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Aging Comparison of the RTV and nano RTV insulator coatings due to thermal and electrical stress

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Abstract

RTV silicone rubber offers excellent high and low temperature resistance as well as UV and weathering resistance and has a bright future in the aerospace and electronics industries. On the other hand, the thermal decomposition behavior of polymeric materials significantly affects their aging process and there are many studies on improving the specifications of nanocomposites by adding different types of nanoparticles. In this work, silicone rubber RTV nanocomposites with low content of modified nano-ZnO particles and pure RTV were compared in terms of their degradation behavior by heat and electrical stress. The coatings were prepared and the products were subjected to various experimental tests, including thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis. The TGA results of the study suggest that the residual weight of the aged samples is higher than that of the unaged samples. The FTIR analysis results show that the aging performance of Nano-RTV is better than that of RTV, which is concluded from the smaller absorption area of the functional groups of Si-CH3 and Si-O-Si. The numeric value of Critical flashover voltage in Nano-RTV coating was higher compared to the RTV coating as a result of the enhanced electrical insulation characteristics. This can confirm the improvement of thermal aging of Nano RTV compared to pure RTV and may prove useful to estimate the expected lifetime of the coatings, which is valuable for estimating the reliability of porcelain insulators

Keywords: Aging characterization; Thermal stability; High voltage Room temperature vulcanized (RTV) coatings ; Nanoparticles; Critical flashover voltage

1. Introduction

Polymeric insulators found rapid growth in their construction, design and types as they have many advantages over conventional ceramic insulators such as light weight, flexibility, easy installation, excellent performance in contaminated environment, better dielectric strength and single unit construction. However, due to their organic nature, polymeric materials have the problem of aging especially in outdoor environment. Ultraviolet (UV) radiation, heat, humidity, acid rain, and fog are some examples of environmental stresses[1]–[4]. Nanoparticles have contributed significantly to the advancement of various branches of science by improving material properties [5]. Since the turn of the century, numerous research publications on the use of inorganic nanoparticles to improve polymer performance have been published. Nanocomposites, which are made by combining tiny inorganic particles with a polymer matrix, have a wide range of uses. There are also some studies such as [6] which concentrate on surface modification of ZnO and SiO_2 particles to compare performance of nanoparticles and modified ones in various aspects especially agglomeration. Also, some research studies have focused on the effects of using different materials as modifier[7], [8]. In fact, the effects of nanoparticles content on enhancing polymeric composition such as RTV is a research area open to the scholars in the field[8]–[10]. The bulk of these studies focus on investigating the effects of different ratios of these particles on mechanical and electrical properties of materials.

Although RTV as a hydrophobic coating is extremely important for outdoor insulators, there have been few studies on Nano ZnO RTV compositions and their thermal stability improvement in the presence of these nanoparticles. Thermal stability properties besides electrical and mechanical aspects are significant in estimating the operating life of electrical equipment [11]. Therefore, it is vital to study the thermal behavior of nano-based RTV coatings.

In this paper, Aging characterization of RTV coating was investigated in the presence of ZnO nanoparticles. Aging behavior was investigated by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis. The rest of the paper is arranged as follows: Section 2 includes information about materials and experimental tests that were used in the study and sample preparation procedure. Results and discussion related to each analysis are discussed in Section 3. Finally, Section 4 presents conclusion of the study.

and safety. In most articles, such as the article above-mentioned, the greatest attention is paid to the minimum path length, and sometimes the smooth or safe path is considered. In addition to the above mentioned, in our article, the minimum length is also considered as the second objective. Furthermore, the environment is assumed offline, and the criteria or objective function considered for the safest is different. In addition, we examined more different complex workspace for testing our model and algorithm.

The rest of this paper is organized as follow. Section 2 states the proposed objective function. Then, the problem formulation is discussed in Section 3. Afterwards, Section 4 explains the proposed algorithm and numerical results and finally, conclusions are given in Section 5.

2. Materials and Methods

This section presents information about material, which is used in this study besides describing process of preparation of nanocomposite samples. Furthermore, experimental tests employed in the study are described.

2.1. Materials

Commercial RTV silicone rubber manufactured by Wacker Co was used in the study. Also, nano ZnO with an average particle diameter of 50 nm and nano SiO_2 with average particle size of 30 nm were utilized in this study. Furthermore, (Amino propyl) triethoxysilane was purchased from Merck Company as the nanoparticles' surface treatment agents.

2.2. Sample Preparation

Based on the preparation methods typically employed in research on ZnO nanoparticles to improve RTV properties, e.g. [12], [13], in this paper two different samples were considered as described below. APTES was chosen as surface modifiers to investigate their performance as surface modifying agents based on the studies reported in [8], [14], [15].

Sample 1. Nano ZnO particles heated in oven at 150 ℃for 2 hours were modified by mixing with (Aminopropyl) triethoxysilane at a ratio of 100:2 in acetone solution. The mixture was mechanically agitated for two hours and sonicated for 20 minutes in that order. Then the mixed liquid was filtered and the nanoparticles were dried in an oven at 100 ℃ for 24 hours. The modified ZnO particles were added to the RTV matrix by the proportion of 1.5% and were mechanically mixed and sonicated [16].

Sample 2. This sample is pure RTV

2.3. Test Setup and Methods

Water soluble and insoluble surface contaminants are the main causes of flashover on insulator surfaces and they have significant effects on electrical stress withstand of the insulators. Soluble variety consists of diverse types of salinity. According to [17], there are different types of pollutions including sand-based pollution or ground dust,

industrial pollution with large amounts of solid deposits, chemical pollution, and smokes.

Flashover process in insulators is accomplished through separate steps. The applied voltage wave, referred to as AC and DC voltages, has a significant effect on the severity of this process. In the case of AC voltages arc-propagation across the insulator surface takes several cycles [18]. Surface characteristics also play an important role in the pollution flashover process of insulators. Insulator surface can be categorized as hydrophilic or hydrophobic [12], [19]. While hydrophilic surfaces are usually associated with glass and ceramic insulators, hydrophobic surfaces are characterized with polymeric insulators or porcelain insulators with polymeric coating, such as RTV or modified RTV with nanoparticles in order to enhance insulator properties [13], [20]. To evaluate electrical stability and hydrophobicity of samples described in the previous section, clean fog test and contact angle measurement test were performed in the study that are described presently.

2.3.1. Critical flash over voltage (clean fog test)

The pollution tests of porcelain insulators were carried out in an artificial fog chamber of 2.0 m × 2.0 m × 2.0 m, and the power was supplied from a 150 kV/900 kVA high voltage transformer. The solid layer method was used to produce uniform pollution layers on insulators' surfaces. In order to obtain artificially polluted surfaces, the procedure described in [21] was used. Composition of the contaminating suspension was based on kaolin containing 40 g Kaolin, 1000 g demineralized water, and some NaCl of commercial purity**.** The insulators' surfaces were cleaned by demineralized water before spraying the contaminating suspension. The prepared suspension was applied through spraying on the whole sample surfaces and the samples were dried during the rest time which was 24 hours for all samples. In addition, variations were considered in the duration of spraying to obtain five contamination levels for each insulator. There are different criteria for determining severity of artificial contamination [17]. The pollution severity can be explained by equivalent salt deposit density (ESDD) and non-soluble material deposit density (NSDD). The level of contamination ranges between very light, light, moderate, heavy, and very heavy [22]. Clean fog chamber demonstrated was equipped with a digital sensor that makes it possible to measure the level of humidity and temperature. After spraying different levels of pollution suspension on insulators by prolonging or shortening the spraying time and the waiting period to dry, insulators were hanged in the fog chamber concurrently so that the test condition was the same for all samples making comparison results reliable for life expectation analysis. After 15 to 20 minutes waiting time in order to wet the insulator surfaces, the applied voltage was increased by the rate of 2.5 kV/sec until flashover occurred. Flashover voltage tests in each pollution level were repeated 3 times with 5-minute delay between one flashover and the next test to avoid interaction of effects. For each sample, the flashover voltage of the contaminated insulators at each level of pollution was calculated as the mean flashover voltages, reported in the standard form of kV per leakage distance (cm). In order to convert the average critical flashover voltage into electrical withstand value, coefficient of 0 .7 was considered [23]. This assumption is the consequence of allocating 10% for standard deviation. A legitimate criterion for contamination severity of cap and pin insulators is the mean value of ESDD and NSDD. In this paper, equivalent salt deposit density was employed as the touchstone since the amount of NSDD in the calculating results was approximately constant and negligible in comparison with ESDD. The procedure for calculating ESDD values was based on the method suggested in [17].

2.4. Methods

In this subsection, the experimental tests and measurements are explained. These include Fourier Transform Infrared Spectrometer (FTIR) and Thermogravimetric Analysis (TGA).

FTIR: FTIR spectra were recorded using a KBr pellet in a Nicolet avatar FTIR spectrometer for the samples to investigate surface modification of nanoparticles process.

TGA: TGA test was performed at 5-10-20 (C/ min) under air using a TA STD Q600 equipment. Through this analysis decomposition behavior of the samples in the presence of modified nanoparticles was compared with pure samples based on some criteria such as activation energy

3. Result and Discussion

3.1.Critical flashover voltage

The following relation is proposed between critical flashover voltage representatives of electrical withstand value and ESDD values as a contamination severity criterion for each cases based on the findings of [1], [11], [19], [29]:

$$E_s = \lambda(ESDD)^{-\mu} \qquad (1)$$

Where λ and μ are related to the material and shape of the insulators. Using experimental data of the clean fog test, which was applied on contaminated insulators in different ESDD levels the results in Table 1, were obtained. In order to obtain these data for the samples, values of ESDD should be calculated based on the procedure described in [13]. The flash over voltages in the five different contamination severities are reported in Table 1.

Table 1. The amount of Critical flashover voltage versus ESDD values

RTV	**Critical flashover voltage (kV/mm)**	1.5000	1.3316	1.2737	0.7874	0.6947
	ESDD values	0.9263	0.6947	0.6316	0.5789	0.5442
Nano RTV	**Critical flashover voltage**	0.1600	0.3900	0.4400	0.7500	1.3500
	ESDD values (kV/mm)	0.3900	0.8600	1.3000	1.3500	1.6000

As Table 1 suggests, the numeric value of Critical flashover voltage in nano-RTV coating was higher compared to the RTV coating as a result of the enhanced electrical insulation characteristics.

3.1 Thermal decomposition of RTV nanocomposites

In order to investigate thermal stability of coatings, TGA was used to obtain the required data. To evaluate the thermal stability of silicone rubber before and after aging, the TGA test is used, which is one of the study tools of polymers and silicones HTV[1] and RTV. It is performed by decomposition or water loss and weight gain by absorption or oxidation with this device. In contrast to, mass measurements with chemical balances, the measurement time for TGA is very long. For this reason, stability and anti-vibration properties must be taken into account.

Fig. 1 depicted the result of this analysis for pure RTV and ZnO/RTV, respectively before aging, at three different heating rates of 5, 10, and 20. From Fig. 1, it can be found that by increasing the heating rate, the temperature of decomposition stages rised in all samples. Thermal decomposition behavior of RTV samples can be divided into 2 main stages. The first stage refers to losing the moisture of the sample, which occurred within the range of 200 ℃. The main decomposition for polymer material is often considered to happen at the temperature of the second or third stages. Furthermore, analysis of the results in Fig. 1 revealed that ZnO/RTV sample showed enhancement in thermal stability performance in comparison with pure RTV. Consequently, the thermal conductivity of ZnO nanoparticles was much higher than RTV [12].

According to Fig. 1, the first weight loss in the diagram is mainly due to the dehydration of the ATH filler at 200 to 350 ° C. LMW molecules may also occur in this range and overlap with water.The second weight loss is due to the destruction of silicone rubber, and finally the percentage of residual weight includes ash. The first weight loss is due to the decomposition of ATH according to the equation (2). To some extent, relationship (3) also includes.

$$Al(OH)_3 \rightarrow Al(O)OH + H_2O \quad (2)$$

$$2\,Al\,(O)OH \rightarrow Al_2O_3 + H_2O \quad (3)$$

ATH plays an essential role in strengthening the polymer's resistance to erosion and corrosion. Of course, too much of it also leads to loss of hydrophobic insulation. The amount of ATH is chosen so that the two parameters of erosion and hydrophobicity are in balance. Therefore, a precise control of the ATH content in the polymer is of particular importance and the TGA test is a suitable method for evaluation.

It can be concluded that a certain amount of the organic materials has already been lost to the air dur-ing the thermal cycling treatment time and a large amount of inorganic fillers remain in the RTV silicone rubber samples:

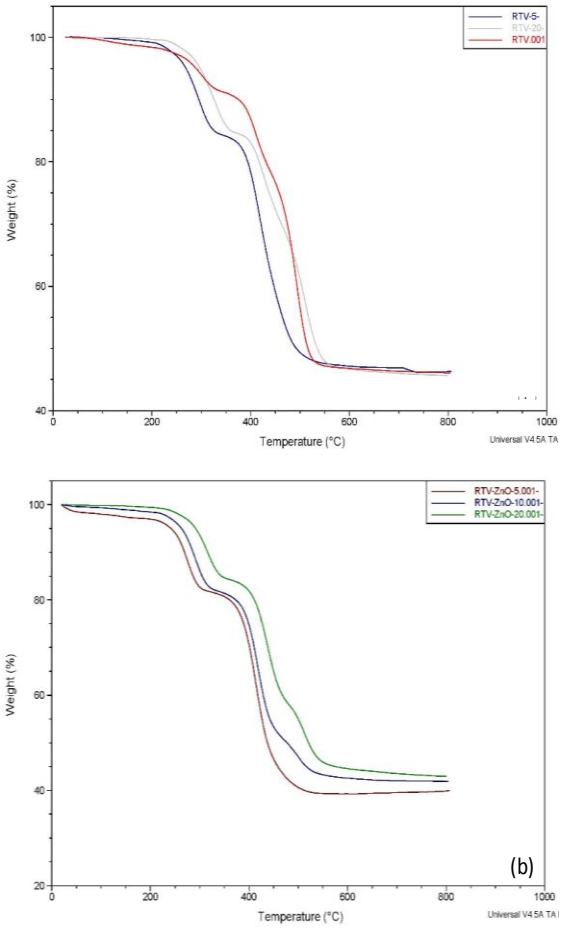

Fig. 1.. TGA curves of (a) RTV, (b) ZnO/RTV at different heating rates before aging

1- High temperature volcanize

3.2. FTIR analysis of RTV nanocomposites

Fourier transform infrared spectroscopy (FTIR) is used to determine the bands and operating groups of polymeric materials. A unique peak is produced as each band and working group absorbs a fixed frequency, the presence or absence of chemical bonds or working groups in the sample is determined from the absorbed curves.The test is similar to the absorption spectrum called ATR. Which includes a reflectance spectrum . The basis of this method is the internal reflection of all light between the inner surfaces of two environments with different refractive indices.

Fig. 4 shows the FTIR spectra of RTV after aging. Table 1 shows the wavelengths assigned to the different functional groups in silicon. The quantitative analysis of FTIR is based on Beer-Lambert's law. The absorption of light in each wavenumber is expressed by the relation (4)[1])

$$A(v) = lg\frac{1}{T(v)} = a(v)bc \qquad (4)$$

In the ratio T(v) and A(v) represent the passage and absorption of the wavenumber v, respectively. a(v) is the absorption coefficients at wavelengths v, b and c represent the length of the light path and the continuity of the sample, respectively.

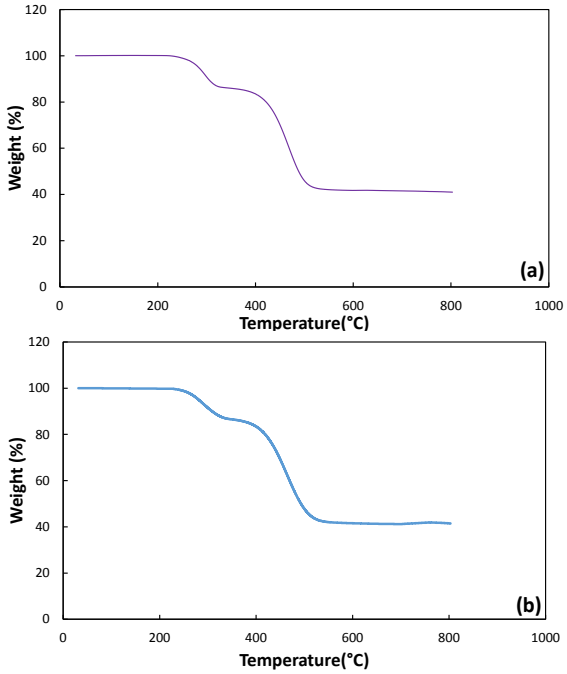

Fig. 2.. TGA curves of (a) RTV, (b) ZnO/RTV at after aging

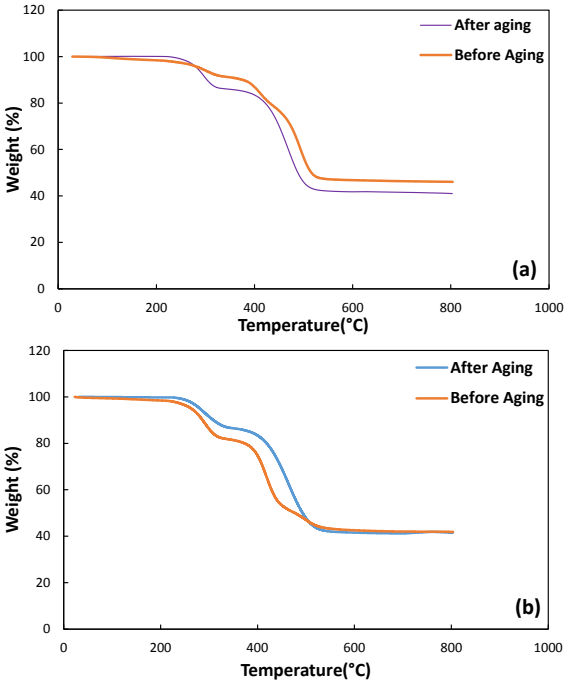

Fig. 3. TGA curves of (a) RTV, (b) ZnO/RTV before and after aging

3.2. FTIR analysis of RTV nanocomposites

Fourier transform infrared spectroscopy (FTIR) is used to determine the bands and operating groups of polymeric materials. A unique peak is produced as each band and working group absorbs a fixed frequency, the presence or absence of chemical bonds or working groups in the sample is determined from the absorbed curves.The test is similar to the absorption spectrum called ATR. Which includes a reflectance spectrum . The basis of this method is the internal reflection of all light between the inner surfaces of two environments with different refractive indices.

Fig. 4 shows the FTIR spectra of RTV after aging. Table 2 shows the wavelengths assigned to the different functional groups in silicon. The quantitative analysis of FTIR is based on Beer-Lambert's law. The absorption of light in each wavenumber is expressed by the relation (3)[1])

$$A(v) = lg\frac{1}{T(v)} = a(v)bc \qquad (3)$$

In the ratio T(v) and A(v) represent the passage and absorption of the wavenumber v, respectively. a(v) is the absorption coefficients at wavelengths v, b and c represent the length of the light path and the continuity of the sample, respectively.

Table 2. Characterisation absorption bands of each group of silicone rubber[4]

Group	Approximate position of the absorption (cm^{-1})
Si- of Si-(CH3)3	700
Si-O of O-Si(CH3)2-O	840~790
Si-(CH3)2	807-800~855
Si-O of O-Si(CH3)3	870~850
Si-O-Si	1110~1000
Si-(CH3)3	1266；1250~840
Si-CH3	1601~1640
-OH of H2O	1270~1255
functional group of ATH	2361~2356
C-H of CH3	2963~2960
-OH of Si-OH and ATH	3700~3200

To assess the aging of silicon, peak changes in the Si-O-Si and Si-CH3 functional groups are commonly studied. The peaks seen in the range 1000-1100 cm^{-1} are specific to the Si-O-Si band and the corresponding peak in the wavenumber 1266 cm^{-1} indicates the change in the symmetric shape of the Si-CH3 band. In the analysis of the FTIR study, the degradation of the insulator due to the action of UV oxygen and energy from electrical discharges is revealed by the removal of the C-H and Si-CH3 bands at 2960 cm^{-1} and 1260 cm^{-1}, respectively. These bonds are removed as a result of the breaking of the carbon-silicon bond in the material. Due to the radical nature of this reaction, the silicon material loses its methyl groups and Polar groups of silanols replace them. As a result, it loses the hydrophobic properties of silicon. Therefore, in many works, the FTIR peak at a wavenumber of 1260 cm^{-1} is considered to indicate the hydrophobicity of the insulator[1]–[4]. There are two quantitative methods for FTIR analysis, one is to measure the absorbed wave peak and the other is to measure the absorbed wave peak area. Using peak area to perform quantitative analysis is more accurate than using peak height[1].

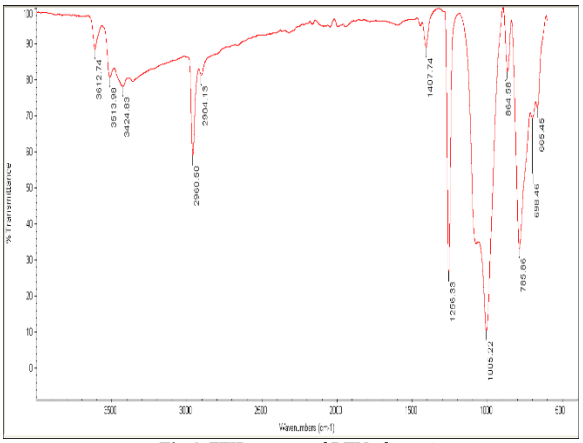

Fig.4. FTIR spectra of RTV after aging

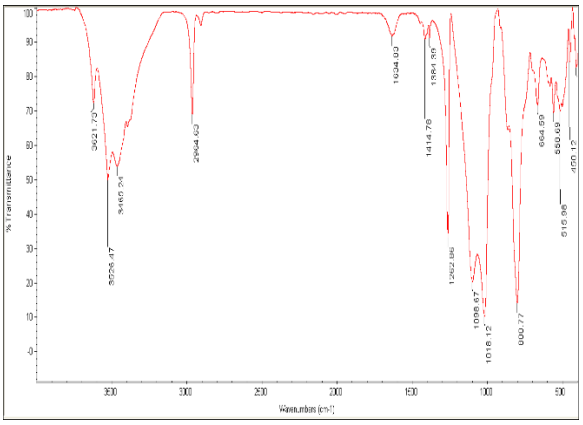

Fig.4 shows the FTIR spectra of RTV after aging. The absorption areas of the functional groups of Si-CH3 and Si-O-Si have a close relationship with the degree of aging. Based on the basic theory about macromolecules, the smaller the absorption area of the functional groups of Si-CH3 and Si-O-Si, the stronger the aging degree. With aging, the peak of the functional groups de-creases, so that a conclusion about the increase or decrease of this group can be generalized from the change in the absorption peak value. And from the change of absorption peak value in the range of 1110 cm-1-1000 cm-1, the increase or decrease of Si-O-Si can also be concluded[4].

Fig. 5 shows the FTIR spectra of nanoZnO- RTV after aging. As can be seen, The addition of nanoparticles reduced aging compared to the coating without nanoparticles. According to the results obtained in current study, the most improvement of electrical insulation performance is related to the nano RTV sample, which is due to the great properties of ZnO nanoparticles. ZnO additive has outstanding physical and chemical properties, such as high dielectric constant[24], [25]

4. Conclusion

In this paper, aging characterization of RTV coating was investigated in the presence of ZnO nanoparticles. The TGA results of the study show that the residual weight of the aged samples is higher than that of the unaged samples. The FTIR analysis results show that the aging performance of nano-RTV is better than that of RTV, which is concluded from the smaller absorption area of the functional groups of Si-CH3 and Si-O-Si. the numeric value of Critical flashover voltage in nano-RTV coating was higher compared to the RTV coating as a result of the enhanced electrical insulation characteristics. This can confirm the improvement of thermal aging of nano-RTV compared to pure RTV and may prove useful to estimate the expected lifetime of the coatings, which is valuable for estimating the reliability of porcelain insulators. This

improvement in aging behaviour of RTV nanocomposites has a significant effect on their expected lifetime.

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