Dielectric properties and AC conductivity for (Niₓ/Bentonite) composites

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Abstract
We have studied the dielectric properties and electrical conductivity for pure bentonite (Ben) and Ben loaded with 1.0%, 3.0% and 10.0% Ni composition within the temperature range 25°C–110°C and over the frequency range (100 Hz–0.3 MHz). The dielectric permittivity of pure Ben and Ni/Ben composite decreased with increasing frequency and temperature. We observed two relaxation processes in the characteristics of the dielectric modulus as a function of frequency and temperature. For both pure Ben and Ni/Ben, the activation energy decreased with increasing frequency and further decreased by adding 1.0, 3.0 and 10.0 wt.% Ni. Thus, the conduction mechanism in Ni/Ben has been associated with small polaron tunnelling.

1. Introduction
Recently, nanocomposites received considerable attention because of their interesting physical properties and wide range of applications including chemical and bio-applications [1]. Due to the quantum size effects, the properties of nanomaterials are different from the bulk counterpart [2]. Among various natural materials, bentonite (Ben) is one of the important clays. Ben is a porous clay mineral with a layered structure, and is an abundant mineral resource, and exhibits the characterisation of low cost and environmental compatibility, which widely used in many applications [3,4].

Ben has excellent inherent acidity, thermal stability, and structure control flexibility, rendering it as promising support [5]. The main issue with Ben is the dielectric, thermal and optical properties. Therefore, the researchers tried to modify the dielectric, optical and thermal properties of Ben by impregnating with silica [6], calcium [7], graphite [8], and nickel hydroxide [9], etc. During the study of the former-cited research work and the literature survey, it was observed that the impregnations of Ben carried out are not quite enough to module the properties of the Ben as per the industrial requirements. Therefore, it was realised to dope Ben by some other suitable doping agents which might improve the dialectical proprieties further.

Amongst various nanomaterials, metal oxides are gaining importance in a variety of fields because these materials are potentially attractive; exhibiting unique chemical and physical properties that are important for varieties of optical and electronic applications [10]. Among the different applications of nano-metal oxides, the dielectric and optical features are very important as the various industries are demanding low to high-class conductivity materials. For instance, ferrite–magnesium oxide, nickel-titanium di-oxide, and copper/nioibium are a few of the nanocomposites that were utilised in different car industries and common mechanical applications, such as aviation, hardware, microelectronics, non-linear optics, and sensors [11].

The nickel oxide is one of the foremost utilised components within the manufacturing sequence of stainless steel, super-alloys, metallic alloys, coins, batteries, etc. Additionally, nickel oxide, compared to noble metal, is known to be cost-effective and naturally friendly material for supercapacitor terminals [12].

Nickel oxide has a very low electrical conductivity of fewer than 10⁻¹³ ohm⁻¹ cm⁻¹ at room temperature is classified as a ‘Mott-Hubbard Insulator’ [13]. This may be used to the controlled conductivity of the Ben. On the other hand, the studies on the electrical properties of nanostructured Nickel oxide are still limited and need to be investigated deeper. The thickness, volume fraction, continuity and degree of heterogeneity of grain boundaries are among the main factors that are expected to significantly affect the AC conductivity of Ni nanoparticles. In the domain of nanostructured materials, the conductivity exhibits an interesting and important dependence on the average size of the nanoparticle. Keeping all these facts into consideration, it was considered worthwhile to synthesise Ni-doped Ben by impregnation with 1.0, 3.0, and 10.0 nickel. The effect of nickel into Ben was studied in terms of AC conductivity and dielectric properties. The results are given herein.
2. Experimental

2.1. Materials

Bentonite (CAS Number 1302-78-9) was obtained from Sigma-Aldrich (USA). Nickel Chloride was ordered from “ASAGGAF-Pharma-HOLYLAND” (production made in K.S.A). All chemicals and solvents were used without any purification.

2.2. Preparation of Ni/Ben composites

The high purity powders of NiCl\textsubscript{2} and Ben were employed to act as the starting materials for the preparation of the composites. The composites were prepared by the incipient wet impregnation method following the procedure described earlier [14].

The proper weight of NiCl\textsubscript{2} was prepared and dissolved in deionised water. To obtain a fully swelling Ben, the Ben suspension (in water) was warmed to 70°C with a 200 r·min\textsuperscript{-1} agitation for 0.5 h. At that point, the NiCl\textsubscript{2} solution was added dropwise to the Ben suspension with a 200 r·min\textsuperscript{-1} agitation at 70°C for 4 h, to get a slurry. The slurry was dried at 120°C for 12 h. The resulting composite with a Ni loading of 1.0 wt.% was assigned as 1.0%Ni/Ben. The other two composites preparation strategy was the same to obtain 3.0%Ni/Ben, and 10.0%Ni/Ben.

The pellets were prepared as follows:

The samples were turned into fine powder utilising a mortar and pestle. Achieving fine powder is essential as coarse particles would prevent the formation of a smooth pellet. A small amount of the fine powder sample (0.30 g) was then compressed into a hard pellet using a die-set kit of a hydraulic compressor.

3. Results and discussions

3.1. Dependent in frequency

The dependence of the dielectric permittivity $\epsilon'$ on the frequency for Ni/Ben at various temperatures is presented in Figure 1.

Clearly, for all samples, the dielectric permittivity $\epsilon'$ decreased as the frequency increased. This might be attributed to the decrease in the number of dipoles. It is also possible that the dipoles are unable to respond to the oscillating electric field. On the other hand, the high dielectric permittivity at low frequency is associated to the Maxwell Wagner type polarisation occurring at the large area sample-electrode interface.

Obviously, the dielectric permittivity remains almost saturated over a wide range of frequency from 10 kHz to 0.3 MHz. We stress that these behaviours of the dielectric permittivity versus the frequency at different temperatures (Figure 1) are common to all Ni/Ben samples.

Also, the values of $\epsilon'$ for 0.1 wt.% of Ni/Ben is higher than the pure Ben, while those for the 3.0% and 10.0% Ni/Ben exhibited relatively lower dielectric constant than that for the pure Ben [15]. Another important parameter for the dielectric property is the dielectric loss, we consider the dielectric loss (tan $\delta$), which can be regarded as a measure of the power dissipation in the sample due to charge transport. Figure 2 shows tan $\delta$ versus the frequency with a temperature as a parameter for all samples.

The patterns of tan $\delta$ as a function of the frequency (Figure 2) exhibited peaks that can be associated with dipolar effects. The position of these dipolar peaks is slightly temperature dependent.

We notice that the magnitude of the dipolar peaks (or maximum tan $\delta$) increased with increasing temperature, however, the peaks themselves did not shift towards higher frequencies with increasing temperatures. Owing to the distribution of the molecular weight or cooperative movement of adjacent chains, a spread of relaxation times was expected to occur. These are well-known features characterising the freezing of dipolar motion with no longer-range correlations [16].

Figure 3 illustrates the dependence of the dielectric modulus $M''$ (for Ni/Ben) on the frequency for different temperatures. It is shown that the values of $M''$ at low temperature tend to be zero, suggesting the disappearance of the electrode polarisation for 1.0%, 3.0% and 10.0% of Ni content. Also, one peak at low frequency for 10.0% Ni content corresponded to $\alpha$ relaxation process associated with micro-Brownian motion. While a second peak shows at high frequency for all samples attributed to the conductivity current relaxation [17].

The AC conductivity dependent on frequency can be calculated by $\sigma_{ac} = \omega \varepsilon_0 \tan \delta$, with $\omega$, $\varepsilon_0$, and $\tan \delta$, representing the angular frequency, the permittivity of the free space and loss tangent, respectively. The frequency dependence of $\sigma_{ac}$ for (Ni/Ben) composites at different fixed temperatures are shown in Figure 4.

The conductivity followed a linear frequency dependence at high frequency range, (Figure 4) indicating that the charge carrier transport mechanism is governed by hopping between defect sites along the chains. The distribution of Ni facilitates the formation of conductive paths throughout the composite networks, stimulating the charge carrier hopping between conducting clusters. It is also obvious that the conductivity decreased by increasing the Ni content. It’s observed that $\sigma_{ac}$ increased with frequency. This is due to the increase of the absorbed energy from the electric field which increased the number of charge carriers in the conduction process.

The variation of AC conductivity with frequency (Figure 4) may act as a manifestation that the polarons hopping are responsible for charge carrier conduction in (Ni/Ben) composites. The AC conductivity dependence of frequency is given by $\sigma_{ac} = B\omega^s$, where s is the universal exponent. The variation of $\ln \sigma_{ac}$ versus $\ln (f)$ for (Ni/Ben) at different temperatures are shown in
Figure 1. Frequency dependence of dielectric permittivity $\varepsilon'$ for (Ni$_x$/Ben) at different temperatures.

Figure 2. Frequency dependence of tan $\delta$ for (Ni$_x$/Ben) at different frequencies.
Figure 3. Frequency dependence of $M'^\ast$ for (Ni/ Ben) at different frequencies.

Figure 4. Frequency dependence of $\sigma_{ac}$ for (Ni/ Ben) at different temperatures.
Figure 5. $\ln(\sigma_{ac})$ vs. $\ln(f)$ for (Ni$_x$/Ben) at different temperatures. Note: the solid lines are the fitting according ($\sigma_{ac} = B\omega^s$).

Table 1. The fitting exponent $s$ for (Ni$_x$/Ben) at different temperatures.

| Temperature | Pure | 1.0% | 3.0% | 10.0% |
|-------------|------|------|------|-------|
| 25°C        | 1.352| 1.577| 1.104| 0.608 |
| 50°C        | 1.669| 1.587| 1.285| 0.864 |
| 75°C        | 1.780| 1.775| 1.682| 1.303 |
| 100°C       | 1.867| 1.837| 1.784| 1.646 |

Figure 5 where the values of the exponent $s$ from the linear fitting are listed in Table 1.

The values of $s$ were larger than unity and increased with increasing temperatures. This suggested that the conduction mechanism is pertinent to small polaron tunnelling (SPT) [18].

3.2. The temperature dependence

The characteristics of the dielectric constant as a function of the temperature are stable over a wide range of frequencies from 10 kHz to 0.3 MHz shown in Figure 6.

The values of the $\varepsilon'$ decreased with increasing temperatures for all the samples. Additionally, $\varepsilon'$ decreased for samples with 3.0% and 10.0% Ni due to the Ni contribution to the polarisation. This result can be explained assuming that the Ni was masked by Ben, while the increase in polarisation for 1.0% Ni sample might be attributed to the space charge polarisation.

Figure 6. Temperature dependence of $\varepsilon'$ for (Ni$_x$/Ben) at 0.1 MHz.

Figure 7 shows the temperature dependence of dielectric modulus $M''$ for pure Ben and Ben containing 1.0, 3.0, 10.0 wt.% of Ni at different frequencies. $M''$ increased with increasing temperature due to the thermally activated nature of the transport in our samples. Asymmetric peak was observed around 85°C for pure Ben. Also, a small peak was observed around 45°C within 0.1 and 1 kHz for 1.0% Ni-doped Ben. This peak is due to $\alpha_a$-relaxation which is attributed to the micro-Brownian motion. In addition, $M''$ increased with Ni content, this behaviour is related to the structural parameters.
Figure 7. Temperature dependence of $M^*$ for (Ni$_x$/Ben) at different frequencies.

Figure 8. The ac conductivity ($\ln(\sigma_{ac})$) as a function of ($1000/T$) for Ni$_x$/Ben at fixed frequencies.
The activation energy ($E_a$) for Ben and Ni/Ben composite was calculated by Arrhenius relation $\sigma_{ac} = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$. The AC conductivity ($\ln \sigma_{ac}$) versus $(1000/\nu)$ for $N_i$/Ben are illustrated in Figure 8. Obviously, $\sigma_{ac}$ increased with temperature. This is due to the increase in the absorbed energy which enhanced the number of charge carriers in the conduction process. The values of $E_a$ for all investigated samples at $\nu = 0.1$ kHz to 0.1 MHz are listed in Table 2.

The values of $E_a$ for Ben are decreased with increasing the content of Ni, leading to an increase in the number of charge carriers. The values of $E_a$ changed from 0.1 to 1.2 eV, indicating that the conduction mechanism in all the investigated samples is ionic.

4. Conclusion

The dielectric properties of pure Ben and Ni/Ben composite as a function of temperature and frequency were investigated. The values of dielectric permittivity $\varepsilon'$ decreased with increasing frequency and temperature. The values of $\varepsilon'$ of pure Ben increased by adding 1 wt.% Ni, while decreased by adding 3.0 and 10.0 wt.% of Ni. Different relaxation processes have been identified, the first one is at low frequency for 10% Ni content corresponded to $\alpha$ relaxation process which is attributed to micro-Brownian motion. The other is attributed to the conductivity current relaxation showed at high frequency for all the samples. The AC conductivity of pure Ben and Ni/Ben composite increased with increasing frequency. The conduction mechanism could be small polaron tunnelling. The activation energy $E_a$ of pure Ben and Ni/Ben composite decreased with increasing frequency and decreased by adding 1.0, 3.0 and 10.0 wt.% Ni. These results may reflect the importance of pure Ben and Ni/Ben composite in dielectric applications.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Table 2. Activation energies of pure Ben and Ni/Ben composite according to the Arrhenius relation.

| Temperature (degree C) | 0.1 KHz | 10 KHz | 50 KHz | 0.1 MHz |
|------------------------|---------|--------|--------|----------|
| Pure                   | 1.170   | 0.365  | 0.151  | 0.130    |
| 1.0% Ni                | 0.697   | 0.399  | 0.886  | 0.638    |
| 3.0% Ni                | 1.0599  | 0.856  | 0.141  | 0.102    |
| 10.0% Ni               | 0.912   | 0.5617 | 0.279  | 0.135    |

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