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Physical and Chemical Investigations on Silicone Insulating Rubber (SiR) Composite

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Abstract

This article presents a physical and chemical investigation of Silicone insulating Rubber (SiR) composite insulators. The study employs durometer shore A measurements, Thermogravimetric Analysis (TGA), and ATR with Fourier Transform Infrared Spectroscopy (FTIR) to evaluate various types of SiR, including 420 kN/800 kV, 210 kN/500 kV, 160 kN/400 kV, 120 kN/400 kV, 90 kN/66 kV, 70 kN/220 kV, 45 kN/25 kV, to assess their performance as insulators for power sector applications. The TGA, conducted according to ASTM E1131, provides a detailed thermal decomposition analysis of SiR and determines filler content and characteristic values unique to the material. Similarly, FT-IR analysis, performed as per ASTM E1252, identifies specific chemical groups and characteristic bands of the material. SiR is primarily composed of polydimethylsiloxane (PDMS) and is enhanced with inorganic fillers such as Alumina Trihydrate (ATH) for High-Temperature Vulcanized (HTV) applications. The TGA study indicates that thermal decomposition occurs in two key stages: the release of highly volatile organics and the breakdown of organic components within the silicone polymer. Notable findings from the FT-IR analysis confirm the presence of PDMS and the hydroxyl (OH) group of ATH in SiR. The hardness of SiR is measured using the IEC 62217 method. Results indicate that the silicone content of SiR ranges from 31% to 37% according to TGA, and hardness values increase from 68 to 71 due to the aging process. Remarkably, a maximum increase of 4 in hardness was observed after aging. This research emphasizes the strength and reliability of SiR composite in demanding power sector applications.

Keywords: Chemical Investigation, Fourier Transform Infrared (FTIR) Spectroscopy, Hardness, Silicone Insulating Rubber (Sir), Silicone Content, Thermogravimetric Analysis (TGA)

1. Introduction

Composite insulators play a crucial role in electrical equipment by effectively supporting and isolating electrical conductors. Their design ensures that current does not flow through the insulators, thereby enhancing safety and reliability in electrical systems. Composite insulators are made of a mixture of polysiloxane fillers, vulcanizers, additives, carbon blacks, aluminum trihydrate, and aluminum hydroxide (ATH). The electrical insulator is a vital component of electrical distribution/transmission lines and substations. Glass, ceramic, and porcelain insulators have good mechanical, surface, and UV resistance characteristics. The main disadvantages of ceramic and glass insulants for High Voltage (HV) insulating applications, however, are their heavy weight, brittleness, and surface wettability[1,2]. The two fundamental polymeric insulators, Ethylene-Propylene-Diene-Monomer rubber (EPDM) and silicone rubber (SiR) have been extensively utilized for high-voltage applications since the 1970s[3]. Because of their superior mechanical, thermal, and electrical qualities, ease of installation and transportation, lightweight design, and superior insulation, polymeric insulators are gradually replacing traditional ceramic and glass insulators in high-voltage distribution and transmission systems[4]. These insulators are primarily composed of silicone insulating rubber (SiR), which uses polydimethylsiloxane (PDMS) as its base polymer. The chemical structure of SiR is illustrated in Figure 1. Additionally, inorganic fillers such as Alumina Trihydrate (ATH) are used in High-Temperature Vulcanized (HTV) silicone insulator rubber, while fumed silica is utilized in Liquid Silicone Rubber (LSR).

Silicone rubber is a polymeric insulation material, which is mostly used in high-voltage applications as insulating

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materials. Silicone rubber is technically called an elastomer, which is made of silicone polymer having silicon composed of carbon, hydrogen, and oxygen. Silicone rubbers are extensively used in various industries, especially in the power industry, and have multiple compositions. Silicone rubbers are versatile materials available in one- or two-part formulations, often enhanced with fillers to improve performance and provide cost-effective solutions. Silicone rubber is a highly effective material, known for its non-reactive nature, stability, and ability to endure extreme temperatures from −55 to 300°C while maintaining its essential properties[5]. Composite insulators equipped with silicone rubber insulation deliver outstanding performance and are installed all over the world[6].

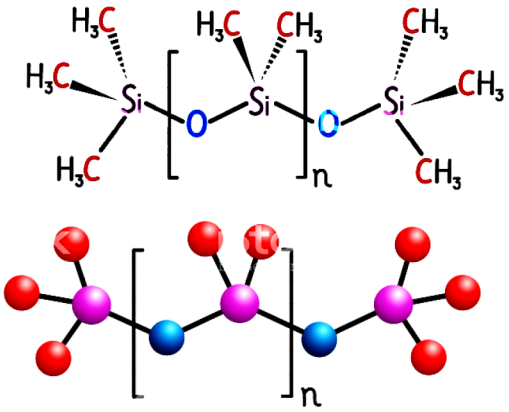


Figure 1. Chemical structure of raw PDMS.

2. Preparation of Silicone Composite Insulators

Generally, silicone rubber is produced through the direct Müller-Rochow synthesis, named after German scientist Richard Gustav Müller and American scientist Eugene George Rochow[6]. They independently invented the catalytic preparation of methylchlorosilane around 1940-1941, marking a significant advancement in materials engineering[6]. The composition and purity of the initial materials used significantly influence the quality of the reaction products. Silicon dioxide (SiO_2) is utilized in powdered form, with particle sizes ranging from 45 to 250 micrometers. Copper acts as a catalyst in this reaction, which occurs at temperatures between 250 – 300 °C. The silane mixture produced, which primarily consists of dimethyldichlorosilane, is isolated through distillation. Dimethyldichlorosilane is then converted into polysiloxane, a precursor for silicone rubber, through a hydrolysis process. To create "silicone rubber semi-finished parts," silica, additional fillers, and various additives are incorporated, along with the necessary peroxides and catalysts essential for vulcanization.

The primary components of silicone rubber may include:

- Polysiloxanes with various functional groups (–OH, –C=CH2, –H, and others).
- Fillers, including pyrogenic or precipitated silica and quartz powder.
- Vulcanizers, such as peroxides and H-siloxane.
- Catalysts, including platinum compounds, tin compounds, and others.
- Additives, such as adhesive agents, softening agents, pigments, and more.
- Carbon blacks, categorized into pigment types, conductivity types, and special types.
- Aluminum trihydrate and aluminum hydroxide (ATH).

3. Common Features and Applications of Silicone Material

The term "silicone" introduced by Kipping in 1901 due to its similarity to ketones, describes innovative compounds with the formula (R2SiO)n. Recognized for their polymeric nature, silicone insulators have been commercially produced since the 1940s. These compounds quickly garnered attention for their polymeric nature and similarities to polydialkylsiloxanes. Since the 1940s, silicone insulators have been produced commercially. They are known for being non-reactive, stable, and able to withstand severe environmental conditions, while maintaining their useful properties across a wide temperature range, from -55 °C to +300 °C[7,8]. These outstanding attributes make silicone rubber an ideal choice for high-voltage insulation and industries such as construction, aerospace, cosmetics, and transportation, where reliability and performance are critical. Silicone rubber is known for its excellent properties, such as thermal stability, resistance to oxidation, and durability against weathering. These characteristics arise from the strong SiO bonds present in its polymer structure.

Additionally, due to its low surface energy, silicone insulators display qualities of both inorganic and organic materials. This unique combination has several advantages over other organic polymers[9]. The dual character of silicone also significantly affects how particles (fillers) interact within the polymer matrix. Silicones are often combined

with various fillers to improve their mechanical, thermal, and other behavior[10]. To enhance the electrical, thermal, and mechanical properties effectively, utilizing micro and nano-sized fillers is crucial as they significantly improve the interaction between filler particles and the base rubber[11,12]. Silicone rubbers are remarkable for their high insulation resistance, ranging from 1TΩ to 100TΩ[7]. Their insulating capabilities remain stable across a wide range of temperatures and frequencies, and their performance is unaffected even when submerged in water, making them excellent insulating materials. Their strong corona resistance under high voltage further enhances their reliability. Thus, silicone rubbers are ideally suited for high-voltage applications in extreme environments[13].

4. Experiments

Table 1. Methods explored for SiR fingerprinting

Techniques	Parameters	Primary property evaluated
Shore A	Physical	Hardness
TGA	Thermal	Thermal degradation stability
FT-IR	Spectroscopic	Confirm the presence of functional groups in SiR

Thermogravimetric analysis (TGA) is an essential technique that quantitatively measures the variation in mass of a specimen as a function of temperature over time, providing critical insights into material properties. In this study, TGA was performed using TA Q500 as per ASTM E1131[14]. The innovative design features a microbalance that is permanently integrated with the sample holder, while a precise thermocouple monitors temperature fluctuations within the sample chamber. The typical temperature range for TGA is between 25°C and 950°C. Each sample weighing 25-40 mg was carefully placed in a platinum crucible and subjected to a systematic heating process, reaching a peak temperature of 950°C at a controlled rate of 20°C per minute. The tests were conducted in two different environments: the samples were first heated in a nitrogen atmosphere from Room Temperature (RT) to 600°C, followed by exposure to an oxygen atmosphere from 600°C to 950°C.

ATR with Fourier Transform Infrared Spectroscopy (FTIR) is an actual analytical method for detecting molecular bonding at depths of up to 10 µm, utilizing an Infrared (IR) frequency between 400 cm^{-1} to 4000 cm^{-1}. In this study, we used a Bruker FTIR spectrometer, Frontier model, equipped with a diamond crystal in a horizontal Attenuated Total Reflection (ATR) accessory. Before measurement, each diamond crystal sample is thoroughly cleaned; otherwise, residues from previous specimens can interfere with the spectrum of the material being analyzed. To ensure accuracy, sixteen scans are conducted, and the average value is reported. Fourier Transform Infrared Spectroscopy (FTIR) is utilized to identify chemical bonds that either create a dipole moment when excited by IR radiation or modify an existing dipole moment as per ASTM E1252[15].

The hardness test was conducted as a relative comparison before and after an aging test, by IEC 62217[16]. The Shore A hardness of the 4 mm thick silicone insulation rubber (SiR) was measured using a Shore A durometer at an ambient temperature of 25-27 °C and relative humidity of 48-50 %. Following an aging process where the SiR was exposed to a boiling solution containing 0.1% by weight of sodium chloride for 42 hours, the hardness was measured again under the same ambient conditions. The general method of explored SiR fingerprinting is given in Table 1.

5. Results and Discussion

5.1 Thermal Degradation Study of Silicone Insulator Rubber Composite

Thermogravimetric Analysis (TGA) is a method used to monitor the weight change of a material as the temperature increases, providing insights into its thermal stability. As the temperature rises, weight loss can occur due to the release of volatiles resulting from the material's degradation. Ultimately, only non-volatile residue remains. For silicone rubber, thermal degradation undergoes various chemical reactions, depending on the condition of the environment. These processes include the hydrolysis and exchange of siloxane bonds, degradation of hydrocarbon that forms cross-links and side products, condensation and depolymerization of silanol groups, and silica formation. Such mechanisms can reduce effective cross-link density, which is vital for material performance. Importantly, TGA efficiently identifies loss of weight linked to the generation of cross-link compounds due to depolymerization and gases released from hydrocarbon degradation in the presence of oxygen. TGA of SiR of 210 kN/500 kV was conducted in nitrogen from 25°C to 600°C, then by oxygen from 600°C to 950°C, as shown in Figure 2.

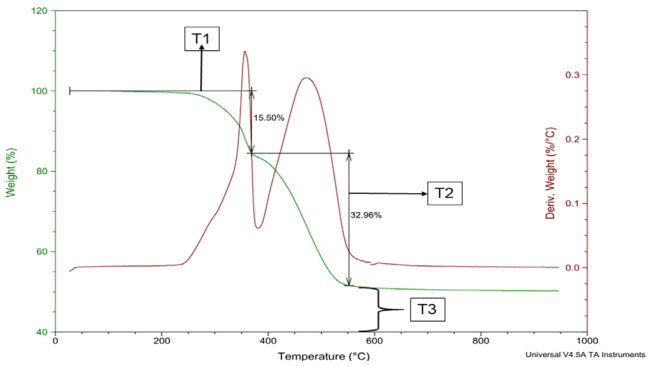


Figure 2. Thermogram of 210kN/500kV by Thermogravimetric Analysis (TGA).

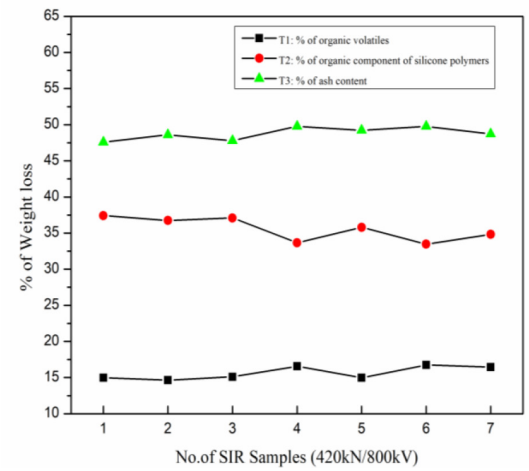


Figure 3. Percentage of weight loss versus no. of 420kN/800kV insulators.

The results shown in Figures 3 to 9 reveal two distinct degradation steps in the thermograms of silicone composite insulators that have been pyrolyzed in both oxygen and nitrogen environments. These steps include T1, which represents the percentage of organic volatiles, T2, which indicates the percentage of the organic component of silicone polymers, and T3, which refers to the percentage of ash content. The rates of weight loss and the total weight loss during each stage differ significantly[17]. In the first stage, which occurs at temperatures between 300 and 420°C, the weight loss is attributed to the degradation of highly volatile organic compounds, resulting in a weight loss of 13-17 wt%. The second stage occurs between 420°C and 600 °C, where weight loss is due to the degradation of the organic component of the silicone polymer, leading to a weight loss of 32-37 wt%. The remaining ash content is between 47-52 wt%. Figures 3-9 show the weight loss of T1, T2, and the residue T3 for all grades of the silicone composite insulator.

The TGA results of HTV-filled silicone insulator rubber provide key insights into ATH filler content. At temperatures above 330°C, a significant second weight loss phase occurs, ending around 570°C. This loss, identified within the 330°C to 570°C range, is due to volatile components released from the silicone rubber matrix, indicating active pyrolysis. The remaining weight >570°C primarily comes from silica filler and Al_2O_3 formed from ATH dehydration, which occurred between 270°C and 330°C. Understanding these thermal behaviors is essential for optimizing the applications of HTV-filled silicone insulator rubber[18].

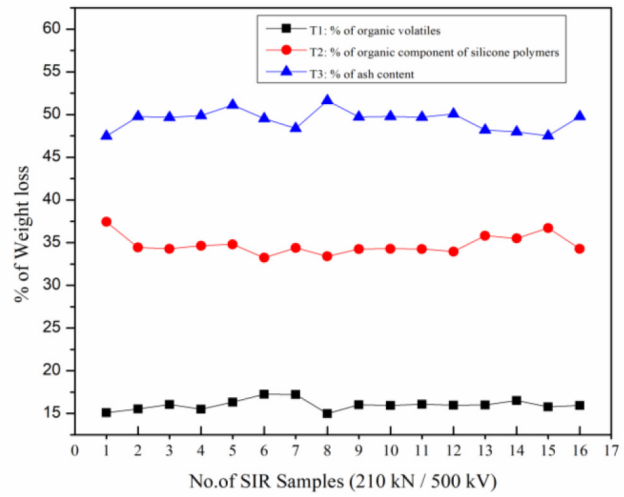


Figure 4. Percentage of weight loss versus no.of 210kN/500 kV insulators.

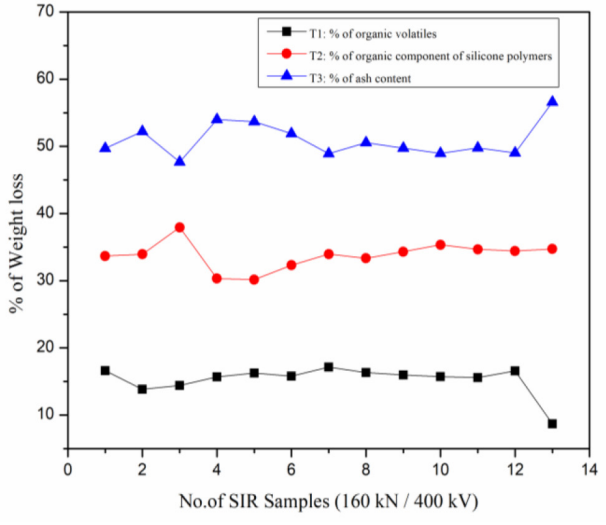


Figure 5. Percentage of weight loss versus no. of 160kN/400 kV insulators.

It is essential to recognize that the temperature for extreme rate of descent in first weight loss (270°C to 330°C) and second weight loss (330°C to 570°C) is significantly influenced by ATH filler content. This behavior highlights ATH filler's involvement in the pyrolysis of silicone rubber matrix. The first peak, which reflects ATH filler dehydration, necessitates longer heating times with increased filler content, leading to higher temperatures for maximum descent.

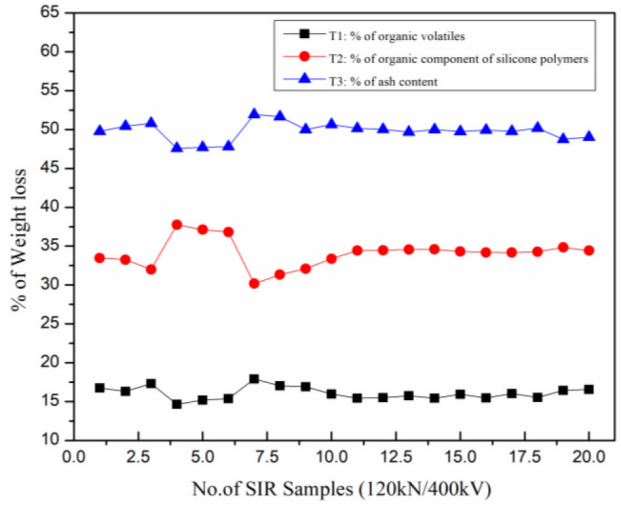


Figure 6. Percentage of weight loss versus no. of 120kN/400 kV insulators.

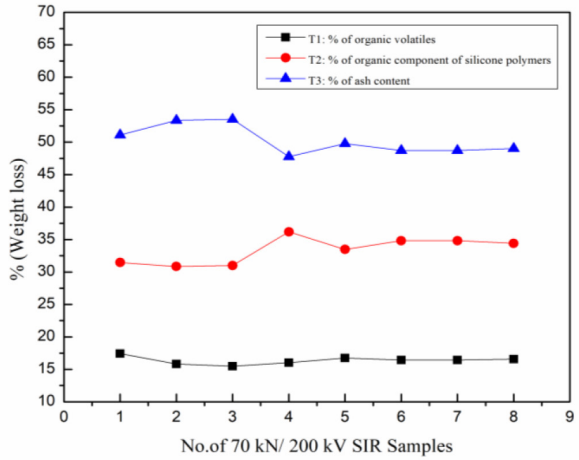


Figure 7. Percentage of weight loss versus no. of 70kN/200 kV insulators.

Furthermore, ATH filler interferes with the arrangement of PDMS polymer chains, resulting in a decrease in crosslink density within the PDMS matrix[18]. Liu *et al.*[21] and Sidharthan *et al.*[22] have conducted experimental studies that explore how fillers disrupt the packing of polymer and PDMS chains. Consequently, this reduction explains the lower temperature for the maximum descent of the second peak, associated with the pyrolysis process. Understanding the effects of ATH filler content is thus crucial for optimizing the thermal properties of silicone rubber materials.

Hence, as shown in Figures 3-9, the silicone content of various SiRs was maintained between 32-37 wt%, organic volatiles at 13-15 wt%, and the remaining ash content at 48-52 wt%.

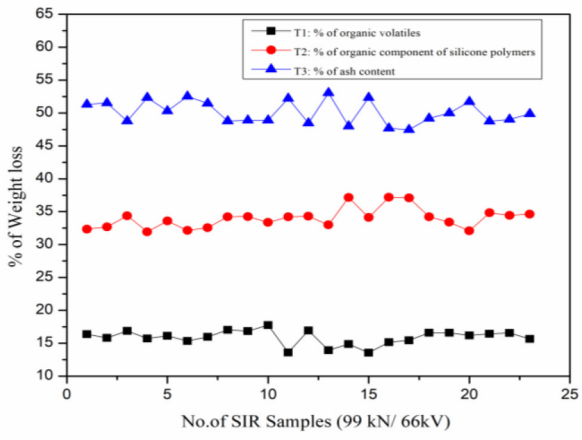


Figure 8. Percentage of weight loss versus no. of 99kN/66 kV insulators.

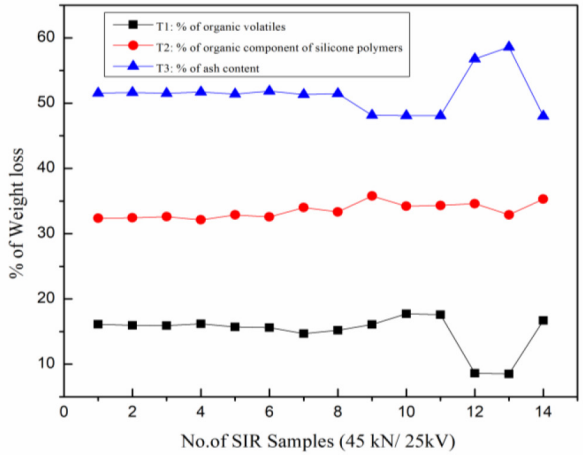


Figure 9. Percentage of weight loss versus no. of 45kN/25 kV insulators.

5.2 Fourier Transform Infrared Spectroscopy (FTIR) Studies on SiR

Silicone Insulating Rubber (SIR) is primarily composed of a base polymer called polydimethylsiloxane (PDMS),

which contains inorganic fillers such as Alumina Tri-Hydrate (ATH) for High-Temperature Vulcanized (HTV). Fourier Transform Infrared (FT-IR) spectrometry was utilized to analyze the structural confirmation of the functional groups present in SiR[19]. The FT-IR analysis revealed several characteristic bonds in all examined silicone insulators: C-H symmetric stretching in the methyl (CH_3) group was observed at 2980-2960 cm^{-1}, while CH_3 asymmetric stretching appeared at 1270-1255 cm^{-1} as shown in Figure 10. Additionally, Si-O-Si symmetric stretching was identified at 1100-1000 cm^{-1}, and $Si(CH_3)_2$ Si-C symmetric stretching was noted at 861-790 cm^{-1}, indicating the presence of PDMS. Furthermore, four peaks at 3617, 3436, and 3370 cm^{-1} within the 3700-3200 cm^{-1} range were detected, which can be attributed to -OH groups in ATH. Specifically, these peaks corresponding to –OH and hydrogen bonding in the Aluminum Tri-Hydroxide (ATH) filler were present in the RTV with ATH samples but absent in the RTV samples without ATH. Other significant FT-IR peaks at 2962, 1257, 1007, and 786 cm^{-1} further confirmed the presence of PDMS in RTV samples. In summary, FT-IR spectra confirm the chemical structure of Silicone Insulating Rubber.

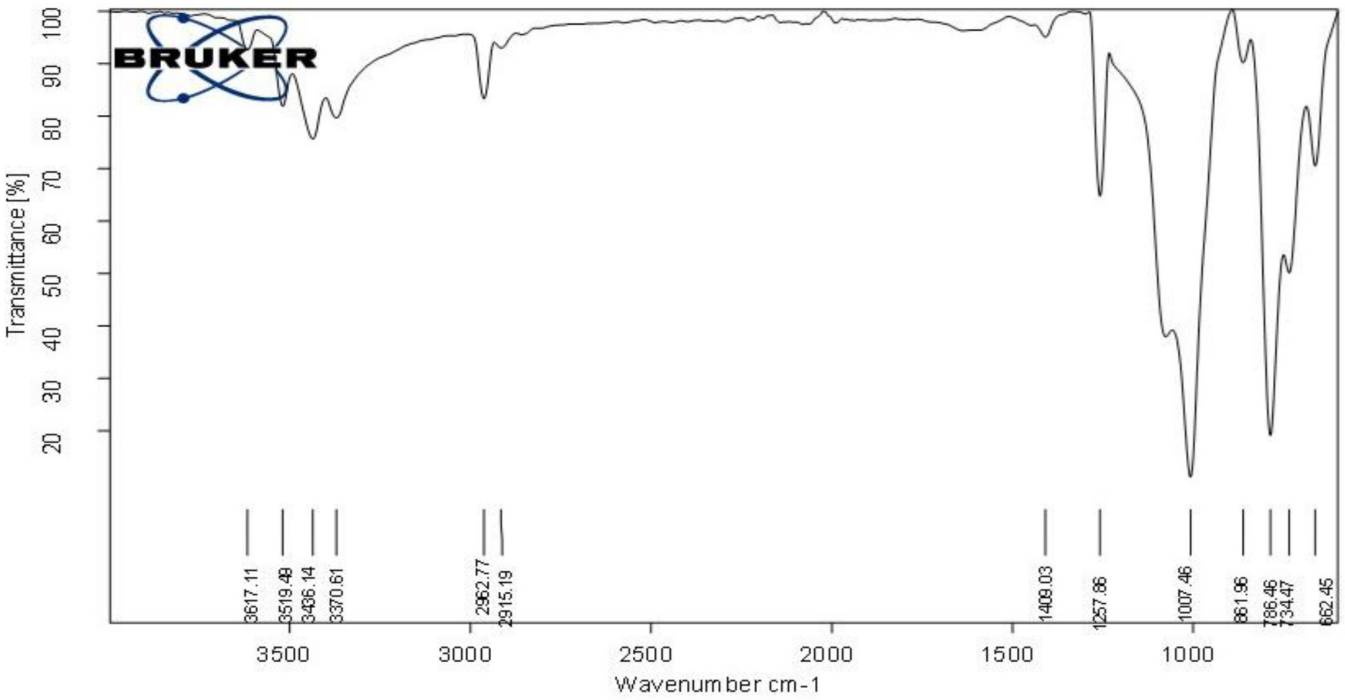


Figure 10. Fourier transform infrared spectroscopy of SiR.

5.3 Hardness Testing of SiR

The hardness of the SiR samples was evaluated according to IEC62217[16]. Initially, before aging termed as pre-boiled, the hardness of the 4 mm thick SiR samples was measured at ambient temperature (25 °C, relative humidity: 48%) using a Shore A durometer. After aging termed as post-boiled, the hardness was measured again under the same ambient conditions. Overall, the hardness of both the pre-and post-boiled SiR samples did not exceed 3. The observed increase in hardness after the boiling test can be attributed to the fact that insulators tend to become harder as they age[23]. The hardness of the various pre- and post-boiled SiRs is shown in Figure 11. It was noted that polymers with a higher filler content typically exhibit increased hardness[20]. The hardness of silicone rubber (SiR) increases with a higher filler content. This observation indicates that there is a direct correlation between the results of Thermogravimetric Analysis (TGA) and hardness studies, confirming that the hardness of SiR is directly related to the amount of filler used.

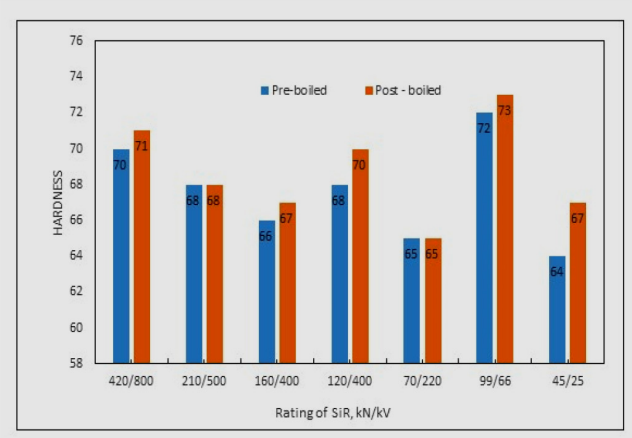


Figure 11. The hardness of the various pre- and post-boiled SiR.

6. Conclusion

The investigation into the chemical and physical properties of Silicone Insulator Rubber (SIR) has provided significant insights through the thorough testing of multiple samples. The analysis leveraged TGA, FTIR, and hardness assessment to evaluate silicone content and its filler content effectively.

The TGA results revealed two critical thermal degradation steps that are fundamental to understanding SIR's behavior. During the TGA process, specific weight loss patterns indicated two distinct peaks in the derivative TGA curve. The first peak, associated with the dehydration of aluminum trihydroxide (ATH) filler, and the second peak, representing the pyrolysis of the silicone rubber matrix, highlight the complex interactions within the material. It was demonstrated that the ATH filler significantly influences the pyrolysis of the SiR, reiterating the importance of TGA analysis in discerning the composition of silicone insulator rubber. Furthermore, FTIR analysis distinctly confirmed the presence of ATH filler, revealing three stretching frequencies of hydroxyl groups (-OH) at 3610, 3525, and 3447 cm^{-1}, indicative of -OH and hydrogen bonding within the ATH. Other notable FTIR peaks at 2960, 1260, 1008, and 795 cm^{-1} provided a clear confirmation of polydimethylsiloxane (PDMS). This technique not only identified specific chemical groups but also established vital characteristic data. The hard tests showed meaningful variations between pre-boiled and post-boiled SiR samples. This comprehensive study enhances our understanding of the physical and chemical characteristics of silicone rubber insulators across different ratings, revealing that these essential properties remain unchanged regardless of the rating. The findings underscore the reliability and consistency of SiR, making it a compelling choice for various applications in the industry.

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