

DEVELOPMENT OF CHITOSAN–ZnO NANOCOMPOSITES FOR FLEXIBLE PIEZOELECTRIC AND MECHANICAL SENSING APPLICATIONS

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ABSTRACT

Chitosan–zinc oxide (ZnO) nanocomposites are bio-based, flexible materials used for piezoelectric and mechanical sensing applications. [1, 2, 3]

Key Performance and Properties

- Piezoelectric Coefficient (d_{33}): Reaches peak values up to 65.9 pC/N at an optimal concentration of 15 wt.% ZnO nanoparticles (NPs) in chitosan-ZnO films. [1, 2]
- Mechanical & Dielectric Synergy: Young's modulus, dielectric constant, and piezoelectric response all reach maximum performance around 15 wt.% ZnO before declining due to particle agglomeration. [1, 2]
- Interfacial Model: A three-phase model (chitosan matrix, ZnO nanoparticles, and a high-dielectric interfacial layer) explains how strong hydrogen-bonding and side-group interactions boost overall energy-conversion efficiency. [1, 2]
- Biocompatibility & Eco-Friendliness: Chitosan provides flexible, biodegradable, and non-toxic polymer backbones, making these composites ideal for wearable electronics, real-time biomedical patient monitoring, and self-powered nanogenerators. [1, 2]

KEYWORDS- chitosan, nanocomposites, piezoelectric, sensing, mechanical

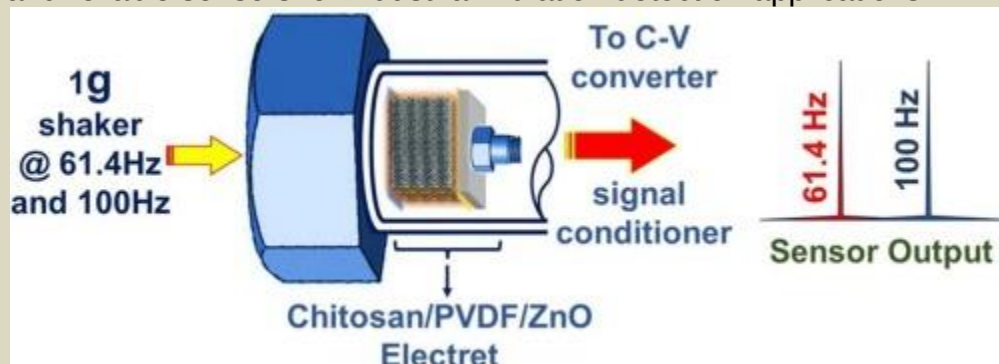
INTRODUCTION

Dielectric, conductivity, mechanical, and piezoelectric properties are assessed by using thermogravimetry, FTIR, XRD, mechanical, and dielectric spectroscopy measurements. These analyses reveal that the dielectric constant, Young's modulus, and piezoelectric constant (d_{33}) exhibit a strong dependence on nanoparticle concentration such that maximum values of referred properties are obtained at 15 wt.% of ZnO NPs. The piezoelectric coefficient d_{33} in CS-ZnO nanocomposite films with 15 wt.% of NPs ($d_{33} = 65.9$ pC/N) is higher than most of polymer-ZnO nanocomposites because of the synergistic effect of piezoelectricity of NPs, elastic properties of CS, and optimum NPs concentration. A three-phase model is used to include the chitosan matrix, ZnO NPs, and interfacial layer with dielectric constant higher than that of neat chitosan and ZnO. This layer between nanoparticles and matrix is due to strong interactions between chitosan's side groups with ZnO NPs.[1,2,3] The understanding of nanoscale properties of CS-ZnO nanocomposites is important in the development of biocompatible sensors, actuators, nanogenerators for flexible electronics and biomedical applications. To accomplish this task, we have also developed a computer program to fit our experimental data. It is noteworthy that as a rule, the effective dielectric constant ϵ and conductivity σ of a two-component mixture with different ϵ and σ can be calculated by using models such as the Maxwell, Bruggeman, Lichtenecker and other classical percolation models. In the literature, there are on the order of thousand papers which used these models. However, the use of such classical models fails to capture the correct physics due to low conductivity of CS-ZnO and the application of the three-

phase model allows correct describe properties of CS-ZnO nanocomposites. Due to the low volume fraction of ZnO NPs in CS-ZnO films (from 0 to 0.15 wt.%; see below the volume fraction calculation). Therefore, the effective conductivity of nanocomposites practically depends upon the conductivity of neat CS (ca. 10^{-7} S/cm). The conductivity of neat CS is related to the Grotthuss mechanism in which the protons are originated from the protonated amino groups and can move along the hydrated molecule in the hydrogen-bonding network via hopping process [50]. Due to the strong interaction of reactive CS side groups with ZnO NPs (as probed by FTIR measurements) the number of generated protons and the number of hydrated molecules decrease (TGA measurements); this plausible scenario is responsible for the decreasing of nanocomposite's conductivity".

DISCUSSION

Zinc oxide (ZnO) nanoparticles, polyvinylidene fluoride (PVDF), and chitosan have been employed to develop a hybrid bio-nanocomposite-based piezoelectric sensor. With various chitosan concentrations, the piezoelectric characteristics of the resultant ZnO/PVDF/chitosan composites were systematically investigated. XRD, FTIR, Raman spectroscopy, SEM, TEM, and XPS investigations verified that ZnO was effectively incorporated within the polymer matrix after its fabrication using the hydrothermal technique.[4,5,6] P-E hysteresis measurements were used to examine the ferroelectric properties of the composites, and the ZnO/PVDF/CS15 mixture showed increased residual polarization. A mechanical sensitivity of 6.3 mV g^{-1} and a maximum piezoelectric strain coefficient (d_{33}) of 3.9 pC N^{-1} have been measured. These results show that ZnO/PVDF/chitosan-based films may be utilized as biocompatible, flexible, and reliable sensors for industrial vibration detection applications.



Biomaterials are substances that can interact with biological systems to improve or supplant natural processes. They can be organic, synthetic, living, or non-living. Both biological and inorganic materials can turn mechanical force into electrical, and the other way around. Inorganic piezoelectric crystals develop piezoelectricity because of the arrangement of ions in the non-inverse symmetric structure of the dielectric materials [1]. An electrical field forms across the material's boundary due to the applied stress linear change in the internal polarization of the material [[2], [3], [4], [5], [6]]. The molecular structure and orientation of the polymer cause the piezoelectric action in organic piezoelectric polymers [7]. A chitin-based biomaterial with a wide range of chemical and mechanical properties of chitosan [[8], [9], [10], [11], [12]]. The four basic processes used to remove the chitosan from the shells of crabs, shrimp, and pawns, among other creatures, are demineralization, deproteinization, decoloration, and

deacetylation [13,14]. The amino and hydroxyl groups of chitosan are altered with a predilection effect of ion for a variety of uses [15,16]. Chitosan is the perfect material for biomedical applications because it combines stretchability with biocompatibility, biodegradability, non-toxicity, antioxidant, and antibacterial activity [[17], [18], [19], [20], [21], [22]]. Because chitosan is capable of creating films, it may also serve as a framework for host fillers (such as nanoparticles and nanorods) to produce flexible, functionalized films [23,24]. Numerous investigations have shown that chitosan comprises non-centrosymmetric structures [25], with the degree of acetylation and the type of solution used to dissolve the chitosan serving as the main variables governing its dielectric and piezoelectric responses [[26], [27], [28]]. The flexibility of PVDF polymer, which makes it easier to mold on Curved surfaces, is only one of many advantages it has over ceramic [29]. Additionally, resilient, creep-resistant, and photo-stable, PVDF is chemically inert. Due to its low density and weak dielectric permittivity, it also possesses a very high voltage coefficient [[30], [31], [32]]. PVDF is a semicrystalline polymer that can be classified into five phases: α , β , γ , δ , and ϵ [33]. The β phase is the only one of the four unique phases that PVDF may take that displays spontaneous polarization [7,8,9] and consequently piezoelectricity. PVDF with a β -phase structure is generally used because molecules with this structure have the greatest piezoelectric effect when compared to other phases [34]. The four atoms in the β -phase are all Trans (TTTT) [35] and form a flat zigzag form with minimum deflection. The surface resistivity and β - a fraction of PVDF polymer are connected to the electrical properties, such as piezoelectricity [36]. Because molecules with this structure have the highest piezoelectric effect when compared to other phases, PVDF with α -phase structure has recently undergone extensive development [37]. Praveen et al. [3,38] have reported that the Bio-nanocomposite electret, which is made up of nano ZnO embedded in chitosan and senses vibration at 80 Hz, has been successfully produced. Adding chitosan to the collagen polymer enhances the piezoelectric strain constant considerably (d14) [39]. Recently, piezoelectric, ferroelectric materials such as ZnO and BaTiO₃ were embedded in chitosan polymer and employed for mechanical excitation detection, with the piezoelectric characteristics of ZnO and BaTiO₃ being highlighted and the electret being evaluated for mechanical sensing applications [40]. The vibration-detecting behavior of biopolymer chitosan and ZnO at 80 Hz has been reported by Praveen et al. [3,38]; however, the sensitivity within the intended range for industrial applications was not addressed.[10,11,12]

RESULTS

An innovative piezoelectric device was fabricated using a polymer nanocomposite of flower-shaped tungsten trioxide (WO₃) nanomaterial embedded in a polyvinylidene fluoride (PVDF) matrix, paving a viable path towards flexible, wearable, highly efficient, energy-harvesting, pressure-sensing devices.

The conversion of mechanical energy to electrical energy is always a topic of great interest since it involves converting day-to-day activities to useful forms of energy and researchers on the lookout for new methods for the same.

Researchers at the Centre for Nano and Soft Matter Sciences (CeNS), Bengaluru, an autonomous institute of the Department of Science and Technology (DST) employed a

systematic experimental approach to explore the interactions between polymers and nanomaterials.

They used the same nanofiller to trace their interactions with varying morphologies, crystal structures, and surface charges. Out of the four dissimilar morphologies examined, the nanoflowers characterized by a crystal system with three axes of unequal length and three unequal angles and the highest surface charge (zeta potential: -58.4 mV) demonstrated the most effective interaction with the PVDF matrix, leading to the highest piezoelectric phase. To further enhance energy generation, an optimization process was carried out to determine the ideal nanofiller concentration within the PVDF matrix. This involved the fabrication and testing of self-powered energy-harvesting devices.[13,14,15]

The research which involves mixing of flexible piezoelectric polymer and nanoparticles and systematic study of the resultant mechanical energy conversion efficiency gives an insight into understanding/classifying what type of nanoparticle can enhance the piezoelectric properties of a piezoelectric polymer.

The high sensitivity and energy efficiency of this nano-engineered system make it ideal for biomedical uses. In particular, it can be incorporated into wearable health monitoring systems that can capture biomechanical energy from minor to major body movements like heartbeats, pulses, breathing, walking, etc., and transform it into electrical signals. By using these signals, physiological parameters can be monitored in real time without requiring external power sources.

Zinc oxide (ZnO) nanocomposites have emerged as multifunctional materials due to their unique optical, electrical, and physicochemical properties. The incorporation of ZnO nanoparticles into diverse matrices has significantly enhanced their applicability in biomedical, environmental, and industrial domains. This review presents a comprehensive overview of the synthesis strategies and characterization techniques for ZnO nanocomposites, highlighting sol-gel, hydrothermal, and green synthesis methods as effective and scalable approaches. The structural and morphological properties of these nanocomposites, investigated through techniques such as SEM, TEM, XRD, and FTIR, confirm their tunable features, enabling controlled functionalization for target-specific applications. Biomedical applications, especially antimicrobial, anticancer, and wound-healing functionalities, have shown promising results due to the enhanced reactive oxygen species (ROS) generation and cellular interaction of ZnO-based materials. In the environmental sector, ZnO nanocomposites have demonstrated efficacy in water purification, photocatalytic degradation of pollutants, and as sensors for detecting environmental toxins.[16,17,18] Additionally, their integration into electronic and optoelectronic devices underscores their versatility. The review also touches upon the toxicity and biocompatibility issues, emphasizing the need for careful design and assessment for safe biomedical use. Future directions focus on optimizing synthesis protocols, enhancing biocompatibility, and expanding application horizons through interdisciplinary approaches. Overall, ZnO nanocomposites hold significant potential in advancing next-generation nanotechnological innovations.

Zinc oxide (ZnO) nanocomposites have gained attention in recent years due to their remarkable versatile synthesis approaches, physicochemical properties and wide-

ranging applications across various fields. ZnO, a well-known semiconductor with a wide bandgap (3.37 eV) and high exciton binding energy (60 meV), possesses exceptional optical, electrical, and mechanical characteristics, make it suitable for nanocomposite formation. When it is combined with other materials such as polymers, metals, metal oxides, and carbon-based nanostructures, ZnO nanocomposites exhibit enhanced functionality, improved stability, and tailored properties suitable for advanced technological applications [1-7]. The synergy between ZnO and other components enables superior photocatalytic efficiency, antibacterial activity, enhanced electrical conductivity, and mechanical robustness, which are high application in biomedical, environmental, and energy-related devices [8]. The synthesis of ZnO nanocomposites involves various techniques, ranging from chemical and physical methods to green synthesis approaches, each offering distinct advantages in terms of particle size control, morphology, and crystallinity. Chemical methods such as sol-gel synthesis, hydrothermal and solvothermal techniques, co-precipitation, and chemical vapor deposition allow for precise tuning of the nanocomposite's structural and functional attributes. Physical methods, including sputtering, laser ablation, and mechanical milling, provide alternative routes for fabricating ZnO-based hybrid structures with controlled nanoscale features. Furthermore, the emergence of eco-friendly synthesis techniques using plant extracts, microorganisms, and bio-molecules has revolutionized nanomaterial fabrication, reducing toxic byproducts and promoting sustainable nanotechnology. The choice of synthesis method plays a crucial role in determining the physicochemical characteristics of ZnO nanocomposites, influencing their effectiveness in diverse applications [9-13]. ZnO nanocomposites has applications in numerous sectors such as healthcare, electronics, environmental remediation, and energy storage. Their antibacterial and antifungal properties make them promising role for biomedical applications, such as drug delivery systems, wound healing materials, and antimicrobial coatings. In electronics and optoelectronic devices, ZnO-based nanocomposites are employed in sensors, transistors, and light-emitting diodes due to their superior electron mobility and optical transparency. [14-17] The photocatalytic efficiency of ZnO composites has been widely explored for environmental applications, especially in wastewater treatment, air purification, and degradation of organic pollutants. Additionally, ZnO nanocomposites play a significant role in energy storage and conversion, where they are integrated into lithium-ion batteries, supercapacitors, and solar cells to enhance energy efficiency and durability. The multifunctional nature of ZnO nanocomposites has attraction in research efforts toward their development and optimization for next-generation technologies [18-20]. This review provides an in-depth analysis of ZnO nanocomposites, focusing on their key applications of zinc oxide. Furthermore, the diverse range of applications of ZnO nanocomposites will be explored, emphasizing their role in emerging technologies and potential future advancements. By examining the latest research trends and technological innovations, this review aims to highlight the significance of ZnO nanocomposites as a crucial component in modern nanotechnology and materials science.[18,19,20]

CONCLUSIONS

Zinc oxide (ZnO) nanocomposites represent a rapidly evolving class of advanced materials with wide-ranging applications across biomedical, environmental, and technological fields. Their exceptional physicochemical properties—such as high

surface area, semiconducting behavior, photocatalytic activity, and biocompatibility—make them ideal for multifunctional applications. This review has highlighted various synthesis techniques, including sol-gel, hydrothermal, and green synthesis methods, which offer versatility in tailoring morphology and improving dispersion within matrices. ZnO nanocomposites have demonstrated remarkable performance in areas like antimicrobial coatings, drug delivery systems, photocatalysis for pollutant degradation, energy harvesting, supercapacitors, and biosensors. Additionally, their role in emerging fields such as vaccine delivery and immunotherapy underscore their potential in precision medicine. However, despite significant progress, challenges remain—particularly in achieving large-scale, cost-effective, and reproducible synthesis, controlling particle agglomeration, and understanding long-term biocompatibility and environmental safety. Addressing these limitations requires an interdisciplinary approach that integrates nanotechnology, materials science, biology, and environmental engineering. Future research should focus on optimizing fabrication methods, enhancing the stability and targeted functionality of ZnO nanocomposites, and exploring their interactions at the nano-bio interface. With continued innovation and rigorous evaluation, ZnO nanocomposites are poised to play a transformative role in next-generation technologies and sustainable development.[20]

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