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Fractal Approach to Dielectric Properties of Single Walled Carbon Nanotubes Reinforced Polymer Composites

Aykut ILGAZ *1, Mehmet BAYIRLI1

Abstract

In this paper, the internal structure and dielectric properties of unsaturated polyester resin-based neat and single-walled carbon nanotube reinforced composites were comprehensively evaluated with the fractal analysis using the Fast Fourier Transform (FFT). The greyscale images, bitmap (BMP) images and 3D tomographic images were obtained by converting the scanning electron microscope images of the materials. It was observed that the distributions of components in the resin for both materials are irregular and their surfaces exhibit anisotropic behaviors. The surface coating rate (SCR) and fractal dimensionality (FD) of the materials were also calculated using the power spectrum. It has been observed that the fractal dimensionality of the composites can be changed by the doping process and the fractalization of the nanotube doped sample increases compared to the pure material due to nanotube agglomeration, spatial distribution and the orientation. The increase in fractalization as a result of this agglomeration and orientation in carbon nanotubes explains the high dielectric constant values observed at low frequencies by increasing the number and size of carbon nanotubes clusters that act as micro capacitors in certain regions of the matrix. It has been reported that the calculations for the surface coverage ratios for both samples also support these results.

Keywords: Fast Fourier Transform, fractal analysis, power spectrum, dielectric properties, carbon nanotubes

1. INTRODUCTION

In recent years, studies on the doping of nanomaterials with various ratios in order to improve the performance of polymer composites in charge storage capacitor applications have led to the production of composite materials with high dielectric constants [1-4]. Single-walled carbon nanotubes are nanomaterials with superior mechanical properties as well as unique dielectric properties. Ultra-high dielectric constant values can be obtained in nanotube-doped polymer composites due to polarizations occurring at the interfaces as a result of the combination of carbon nanotubes with conductive nature and insulating composites [5]. Samir et al. estimated dielectric permittivity for different concentrations of nanotubes. It was stated that adding 0.5 wt. % nanotubes to the neat sample increased the dielectric constant about 30

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times [6]. Belhimria et al. studied effect of CNT and graphite reinforcements on dielectric behaviours of polyester based neat composite. It has been reported that nanotubes and graphite additives significantly increase the dielectric constant of the material, even at small concentrations [7].

In addition to experimental efforts, the properties of doped composites and solids can also be explained with a theoretical model that includes the fractal characteristics, morphological and topographic properties. For this purpose, studies have been carried out to analyze the correlation between properties and morphological characteristics of materials in recent years [8-12]. The relationship between the fractal dimension and dielectric relaxation mechanism of the carbon nanotube doped epoxy-based polymer composites using small angle neutron scattering (SANS) and impedance spectroscopy (IS) methods has been studied [9].

Pander et al. investigated CNT forest structure by fractal dimension and lacunarity analysis using a box-counting method [13]. It is determined that the fractalization decreased with the increasing thickness during the fractality analysis of the catalyst particles. Zhang et al. reported a simple method to determine the amount of the interface's surface area and uniformity using fractal dimension calculation based on SEM images [14]. They studied on rubber and plastic composites to directly correlate the fractal dimension of the CNT interfacial surface area with the composite properties. They found that with increasing fractal dimension of the CNT interface surface area, the electrical conductivity of the composites increased exponentially and the tensile strength linearly increased. Hopkins et al. have demonstrated that the fractal dimension is related to the dielectric relaxation process [15].

So far, most of the researches on the dielectric behavior of nanotube-doped polymer composites have used multi-walled carbon nanotubes. We thought that the effect of single-walled carbon nanotubes, which have different mechanical, thermal and electrical properties from multi-walled carbon nanotubes, on the dielectric properties of composite materials should be investigated. Additionally, there are not enough studies in the literature to fully reveal the relation between the capacitor behaviors of the single-walled carbon nanotube doped material and its morphological structure.

This motivated us to consider a detailed and systematic study to understand the correlation between them. Therefore, the main purpose of this study is to reveal the degree of correlation between the experimentally determined dielectric performance of pure and nanotube loaded composites and fractal analysis parameters.

2. MATERIAL AND METHOD

2.1. Material

Pure and nanotube-filled polymer composites were manufactured using Sheet Moulding Compound (SMC) method that involves a mixture of glass fiber, thermosetting resin, additives, calcium carbonate, fillers such as carbon nanotube, carbon fiber. In this study, FWR6 glass fiber was (16 μm filament diameter, 2200 roving tex count (g/1000 m)) purchased from Sisecam Turkey. Polipol 3401 orthophthalic-based unsaturated polyester obtained from Poliya was used as resin which has styrene monomer content 37-41% with viscosity value of 350 cps. The 3-methacryloxypropyltrimethoxy silane was employed as a coupling agent that enhances adhesion ratio between resin and glass fibers and improves quality of electrical properties. Single walled carbon nanotubes (Tuball Matrix, OCSiAl, Germany Laboratories) with the average diameter of 20 nm and the length in the range of ~22 μm were used, in which the purity is higher than 93 wt. %.

The materials produced also include methyl ethyl ketone peroxide, calcium carbonate, thickener mixture, zinc sulphide. The above-mentioned components and unsaturated polyester resin were added into the single-walled carbon nanotube suspension, which was subjected to an ultrasonic bath for 1 hour at room temperature. The dough, which became paste-like, was transferred to the conveyor system by mixing with the help of a mechanical stirrer. The dough, on which glass fiber was clipped and pressed again in order to ensure homogeneity, was put into molds until it had the appropriate viscosity and sent to the oven. After the optimum conditions were satisfied, the material removed from the mold was pressed on test plates.

2.2. Method and Morphology

Surface images were obtained using scanning electron microscopy (SEM) and transferred to digital media using Gwyddion free software in order to investigate the surface morphology of the pure and carbon nanotube loaded samples [16]. Five different images with 200 x 200 pixel mesh were selected from the SEM microphotographs to determine the regional fractal morphology features.

Firstly, the particle density ρ (x_i,y_j) according to the location of the particles on the sample surfaces, black cells as one (1), white cells as zero (0) were determined to calculate the surface coating rate (SCR). SCR can be defined as

$$\sigma\,(N,L) = L^{-d} \sum_{i=1,j=1}^{i=L,j=L} \rho(x_i, y_j) \tag{1}$$

where $\sum_{i=1,j=1}^{i=L,j=L} \boldsymbol{\rho(x_i, y_j)}$ is total number of particles, L is the side of the square mesh in BMP image format and d = 2 Euclidean dimension.

Secondly, surface height density can be obtained using following equation:

$$\bar{h}(h, L) = (L^{-d}) \sum_{j=1}^{L} \sum_{i=1}^{L} h_{i,j} \tag{2}$$

where $\sum_{j=1}^{L} \sum_{i=1}^{L} h_{i,j}$ is the total value of image density on the total grayscale of the surface. The $h_{i,j}$ value is the number of data points and the height value at each data point on the surface of the composite material displayed in 3 dimensions. In the matrix array representing the composite surface, the height value for each pixel in the image is defined as follows:

$$h_{i,j} = \begin{cases} 0 & \text{black pixels} \\ \text{from 0 to 255} & \text{grey pixels} \end{cases} \tag{3}$$

In this model, the height value of each pixel on the surface of the composite is an integer and takes values between 0 and 255 on the grayscale.

The power spectrum is one of the useful methods for fractal dimension calculation of the material and is based on the power spectrum dependence of the irregular Brownian motion [17-19]. To find the fractal dimension of an image, the intensity distribution in a particular aspect of the image converted to gray scale is determined using appropriate image processing software. The Fast Fourier Transform (FFT) of the obtained data is extracted. The square of the amplitude of the Fourier transform is the power spectrum w(f) which is defined as proportional to β

$$w(f) \sim k^{-\beta} \tag{4}$$

where f is the frequency and $k = 1.37\times10^{-23}$ J/K is the Boltzmann constant. The calculated $\beta = 7 - 2d_f$ value is related to the fractal dimension d_f. Integrating Eq. (4), we have

$$\log w(f) = -\beta \log k + c \tag{5}$$

where c is the integration constant. However the calculated fractal dimension values have a relative measurement uncertainty which can be expressed as

$$\frac{\Delta d_f}{\overline{d_f}} = \frac{d_f - \overline{d_f}}{\overline{d_f}} \tag{6}$$

where $\overline{d_f}$ is the average of the regional fractal dimension values of the composite.

3. IMPEDANCE SPECTROSCOPY

The frequency dependent impedance measurements were carried out at room temperature in the frequency range from 10^{-2} Hz to 1 MHz. The samples in the form of 3 mm thick square plates with 20 mm side length were placed between two parallel plate electrodes. The results extracted from these measurements are used to determine complex impedance (Z*) of the specimens. The real part (Z') of the represents the resistance of the material, while the imaginary part (Z") defines the loss factor [20]. Using the impedance data, the real (ε') and imaginary parts (ε") of the complex dielectric permittivity (ε*) of the polymer material are obtained with the following formulas [7].

$$\varepsilon'(\omega) = Z''/_{2\pi f C_0 Z^2}$$
$$\varepsilon''(\omega) = Z'/_{2\pi f C_0 Z^2} \qquad (7)$$

where C_0 is the capacitance of sample.

4. RESULTS

The surfaces of neat and nanotube-doped samples are given in Fig. 1 as typical greyscale images and bitmap (BMP) images. When the surface morphology of the neat sample is examined, it is reported that a systematic and symmetrical distribution is not observed and the structure is irregular. The cylindrical fiber structures are randomly distributed along the upper and lower lateral edges of the lattice and the sizes of the particles that form the matrix appear to be different from each other.

On the other hand, the components were distributed relatively more homogeneously in the resin and the carbon nanotubes exhibited a different structure by adhering randomly to the materials forming the matrix in the carbon nanotube doped sample. In addition, agglomerations of carbon nanotubes clusters were observed in certain regions in the matrix.

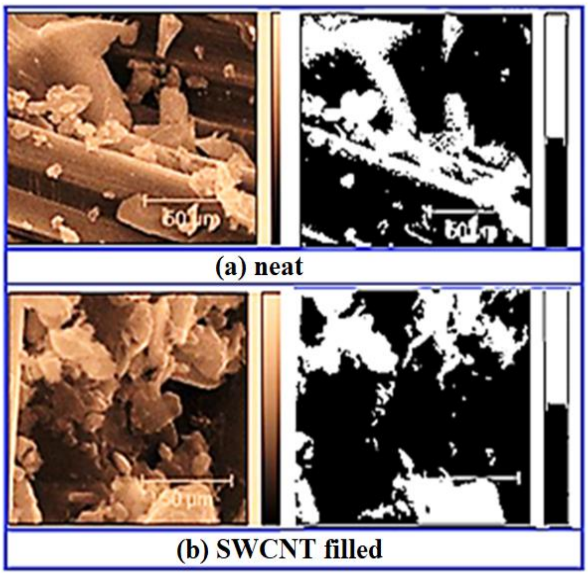

Figure 1 The greyscale and BMP images of the neat and SWCNT filled materials

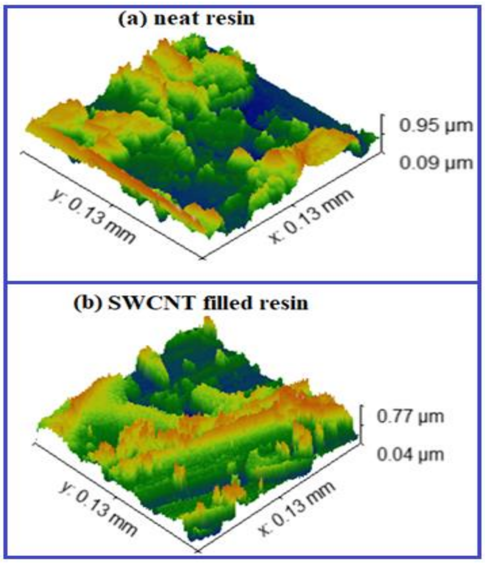

Figure 2 The tomographic images of the neat and SWCNT filled materials

The surface coating rate (SCR) value calculated from BMP image format for the pure material varies between 36.82% and 58.29%, with an average value of 45.08%. The SCR value for the carbon nanotube composite varies between 42.48% and 52.32%, and the average value was calculated as 47.51%. This situation was attributed to the balanced distribution of carbon nanotubes in the matrices and interfaces.

The morphologies of the surface formations of the specimens were examined by 3D tomographic images as given in Figure 2. It was revealed from images that internal structures of the polymer composites were heterogeneous and irregular.

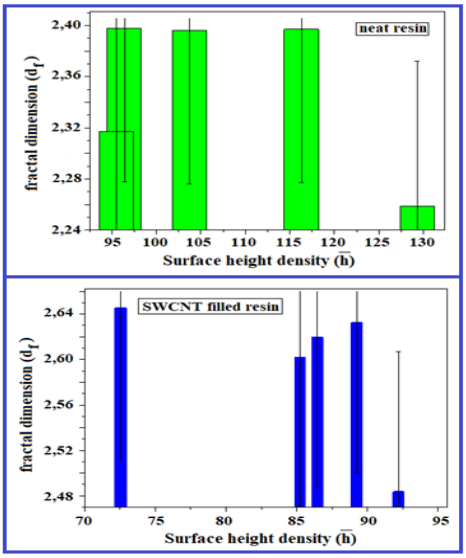

Figure 3 Surface height density versus fractal dimension graph of the neat and SWCNT filled materials

Fig. 3 shows the relation between surface height density and fractal dimension for both samples. $\overline{(h)}$ varies between 95.518 and 129.296 with an average value of 108.246 neat composites. Surface height density $\overline{(h)}$ value is between 85.139 and 92.22 for nanotube added polymer and its average value was calculated as 87.247.Error lines have been added on the bar chart. The regional surface densities were found to be different from each other due to the fact that the carbon nanotubes added to the polyester-based composite were not homogeneously dispersed into the polymer composite.

The fractal dimension parameter (d_f) are obtained by β value from the slope of log w (f)-log k graph as illustrated in Fig. 4 of the power spectrum [19]. It was revealed that the fractal dimension values of the pure sample obtained by the Fourier spectral analysis method ranged from 2.259 to 2.398 and the average value was 2.353. The fractal dimension value of the carbon nanotube added sample increased from 2.483 and 2.632 and the average value was calculated as 2.636.

The measurement uncertainty for the pure and doped sample was calculated as 0.022 and 0.027, respectively. The d_f value of the carbon nanotube added samples was found to be higher than the undoped samples. This situation can be attributed to the possible existence of high fractalization and surface anisotropy in the doped material. Experimental data reported that while the value found by spectroscopy is between 2.02 and 2.21, the value found by SANS technique is between 2.29 and 2.31 [9]. It should be noted that the obtained dimensionality parameters take values closer to 3 rather than 2. That is, they are higher than the surface size but smaller than the volume dimension. The reason for this can be interpreted as that not only carbon nanotubes and other components shape the agglomeration, but also the chemical surface properties have an active role in this case [21].

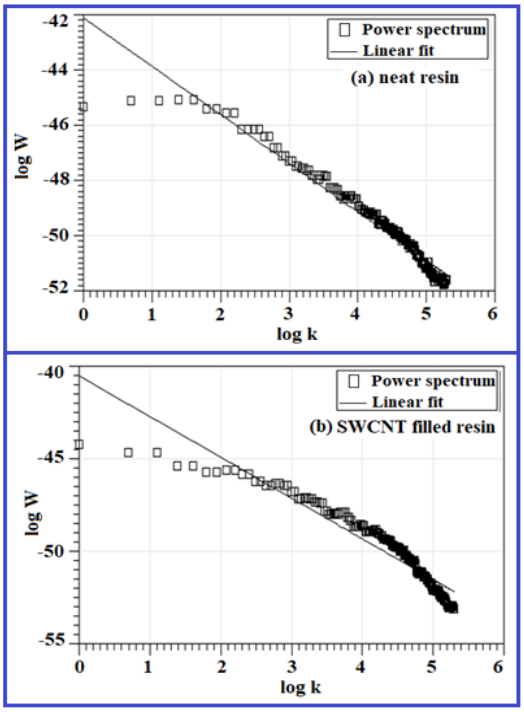

Figure 4 log w (f)-log k graph of the neat and SWCNT filled materials

Fig. 5 (a) and (b) provides plots of the dielectric constant dielectric loss factor of neat and SWCNT filled resin. It is seen that the dielectric constant values found for the neat resin are almost independent of frequency. However, the nanotube doped sample has high dielectric constants at low frequencies.

This can be attributed to the fact that the electric field generated in the material prevents charge accumulation at the interface between the matrix and the single-walled carbon nanotubes. Another reason can be considered as polarization and Maxwell-Wagner-Sillars interaction effects in the low frequency region [22].

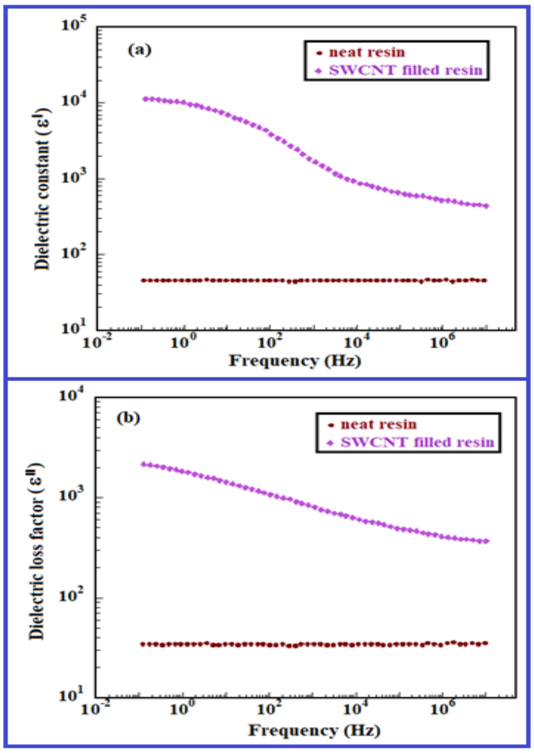

Figure 5 (a) Dielectric constant and (b) dielectric loss factor of neat and SWCNT filled resin.

The fact that carbon nanotubes act as capacitors in the matrix as a result of aggregation which is presented by fractal analysis is also one of the factors that increase the dielectric constant. At high frequencies, the dielectric constant decreases as the polarization effects weaken and carbon nanotubes act as conductive sources. As can be seen from the graphs, no loss peaks were observed within our frequency limits measured in the loss spectrum. The loss factor, which is high at low frequencies, gradually decreases with increasing frequency due to the interfacial polarization and direct current conductivity contributing to the dielectric relaxation process.

5. CONCLUSIONS AND DISCUSSION

The polymer-based composites are known to be ideal candidates for designing materials with high dielectric permeability over a wide frequency range. However, in the last two decades, it has been revealed that adding carbon nanotubes to polymer-based composites improves the dielectric properties of the material. At the same time, there are studies in which this effect is related to the morphological structure and fractal behavior of the material. In this study, pure and single-walled carbon nanotube doped materials were manufactured to test this correlation between dielectric properties and morphological structure. Firstly, the real (dielectric constant) and imaginary (dielectric loss factor) components of complex permittivity for materials were obtained using the impedance spectrum data.

It has been observed that the pure sample has a dielectric value that is almost unaffected by the frequency, however, the dielectric properties of the carbon nanotube added material show frequency-dependent behaviors. Doping has been found to increase fractalization due to the agglomeration and orientation of carbon nanotubes. It has been interpreted that increasing nanotube clusters also act as a microcapacitor at low frequencies and increase the dielectric constant. At high frequencies, due to their conductive nature, they become conductive and the dielectric constant begins to decrease as Belhimria et al. stated in literature [9]. Similar interpretations can be made for the dielectric loss factor in parallel with the values found by Samir et al [6].

Since it is known from that the polarization effects and dielectric performance of the composite material affect by the homogeneity of structure and material morphology, a theoretical model that includes fractal geometry has been used to evaluate different parameters such as fractal dimension, surface height density, and surface coating rate. The gray scale, BMP and 3-dimensional fractal graphics are observed to better define the surfaces of materials. The fractal dimension (d_f) of the carbon nanotube added samples was found to be higher than the undoped samples as expected. The average fractal dimension extracted from Fourier spectral analysis method was 2.3 for neat and 2.5 for nanotube filled matrix. The fractal dimensions found in the literature are between 2.02 and 2.21 by impedance spectroscopy and between 2.29 and 2.31 by the SANS method [9].

As a result of, dielectric properties have been studied in detail both experimentally with impedance results and theoretically with fractal approach. The results show that the fractalization method can be used as a useful tool to evaluate the additive dispersion character in the polymer composite mixture and to predict effect of filler on the properties of the material. In other studies, the contribution of the area-perimeter relationship of the components on the surface to the AC conductivity can be discussed.

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The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

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The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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