A Comprehensive Study on Dielectric Properties of Volcanic Rock/PANI Composites

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Abstract. Basalt is a very well-known volcanic rock that is dark colored and relatively rich in iron and magnesium, almost located each country in the world. These rocks have been used in the refused rock industry, to produce building tiles, construction industrial, highway engineering. Powders and fibers of basalt rocks are widely used of radiation shielding, thermal stability, heat and sound insulation. This study examined three different basalt samples (coded CM-1, KYZ-13 and KYZ-24) collected from different regions of Van province in Turkey. Polyaniline (PANI) is one of the representative conductive polymers due to its fine environmental stability, huge electrical conductivity, as well as a comparatively low cost. Also, the electrical and thermal properties of polymer composites containing PANI have been widely studied.

The dielectric properties of Basalt/Polyaniline composites in different concentrations (10, 25, 50 wt.% PANI) have been investigated by dielectric spectroscopy method at the room temperature. The dielectric parameters (dielectric constants, loss and strength) were measured in the frequency range of 10^2 Hz-10^6 Hz at room temperature. The electrical mechanism change with PANI dopant. A detailed dielectrically analysis of these composites will be presented.

1. Introduction
Basalt is the generic term for solidified volcanic lava that is dark colored and relatively rich in iron and magnesium, almost located every country in the world. Basalt rocks include a variety of crucial elements (Fe, Mg, Ca, K, P, and S) along with helpful elements (Si and Na) for plants. Also, they are intrinsically obtainable and environmentally sound as a soil amendment. There is growing interest in reinforcing polymer matrix composites with mineral basalt because of their moderate cost, high stiffness and strength, excellent corrosion and oxidation resistance, and heat resistance and thermal stability [1]. Conducting polymers breakthrough provides many new applications for polymeric components. The conducting polymers have been studied for the last 20 years, because of their essential physical attributes and potential applications in numerous electronic devices, e.g., organic field effect transistors, light emitting diodes, and chemical sensors [2].

Among the conducting polymers, Polyaniline is an excellent example of Π-conjugated polymer. The conductivity and I-V characteristics of Polyaniline depend on different experimental conditions like temperature, pH value, the concentration of oxidant and on the nature of dopant. Among different methods of synthesize of Polyaniline, the chemical oxidation and electrochemical synthesis are prominent [3]. It is one of the members of the intrinsically conducting polymer family. Due to possessing a high molecular weight. Also, PANI indicates high conductivity and good environmental stability in contrast to other conducting polymers [2].
The main goal of this study was to examine the effect of PANI on basalt and to evaluate the dielectric properties by varying the PANI concentration. The real and imaginary parts of the complex dielectric permittivity, dielectric strength and a.c. conductive mechanism of composites have been investigated by the dielectric spectroscopy method at the room temperature.

2. Experimental Procedure

2.1. Materials
Basalt samples collected from Van city, Turkey. The basalts were taken from volcanic fields erupted from extensional fractures in different periods of time in the Pliocene to Quaternary. Petrology and volcanology of the volcanic regions are examined in detail by [4]. Chemical analyses of the basalt samples are taken by X-ray fluorescence (XRF) instrument. Operating conditions of the Philips PW-2400 XRF instrument were set at 60 kV and 50 mA. The results of chemical analysis of basalt samples are given in Table 1. According to the chemical analysis of basalt samples, SiO$_2$ has pure basic character [5].

| Compound | CM-1  | KYZ-13 | KYZ-24 |
|----------|-------|--------|--------|
| SiO$_2$  | 41.668| 47.790 | 47.086 |
| TiO$_2$  | 2.0800| 1.3950 | 1.7910 |
| Al$_2$O$_3$ | 13.106| 16.918 | 17.574 |
| Fe$_2$O$_3$ | 13.823| 10.878 | 11.493 |
| MnO      | 0.1920| 0.1630 | 0.1720 |
| MgO      | 9.7540| 7.6190 | 8.6710 |
| CaO      | 10.602| 11.357 | 9.9660 |
| Na$_2$O  | 5.2610| 3.1370 | 2.9340 |
| K$_2$O   | 1.7370| 0.5190 | 0.1210 |
| P$_2$O$_5$ | 1.7770| 0.2240 | 0.1920 |

Polyaniline (emeraldine base, average Mw ~5000) was purchased from Sigma-Aldrich. To investigate effects of PANI additive percentages (10.0, 25.0, 50.0 wt.%) on the electrical properties of basalt mechanically modified by PANI, Basalt/PANI composites were prepared by mixing of basalt samples with PANI. The prepared materials of composites were compression molded in a cold press at room temperature. Each one of these mixtures prepared as a pellet having 13 mm diameter, 0.500 g weight and 2 mm thickness.

2.2. Dielectric Measurements
The dielectric measurements were carried out with a two-point probe arrangement. The measurements at room temperature with a high accuracy (0.17% typ.) of the samples were measured by an HP 4194A Impedance Analyzer. The dielectric parameters were measured in the frequency range of 100Hz–15 MHz, using an impedance analyzer interfaced with a computer.

3. Result and Discussion
Dielectric spectroscopy (DS) is a well-known and powerful technique which has been effectively used for the characterization of electrical properties of materials as a function of frequency and temperature [6,7]. The dielectric permittivity, energy loss and dielectric relaxation strength are important parameters for material science because these parameters used to decide on the suitability for a given application. The frequency dependence complex dielectric permittivity $\varepsilon'(\omega)$ is given by

$$\varepsilon'(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

(1)
Here, $\omega$, $\varepsilon'(\omega)$, and $\varepsilon''(\omega)$ are the angular frequency, the real and the imaginary part of the complex dielectric permittivity, respectively. The $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for samples have been shown in Fig. 1. When the three types of basalts are doped by different weight percentage of PANI, the dielectric constant is decreased in low frequencies. Moreover, the $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ have large values in the low-frequency region and decreases rapidly in 10.0 wt.% PANI composites. Therefore the complex conjugates of dielectric can be written as [8],

$$\varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$

(2)

In this expression, $\varepsilon'_s$ and $\varepsilon'_\infty$ are low and high frequency dielectric constants. In the dielectric spectroscopy technique, the dielectric relaxation strength $\Delta\varepsilon'$ is the difference between the dielectric values at low and high frequencies $\Delta\varepsilon'$ is given by;

$$\Delta\varepsilon' = \varepsilon'_s - \varepsilon'_\infty$$

(3)

The $\varepsilon'_s$, $\varepsilon'_\infty$ and $\Delta\varepsilon'$ values have been shown in Table 2. The highest value was obtained in CM-1/10.0 wt.% PANI sample in terms of dielectric strength parameters. It is also observed that the dielectric strength $\Delta\varepsilon'$ decreases with the increasing PANI doping concentrations.

| Sample       | $\varepsilon'_s$ | $\varepsilon'_\infty$ | $\Delta\varepsilon'$ |
|--------------|------------------|------------------------|----------------------|
| CM-1/ 10.0 wt.% PANI | 222.56           | 24.76                  | 197.80               |
| CM-1/ 25.0 wt.% PANI | 83.13            | 30.59                  | 52.54                |
| CM-1/ 50.0 wt.% PANI | 58.67            | 25.86                  | 32.81                |
| KYZ-13/ 10.0 wt.% PANI | 148.94           | 28.40                  | 120.54               |
| KYZ-13/ 25.0 wt.% PANI | 74.91            | 18.99                  | 55.92                |
| KYZ-13/ 50.0 wt.% PANI | 42.45            | 9.49                   | 32.96                |
| KYZ-24/ 10.0 wt.% PANI | 132.15           | 10.11                  | 122.04               |
| KYZ-24/ 25.0 wt.% PANI | 98.55            | 30.74                  | 67.81                |
| KYZ-24/ 50.0 wt.% PANI | 65.03            | 29.74                  | 35.29                |
Figure 1 The variation of (a, c, e) the real part and (b, d, f) the imaginary part of dielectric constant with angular frequency for the Basalt/PANI composites.

In dielectric spectroscopy, to characterize the electrical properties of materials, usually measurements of alternating current (a.c.) conductivity are preferred. The alternative current (a.c.) conductivity ($\sigma_{ac}$) was calculated using the empirical equation:

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon''$$  \hspace{1cm} (4)
where, $\omega$, $\varepsilon_0$, and $\varepsilon''$ are the angular frequency, dielectric constant of free space, and imaginary part of the dielectric constant, respectively. The frequency dependent conductivity in solids is generally analyzed using Jonscher’s power law [9]:

$$\sigma_{ac} = \sigma(0) + \sigma(\omega) = \sigma_{dc} + A\omega^s$$  

(5)

Where, the first term is frequency independent conductivity ($\sigma(0)$) which is d.c. part of conductivity, and the second term is frequency dependent conductivity ($A\omega^s$) which is a.c. part of conductivity. Here, “A” is the coefficient, “s” represents the degree of interaction between mobile ions with the lattices around them and generally in the range of $0 < s < 1$ [10,11]. While $s \approx 0$ corresponds to D.C. conductivity [12], $s \approx 0.5$ corresponds to Correlated Barrier Hoping (CBH) Mechanism [13] and $s \leq 0.7 < 1$ conditions represent Quantum Mechanical Tunneling (QMT) model [14].

The frequency exponent, $s$ has been calculated by the slope of $\ln \sigma_{ac} = f(\ln \omega)$ function of the samples for two frequency regions (I. regions: $\sim 100$ Hz – 3.8 kHz, II. Regions: $\sim 3.81$ kHz – 15 MHz) given in Fig. 2. The results have been summarized in Table 3. It is clear that the curves tend to merge with a constant slope. The ionic conductivity mechanism all the samples correspond to the Quantum Mechanical Tunneling (QMT) model in the two frequency regions.

![Figure 2](image)

**Figure 2** The $\ln \sigma_{ac} = f(\ln \omega)$ curves for the Basalt/PANI composites.
4. Conclusion

This research represents the results of our investigation on the dielectric properties of three type Basalt/PANI composite using dielectric spectroscopy. All composites show that Pani additivities reduce the dielectric constant and strength at low frequencies. CM-1 with 10.0 wt% exhibits the highest strength. Also, these composite obey to mechanism of Quantum Mechanical Tunneling according to ionic conductivity.

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Table 3 The s parameters and conductivity mechanism for the samples.

| Sample   | s parameter | I. Region | II. Region |
|----------|-------------|-----------|------------|
| CM-1/ 10.0 wt.% PANI | 0.676       | 0.925     |
| CM-1/ 25.0 wt.% PANI | 0.913       | 0.973     |
| CM-1/ 50.0 wt.% PANI | 0.945       | 0.982     |
| KYZ-13/ 10.0 wt.% PANI | 0.675       | 0.964     |
| KYZ-13/ 25.0 wt.% PANI | 0.845       | 0.964     |
| KYZ-13/ 50.0 wt.% PANI | 0.834       | 0.978     |
| KYZ-24/ 10.0 wt.% PANI | 0.617       | 0.928     |
| KYZ-24/ 25.0 wt.% PANI | 0.839       | 0.973     |
| KYZ-24/ 50.0 wt.% PANI | 0.943       | 0.982     |
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