

Biocompatible Neem Gum-Modified Polyvinyl Alcohol Nanocomposite as Dielectric Material for Flexible Energy Devices

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Abstract

In the pursuit of a flexible energy storage system, we have integrated naturally accessible neem tree gum with polyvinyl alcohol nanocomposite polymers (bc-Ng/PVA). This bio-inspired approach leverages the unique properties of neem gum for both the bio-electrolyte and bio-electrode components. The resulting bc-Ng/PVA nanocomposites exhibit superior dielectric strength and versatility, outperforming traditional inorganic ceramic dielectrics in advanced electronics and pulsed power systems. Our study delves into the dielectric characteristics, conductivities, electric modulus, and impedance parameters of Pure PVA and Ng-doped PVA composites. The variation in Ng concentration in the matrix leads to notable improvements in dielectric characteristics and relaxation factors, emphasizing the significance of polymer co-

operative chain segmented movement. We further explore the relaxation time and conductivity properties of bc-Ng/PVA polymer composite films, showcasing their enhanced electrical and dielectric properties. The increased performance of these neem gum-blended PVA composite materials underscores their promise as a valuable resource in the realm of flexible energy storage.

Keywords: Polymer blends; Neem gum; Nanocomposite; Dielectric properties; Bio-electrode; Energy storage.

1. Introduction

The global population and the utilization of fossil fuels are expanding rapidly. In this context, the development of renewable energy technologies is crucial for future energy generation, storage, and utilization [1-3]. Dielectric materials exhibit outstanding features that make them valuable for electronics due to their adaptability, versatility, and eco-friendliness [4]. Compared to ceramics, polymers offer greater flexibility, processability, and lightweight properties, overcoming several limitations associated with ceramics such as embrittlement, processing challenges, and low stability [5]. Numerous researchers have successfully developed super-absorbent polymeric hydrogels with the capability to store a significant amount of water and biological fluids within their cross-linked polymeric network structure. In recent years, there has been an increased interest in the biocompatibility and pH sensitivity of these hydrogels [6, 7].

Indeed, all these electrolytes involve complicated manufacturing procedures, which could make them suitable for the future direction of an environmentally conscious energy production system. The combination of solid materials and polymer electrolytes has recently gained attention due to its benefits in terms of safety and environmental friendliness. For example, Lee et al.

reported on clay nanocomposites with elevated ionic conductivities, mechanical robustness, and flexibility [8]. Yan et al. reported on a disposable bacterial cellulose-supported quasi-solid electrolyte [9], which exhibits better stability with temperature variations and a higher decomposition rate. Additionally, Wang et al. developed a high-performance lithium battery [10] by incorporating a polymer-laden lignin electrolyte.

Neem gum (Ng), a naturally occurring water-soluble polysaccharide, is derived from the exudates of *Azadirachta indica*, a member of the Meliaceae family [11]. Ng has been explored in pharmaceutical dosage forms, serving as a binder and excipient [12–14]. Gums extracted from various trees, including Neem, offer non-hazardous, renewable, biocompatible, and cost-effective electrolyte options, presenting several advantages [15, 16]. These tree gums, as a class of renewable and sustainable polymers, are natural exudates from diverse tree species. Widely accessible, these tree gums boast strong biodegradability, non-toxicity, affordability, and versatile physical and chemical properties. Processed exports of these tree gums present significant opportunities for income growth.

However, using naturally derived polysaccharides comes with certain disadvantages, including the potential for microbial presence, unregulated hydration, and changes in viscosity over time. Various strategies are employed to modify the properties of the polymer to enhance and maintain consistency. Grafting has been the most frequently utilized modification method in recent decades, alongside mixing and curing [17]. The applications of cross-linked hydrogels in pharmaceutical drug delivery and biomedical fields, such as tissue engineering and wound dressing, have been widely explored [18]. The addition of hydrophilic groups like NH_2 , COOH , OH , SO_3 , and CONH_2 to native polysaccharides significantly increases their water absorption capacity. The robust three-dimensional structure of polysaccharides allows for the effective

retention of water or biological fluids within the polymeric system. Graft copolymers, known for their ability to keep soil moist, have been employed in agricultural practices. This characteristic has shown potential in reducing plant mortality during irrigation, conserving water, and improving plant development and soil fertility. In arid conditions, graft copolymers have been reported to preserve soil moisture content, contributing to their use in desert areas [19, 20].

In this study, we developed a PVA/Ng polymer composite for flexible energy applications by blending naturally accessible neem tree gum with PVA. Comprehensive analyses using XRD, FTIR, SEM, impedance analyzer, and dielectric investigations demonstrate that the Neem gum/PVA composite polymer exhibits favorable physicochemical and dielectric properties. The dc conductivity of the PVA blended with 5% Ng ranged from 7.19×10^8 to 5.49×10^7 S/cm. Variations in the Ng concentration within the host matrix lead to notable improvements in dielectric characteristics and relaxation factors, indicating significant changes in polymer supportive chain segmental movement.

2. Experimental section

2.1. Collection and purification of neem (Azadirachta Indicia) gum

Neem (*Azadirachta Indica*) dried gum was obtained by puncturing the bark of locally grown *Azadirachta indica* trees. The moisture was eliminated by desiccating Ng, exposing it to direct sunlight continuously for 7 days. Subsequently, the gum was finely powdered using a mortar and pestle. Three grams of Ng were dissolved in 50 ml of deionized water with constant stirring at room temperature for 4-6 hours. The solution was filtered using Whatman filter paper to remove any impurities present in the Ng. The resulting Ng solution was stored at room temperature for further experimental processes.

2.2. Synthesis of PVA/Ng composites

The solution casting technique was employed to fabricate the blend polymer consisting of PVA and Ng at different ratios. In this method, double-distilled water served as the solvent for preparing a biopolymer membrane. Initially, a fixed amount (2g) of PVA solution and various ratios (1%, 2%, and 3%) of Ng solutions were prepared. These solutions were mixed and stirred overnight. The resulting mixtures of pure biopolymer (PVA) and polymer composites were allowed to dry in a hot air oven at 60 °C. Figure 1 illustrates the experimental procedure for preparing the PVA/Ng composite.

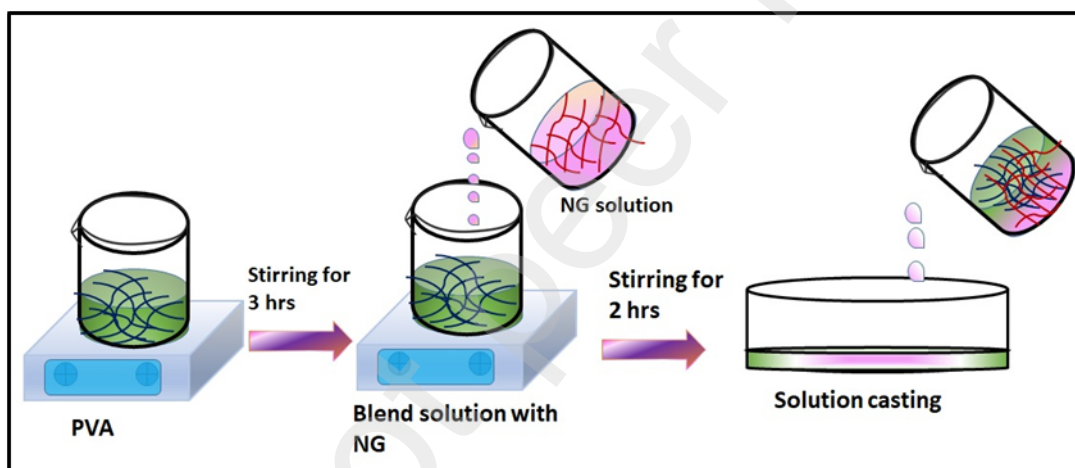


Figure 1: Experimental method of preparing PVA/Ng composite.

2.3. Characterization of PVA/Ng composites

The structure of the composite films was analyzed using an X-ray diffractometer with a wavelength source of 1.540 Å, in steps of 0.05°, covering the range from 10 to 60°. The chemical composition of the prepared samples was assessed using a Shimadzu IR Tracer 100 spectrometer within the range of 4000-400 cm⁻¹. The surface morphology of the prepared pure PVA and its composite films was examined using scanning electron microscopy (SEM) (Model: ZEISS-EVO 18

Research, Japan). The response of the prepared samples was analyzed using a Hioki 3532-50 LCR Hi-tester with an applied voltage at a frequency range from 42 Hz to 1 MHz. The polymer film was placed between two silver electrodes in an LCR Hi-tester, and Z-view fitting software was utilized to determine the overall resistances of the prepared samples.

3. Results and discussion

3.1. Structural and morphological properties of PVA/Ng composites

The structural and morphological characteristics of the PVA/neem gum (Ng) composites were investigated to understand the impact of neem gum on the polymer matrix. Figure 2 illustrates the XRD pattern of pure PVA and (1%, 3%, and 5%) Ng-added bc-Ng/PVA composite samples. The broad peak observed at nearly $2\theta=19^\circ$ corresponds to PVA's semi-crystalline property [21]. The addition of Ng has increased the intensity of the peak, contributing to the enhancement of the crystallinity of the polymer composite [22]. Crucial for a polymer to exhibit dielectric properties are crystallinity and planar orientation. The addition of Neem gum improves interfacial interactions, inducing crystallinity in PVA, and is expected to enhance the dielectric properties. Various factors, including preparation methods and the presence of Ng within the polymer, are responsible for the higher crystallinity observed in the PVA composites.

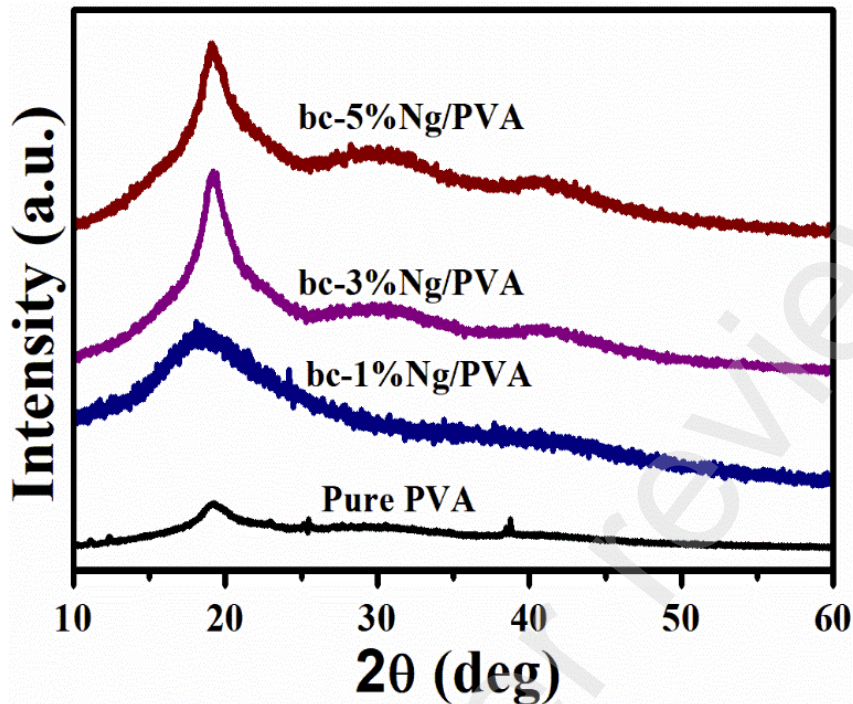


Figure 2: XRD patterns of PVA and bc-Ng/PVA composites

Figure 3 displays the FTIR spectra of pure PVA and (1%, 3%, and 5%) Ng added bc-Ng/PVA samples. In the FTIR spectrum of pure PVA, a broad peak at 3410 cm^{-1} signifies -OH stretching, indicative of intermolecular and intramolecular hydrogen bonds. A peak near 2960 cm^{-1} results from -C-H stretching of -C-O-CH₃. The appearance of a peak at 1728 cm^{-1} is attributed to stretching vibrations of -C=O in the polymer. In the FTIR spectrum of Neem gum incorporated with the PVA matrix, bands at 3406 cm^{-1} indicate -OH stretching vibrations in the gum polysaccharide [23]. Peaks at 2931 cm^{-1} and 2121 cm^{-1} arise from the -C-H stretching mode of -CH₃ groups in the gum and the overtones of -C-O stretching vibrations. Peaks at 1738 cm^{-1} and 1627 cm^{-1} correspond to C=O stretching vibrations of carboxylic acid and amide in the gum. Absorption peaks at 1421 cm^{-1} are due to C-H deformation of methylene groups in the gum, while those at 1248 cm^{-1} are due to C-O-C asymmetric stretching vibrations.

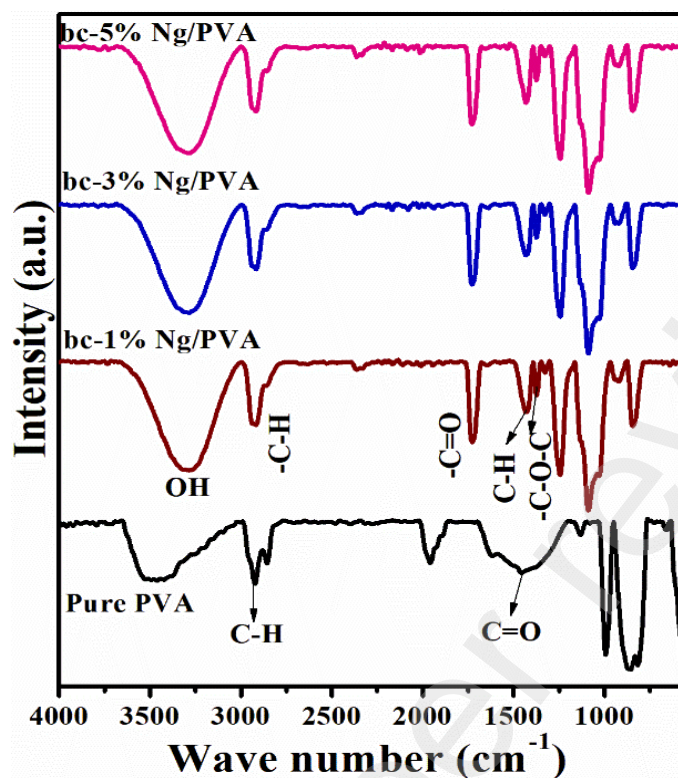


Figure 3: FTIR spectra of pure PVA and bc-Ng/PVA composites

SEM is an effective method for investigating material morphology. In Figure 4(a), the SEM image of Pure PVA shows a homogeneous and consistent surface. The introduction of Ng into pure PVA alters the surface morphology, as depicted in Figure 4(b-d). Significant changes occur with increasing weight percentage of Ng in pure PVA. The 5% Ng addition (Figure 4(d)) shows increased surface change distribution, confirming interfacial contact between pure PVA and Ng. The observed nanostructures in PVA/Ng composites indicate the presence of different Ng contents, enhancing ionic mobility, ion dissociation, and improving the mechanical strength of the polymer. The strong interfacial bond between Ng and the polymer matrix contributes to reinforced dielectric properties in these nanocomposites.

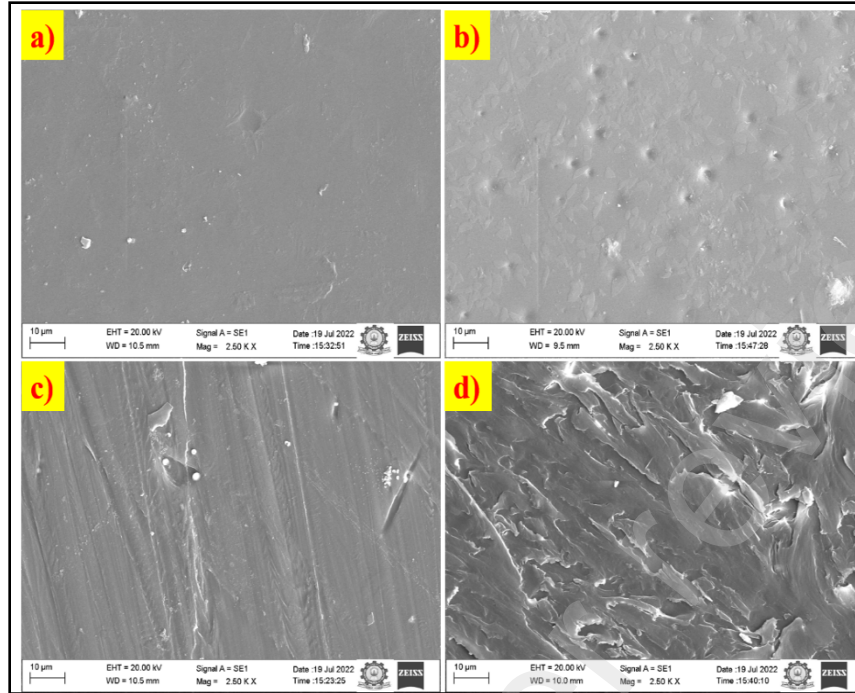


Figure 4: SEM Analysis of Pure PVA and bc-Ng/PVA Composites

3.2. Dielectric properties of the nanocomposite films

The AC conductivity of the prepared samples is calculated using the formula:

$$\sigma_{ac} = 2 f \epsilon_0 \epsilon'' \quad (1)$$

Where, f is the applied frequency, ϵ_0 is the vacuum permittivity, and ϵ'' is the dielectric loss.

Figure 5(a-b) illustrates the impedance and differences in AC conductivity for composites with varying Neem gum (Ng) doping levels and a pure PVA sample at different frequencies. As the neem content increases, the AC conductivity rises until reaching a 5% weight concentration. Beyond this concentration, conductivity decreases, primarily due to the combination of low-surface-area components forming larger structures [24]. The increased film conductivity is attributed to the formation of complexes in the composite samples and the presence of polar functional groups [25, 26].

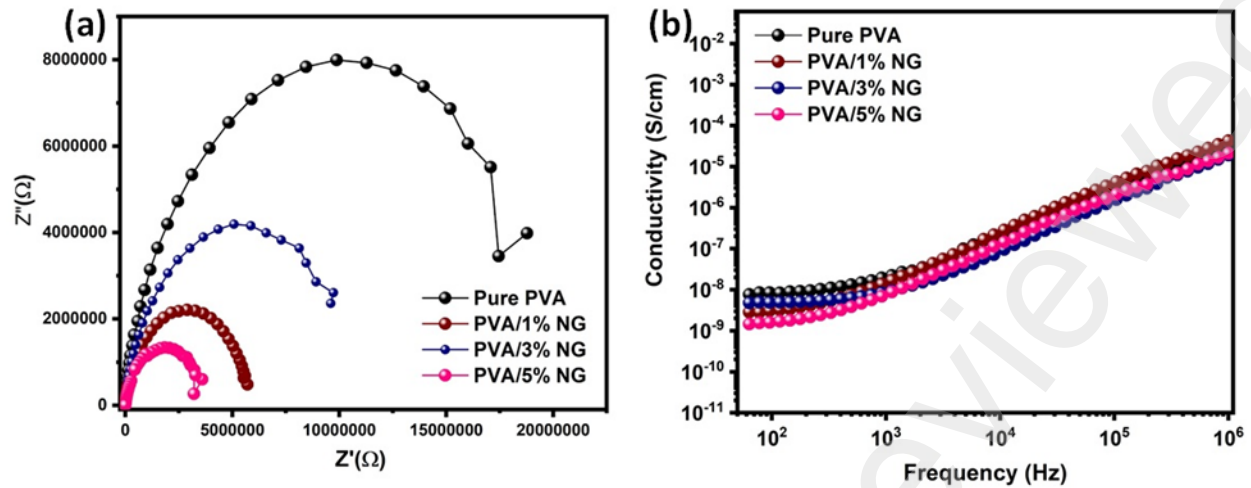


Figure 5: a) Impedance and b) Variation of ac conductivity with frequency for pure and different Ng (1, 3 and 5%) added PVA composites films.

Figure 6 depicts the frequency dependence of the real and imaginary parts of the dielectric constant. The dielectric constant is higher at lower frequencies, and the reverse effect is observed at higher frequencies, attributed to Maxwell-Wagner polarization predominantly caused by conductor-insulator interactions, indicating interfacial polarization. In the low-frequency range, space charges have sufficient time to respond to an applied electric field. In the higher-frequency range, alterations in the applied electric field occur too rapidly for space charges to compensate, and polarization cannot occur. PVA with 5% biocompatible Neem gum doping exhibits the highest dielectric constant, suggesting percolation. The dielectric constant tends to decrease above this percolation threshold [27-29].

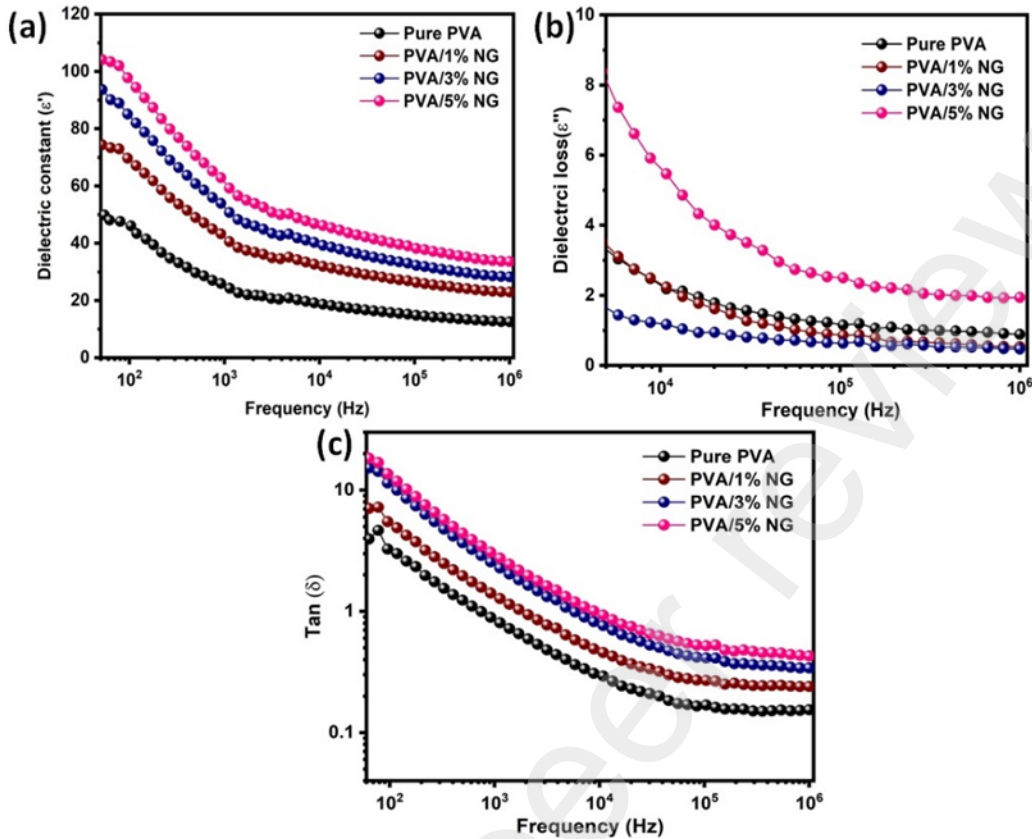


Figure 6: Frequency dependence of a) real dielectric constant, b) dielectric loss (ϵ'') and c) dielectric loss factor for Pure PVA and PVA with (1, 3 and 5%) added Ng polymer composite films

Figure 6b illustrates the decrease in dielectric loss (ϵ'') as frequency increases. At higher frequencies, the reduction in dielectric loss is attributed to the diminished accumulation of polarization-induced charges due to the difficulty in generating space charges under the applied electric field [30]. Figure 6c demonstrates the frequency-dependent evolution of the dielectric loss factor for all films. The graph indicates a decrease in the loss tangent as frequency rises.

The electric modulus $M^*(\omega) = 1/\epsilon^*(\omega)$ can determine the complex permittivity $\epsilon^*(\omega)$ of the composite dielectric material. After accounting for impurities, electrode-dielectric interaction, and electrode polarization effects, these spectra validate the bulk response [31]. Figure 7 displays

the real M' and imaginary M'' sections of the electric modulus calculated using permittivity profiles for pure PVA and various neem gum-added PVA composite polymers. The M' value increases rapidly at high frequencies, indicating the dominance of non-Debye type relaxation behavior, particularly the Maxwell-Wagner-Sillars (MWS) relaxation mechanism. The widening peak at higher frequencies suggests the presence of PVA chain segment motions (-relaxation) in the studied composites [32, 33]. The enhanced dielectric properties observed in the PVA/neem gum composite films, especially at a 5% Ng concentration, can be linked to the improved structural features and increased interfacial contact between PVA and Ng. The favorable dielectric strengths at higher frequencies make these composites suitable for applications in advanced electronics and energy storage devices.

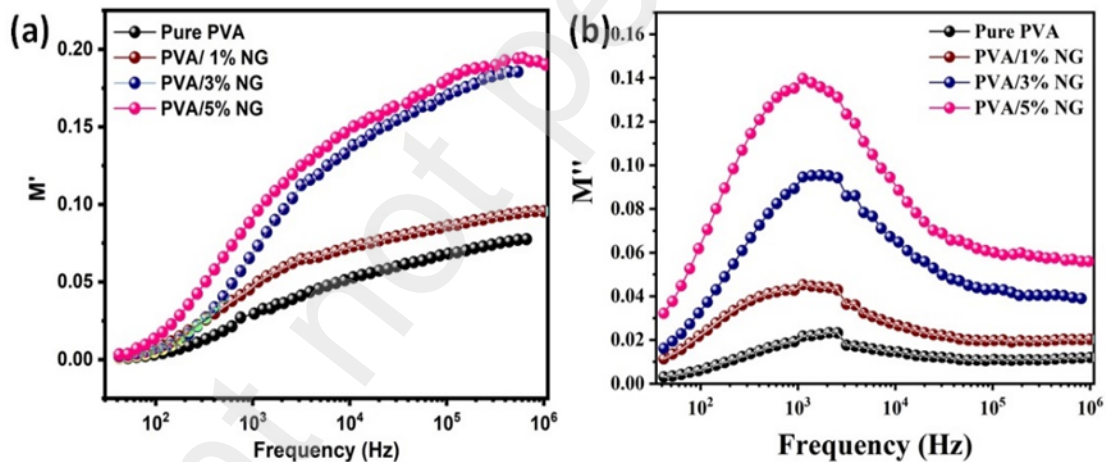


Figure 7: Frequency-dependent real part M' and loss part M'' for pure and different Ng added (1, 3 and 5%) added PVA nanocomposite films.

4. Conclusion

The solution casting technique was employed to fabricate PVA polymer composites with varying neem gum (Ng) concentrations. The XRD patterns confirmed the successful production of blended

composites. FTIR spectra highlighted the interaction between Ng and the polymer, resulting in complex formation through hydrogen bonding. The addition of Ng enhanced both electrical and dielectric properties, with the optimal improvement observed at a 5 wt% Ng concentration compared to pure PVA and other composite samples. The composites exhibited favorable dielectric strengths at higher frequencies, suggesting potential applications across a wide range of devices. The incorporation of Ng into the PVA matrix not only improved structural features but also demonstrated enhanced dielectric capabilities, making these composites promising for diverse device applications.

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