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STUDY OF DIELECTRIC PROPERTIES OF NANOPOLYMER FILMS SYNTHESIZED BY SOLUTION CASTING TECHNIQUE

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Abstract: The dielectric properties of polymer nanocomposites (PNCs) are analyzed in relation to the incorporation of nanoparticles, which can significantly enhance dielectric constant and reduce loss. These materials are studied for various applications, including energy storage and electrical insulation, where enhanced dielectric properties are crucial. Research focuses on understanding how factors like nanoparticle type, concentration, and interphase regions influence the overall dielectric behavior of the composite. In this paper, the dependence of dielectric constant, dielectric losses and conductivity of nanopolymers with variance of frequency and temperature were presented.

Keywords: Dielectric constant, dielectric loss, frequency response, temperature and conductivity.

1. INTRODUCTION TO DIELECTRIC PROPERTIES

The dielectric properties of nanocomposite films are crucial for analyzing energy storage capacity, conduction mechanisms, structural transitions, and molecular mobility in polymeric films, along with determining the appropriate applications for NCFs [1,2,3]. The dielectric constant, a complex permittivity, is expressed as

$$\varepsilon^* = \varepsilon' - i\,\varepsilon'',$$

Where ε' represents the dielectric constant (real part) and ε'' denotes the dielectric loss (imaginary part). The value of ε′ indicates the energy storage within the material and is calculated using the equation:

$$\varepsilon' = Cpd/\varepsilon o\, A,$$

where Cp stands for parallel capacitance, d is the thickness of the circular film, A represents the cross-sectional area, and εo is the permittivity of free space. The dielectric loss, ε'', reflects the energy loss in the material and is determined using the equation [3-5]:

$$\varepsilon'' = \varepsilon' \tan\delta,$$

where tanδ signifies the tangent loss. The dielectric behavior of polymer NCFs is influenced by various polarization mechanisms—including dipolar, ionic, and interfacial polarization—which are active in the films when subjected to an alternating field [6,7].

2. FREQUENCY DEPENDENCE OF DIELECTRIC CONSTANT AND DIELECTRIC LOSS

The variations in ε' and ε" values of the synthesized polymer films were examined across a frequency range from 100 Hz to 5 MHz, as depicted in Figure 1. It is clear from these figures that both ε' and ε" values are elevated at lower frequencies but decline as frequency increases, stabilizing after 100 kHz. This phenomenon is elucidated by Koop's theory referenced in the literature [8]. According to this theory, a polycrystalline material comprises grains and grain boundaries, with grains being less resistive than grain boundaries. When subjected to an alternating electric field, charge carriers orient themselves. This results in charge accumulation at the interfaces of grain boundaries, forming dipoles. The enhancement of charge carriers leads to Maxwell- Wagner interfacial or space charge polarization [3]. Consequently, at lower frequencies, a greater number of charges are captured at the NACMC interfaces due to the high resistivity of grain boundaries, causing significant space charge polarization and consequently high ε' and ε" values. Furthermore, at higher frequencies, ε' and ε "values decline because electric dipole orientations struggle to keep up with the rapidly alternating electric field. This reduction is attributed to decreased charge accumulation at interfaces and the lower resistivity of grain boundaries at high frequencies. This process is known as anomalous dielectric dispersion [15-9]. Figure 1 presents the dielectric constant versus frequency plots at room temperature for pure NACMC and its compounds with varying doping concentrations. It is noticeable that the pure SA film exhibited lower ε' values compared to NHM 0. 2, NHM 0. 4, NHM 0. 6, and pure MnO 2. The highest ε' value at room temperature was observed for the MnO 2 16 film. Additionally, the ε' values increased with higher concentrations of MnO 2 nanoparticles due to interfacial polarization, which traps more charge carriers at the interfaces because of the availability of free charges with doping. Figure. 1 also illustrates the frequency dependence of dielectric loss at room temperature for the studied films. A similar trend observed for ε' is noted for ε". It was verified that electric dipoles had ample time to align in the field direction, resulting in elevated ε" values at lower frequencies. Moreover, doping NPs into the SA matrix improved ε" values at a lower frequency (100 Hz) while suppressing ε" values at a higher frequency (5 MHz). This behavior of low ε" at elevated frequencies is advantageous for embedded passive applications [1, 10].

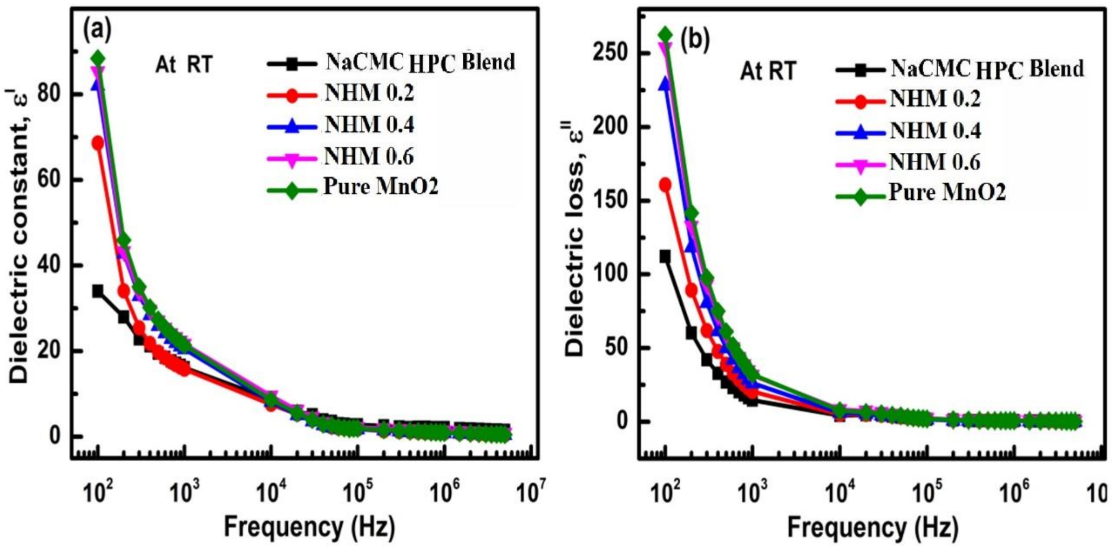

Figure 1: Frequency dependence of dielectric constant, dielectric loss of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MNO_2 nanocomposite films at room temperature., NHM

3. TEMPERATURE DEPENDENCE OF DIELECTRIC CONSTANT AND DIELECTRIC LOSS

Figure 2 illustrates the temperature-dependent behavior of ε' and ε" values for pure MnO2 and NaCMC at a frequency of 100 Hz, showing how the dielectric constant varies with temperature from room temperature to 100 °C. As temperature rises, ε' values increase due to several mechanisms. Firstly, the decreasing viscosity of the polymer NCFS allows electric dipoles to orient more easily in the direction of the electric field, enhancing polarization and thereby increasing ε' values with temperature [2]. Secondly, as the polymer's specific volume grows, some crystalline phases dissolve and convert to an amorphous phase, which also leads to higher ε' values [18-19]. Additionally, at a specific frequency and elevated temperatures, the thermal activation of charge carriers significantly occurs. This increase in thermal activation results in enhanced polarization, contributing to the higher ε' values, confirming the thermally activated behavior of nanocomposite films [13-15]. Figure 2 also depicts the temperature dependence of dielectric loss at 100 Hz, highlighting that ε" values rise with temperature. This increase is due to the relaxation of dipoles, accompanied by a reduction in relaxation time [16-17], which is evidenced by the peak in the plot indicating a phase transition around 90°C across all films studied. This transition corresponds to the glass transition temperature of the films, suggesting the presence and improved dispersion of nanoparticles within the SA matrix. The high dielectric constant values noted with varying frequency and temperature in NCFs are largely due to the enhanced dispersion of MnO2 nanoparticles in the NaCMC matrix, as well as the high ε' values of the nanoparticles. Thus, these composites present opportunities for use in potential electronic applications.

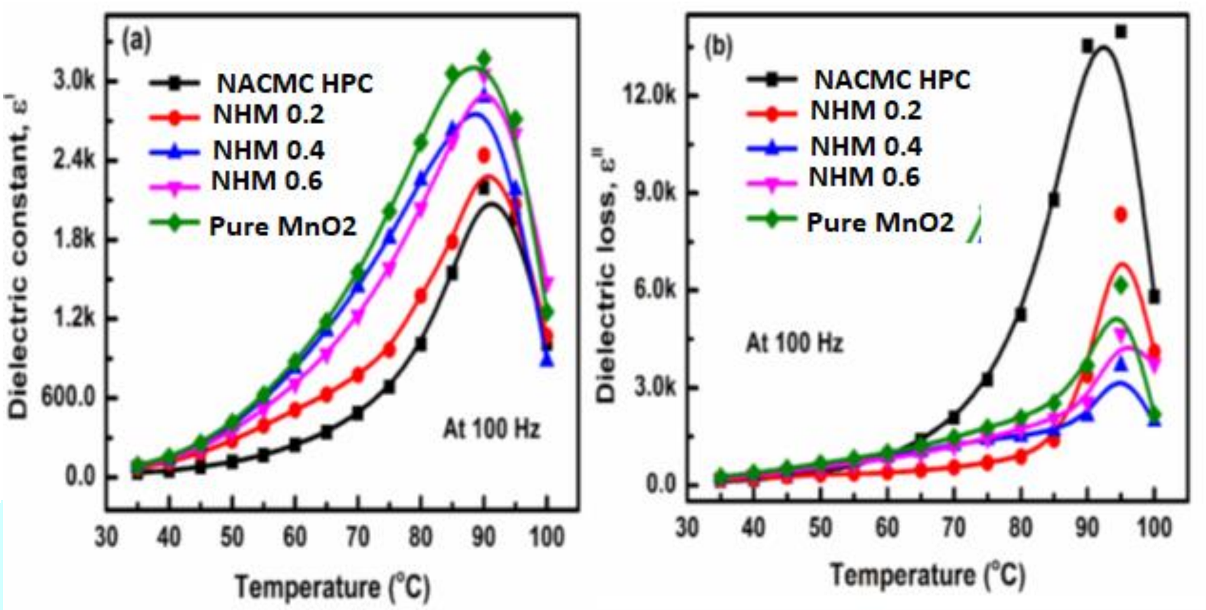

Figure 2: Temperature dependence of dielectric constant, dielectric loss at 100 Hz of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MNO_2 nanocomposite films.

4. VARIATION OF AC CONDUCTIVITY WITH FREQUENCY AND TEMPERATURE

To assess the influence of NPs on the ac conductivity of pure NACMC and HPC with MnO2 nanocomposite films, ac conductivity is calculated using the formula σac = εoε″ω, where ω represents the angular frequency. The ac conductivity's temperature dependence adheres to the Arrhenius relationship [2], expressed as σac = σoexp(-Ea /kT), with σo as the pre-exponential factor, Ea as the activation energy, k as the Boltzmann constant, and T as the absolute temperature.

Figure 3 illustrates the variation of ac conductivity σac with frequency for pure NACMC and NACMC-MnO2 NCFs. The figure indicates that σac increased with frequency across all films studied, which is typical for polymer nanocomposites [4]. This increase in σac values with frequency is attributed to the hopping of charge carriers. Similar findings have been reported in the literature for various polymers [2]. At higher frequencies, the electric dipoles oscillate more rapidly, resulting in elevated σac values for the nanocomposite films investigated. The highest σac values at a frequency of 5 MHz were recorded at room temperature (Table 1). Figure 4 shows how σac changes with temperature for the films studied. The figure clearly reveals that σac values increased with temperature in both pure NACMC and NACMC NCFs. This effect is due to the rapid movement of charge carriers, driven by the thermal energy generated at elevated temperatures [3]. Consequently, σac becomes more significant at higher temperatures. Generally, elevated temperatures enable the polymer chain to adopt faster internal modes, resulting in segmental motions from bond rotations. This facilitates quicker movement of inter-chain and intra-chain charge carriers, leading to enhanced conductivity [13]. However, a reduction trend in σac values was noted with the addition of MnO2 NPs to the NACMC matrix. This decline is due to a decrease in the flexibility of the NCFs upon doping compared to pure NACMC, as the doping resulted in a crystalline phase. In the crystalline phase, the polymer chains exhibit reduced flexibility, which diminishes conductivity [8-9]. This supports the observed decrease in σac values with increasing MnO2 nanoparticle content. The abrupt decrease in σac values at 100 °C is attributed to an error, likely because 100 °C represents the temperature limit of the measurement technique employed. Notably, high σac values were recorded for all films at 95 °C (Table -1).

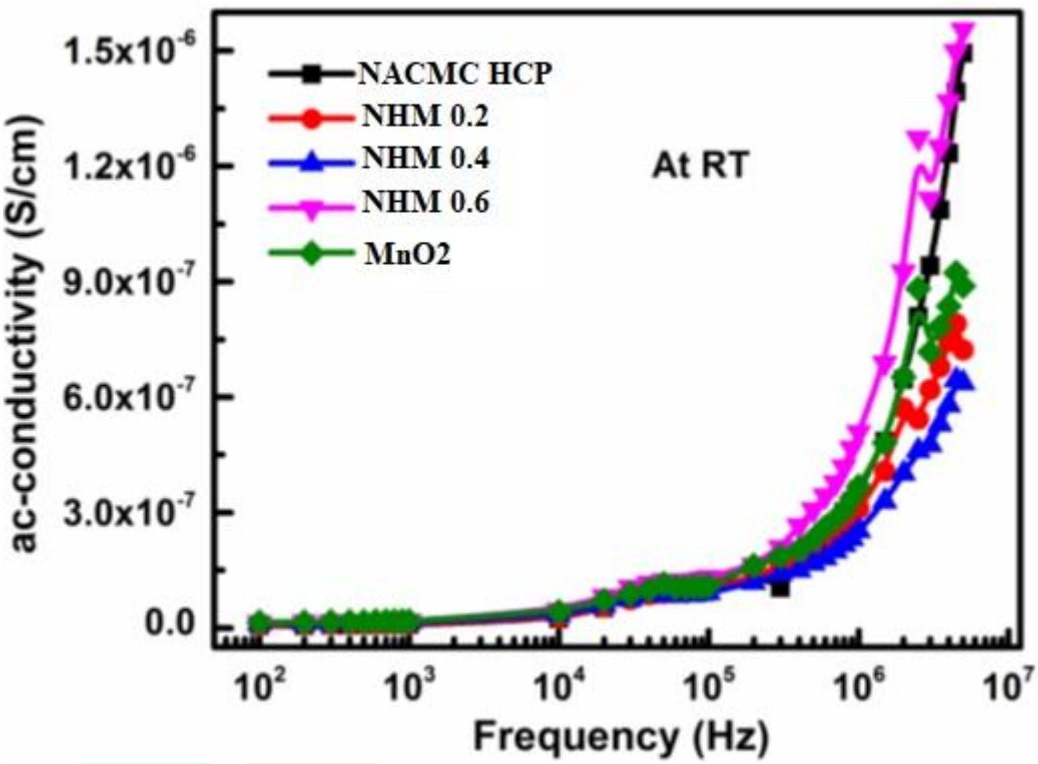

Figure 3: Variation of ac conductivity with the frequency of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MnO_2 nanocomposite films at Room temperature.

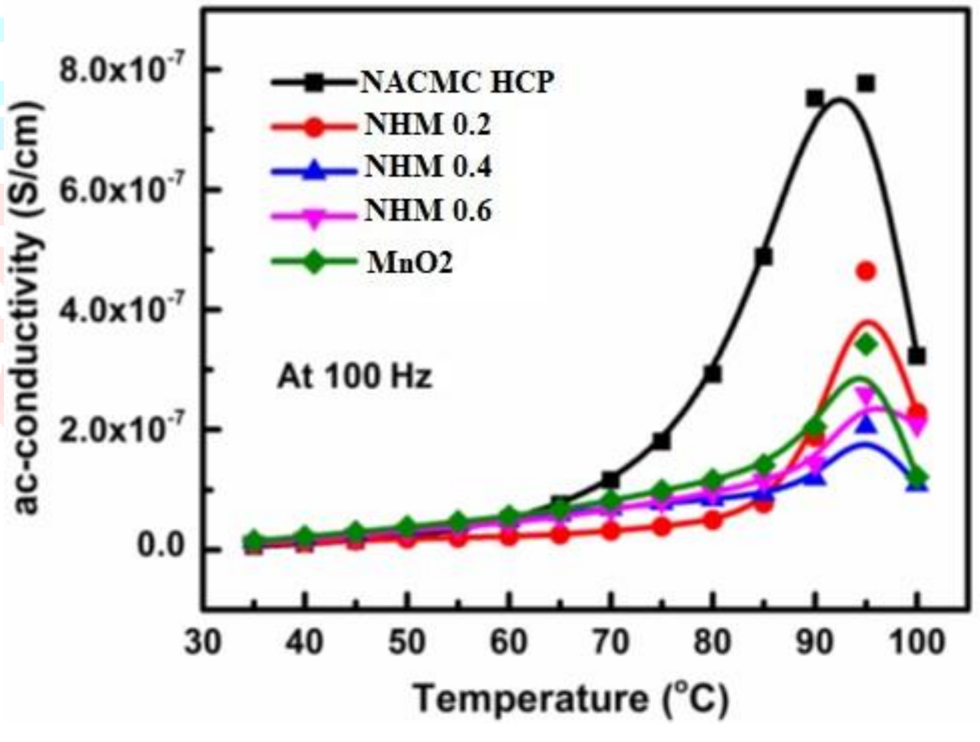

Figure 4**:** Variation of ac conductivity with the temperature of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MnO_2 nanocomposite films at 100 Hz.

The plots of lnσac as a function of 1000/T for all the synthesised NACMC films are depicted in Figure.5 to determine the activation energies by following the Arrhenius relation [3-4]. The slope of the Arrhenius plot provides the activation energies. The activation energies of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 films were lower than those of the pure film and are listed in Table-1. This suggests the tunneling phenomena of ac conductivity of the investigated nanocomposite films [3]. The magnitude of Ea is less than 1eV for all the films. A similar trend was observed for different NCFs in the literature in the magnitude range of Ea values. Shameem et al. investigated the nanocomposites of NaLiS nanoparticles on the Alginate matrix and obtained the Ea as 0.31ev and 0.75ev [21]. Sheela et al. reported the values of Ea in the range 0.41 ev and 0.38 ev for LiClO4/PVA/NaAlg polymer composites [16].

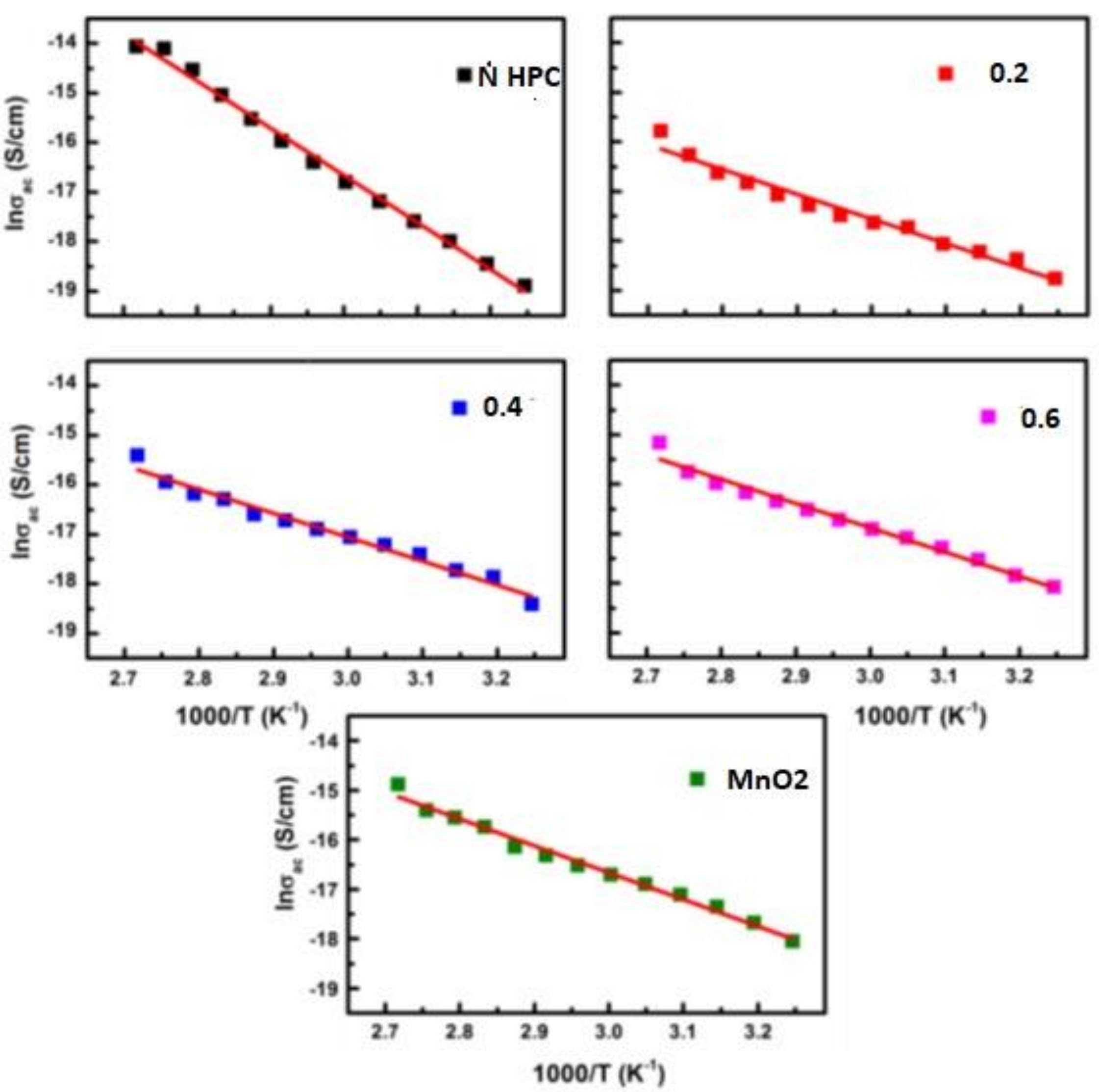

Figure 5: Arrhenius plots of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MNO_2 nanocomposite films.

Table-1. Dielectric parameters of NACMC, NHM 0.2, NHM 0.4, NHM 0.6 and MNO_2 nanocomposite films.

Dielectric parameters	NaCMC	NHM 0.2	NHM 0.4	NHM 0.8	MnO2
ε' at RT	34.04	68.64	82.09	85.27	88.34
ε' at 900C	2192	2441	2883	3050	3173
σac at RT (10^{-7} S/cm)	14.941	7.224	6.367	15.542	8.881
σac at 950C (10^{-7} S/cm)	7.77	4.64	2.054	2.595	3.431
Ea (eV)	0.817	0.43	0.41	0.42	0.46

5. CONCLUSION

From Figure 1 illustrate the frequency dependence of dielectric loss at room temperature for the studied films. A similar trend observed for ε' is noted for ε". It was verified that electric dipoles had ample time to align in the field direction, resulting in elevated ε" values at lower frequencies. Moreover, doping NPs into the SA matrix improved ε" values at a lower frequency (100 Hz) while suppressing ε" values at a higher frequency (5 MHz). This behaviour of low ε" at elevated frequencies is advantageous for embedded passive applications.

The high dielectric constant values noted with varying frequency and temperature in NCFs are largely due to the enhanced dispersion of MnO_2 nanoparticles in the NaCMC matrix, as well as the high ε' values of the nanoparticles. Thus, these composites present opportunities for use in potential electronic applications.

Figure 3 illustrate the variation of ac conductivity σ_{ac} with frequency for pure NACMC and NACMC-MnO_2 NCFs. The figure indicates that σ_{ac} increased with frequency across all films studied, which is typical for polymer nanocomposites.

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