 is a summary of these upper limits for different values of $\theta_{\text{MI}}$.

Table 4.2. Mathematical upper limit for $\theta_{\text{water}}$ for selected values of $\theta_{\text{MI}}$ in order to have nonnegative surface energies when using the harmonic mean approximation to calculate the surface energies.

<table>
<thead>
<tr>
<th>$\theta_{\text{water}}$ (degrees)</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
<th>70</th>
<th>75</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum possible $\theta_{\text{water}}$ (degrees)</td>
<td>101</td>
<td>102</td>
<td>103</td>
<td>104</td>
<td>106</td>
<td>107</td>
<td>108</td>
<td>112</td>
<td>113</td>
</tr>
</tbody>
</table>

In other words, in practice, if the difference between the measured contact angles of droplet of MI and water goes beyond a certain amount, this method cannot calculate the surface energy of the material under study.

Figures 4.10—4.12 show the contour map of the surface energies $\gamma_{\text{sd}}$, $\gamma_{\text{sh}}$ and $\gamma_{\text{s}}$, respectively, in the plane of $\theta_{\text{water}}$ and $\theta_{\text{MI}}$. Numbered curves in these figures represent the surface-energy-equal-to-constant curves as a function of $\theta_{\text{water}}$ and $\theta_{\text{MI}}$ and the numbers are the values of the constant surface energies.

From these figures it is understood that measuring the contact angle of only one liquid on the surface of an insulator cannot give an exact explanation of how the composition of the surface is changing. Combined tracking of the changes in the pair of contact angles, on the other hand, will give an understanding of what components of the surface energy is changing. For instance, a certain $\theta_{\text{water}}$ corresponds to different values of $\gamma_{\text{s}}$. Only with knowing the corresponding $\theta_{\text{MI}}$ the right $\gamma_{\text{s}}$ and its components can be distinguished. That
explains why we need to know the changes in the contact angle of two different liquids on the surface in order to know how the surface composition of an insulator is changing. Knowing the changes in the contact angle of only one fluid may only give the information about whether $\gamma_s$ is increasing or decreasing (with very few exceptions), but cannot explain how.

Finally, Figure 4.13 shows the 3D realization of the dependency of the surface energies $\gamma_{sh}$, $\gamma_{sd}$ and $\gamma_s$ of a solid on the contact angle of droplets of water and MI on its surface.

From this figure it can be concluded that, generally speaking, with an increase in the contact angle of any of the liquids, water or MI, $\gamma_s$ will decrease (with very few exceptions where $\theta_{water}$ is greater than 90° and $\theta_{MI}$ is small). In addition, $\gamma_{sh}$ and $\gamma_{sd}$ seem to be more sensitive to the changes in $\theta_{water}$ and $\theta_{MI}$, respectively. A similar analysis of the surface energies was reported in [56].

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Figure 4.1. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_\sigma$, for $0 \leq \theta_{\text{water}} \leq 150^\circ$ and $\theta_{\text{ML}}=40^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_\sigma$, for $50^\circ \leq \theta_{\text{water}} \leq 120^\circ$ and $\theta_{\text{ML}}=40^\circ$; the vertical line shows the upper limit for $\theta_{\text{water}}$ to have valid surface energies.
Figure 4.2. Top: solutions for the variables \( \gamma_{sd} \) and \( \gamma_{sh} \) of (4.8) and their sum, \( \gamma_s \), for \( 0 \leq \theta_{water} \leq 150^\circ \) and \( \theta_{MI}=45^\circ \) as input parameters; Bottom: acceptable solution (solution 1) for \( \gamma_{sd} \) and \( \gamma_{sh} \) and their sum, \( \gamma_s \), for \( 50^\circ \leq \theta_{water} \leq 120^\circ \) and \( \theta_{MI}=45^\circ \); the vertical line shows the upper limit for \( \theta_{water} \) to have valid surface energies.

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Figure 4.3. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_o$, for $0 \leq \theta_{water} \leq 150^\circ$ and $\theta_{MI}=50^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_o$, for $50^\circ \leq \theta_{water} \leq 120^\circ$ and $\theta_{MI}=50^\circ$; the vertical line shows the upper limit for $\theta_{water}$ to have valid surface energies.
Figure 4.4. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_s$ for $0 \leq \theta_{\text{water}} \leq 150^\circ$ and $\theta_{\text{Mi}}=55^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_s$ for $50^\circ \leq \theta_{\text{water}} \leq 120^\circ$ and $\theta_{\text{Mi}}=55^\circ$; the vertical line shows the upper limit for $\theta_{\text{water}}$ to have valid surface energies.
Figure 4.5. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_s$, for $0 \leq \theta_{water} \leq 150^\circ$ and $\theta_{MI}=60^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_s$, for $50^\circ \leq \theta_{water} \leq 120^\circ$ and $\theta_{MI}=60^\circ$; the vertical line shows the upper limit for $\theta_{water}$ to have valid surface energies.
Figure 4.6. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_o$ for $0 \leq \theta_{\text{water}} \leq 150^\circ$ and $\theta_M=65^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_s$, for $50^\circ \leq \theta_{\text{water}} \leq 120^\circ$ and $\theta_M=65^\circ$; the vertical line shows the upper limit for $\theta_{\text{water}}$ to have valid surface energies.
Figure 4.7. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_s$, for $0 \leq \theta_{\text{water}} \leq 150^\circ$ and $\theta_{Ml}=70^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_s$, for $50^\circ \leq \theta_{\text{water}} \leq 120^\circ$ and $\theta_{Ml}=70^\circ$; the vertical line shows the upper limit for $\theta_{\text{water}}$ to have valid surface energies.
Figure 4.8. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_s$, for $0 \leq \theta_{water} \leq 150^\circ$ and $\theta_{MI} = 75^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_s$, for $50^\circ \leq \theta_{water} \leq 120^\circ$ and $\theta_{MI} = 75^\circ$; the vertical line shows the upper limit for $\theta_{water}$ to have valid surface energies.
Figure 4.9. Top: solutions for the variables $\gamma_{sd}$ and $\gamma_{sh}$ of (4.8) and their sum, $\gamma_{s}$, for $0 \leq \theta_{water} \leq 150^\circ$ and $\theta_{MI}=80^\circ$ as input parameters; Bottom: acceptable solution (solution 1) for $\gamma_{sd}$ and $\gamma_{sh}$ and their sum, $\gamma_{s}$, for $50^\circ \leq \theta_{water} \leq 120^\circ$ and $\theta_{MI}=80^\circ$; the vertical line shows the upper limit for $\theta_{water}$ to have valid surface energies.
Figure 4.10. Contour map of $\gamma_{sd}=$-constant curves in the plane of $\theta_{water}$ and $\theta_{MI}$.

Figure 4.11. Contour map of $\gamma_{sh}=$-constant curves in the plane of $\theta_{water}$ and $\theta_{MI}$.
Figure 4.12. Contour map of $\gamma_s$=constant curves in the plane of $\theta_{\text{water}}$ and $\theta_{\text{MI}}$.

Figure 4.13. 3D realization of the surface energies $\gamma_{sh}$, $\gamma_{sd}$ and $\gamma_s$ of a solid as a function of the contact angle of droplets of water and MI on its surface.
4.3 Experimental Procedures

4.3.1 Preparation

EPDM specimens were cut into 1cm×1cm×(0.5–0.8)cm pieces from the sheds of a new 46 kV outdoor insulator. To remove any previous contamination from the surface of the specimens, they were washed in a Branson B-220 ultrasonic cleaner with 5% acetic acid diluted with water (with the ratio of 1 to 10) for two minutes, rinsed with distilled water and dried at room temperature.

Four different salinity levels $5\times10^{-3}$ (lowest possible, distilled water), 1, 10, 100 (saturated) mS/cm and also stationary air were used to age the specimens at 75 °C. A VWRbrand 1350GM microprocessor-controlled gravity convection oven was utilized to ensure the constant temperature of 75 °C during the experiments.

Saline solutions were prepared by adding table salt (NaCl) to distilled water at room temperature until the desired conductivity was reached. A Horiba ES-12 digital conductivity meter was used to measure the conductivity. Distilled water was taken from a Barnstead NANOpure DIamond UV water purification system.

4.3.2 Measurement of the Contact Angles of Water and of Methylene Iodide

The contact angles of water and of methylene iodide on the surface of all virgin specimens were measured prior to being aged. The specimens then were put in sealed glass containers, in stress conditions explained above, for up to 1500 h. The contact angles of water and methylene iodide on their surface were measured intermittently during the aging process.

Prior to each reading, specimens were taken out of their containers, cleaned and dried at room temperature for less than ten minutes. To clean the specimens they were washed in the ultrasonic cleaner with distilled water for two minutes.

Each contact angle was determined by averaging at least five different readings for each specimen. For each reading, a droplet of liquid was placed on the surface of the specimen
by a small syringe and a goniometer was used to read the contact angle with an accuracy of 1°. This method of reading the contact angle was explained in more details in Chapter 2. To keep the consistency of the measurements, droplets of liquid with a size of about 5 μl have been used and the readings took place within 10 s. Room temperature and humidity were also measured to be 25±3 °C and 60±10%, respectively, during the experiments.

Variations in the contact angles of water and MI were closely monitored during the measurements to avoid unwanted reading errors. That means as soon as an unexpected change was observed in a reading, another reading would be taken immediately to ensure the reproducibility of the measurement.

4.3.3 Calculating the Surface Free Energies

Following the measurements of the contact angles, a Microsoft Excel spreadsheet was used to calculate and manipulate the surface energies, $\gamma_{sd}$, $\gamma_{sh}$ and $\gamma_s$, based on the method described in 1.2.3.1. The interfacial energy of liquid and solid, $\gamma_{si}$, and the energy of adhesion on the surface, $W_{si}$, were also calculated for all stress conditions using (4.4) and (4.5).

4.4 Results

Figures 4.14–4.18 show the time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen aged in 5×10⁻³, 1, 10, 100 mS/cm solutions and also stationary air, at 75 °C.

Figure 4.19 shows the restatement of the collected data (θ_MIL, $\gamma_{sh}$, $\gamma_{sd}$ and $\gamma_s$) from all stress conditions (stationary air and 5×10⁻³, 1, 10 and 100 mS/cm solutions, at 75 °C), as introduced in Figures 4.14–4.18, and also the corresponding calculated $W_{si}$ and $\gamma_{si}$, as a function of the contact angle of water (θ_water). In a similar study [44], the values of $\gamma_{sh}$, $\gamma_{sd}$ and $\gamma_s$ were reported as 7.95, 15.05 and 23 mJ/m², respectively, for the un-aged EPDM. After aging, these became 50.55, 0.67, 51.22 mJ/m².
Figure 4.14. Time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen during aging in stationary air at 75 °C.
Figure 4.15. Time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen during aging in distilled water ($5 \times 10^{-5}$ mS/cm) at 75 °C.
Figure 4.16. Time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen during aging in 1 mS/cm saline solution at 75 °C.
Figure 4.17. Time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen during aging in 10 mS/cm saline solution at 75°C.
Figure 4.18. Time variation of the measured contact angle of distilled water and methylene iodide and also the calculated surface energies of the EPDM specimen during aging in 100 mS/cm saline solution at 75 °C.

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Figure 4.19. Restatement of the collected data ($\theta_{\text{Ml}}, \gamma_{\text{sd}}, \gamma_{\text{sh}}$ and $\gamma_{\text{s}}$) from all stress conditions (stationary air and $5 \times 10^3$, 1, 10 and 100 mS/cm solutions, at 75 °C), described in Figures 4.14–4.18, and also the corresponding calculated $W_{\text{s,t}}$ and $\gamma_{\text{st}}$ as a function of the contact angle of water ($\theta_{\text{water}}$).
4.5 Discussions

From the results it can be concluded that:

- Generally speaking, in EPDM an increase in either $\theta_{\text{water}}$ or $\theta_{\text{MI}}$ is an indication of the decrease in surface free energy. That is why we can usually use either of them alone to quickly investigate the hydrophobicity of EPDM specimens, although water seems to be more sensitive to the changes in the surface energy and hydrophobicity than MI. This is also in agreement with our findings in the mathematical analysis.

- In EPDM, the component mostly responsible for the changes in the surface free energy during the aging process is $\gamma_{sh}$ which corresponds to the polar component of the surface free energy and is due to the hydrogen bonding forces. This is consistent with what reported for other polymers in [5, 54].

The above observations suggest that in EPDM during the aging process something must have happened to the hydrogen bonding on the surface, which might be explained with the migration of the LMW fluid from the bulk to the surface of the insulator and causing the change in the composition of the surface. This behavior, which was also reported in [44, 52], will be discussed in more details in the following chapters.
5. Recovery

5.1 Introduction

A study of the aging characteristics of an EPDM insulator was reported in the previous chapters. EPDM specimens were aged in stationary air and water with different salinity levels at different temperatures. The contact angle of a droplet of water and the changes in the weight and the surface roughness of the specimens during the aging process were measured and reported in Chapter 2.

This chapter reports on the study of the recovery of aged EPDM specimens after removing them from the stress conditions and keeping them in stationary air at room temperature for up to 4000 h. The contact angle of a droplet of water on the surface of the specimens and variations in the weight of the specimens during the recovery process were used to determine the hydrophobic behavior of the EPDM insulator.

5.2 Experimental Procedures

One specimen among the three specimens subjected to heat and salinity stresses, which were previously used for the aging process in Chapter 2, was used for the recovery. To remove any contamination deposited during the aging process from the surface of the specimens, they were washed with diluted acetic acid and brushed in distilled water as described in 2.2. The specimens were then kept in stationary air at room temperature for about 4000 h and their weight and the contact angle of water on the surface were measured intermittently during the recovery process. Measurement tools and techniques are as previously described in 2.2.2. Room temperature and humidity were also measured to be 25±3 °C and 60±10%, respectively, during the experiments.
5.3 Results

5.3.1 Variations in the Contact Angle

Figures 5.1–5.5 show the time variation of the contact angle of distilled water on the surface of EPDM specimens recovered in stationary air at room temperature. These specimens were aged in different salinities and in air, and in various temperatures (0, 25, 50, 75 and 98 °C) for about 6000 h. Details of the study on the aging characteristics of similar specimens under the same stress conditions were reported in Chapter 2.

From Figure 5.1, the contact angle of the specimens aged in 0 °C did not show much of a change during the recovery period, except for the specimen aged in 100 mS/cm saline solution, for which the contact angle increased from 84°, at the beginning of the recovery, to 95° after a few hundred hours. At 25 °C (Figure 5.2) the contact angles remained almost constant for all specimens during the recovery. At 50 °C, Figure 5.3, the only contact angle that changed was that of the specimen aged in air, which increased rapidly from 98° to 110° during the first 10 h and then gradually to 115° from then on. At 75 °C (Figure 5.4), the contact angle of the specimen aged in 10 mS/cm recovered gradually from 96° to 107°; whereas, that of the specimen aged in 100 mS/cm decreased from 115° at the beginning of the recovery to 103° at the end. Changes of the contact angle of the rest of the specimens at 75 °C were negligible. At 98 °C (Figure 5.5), however, the contact angle of almost all specimens, except the one in 100 mS/cm, increased considerably (about 20°) during the recovery. In 100 mS/cm, the contact angle increased rapidly from 100° to around 110° during the first 400 h and then returned gradually to 103° at the end of the recovery.

Table 5.1 shows the comparison between the contact angles of the specimens at three stages of the aging and recovery process: (1) contact angle of the virgin specimens before aging, (2) contact angle after aging and at the beginning of the recovery process, and (3) contact angle at the end of recovery. The specimens were aged for about 6000 h in different stress conditions as described in Chapter 2 and then recovered in air at room temperature for more than 4000 h.
From Table 5.1, specimens can be divided into the following categories based on the changes in their contact angles during the aging and recovery process:

- The contact angle recovered to its original value (contact angle of the virgin specimen, 95±3°) after recovery, including specimens aged in: 0 °C and 100 mS/cm, 75 °C and 10 mS/cm, 75 °C and 100 mS/cm, 98 °C and 1 mS/cm, and 98 °C and 10 mS/cm.

- The contact angle did not recover after aging, including specimens aged in: 0 °C and 0.005 mS/cm, 25 °C and 0.005 mS/cm, 25 °C and 100 mS/cm, 50 °C and 1 mS/cm, 50 °C and 10 mS/cm, and 75 °C and air.

- The contact angle recovered to a different value rather than its original value (contact angle of a virgin specimen, 95±3°), including specimens aged in: 50 °C and air, 98 °C and air, and 98 °C and 0.005 mS/cm.

- The contact angle retained its original value (contact angle of a virgin specimen, 95±3°) after aging and also at the end of recovery, although in some cases it changed during those processes. The rest of the specimens not mentioned above are in this category.

Table 5.1. Comparison between the contact angles of EPDM specimens at different stages: (1) contact angle of the virgin specimens before aging, (2) contact angle after aging for about 6000 h and at the beginning of the recovery process, (3) contact angle after recovery for more than 4000 h.

<table>
<thead>
<tr>
<th>Contact angle (degrees)</th>
<th>(1) virgin specimen, (2) beginning of recovery, (3) last recovery measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ageing temp. (°C)</td>
<td>Aging salinity (mS/cm)</td>
</tr>
<tr>
<td>Air</td>
<td>0.005</td>
</tr>
<tr>
<td>0</td>
<td>95 93 93 93 105 97 95 96 96 97 93 91 95 100 84 95</td>
</tr>
<tr>
<td>25</td>
<td>94 98 96 96 87 86 97 89 95 96 95 95 100 99 86 85</td>
</tr>
<tr>
<td>50</td>
<td>96 98 115 96 102 104 95 108 106 95 113 110 95 105 100</td>
</tr>
<tr>
<td>75</td>
<td>95 104 106 94 105 103 98 100 101 106 96 107 97 115 103</td>
</tr>
<tr>
<td>98</td>
<td>94 66 84 94 94 113 96 82 104 105 81 100 101 100 103</td>
</tr>
</tbody>
</table>

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Figure 5.1. Time variation of the contact angle of distilled water on the surface of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 0 °C (Chapter 2).
Figure 5.2. Time variation of the contact angle of distilled water on the surface of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 25 °C (Chapter 2).
Figure 5.3. Time variation of the contact angle of distilled water on the surface of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 50 °C (Chapter 2).
Figure 5.4. Time variation of the contact angle of distilled water on the surface of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 75 °C (Chapter 2).
Figure 5.5. Time variation of the contact angle of distilled water on the surface of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 98 °C (Chapter 2).
5.3.2 Changes in Weight during Recovery at 25 °C in Air

Figures 5.6–5.10 show the time variation of the percentage of weight loss of EPDM specimens recovered in stationary air at room temperature. These specimens were aged in different salinities and in air, and at various temperatures (0, 25, 50, 75 and 98 °C) for about 6000 h. Details of the study on the aging characteristics of similar specimens under the same stress conditions were reported in Chapter 2.

Table 5.2 is a summary of the percentages of final weight loss or gain of EPDM specimens: (1) during aging for about 6000 h in different stress conditions as described in Chapter 2, and (2) during recovery in air at room temperature for 4000 h.

Table 5.2. percentages of final weight loss or gain of EPDM specimens: (1) during aging for about 6000 h in different stress conditions, (2) during recovery in air at room temperature for 4000 h.

<table>
<thead>
<tr>
<th>Aging salinity (mS/cm)</th>
<th>0.005</th>
<th>1</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.34</td>
<td>-1.09</td>
<td>0.92</td>
<td>-0.53</td>
</tr>
<tr>
<td>25</td>
<td>-0.08</td>
<td>-1.16</td>
<td>2.57</td>
<td>-1.23</td>
</tr>
<tr>
<td>50</td>
<td>0.37</td>
<td>-2</td>
<td>2.49</td>
<td>-1.57</td>
</tr>
<tr>
<td>75</td>
<td>0.74</td>
<td>-3.01</td>
<td>4.76</td>
<td>-1.8</td>
</tr>
<tr>
<td>98</td>
<td>2.21</td>
<td>-5.57</td>
<td>12.19</td>
<td>-2.86</td>
</tr>
</tbody>
</table>

From Figures 5.6–5.10 it can be seen that all specimens aged in air at different temperatures gained weight gradually during the recovery at 25 °C in air. Percentage of weight gain at the end of recovery ranged from 0.04% for 0 °C to 0.42% for 98 °C (Table 5.2).

On the other hand, all the specimens aged in saline solutions in different temperatures lost weight during recovery. Weight lost was faster at the beginning of the recovery and saturated gradually towards the end. The rise time of the saturation of the weight loss curves ranged from about 300 h for the specimens aged at 0 °C to about 1600 h at 98 °C.
Moreover, from Table 5.2 it was observed that the percentage of weight loss was as low as 0.23% for the specimen aged at 0 °C and 100 mS/cm, and topped out at 12.19% for the specimen aged in 98 °C and 0.005 mS/cm. The specimens aged at higher temperatures lost more weight during recovery. In other words, the higher the aging temperature, the higher was the percentage of weight loss of the specimens during recovery. On the contrary, specimens aged at higher salinity levels lost less weight during recovery. In other words, the higher the aging salinity level, the lower was the percentage of weight loss of the specimens. However, there were some exceptions to these general conditions, such as specimens aged at 25 °C and 0.005, 1 and 100 mS/cm, for the first condition (rising temperature), and the specimen aged in 98 °C and 10 mS/cm for the second condition (rising salinity level).

Table 5.3 lists the percentages of the total weight loss of the specimens at the end of the overall process of aging and recovery.

Table 5.3. Percentage of the total weight loss (extracted substance) of the EPDM specimens after being aged for about 6000 h in different stress conditions as listed below, followed by recovery in air at room temperature for more than 4000 h; negative values mean weight gain.

<table>
<thead>
<tr>
<th>Aging temp. (°C)</th>
<th>Aging salinity (mS/cm)</th>
<th>% of total weight loss (+) and weight gain (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air 0.005 1 10 100</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.3 -0.18 0.28 -0.1 -0.15</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>-0.18 1.41 1.26 0.67 0.09</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.14 0.49 0.66 1.16 -0.13</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.4 1.74 2.4 2.08 1.83</td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>1.79 6.62 6.57 5.27 5.99</td>
<td></td>
</tr>
</tbody>
</table>

The results show that some specimens gained weight at the end of the process. Those include the specimens aged at 0 °C and 0.005, 10 and 100 mS/cm; 25 °C and air; and the one aged at 50 °C and 100 mS/cm. Other specimens showed an overall decrease in weight which could be an indication of losing a component during the aging process. This extracted component has previously been introduced as the low molecular weight (LMW) fluid. In the suggested aging mechanism the generation and diffusion of the LMW fluid...
from the bulk of the insulator material to the surface and its migration to the top of the contamination layer [14, 18, 37–39, 65], results in more hydrophobic characteristics. This mechanism will be discussed in details in Chapter 6.

Considerable extractions occurred at aging temperature 98 °C. The maximum amount of the extracted fluid was 6.62%, which corresponds to the specimen aged at 98 °C and 0.005 mS/cm.
Figure 5.6. Time variation of percentage of weight loss of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 0 °C (Chapter 2).
Figure 5.7. Time variation of percentage of weight loss of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 25 °C (Chapter 2).
Figure 5.8. Time variation of percentage of weight loss of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 50 °C (Chapter 2).
Weight loss, %

Figure 5.9. Time variation of percentage of weight loss of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 75 °C (Chapter 2).
Figure 5.10. Time variation of percentage of weight loss of EPDM specimens during recovery in stationary air at room temperature. The specimens were aged in different salinities and in air at 98 °C (Chapter 2).
6. **LMW Fluid Content of EPDM Insulator**

6.1 **Introduction**

In EPDM insulator, low molecular weight (LMW) additives are often used during processing or purposely added as a blend [1, 8, 15, 44]. During aging, the LMW fluid could be generated by either the release of short cyclic chains that were trapped in the structure of the polymer and/or scission of the long molecular chains at higher temperatures [34, 45].

The mechanism responsible for the loss and recovery of hydrophobicity under stress conditions of heat and salinity was suggested to be highly dependent on the generation and diffusion of the LMW fluid from the bulk of the EPDM insulator and its migration to the surface. This was addressed in previous chapters in the following circumstances:

- In Chapters 2 and 3, the generation and diffusion of the LMW fluid and its migration to the surface was suggested to be responsible for the increase in the contact angle of EPDM specimens at higher aging temperatures (75 and 98 °C).

- In Chapter 3, effectively washing the specimens with a brush was suggested to be responsible for the retrieval of the contact angle in the case of higher aging temperatures (75 and 98 °C) by removing the migrated LMW fluid, which had increased the contact angle, from the surface of the specimens.

- In Chapter 3, changes in the absorbance level of C=O stretching bonds in the IR spectrum of different specimens were interpreted as due to the presence of polar groups on the surface of the specimens from diffusion of the LMW fluid during the aging process, resulting in maintenance of the hydrophobic properties of the insulator.

- In Chapter 4, changes in the polar component of the surface energy, and hence the contact angle, were related to the changes in the hydrogen bonding on the surface as a
result of migration of the LMW fluid from the bulk to the surface during the aging process.

- In Chapter 5, the overall weight loss of the specimens at the end of the recovery process was suggested to be an indication of extraction of the LMW fluid from the bulk of the specimens during the aging process.

In this chapter, first the composition of the LMW fluid is investigated by the application of several identification techniques after extracting the fluid from the bulk of the EPDM insulator specimens. Then the aging mechanism of the EPDM insulator is established after performing a few complementary experiments on the EPDM specimens.

6.2 General Preparation

New specimens of EPDM were cut and washed as explained in Chapter 2. Several specimens were used for each set of experiments in order to ensure the reproducibility of the results.

Two high temperature ovens and a precision balance with accuracy of 0.1 mg were used in the following experiments in order to heat and weigh the specimens. The room temperature and the humidity were measured to be 25±2 °C and 60±10% respectively during the experiments.

6.3 Extracting the LMW Fluid

6.3.1 Immersion in Hexane

LMW fluid content of the specimens was extracted by immersing them in analytical hexane, until complete saturation in the weight of the specimens due to absorption of the hexane, followed by evaporation in air [34]. The difference between the weight of the specimens before immersion in hexane and after complete evaporation in air shows the actual amount of the substance which was taken out from the bulk of the specimens by being dissolved in hexane during immersion. This process was followed at both room
temperature and 50 °C for two different specimens. The latter temperature was utilized to accelerate the extraction process.

To ensure that the process of immersion and evaporation extracted all the fluid content of the specimens, two different cases of extraction were followed.

In the first case, immersion and evaporation were repeated three times, for the same specimens, until full absorption and evaporation was accomplished in each stage. To ensure this, the specimens were immersed in hexane each time for 120 h and then dried in stationary air for 240 h. Figures 6.1–6.3 show the percentages of weight gain and loss as a function of time in each stage, for the specimens at room temperature and 50 °C.

In the second case, specimens were immersed in hexane for almost 1000 h followed by 1000 h of evaporation in air. Figure 6.4 shows the percentages of weight gain and loss as a function of time at room temperature and 50 °C.

6.3.2 Results and Comparisons

From Figures 6.1–6.4 it can be seen that, in all cases the weight of the specimens increased and saturated rapidly within the 24 h of immersion in hexane for both temperatures 25 and 50 °C. Saturation occurred faster and to lower percentages in case of 50 °C. Moreover, the percentages of the final increase in the weight of specimens during immersion in hexane in the first extractions (Figures 6.1 and 6.4) were less than those of the second and third extractions (Figures 6.2 and 6.3) for about 10%. An explanation for this is that, the specimens must have absorbed more hexane during the second and third immersions due to the extraction of most of their fluid contents during the first immersion. The evaporation process, on the other hand, seems to be a slower process compared to absorption, and the percentage of weight loss during evaporation always reached to the same steady state (about 37%) after almost 120 h, regardless of how many extractions had been done before, for both 25 and 50 °C, although evaporation, like absorption, occurred faster at 50 °C.
Table 6.1 compares the percentages of extracted fluid from the EPDM specimens, for the three consecutive short-term and the long-term extractions mentioned above.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (h) of Immersion</th>
<th>Time (h) of Evaporation</th>
<th>Extraction Time (°C)</th>
<th>% of extracted fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Stage 1</td>
</tr>
<tr>
<td>Short-term extractions</td>
<td>120</td>
<td>240</td>
<td>25</td>
<td>7.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>8.44</td>
</tr>
<tr>
<td>Long-term extraction</td>
<td>1000</td>
<td>1000</td>
<td>25</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>8.69</td>
</tr>
</tbody>
</table>

From the table, it can be seen that the percentage of the extracted fluid in the second and third stages of the short-term extractions were negligible, compared to the first stage. In addition, the percentages of the total extracted fluid in the short-term and long-term extractions were close within ±0.11% at 25 °C and ±0.09% at 50 °C. These results suggest that the long-term extraction process can be replaced with the short-term process for almost similar results.

Thus, for the purpose of this study, 48 h of immersion in hexane followed by 120 h of evaporation in air, both at 50 °C, were used in order to extract the LMW fluid contents of EPDM specimens. In the literature, 48 h of evaporation at 44 °C has been used for the alloy of EPDM/SIR [55], 96 h of immersion at 40 °C, followed by 12 h of evaporation at room temperature were used for RTV specimens [61], and 96 h of immersion followed by 24 h of evaporation, both in 23 °C, were used for EPDM [60].
Figure 6.1. Top: percentage of weight gain of EPDM specimens during the 1st short-term immersion in hexane at 25 and 50 °C; Bottom: percentage of weight loss of EPDM specimens during the 1st short-term evaporation in air at 25 and 50 °C.
Figure 6.2. Top: percentage of weight gain of EPDM specimens during the 2nd short-term immersion in hexane at 25 and 50 °C; Bottom: percentage of weight loss of EPDM specimens during the 2nd short-term evaporation in air at 25 and 50 °C.
Figure 6.3. Top: percentage of weight gain of EPDM specimens during the 3rd short-term immersion in hexane at 25 and 50 °C; Bottom: percentage of weight loss of EPDM specimens during the 3rd short-term evaporation in air at 25 and 50 °C.
Figure 6.4. Top: percentage of weight gain of EPDM specimens during the long-term immersion in hexane at 25 and 50 °C; Bottom: percentage of weight loss of EPDM specimens during the long-term evaporation in air at 25 and 50 °C.


6.4 Identification of the Extracted Fluid

The composition of the fluid extracted from the EPDM insulator specimens was studied. In order to separate the LMW fluid from hexane, the solution from the extraction process was concentrated down by evaporating its hexane in a rotary evaporator. The latter is a device used in chemical and biochemical laboratories for the efficient and gentle evaporation of solvents. The main components of a rotary evaporator are a vacuum system, consisting of a vacuum pump and a controller, a rotating evaporation flask which can be heated in a heated fluid bath, and a condenser with a condensate collecting flask. The evaporation process only took a few minutes and the remaining product after the process, which was a colorless oily liquid, was mostly consisted of the LMW fluid extracted from the EPDM insulator specimens.

Several identification techniques, including gas chromatography-mass spectrometry (GC-MS), infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, were utilized to identify the concentrated extracted fluid as follows. Each technique was repeated several times on samples of the fluid extracted from different EPDM specimens to ensure the accuracy and reproducibility of the results.

6.4.1 GC

The identification process started with gas chromatography (GC). A Varian CP-3800 gas chromatograph with a flame ionization detector (FID) was used for initial identification of the extracted fluid. The concentrated extracted fluid from the EPDM specimens was dissolved in enough (few μls) acetone and 2 μl of the solution was injected into the CP-Sil 5 CB column of the chromatograph. The initial temperature at the column was held at 50 °C for 2 min and then increased by 15 °C/min up to 300 °C and was held there for 5 min. The analysis took 23.67 min.

Figure 6.5 shows the GC chromatogram of the extracted fluid. Peaks at 15 and 17 min indicate the presence of two different compounds in the fluid under study. The former most likely pertain to the residual hexane and the latter are representing the LMW fluid extracted from the EPDM specimens.
6.4.2 GC-MS

Gas chromatography-mass spectrometry (GC-MS) was used to obtain more information about the extracted fluid. A Varian CP-3800 gas chromatograph and a Varian 1200L Quadropole MS mass analyzer (70 eV) were used to identify the extracted fluid. The concentrated extracted fluid was dissolved in acetone and 2μl of the solution was injected into the carrier gas stream, helium, which passed through the CP-Sil 8 CB column, at a speed of approximately 36 cm/s and a quantity of 1ml/min. The column head pressure was 7.6 psi. The initial temperature at the column was held at 50 °C for 2 min and then increased by 10 °C/min up to 155 °C and then by 30 °C/min up to 300 °C and was held there for 17.5 min. The GC-MS interface’s temperature was 200 °C and that of the injector was 250 °C.

Figure 6.6 shows the GC-MS spectra of the extracted fluid. The spectra clearly confirm the presence of an organic compound with a molecular weight of about 370, appeared at 18 min in the GC chromatogram. The closest match to this compound, suggested by the instrument’s software program from its built-in National Institute of Standards and Technology (NIST) database, is dioctyl adipate with the chemical formula C_{22}H_{42}O_{4} and the Chemical Abstracts Service (CAS) registry number 103-23-1. Figure 6.7 shows the mass spectrum of dioctyl adipate taken from NIST database.

6.4.3 IR Spectroscopy

In order to verify the identification of the extracted LMW fluid, a Bruker Vector 22 spectrometer was used to obtain the infrared spectrum of the extracted fluid. The concentrated extracted fluid was dissolved in acetone and a few drops of the solution were placed on KBr plate and was kept at room temperature for a few minutes for the acetone to evaporate. The sample was then put into the spectrometer and the infrared beam was transmitted through it.

Figure 6.8 shows the IR spectrum of the extracted LMW fluid. Comparing this spectrum to the IR spectrum of dioctyl adipate, taken from [57], in Figure 6.9 leaves no doubt that the extracted fluid contains dioctyl adipate, an ester of octanol and adipic acid.
6.4.4 NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used as the last step of the identification process. A Bruker Avance 500 MHz spectrometer was used to obtain the $^{13}$C and $^1$H NMR spectra of the extracted fluid, with chloroform-$d$ ($\text{CDCl}_3$) as the solvent.

Figures 6.10 and 6.11 compare the $^{13}$C and $^1$H NMR spectra of the extracted fluid with those of the actual dioctyl adipate (from Sigma-Aldrich Co.). Peaks around 77 ppm in the $^{13}$C NMR spectra in Figure 6.10 are representing chloroform-$d$. It can be seen that all the major peaks in the spectra of the extracted fluid closely match the reference spectra.
Figure 6.6. GC-MS spectra of the fluid extracted from EPDM insulator (70 eV).

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Figure 6.7. Mass spectrum of dioctyl adipate (source: NIST database).
Figure 6.8. IR spectrum of the fluid extracted from EPDM insulator.
Figure 6.10. $^{13}$C NMR spectrum of, top: the fluid extracted from EPDM insulator; bottom: dioctyl adipate (source: Sigma-Aldrich Co.).
Figure 6.11. $^1$H (proton) NMR spectrum of, top: the fluid extracted from EPDM insulator (500 MHz); bottom: dioctyl adipate (source: Sigma-Aldrich Co.).
6.4.5 Dioctyl Adipate

It was shown, as a result of the application of several identification techniques in the previous sections, that the LMW fluid extracted from the EPDM specimens contains dioctyl adipate.

Dioctyl adipate or DOA is a colorless oily liquid generally used as a plasticizer in polymers and is sometimes blended with other plasticizers. It features flexibility at low temperatures, good electrical properties, good resistance to weathering, and good stability to heat. DOA is an ester of octanol and adipic acid. Its melting point is -67.8 °C and its boiling point is 214 °C. Its solubility in water is negligible, but it is soluble in ethyl alcohol, diethyl ether, acetone, acetic acid, and most organic solvents. Its chemical formula is \( C_{22}H_{42}O_4 \), with the molecular weight 370.57, and its CAS number is 103-23-1. It has several other names in literature, including: hexanedioic acid, bis(2-ethylhexyl) ester; adipic acid, bis(2-ethylhexyl) ester; bis(2-ethylhexyl) adipate [62, 63]. Figure 6.12 shows its chemical structure [62].

![Chemical structure of dioctyl adipate](image)

*Figure 6.12. Chemical structure of dioctyl adipate \( (C_{22}H_{42}O_4) \) [62].*

In a previous study on EPDM [45], siloxane molecular units \([-\text{Si(CH}_3\text{)}_2\text{-O}]_n\) of \( n=3 \) to \( n=6 \) and cyclo-siloxanes with units of \( n=6 \) to \( n=12 \) were identified as the LMW fluid. A recent study of the extracted LMW fluid from EPDM was also reported in [66].
6.5 Effect of Heat in Regeneration of LMW Fluid

In order to establish the aging mechanism of the EPDM insulator, the following complementary experiments on the effect of heat in regeneration and diffusion of the LMW fluid were performed.

6.5.1 Hexane-Heat-Hexane Test Sequence

Eight EPDM specimens were washed with 5% acetic acid diluted with water (with the ratio of 1 to 10) and dried at room temperature and their weight and the contact angles of water and MI on their surface were measured, as explained in Chapter 2.

The specimens were put in the hexane-heat-hexane test sequence as depicted in Figure 6.13. In this test sequence, first, all the LMW fluid contents of the specimens were extracted by immersing them in analytical hexane for 48 h, followed by evaporation in air for 120 h, all at 50 °C, as described in 6.3.1. The specimens were then heated for 32 h at 100, 150, 175 and 200 °C in air to accelerate the possible regeneration of the LMW fluid. Finally, the specimens were immersed again in hexane to extract any remaining LMW fluid. To ensure the reproducibility of the results, two specimens were used at each heating temperature.

![Hexane-heat-hexane test sequence diagram]

Figure 6.13. Hexane-heat-hexane test sequence

The weight and the contact angles of water and MI on the surface of the specimens were measured intermittently during the test at the following nine steps A to H: A, after the first extraction of the LMW fluid; B–H: at 0.5, 1, 2, 4, 8, 16 and 32 h after the start of the heating process; I, after the second extraction of the LMW fluid.

- 113 -
Figure 6.14 shows the percentage of total (cumulative) and step weight loss of the EPDM specimens at different steps of the hexane-heat-hexane test sequence, for both specimens at each heating temperature 100, 150, 175 and 200 °C.

From Figure 6.14 it can be seen that all specimens lost about 8% of their weight after the first extraction of the LMW fluid (measurement step A). During the heating process (measurement steps B–H) the percentage of weight loss increased with the increase of the heating temperature. The percentage of weight loss after the second extraction (measurement step I) was also slightly higher for the specimens which had been heated at higher temperatures.

Table 6.2 is a summary of the percentage of weight loss of EPDM specimens at different steps of the hexane-heat-hexane test sequence. Each table entry is the average of the percentages of weight losses of two different specimens at each heating temperature, at a given step of the sequence. Measurement steps A–I are as described above.

<table>
<thead>
<tr>
<th>Average % of weight loss (of two samples in each temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement sequence</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Heating temp. (°C)</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
<td>175</td>
</tr>
<tr>
<td>200</td>
</tr>
</tbody>
</table>

In Table 6.2, entries under column A show the percentage of the LMW fluid contents of the virgin specimens. The sum of the percentages of weight loss from steps B to I at each temperature shows the percentage of the total regenerated LMW fluid due to heat, at that
temperature. A portion of this regenerated fluid is evaporated during the heating process. The percentage of the evaporated fluid is the sum of the percentages of the weight loss from measurement step B through H. The rest of the regenerated LMW fluid is extracted in step I.

From Table 6.2 it can be seen that the percentage of the LMW fluid contents of the virgin specimens, under column A, was 7.89±0.05%. However, the percentage of the total regenerated LMW fluid due to heat (sum of B–I) increased with the heating temperature, from 0.54% for 100 °C to 3.77% for 200 °C.

Figures 6.15 and 6.16 show the contact angles of water and MI and surface free energy ($\gamma_s$) of the EPDM specimens at different steps of the hexane-heat-hexane test sequence, for both specimens at each heating temperature 100, 150, 175 and 200 °C.

From Figures 6.15 and 6.16 it can be seen that, almost for all specimens, the contact angles of water and MI increased after the first extraction of the LMW fluid (measurement step A). The average of the original contact angles of water and MI for all specimens were 93 and 53°, and the average amount of the increase of the contact angles after the first extraction were 8 and 5° for water and MI, respectively. Moreover, the contact angles showed an increase during the heating process (measurement steps BH) for all heating temperatures, however, the higher the heating temperature, the higher was the amount of increase in the contact angles. The average of the increase of the contact angles of water and MI for two specimens at each heating temperature, during the heating process (between measurement steps B and H), was as low as 6 and 4° for 100 °C and as high as 10 and 9° for 200 °C, for water and MI, respectively. After the second extraction (measurement step I) the contact angles of water and MI decreased considerably for all specimens.

An explanation for the variations in the contact angles of water and MI during the hexane-heat-hexane test sequence is that during the heating process, LMW fluid is generated and then migrates to the surface of the specimens, lowering the surface energy of the specimens, which results in an increase in the contact angles of the water and MI.
The amount of the generated LMW fluid depends on the heating temperature and is higher for higher temperatures. After the second extraction, most of the LMW fluid contents of the specimens are removed from the bulk and the surface of the specimens. This increased the surface energy and decreased the contact angle of the specimens as shown in Figures 6.15 and 6.16. These results are in agreement with what reported in [17, 18, 34].
Figure 6.14. Percentage of total (cumulative) and step weight loss of the EPDM specimens at different steps of the hexane-heat-hexane test sequence, for heating temperatures 100, 150, 175 and 200 °C (two specimens at each temperature).

Description of the measurement steps:

A: measurement after the 1st extraction of the LMW fluid at 50 °C
B–H: measurement at 0.5, 1, 2, 4, 8, 16 and 32 h after the start of the heating process at different temperatures
I: measurement after the 2nd extraction of the LMW fluid at 50 °C
Figure 6.15. Contact angles of water and MI and surface free energy ($\gamma_s$) of the EPDM specimens at different steps of the hexane-heat-hexane test sequence for both specimens at each heating temperature 100 °C (top) and 150 °C (bottom). Measurement steps are as in Figure 6.14.
Figure 6.16. Contact angles of water and MI and surface free energy ($\gamma_s$) of the EPDM specimens at different steps of the hexane-heat-hexane test sequence for both specimens at each heating temperature 175 °C (top) and 200 °C (bottom). Measurement steps are as in Figure 6.14.
6.5.2 Heat-Hexane-Heat Test Sequence

Four EPDM specimens were washed with 5% acetic acid diluted with water (with the ratio of 1 to 10) and dried at room temperature and their weight and the contact angle of water on their surface were measured, as explained in Chapter 2.

The specimens were put in the heat-hexane-heat test sequence as depicted in Figure 6.17. Four specimens were used for the test to ensure the reproducibility of the results. In this test sequence, first, the specimens were heated for 32 h at 200 °C in air to accelerate the possible regeneration of the LMW fluid. The LMW fluid contents of the specimens were then extracted by immersing them in analytical hexane for 48 h, followed by evaporation in air for 120 h, all at 50 °C, as described in 6.3.1. Finally, the specimens were heated again for 32 h at 200 °C.

![Figure 6.17. Heat-hexane-heat test sequence](image)

The weight and the contact angle of water on the surface of the specimens were measured intermittently during the test at the following three steps: J, after the first heating for 32 h at 200 °C; K, after immersion in hexane for the extraction of the LMW fluid; L, after the second heating for 32 h at 200 °C.

Figure 6.18 shows the contact angle of water on the surface of the four EPDM specimens at, different steps of the heat-hexane-heat test sequence. From Figure 6.18 it can be seen that after the first heating at 200 °C the contact angle of water on the surface of the specimens slightly increased from its original value of about 93 to 95°. After extracting the LMW fluid content from the specimens, the contact angles increased considerably and reached higher values, ranging from 101 to 124°. The average contact angle at this stage...
was 111°. After the second heating, contact angles returned close to their original value to about 92°.

Figure 6.19 shows the percentage of total (cumulative) and step weight loss of the four EPDM specimens, at different steps of the heat-hexane-heat test sequence. From Figure 6.19 it can be seen that all four specimens lost about 9% of their weight during the first heating process (step J). However, the percentage of the extracted LMW fluid (step K) varied between less than 1% and about 6%. Finally, all four specimens lost equally about 2% of their weight during the second heating process (step L).

Table 6.3 is a summary of the average percentage of weight loss of four EPDM specimens at different steps of the heat-hexane-heat test sequence. Measurement steps J–K are described above.

<table>
<thead>
<tr>
<th>ID</th>
<th>Measurement sequence</th>
<th>Average % of weight loss (of four samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>after the 1st heating for 32 h at 200 °C</td>
<td>9.39</td>
</tr>
<tr>
<td>K</td>
<td>after the extraction of the LMW fluid</td>
<td>2.84</td>
</tr>
<tr>
<td>L</td>
<td>after the 2nd heating for 32 h at 200 °C</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>14.26</td>
</tr>
</tbody>
</table>
Figure 6.18. Contact angle of water on the surface of four EPDM specimens at different steps of the heat-hexane-heat test sequence.

Description of the measurement steps:

J: measurement after the 1\textsuperscript{st} heating at 200 °C for 32 h

K: measurement after extraction of the LMW fluid at 50 °C

L: measurement after the 2\textsuperscript{nd} heating at 200 °C for 32 h
Figure 6.19. Percentage of total (cumulative) and step weight loss of four EPDM specimens at the different steps of the heat-hexane-heat test sequence.

Description of the measurement steps:

J: measurement after the 1st heating for 32 h at 200 °C
K: measurement after extraction of the LMW fluid at 50 °C
L: measurement after the 2nd heating for 32 h at 200 °C
7. Conclusion

7.1 Summary of the Results

An extended laboratory study of the aging characteristics and the mechanisms responsible for the loss and recovery of hydrophobicity in EPDM insulator, under heat and water salinity stress conditions was carried out:

- EPDM specimens were aged by placing them in stationary air and in water with different salinity levels, $5 \times 10^{-3}$ (distilled water), 1, 10 and 100 mS/cm, at different temperatures, 0, 25 (room temperature), 50, 75 and 98 °C, for up to 6000 hours. The static contact angle of water droplets on the surface of insulator specimens and variations in the weight of specimens were measured during the aging process. The contact angle of all virgin specimens prior to being aged was 95±3°.

  - The specimens kept in air at all temperatures maintained almost constant contact angles at their original values during the aging process. Few high variations in the contact angle were observed, two of which, at 0 and 98 °C, were as high as 120° at some point, but returned to the normal contact angle after washing.

  - The contact angle of the specimens in water with different salinity levels, at 0 °C also remained almost constant at their original value throughout the aging process.

  - For specimens that were kept in water at temperatures of 25 °C and above, whenever the specimens had not been cleaned with brush and distilled water for a long period of time, as in the early stages of the aging process, the contact angle increased gradually at higher temperatures (75 and 98 °C) and decreased at lower temperatures (25 and 50 °C). It was also observed that, in all cases, the contact angle would maintain its original value again, immediately after using the brush to clean the specimens. A possible explanation for this behavior could be that at lower temperatures (25 and 50 °C), salt from the saline solution and other contaminations leaching from the specimens deposit on the surface of the
specimens during a long period of immersion, and yield low contact angles. In this case, the higher the salinity level, the lower the contact angle. At higher temperatures (75 and 98 °C), however, generation and diffusion of the low molecular weight (LMW) fluid and its migration from the bulk of the insulator material to the surface and even to the top of the contamination layer suppresses the effect of contamination and yields higher contact angles even in high salinity levels. In this case, the higher the temperature, the higher the contact angle is observed to be. Effective cleaning, in both cases, recovers the contact angle to its original value by removing the contamination and the diffused LMW fluid from the surface of the specimens.

- For the specimens kept in air at 0, 25, 50 and 75 °C, the changes in weight is almost negligible, although it shows a very slight decrease over time (less than 1%). At 98 °C, however, the decrease in weight is considerable and is as high as 2.61% at the end of the aging process. In addition, for specimens kept in air at temperatures higher than the room temperature, e.g., 50, 75 and 98 °C, the decrease in weight seems to be occurring with a faster rate in the first few hours, which could be because of instant evaporation of water content of specimens due to the higher temperature of the specimens.

- For specimens immersed in water, on the other hand, almost at all salinity levels and temperatures, the weight starts to increase at a fast rate in the initial hours of immersion, due to instant water uptake in the specimens, and then slows down for the rest of the process. The total increase in weight could get as high as 6.05% for the specimen at 5 μS/cm and 98 °C. The total increase in the weight of specimens immersed in water varies with the stress conditions, i.e., temperature and salinity level of water. In general, at a constant salinity level, the higher the temperature, the higher is the increase in weight. In contrast, for a constant temperature, the higher the salinity level of water, the lower the percentage increase in the weight of the specimens would be. However, there are few exceptions to this rule. For example, specimens in 100 mS/cm saline solution seem to be losing weight at the
higher temperatures, e.g., 75 and 98 °C, in the long run, although they gain weight in the beginning few hundred hours. A possible explanation for this behavior could be that these specimens cannot absorb much water due to the high salinity level and saturated condition of the solution and at the same time lose some of their components as a result of the high temperature.

- The surface of the EPDM specimens was studied to investigate the effect of heat and water salinity during the aging process. ATR-FTIR spectroscopy, SEM and EDS were employed to observe the physical and chemical changes of the surface of EPDM specimens.

  o From the SEM images it was observed that the surface roughness of the specimens increased with increasing aging salinity level. The Surface of the specimen aged at 100 mS/cm completely lost its original shape. However, it seems that the use of brush to clean the specimen that was aged at 10 mS/cm, effectively recovered the surface to its original status.

  o From the energy-dispersive spectra it was observed that the virgin EPDM specimen did not have any significant element on its surface; whereas in aged specimens more intensity of Al, Si and Ca was detected. In addition, the intensity of Al and Si varied with the salinity level and the applied washing method, e.g., the intensity of Al was dominant where the specimen had been cleaned with brush, compared to the specimen with the high salinity level 100 mS/cm, which had high intensity of Si and no Al. The specimen aged in distilled water also showed relatively higher intensity of Al than Si. These results imply that the intensity counts of Al decreased with the aging salinity level and returned to its higher values with the use of effective washing methods as it exposed the original surface.

  o The presence of polar bonds, such as C=O, in ATR-FTIR spectra contribute to the hydrophobic behavior of the EPDM insulator even during the aging process. In addition, changes in the absorbance level of C=O stretching bonds in different
specimens, were interpreted as regeneration of polar groups during the aging process, due to diffusion of the LMW fluid, which resulted in maintenance of the hydrophobic properties of the insulator. There were also significant changes in the absorbance level of OH stretching bonds among the specimens, which could be related to the changes in the composition of ATH particles due to various aging conditions and different washing methods.

- The surface energies of EPDM insulator were calculated during the aging process and were used to study the changes in the composition of the surface of the specimens. It was concluded that changes in the polar component of the surface energy, and hence the contact angle, were related to the changes in the hydrogen bonding on the surface as a result of migration of the LMW fluid from the bulk to the surface during the aging process.

- The hydrophobicity of the EPDM specimens recovered in stationary air at room temperature for up to 4000 h. The specimens were categorized based on the changes in their contact angles during the aging and recovery process, as follows:
  - For specimens aged at: 0 °C and 100 mS/cm; 75 °C and 10 mS/cm; 75 °C and 100 mS/cm; 98 °C and 1 mS/cm; and 98 °C and 10 mS/cm, the contact angle recovered to its original value (contact angle of a virgin specimen, 95±3°).
  - For the specimens aged at: 0 °C and 0.005 mS/cm; 25 °C and 0.005 mS/cm; 25 °C and 100 mS/cm; 50 °C and 1 mS/cm; 50 °C and 10 mS/cm; and 75 °C and air, the contact angle did not recover after aging.
  - For the specimens aged at: 50 °C and air; 98 °C and air; and 98 °C and 0.005 mS/cm, the contact angle recovered to a different value rather than its original value (contact angle of a virgin specimen, 95±3°).
  - For the rest of the specimens not mentioned above, the contact angle retained its original value (contact angle of a virgin specimen, 95±3°) after aging and also at the end of recovery; although in some cases it changed during those processes.
Moreover, it was observed that the higher the aging temperature, the higher was the percentage of weight loss of the specimens during recovery. On the contrary, the higher the aging salinity level, the lower was the percentage of weight loss of the specimens.

Almost all specimens showed an overall decrease in the weight which could be an indication of losing the LMW fluid during the aging process. Considerable lost occurred for the specimens aged in 98 °C. The maximum amount of the extracted fluid was 6.62%, which corresponds to the specimen aged in 98 °C and 0.005 mS/cm.

- LMW fluid content of EPDM specimens was extracted by immersing them in analytical hexane. The composition of the extracted LMW fluid was investigated by the application of several identification techniques, including GC-MS, IR spectroscopy and NMR spectroscopy. It was shown that the extracted LMW fluid contains dioctyl adipate, an ester of octanol and adipic acid.

- The aging mechanism of EPDM insulator was established after performing a few complementary experiments on the effect of heat in regeneration of the LMW fluid. The results of these experiments confirmed that in EPDM insulator, generation of the LMW fluid in the bulk of the insulator material and its migration to the surface and even to the top of the contamination layer maintains the hydrophobicity of the insulator in wet and contaminated conditions.

### 7.2 Suggestion for Future Research

The study of the effect of electrical DC/AC stress and R.F. discharge on the hydrophobicity of EPDM insulator is still to be done and is suggested for future research.
References


Appendix A. Confidence Interval for the Mean

A.1 Introduction [64]

Confidence limits for the mean are interval estimates for the mean. Interval estimates are often desirable because the estimate of the mean varies from sample to sample. Instead of a single estimate for the mean, a confidence interval generates a lower and upper limit for the mean. The interval estimate gives an indication of how much uncertainty there is in our estimate of the true mean. The narrower the interval, the more precise is our estimate. On the other hand, the more an analysis or measurement is replicated, the closer the mean of the results will approach the "true" value, of the sample.

Confidence limits are expressed in terms of a confidence coefficient. Although the choice of confidence coefficient is somewhat arbitrary, in practice 90%, 95%, and 99% intervals are often used, with 95% being the most commonly used.

As a technical note, a 95% confidence interval does not mean that there is a 95% probability that the interval contains the true mean. The interval computed from a given sample either contains the true mean or it does not. Instead, the level of confidence is associated with the method of calculating the interval. The confidence coefficient is simply the proportion of samples of a given size that may be expected to contain the true mean. That is, for a 95% confidence interval, if many samples are collected and the confidence interval computed, in the long run about 95% of these intervals would contain the true mean.

A.2 Definition [64]

Confidence limits are defined as:

\[ \mu = \bar{u} \pm t_{n-1} \frac{s}{\sqrt{n}} \]  

(A.1)

where
\( \mu = "true" \) value or the confidence interval (mean of large set of replicates)

\( \bar{\mu} = \) mean of sample

\( t_{n-1} = \) upper critical value of the t distribution with \( n-1 \) degrees of freedom, a statistical value which depends on the number of data and the required confidence (usually 95%)

\( s = \) standard deviation of sample

\( n = \) sample size

The term \( \frac{s}{\sqrt{n}} \) is also known as the standard error of the mean.

The critical values for \( t \) are listed in Table A.1 [64].

**Table A.1. Critical values of constant \( t \), in the equation (A.1) to calculate the confidence interval [64].**

<table>
<thead>
<tr>
<th>( n-1 )</th>
<th>( t )</th>
<th>( n-1 )</th>
<th>( t )</th>
<th>( n-1 )</th>
<th>( t )</th>
<th>( n-1 )</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.71</td>
<td>11</td>
<td>2.20</td>
<td>21</td>
<td>2.08</td>
<td>35</td>
<td>2.03</td>
</tr>
<tr>
<td>2</td>
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As an example, for a sample with readings \( (n=10) \) with an average of 95 (\( \bar{\mu}=95 \)) and a standard deviation of 2.5 (\( s=2.5 \)) and \( t \) looked up from Table A.1 for \( n-1=9 \), the confidence interval, \( \mu \), is calculated from (A.1) as:

\[
\mu = 95 \pm 2.26 \frac{2.5}{\sqrt{10}} = 95 \pm 1.79 \approx 95 \pm 2.
\]

From (A.1), it can be seen that the width of the interval is controlled by two factors:

1. As \( n \) increases, the interval gets narrower, i.e., one way to obtain more precise estimates for the mean is to increase the sample size.

2. The larger the sample standard deviation, e.g., for noisy data, the larger the confidence interval.
Appendix B. MATLAB Code for Calculating Surface Energies

% a: water contact angle (70,100)
% b: MI contact angle (50,80)
% x: Gsd
% y: Gsh

equation_1=strcat('72.8e-3*(1+cos(deg2rad(a)))-',...
'4*22.1e-3*x/(x+22.1e-3)-',...
'4*50.7e-3*y/(y+50.7e-3))');
equation_2=strcat('50.8e-3*(1+cos(deg2rad(b)))-',...
'4*44.1e-3*x/(x+44.1e-3)-',...
'4*6.7e-3*y/(y+6.7e-3))');

A=solve(equation_1,equation_2);
Gsh=1000*A.y(2); % in mJ/m^2
Gsd=1000*A.x(2); % in mJ/m^2
G=Gsd+Gsh; % in mJ/m^2

%%% begin mesh & contour
domain=[50 100 45 80];

contour ezcontour(Gsh,domain)
axis auto

mesh hold on
ezmesh(Gsh,domain)
ezmesh(Gsd,domain)
ezmesh(G,domain)
axis auto
%%% end mesh & contour

%%% b=40; % b takes values from [40 45 50 55 60 65 70 75 80]

% 1 -->
Gsh subplot(3,2,1); ezplot(subs(Gsh),[0,150])
xlabel ''
ylabel('\gamma_{sh}, mJ/m^2','FontSize',12)
title('Solution 1','FontSize',12)
axis 'auto y'; grid on
subplot(3,2,2); ezplot(1000*subs(A.y(1)),[0,150])
xlabel ''
ylabel ''

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title('Solution 2','FontSize',12)
axis 'auto y'; grid on

%Gsd
subplot(3,2,3); ezplot(subs(Gsd),[0,150])
ylabel(\gamma_{sd}, mJ/m^2','FontSize',12)
title(\theta_{MI} = 40\circ','FontSize',12)
axis 'auto y'; grid on
subplot(3,2,4); ezplot(1000*subs(A.x(1)),[0,150])
ylabel '';
title ''
axis 'auto y'; grid on

%G
subplot(3,2,5); ezplot(subs(G),[0,150])
xlabel(\theta_{water}, degrees','FontSize',12);
ylabel(\gamma_s, mJ/m^2','FontSize',12)
title ''
axis 'auto y'; grid on
subplot(3,2,6); ezplot(1000*(subs(A.y(1)+subs(A.x(1)))),[0,150])
xlabel(\theta_{water}, degrees','FontSize',12);
ylabel ''
title ''
axis 'auto y'; grid on
% <-- 1

% 2 -->
hold on
ezplot(subs(Gsh),[50,120])
ezplot(subs(Gsd),[50,120])
ezplot(subs(G),[50,120])
xlabel(\theta_{water}, degrees','FontSize',12);
ylabel('surface energy, mJ/m^2','FontSize',12)
title(\theta_{MI} = 40\circ','FontSize',12)
text(110,30,'\gamma_{sh}','FontSize',12)
text(110,40,'\gamma_{sd}','FontSize',12)
text(110,50,'\gamma_s','FontSize',12)
axis 'auto y'; grid on
% <-- 2

%%%
**Vita Auctoris**

<table>
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<tr>
<th>Name</th>
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