Dielectric Performance of Polymer Nanocomposites Synthesized by Atmospheric-pressure Plasma-treated Silica Nanoparticles

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ABSTRACT

In this study, atmospheric-pressure plasmas were applied to modify the surface of silane-coated silica nanoparticles. Subsequently nanocomposites were synthesized by incorporating plasma-treated nanoparticles into an epoxy resin matrix. Electrical testing showed that such novel dielectric materials obtained high partial discharge resistance, high dielectric breakdown strength, and enhanced endurance under highly stressed electric field. Through spectroscopic and microscopic analysis, we found surface groups of nanoparticles were activated and radicals were created after the plasma treatment. Moreover, a uniform dispersion of nanoparticles in nanocomposites was observed. It was expected that the improved dielectric performance of the nanocomposites can attribute to stronger chemical bonds formed between surface groups of plasma-treated nanoparticles and molecules in the matrix. This simple yet effective and environmentally friendly approach aims to synthesize the next generation of high-performance nanocomposite dielectric insulation materials for applications in high-voltage power systems.

Keywords: atmospheric-pressure plasma, nanocomposite, partial discharge, dielectric breakdown

1 INTRODUCTION

Polymer nanocomposites, which are synthesized by incorporating nano-metric inorganic fillers into organic polymer matrices, have been attracting interests of researchers who are seeking for the next-generation, high-performance materials for various advanced applications [1-8]. High voltage insulation is one of fields in which the polymer nanocomposites obtain promising advantages over traditional polymers and polymer microcomposites [9]. In the recent decade, extensive researches have been initiated and developed. Lewis firstly proposed the concept of nanometric dielectrics in 1994 and analyzed the consequence if the size of a two-phase dielectric system was reduced to the order of nanometers [10]. Subsequently, Nelson and Tanaka, pioneers in the field of nanocomposite engineering, have carried out systematic studies on the dielectric performance of nanocomposite dielectrics [7, 11], as well as provided theoretical analysis [12, 13] on relevant mechanisms. According to their findings, one significant challenge is that nanoparticles often tend to agglomerate due to the incompatibility between inorganic fillers and polymer matrices. As a result, the sizes of particulates are enlarged and the dielectric performance of composite materials deteriorates.

To overcome this issue, attempts have been carried out using coupling agents to coat organic groups on the surface of the nanoparticles [14]. However, these organic groups often interact poorly with the polymer matrix. Thus the interface region of the nanoparticles and the polymer matrix is often inhibited from forming strong chemical bonds, leading to unsatisfactory improvements of the nanocomposites. Previous work by the authors found that resistance to partial discharges (PD) of the silane coated SiO_2/epoxy resin nanocomposite was marginally improved compared to the pure epoxy resin [15].

Recently, it has been demonstrated that the plasma treatment on nanofillers can improve the chemical interaction between organic-inorganic constituents in a polymeric nanocomposite system [16]. In this study, we propose using the atmospheric-pressure plasma technique to activate the surface of the silane-coated nanoparticles prior to mixing them with the uncured polymer. The synthesized epoxy/plasma-treated silane-coated SiO_2 nanocomposites were characterized by Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM). Their dielectric properties were also extensively investigated. Our results demonstrated that this simple yet effective atmospheric-pressure plasma treatment method can provide improved physical and chemical properties of functional organic-inorganic nanocomposites, thereby advancing their potential applications in many fields.

2 EXPERIMENTAL SECTION

2.1 Materials

Hydrophobic fumed silica nanoparticles (AEROSIL R972) treated with dimethyldichlorosilane (DDS) were provided by Evonik Industries, Germany. These silane-coated nanoparticles had an average particle size of 16

nm and a surface area of 110 m^2/g. The epoxy resin (RX771C/NC) containing bisphenol-A diglycidyl ether (BADGE) was obtained from ROBNOR RESINS Ltd. The curing agent (ARADUR HY 1300 GB) consisted of triethylenetetramine (TETA) was supplied by Huntsman Advanced Materials. This thermoset epoxy resin has been widely used as insulation materials in high-voltage applications.

2.2 Sample Preparation

The process of preparing nanocomposite samples is depicted in Figure 1. A custom-designed atmospheric-pressure plasma reactor was used to modify the surface of the as-received silica nanoparticles. Cold atmospheric-pressure plasma was generated by a 4 kV peak-peak 350 kHz radio frequency (RF) power supply. The plasma was generated in dielectric barrier discharge (DBD) mode using a stainless steel electrode suspended in the glass-made reactor with the ground electrode placed underneath it. Helium was used as the working gas for the discharge. The power density in the plasma region was estimated to be 60 mW/cm^3. During the treatment, nanoparticles were fully covered by the glow discharge plasma. Also, magnetic stirring was constantly applied to ensure a uniform exposure of the surface of nanoparticles to the plasma. Each batch of nanoparticles was treated for 30 min. After the plasma treatment, the temperature of nanoparticles was 55°C.
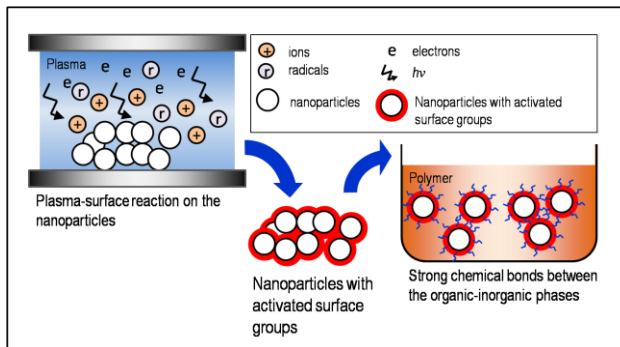

Figure 1: The process of synthesizing nanocomposites with atmospheric-pressure plasma-treated silica nanoparticles.

The nanocomposites were synthesized by introducing 400 mg atmospheric-pressure plasma-treated silica nanoparticles into 10g uncured epoxy resin. High-shear stirring (5000 revolutions per minute) was then performed for 1 min. Subsequently, 4 g hardener agent was added to the mixture, followed by another 1 min of stirring at a constant speed. Afterwards, the 3-part mixture underwent ultrasonication for 15 min followed by degassing under vacuum (less than 100 Pa) for 1 h. Finally, the mixture was poured into premade molds and cured at 40 °C for 2 h followed by 48 h curing at room temperature. The loading ratio of all samples was 3 wt%. The denotation and the recipe of each sample can be found in Table 1.

Sample denotation	Recipes
PER	Pure epoxy resin
UTNC	Epoxy resin/2 wt% untreated silane-coated silica nanocomposite
PTNC	Epoxy resin/2 wt% plasma-treated silane-coated silica nanocomposite

Table 1: Denotation and composition of each sample

2.3 Characterization and Electrical Testing

Fourier transform infrared (FTIR) spectroscopy analysis of the nanoparticles was performed using PerkinElmer Spotlight 400 FTIR spectrometer. Field emission scanning electron microscopy (FESEM) images of each sample were obtained using a Zeiss Ultra Plus microscope. Accelerated electrical ageing test was performed by applying a constant AC high-voltage (7.5 kV root mean square, 300 Hz) to a pair of needle-to-plane electrodes embedded in nanocomposites samples. The distance between the two electrodes was 2 mm. Simultaneously, magnitudes of partial discharge (PD) activities were recorded using the OMICRON MPD600 system with a typical measurement circuit as described elsewhere [15]. Dielectric breakdown tests were carried out complying with the geometry and procedures in ASTM D149 [17]. Specifically, laminar samples (Figure 2) were fabricated and tested by increasing the voltage from 2 kV until occurrence of breakdown with a 0.5 kV step increment for every one minute.
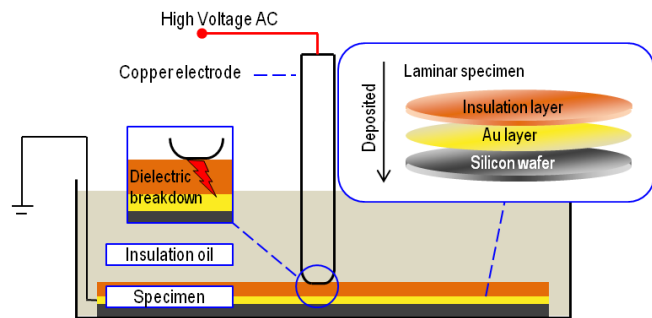

Figure 2: The laminar sample and the electrode geometry employed in the dielectric breakdown measurement system.

3 RESULTS AND DISCUSSIONS

Now we discuss effects of the atmospheric-pressure plasma treatment on silica nanoparticles and synthesized nanocomposites.

FTIR examination was carried out on the untreated and plasma-treated silane-coated SiO$_2$ nanoparticles. The spectrum of pure SiO$_2$ nanoparticles (AEROSIL A380) was also obtained as a control. The spectra of the samples are shown in Figure 3. First, the spectrum of the pure SiO$_2$ nanoparticles features two sharp peaks at 1070 cm^{-1} (Si–O–

Si stretching) and 806 cm^{-1} (Si–O bending). In the spectrum of the silane coated SiO$_2$ nanoparticles, three additional peaks are found around 870, 840 and 760 cm^{-1}. This can be interpreted by the surface structure of the silane-coated SiO$_2$ (Figure 4) [18]. The peaks and the corresponding bonds are listed in the inset of Figure 4. In contrast, one can find that both peaks around 840 and 760 cm^{-1} are reduced from the spectrum of the plasma-treated sample. This result demonstrates that the Si–C bonds are partially broken by the impact of energetic electrons and ions in the plasma. As a result, unpaired electrons are created in the surface groups of the plasma-treated nanoparticles and radicals may form. This will further result in the increase of surface reactivity of the nanoparticles and the tendency of forming chemical bonds with the matrix after being mixed with the host polymer.
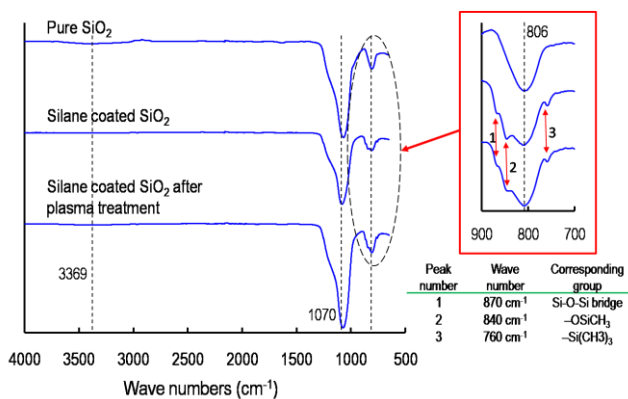

Figure 3: FTIR spectra of pure SiO$_2$, silane coated SiO$_2$, and plasma-treated silane-coated SiO$_2$ nanoparticles.
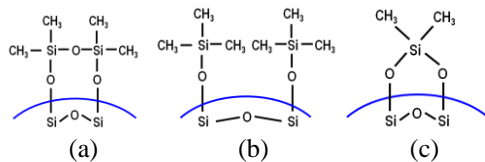

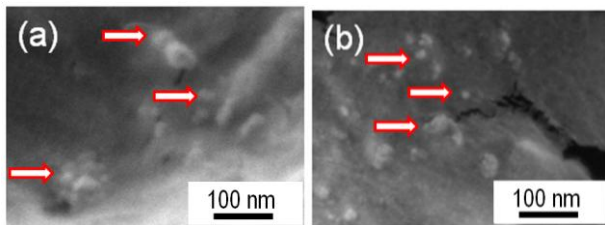Figure 4. Possible surface structures of silane coated SiO$_2$ nanoparticles.

Figure 5: SEM images of (a) epoxy/untreated SiO$_2$ nanocomposite sample and (b) epoxy/plasma-treated SiO$_2$ nanocomposite sample.

Furthermore, we observed the dispersion uniformity of the nanocomposites synthesized by the untreated and plasma-treated SiO$_2$ nanoparticles from SEM imaging (Figure 5). For both samples, the largest size of the nanoparticle clusters was less than 30 nm. This result indicates that the dispersion uniformity was not affected from the introduction of plasma-treated silica nanoparticles into the host polymer.

To investigate dielectric properties of synthesized nanocomposites, accelerated electrical ageing was applied to test samples using needle-to-plane electrodes. Partial discharge magnitudes were simultaneously recorded throughout the test and depicted in Figure 6. From this figure, one can divide the aging process into three phases: 1 voids formation; 2 tree propagation; 3 the ultimate breakdown. It can be explained by the degradation process of nanocomposites under the highly stressed electric field. Initially, gaseous byproducts may lead to the formation of voids within the material. Then, those voids may develop into electrical trees and propagate to the opposite electrode. Eventually, breakdown occurred once any of the electrical trees formed a complete channel linking the two electrodes. The endurance of the PTNC sample was about 19 h, compared to only 14.7 h for the UTNC sample.
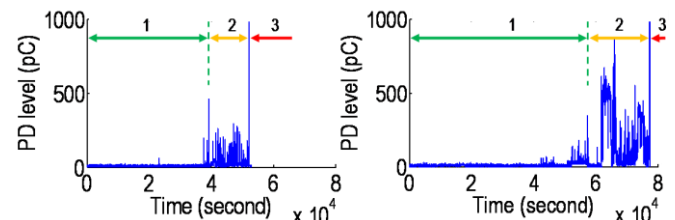

Figure 6: Partial discharge magnitudes of (a) the epoxy/untreated SiO$_2$ nanocomposite and (b) the epoxy/plasma-treated nanocomposite during the aging test. The process can be divided into three phases: 1 voids formation; 2 tree propagation; 3 ultimate breakdown.

From Figure 6, it is obvious that the extended endurance of the PTNC sample was mainly contributed from its prolonged voids formation time (the first phase). This effect can attribute to the stronger chemical bonds formed between the plasma-treated SiO$_2$ nanoparticles and the polymer matrix. In particular, the cross-linking of the epoxy resin polymer is achieved by the C–N bonds which link the epoxide groups of the uncured resin (BADGE) and the amine groups of the curing agent (TETA). As the surface of plasma-treated silane-coated SiO$_2$ nanoparticles were highly reactive, the incorporation of these nanoparticles can lead to the reaction between silicon-based radical groups on nanoparticles and amine groups of the curing agent. Therefore, Si–N bonds may be created instead of C–N bonds, which are expected to form in the pristine epoxy resin polymers.

The chemical bonds in the epoxy resin nanocomposites and their corresponding bond dissociation energy (BDE) are given in Table 2. It is noted that the C–N bonds have the lowest BDE (3.1 eV), while the Si–N bonds (3.7 eV) is relatively stronger. Therefore, more energy from the charge carriers is needed to deform the nanocomposites, leading to a longer voids formation time. Hence a desired stability under highly stressed electric fields is achieved.

Bond	C–C	C–O	C–N	C–H	Si–N
BDE (eV)	3.6	3.7	3.1	4.3	3.7

Table 2: Chemical bonds in epoxy resin nanocomposites and their corresponding bond dissociation energy (BDE)

Moreover, the dielectric breakdown test was carried out and Weibull plots of the dielectric strength of the pure epoxy resin (PER) and the epoxy/untreated nanocomposite (UTNC) sample were obtained (Figure 7). Values of shape parameters (i.e. breakdown strength at the probability of 63.2%) of each specimen are also given in the figure. The breakdown strength of the UNTC was 82 kV/mm, which was significantly higher than that of the PER sample (52 kV/mm). For the PTNC sample, much higher voltage was applied in order to achieve equivalent stress (due to different thickness) and thus the added effect of surface discharges. This can also cause damage to the sample and thus facilitate the breakdown. Nevertheless, we found that no breakdown occurred before the external field was increased to 80 kV/mm. This result implies that the breakdown strength was dramatically improved by replacing untreated nanofillers with plasma-treated ones.

These results therefore demonstrate that this simple atmospheric-pressure plasma treatment indeed effectively improved the dielectric performance of organic-inorganic nanocomposites.
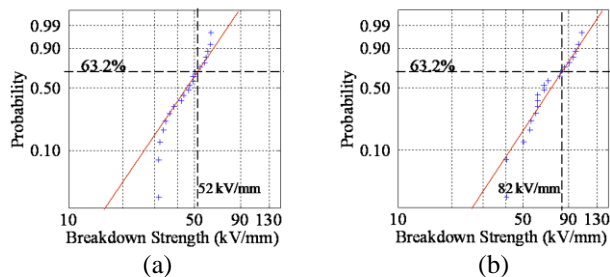

Figure 7. Weibull plots of the dielectric breakdown strength probability of (a) the pure epoxy resin and (b) the epoxy/untreated SiO_2 nanocomposite sample.

4   CONCLUSION

We have demonstrated that the atmospheric-pressure plasma treatment is an easily-accessible, environmentally friendly, and effective approach for development of high-performance nanocomposite dielectric materials. Through microscopic and spectroscopic analysis, we found that surface groups of silane-coated nanoparticles were activated and radicals were formed after the plasma-treatment. When nanoparticles were introduced into the host polymer, those activated surfaces may lead to the formation of stronger chemical bonds between nanoparticles and the matrix. As a result, significant improvement of the aging endurance and dielectric breakdown strength were found in the epoxy/plasma-treated

SiO_2 nanocomposite samples compared to the nanocomposite synthesized with untreated fillers. From a broader perspective, this contribution not only provides a novel approach to synthesize organic-inorganic nanocomposite materials with desired dielectric properties for high-voltage insulation systems, but also can be employed in energy conversion and storage applications.

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