

Effect MnO_3 Nanoparticles On Structural, Optical, And Electrical Properties Of PVP: CMC Blend Films

Assist. Prof. Dr. Bahaa Abbas¹ ,
Assist. Prof. Dr. Widad H. Albanda² ,
Assist. Prof. Enamm S. Abdullah² ,
Assist. Research Esmaeil Jalali Lavasani³
Prof. Dr. Muhammad Hameed Al-Timimi⁴

- 1- Swansea University , Engineering and Science, Materials, Specific Research Group, UK.
- 2- Al-Mustansiriyah University , College of Basic Education , Science Department , Iraq.
- 3- University of Bucharest , Faculty of Physics , 3 Nanosae Centre , Romania.
- 4- University of Diyala , College of Science , Department of Physics, Iraq.

Abstract:

This Study Demonstrates The Potential Of MnO_3 Nanoparticle Addition To Enhance The Properties Of Polymeric Blends, The Effect Of Adding MnO_3 Nps Was Studied In A Polymeric Blend Composed Of Polyvinylpyrrolidone (PVP): Carboxymethylcellulose (CMC) With Different Concentrations Of MnO_3 Nps (3%, 5%, And 7%), And The Study Of Structural, Optical, And Electrical Properties, The Results Show The Energy Gap Of The (PVA: CMC) Film Was Reduced From 4.48 (Ev) To 3.89 (Ev) By Incorporating 7% MnO_3 Nps , This Change Suggests Enhanced Optical Properties, Including Increased Light Transmission And Reflection. Furthermore, The Conductivity Of The Blend Was Increased, Rendering It Suitable For Various Applications Such As, Sensor And Optoelectronics Devices.

Keyword: CMC, PVP, MnO_3 NPs , Structural, Optical, Dielectric Properties.

1. Introduction

Nanocomposites are very important in scientific applications, as they are prepared from mixing a polymeric matrix or composed of several different polymers with nanoparticles, which offer potential advantages in terms of improved optical, electrical, and mechanical properties. These components can be utilized to develop new materials [1]. Carboxymethylcellulose (CMC) is a chemically modified water-soluble cellulose derivative used as a substitute polymer for blending with proteins to produce flexible and strong films. It is chosen for its ability to form a continuous matrix, excellent viscosity, biocompatibility, and availability [2, 3]. CMC is widely used in industries such as pharmaceuticals, packaging and food, due to its non-toxicity, safety, and its ability to enhance the mechanical, thermal, and barrier properties of films [4, 5]. Polyvinylpyrrolidone (PVP) is a water-soluble polymer derived from vinylpyrrolidone monomer. PVP has unique properties, including the formation of stable complexes with various compounds [6]. In care products, PVP is commonly used as a binder, and also in hair styling products. It is also found in skincare products [7, 8]. It is possible to prepare a material with better solubility, stability, and film-forming ability by blending PVP and CMC polymers. MnO_3 nanoparticles are used to further improve these properties. The addition of manganese trioxide (MnO_3) nanoparticles further enhances these properties. MnO_3 nanoparticles are incorporated using a deposition method, which offers advantages such as low cost [9]. The addition of MnO_3 to a PVP: CMC polymer blend improves the material's characteristics, making it more versatile and useful across various applications [10, 11]. This study focuses on preparing the blend using a 50% ratio of PVP and 50% CMC, with the addition of 3%, 5%, and 7% MnO_3 nanoparticles to the polymeric matrix. The incorporation of nanoparticles enhances the structural, optical, and electrical properties of the resulting material. Moreover, the impact of the MnO_3 NPs content on the FTIR and FE-SME, optical, and electrical properties for the produced nanocomposite films.

2. Experimental Part

The casting method is a simple way to prepare PVP: CMC composite films. Using this procedure, PVP and CMC are dissolved at 60°C in a suitable solvent, such as water. The final solution is homogeneous. MnO_3 nanoparticles are added to the solution at varying weight ratios of 3%, 5%,

and 7% to improve the films' characteristics, The solution is then poured onto a flat surface and allowed to dry, forming thin films. By utilizing the solution casting method, researchers can easily fabricate PVP: CMC composite films with improved characteristics, The incorporation of MnO_3 nanoparticles further enhances the properties of these films.

3. Results and discussions

3.1 .FTIR Spectroscopy

The FTIR of the samples were obtained using a Shimadzu Japan-IR Affinity-1 spectrometer in the wavelength range of $450\text{-}4000\text{ cm}^{-1}$. Figure (1) displays the distinctive FT-IR spectra of CMC: PVP and CMC: PVP with 7% MnO_3 filler.

A peak at around 23450 cm^{-1} is indicative of the CMC backbones stretching vibration -CH. The carboxyl bond in CMC has a stretching vibration called -COO-, which has a peak, at about 1650 cm^{-1} , The CMC backbone's -CH bending vibration has a peak at around 1420 cm^{-1} [12, 13]. A peak at 3350 cm^{-1} , corresponding to the amide groups -NH stretching vibration [14, 15], The PVP backbone's stretching vibration -CH has a peak at about 2950 cm^{-1} . The amide group has a stretching vibration that is -C=O, and this vibration has a peak at about 1550 cm^{-1} [16] Furthermore, due to the hygroscopic nature of CMC, Certain overlapping peaks, such as the -OH stretching vibration of water molecules, may also be seen in the FTIR spectra of (PVP: CMC). It is significant to remember that the particular ratio and blending technique employed may have an impact on the (PVP: CMC) FTIR spectra. Peaks of MnO_3 nanoparticles: The -OH stretching vibration of the surface hydroxyl groups on the MnO_3 nanoparticles is represented as a peak at around $3700\text{-}3300\text{ cm}^{-1}$ [17], A peak located between 1600 and 1500 cm^{-1} is indicative of the O-H bending vibration on the MnO_3 nanoparticle surface. In MnO_3 nanoparticles, the vibration of Mn-O bonds is represented as a peak at around $1400\text{-}1300\text{ cm}^{-1}$ [18, 19]. Furthermore, several overlapping peaks, like the -OH vibration of water molecules [20, 21], It is significant to remember that the particular doping concentration of MnO_3 NPs and the preparation technique employed may have an impact on the FTIR spectra of CMC: PVP [22, 23].

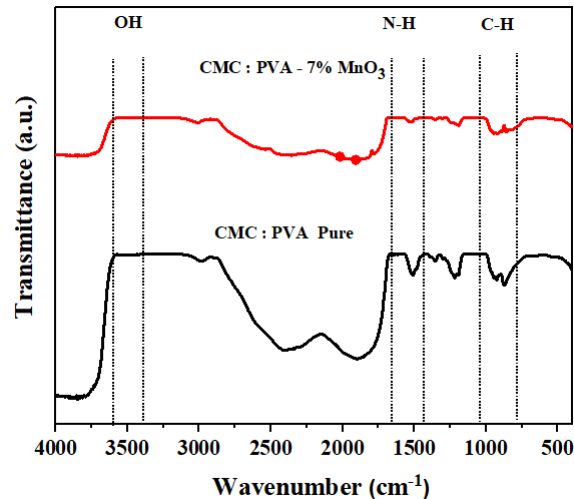


Fig 1. FTIR for the Samples.

3.2 FE-SEM Analysis

Figure (2) displays field-emitting scanning electron microscopy (FE-SEM) images of the sample (PVP: CMC) before (a) and after the addition of MnO_3 nanopowders at different ratios (b). The images reveal that the surface of the (PVP: CMC) film appears rough. When MnO_3 nanoparticles are incorporated, the reinforced polymeric films exhibit even more irregular and rough surfaces, along with increased surface porosity compared to the films prior to reinforcement. This rough and porous surface morphology is attributed to the formation of hydrogen bonding facilitated by the active carboxyl and hydroxyl functional groups present in the nanoparticles [24, 25]. The irregular, rough, and highly porous surface enhances the adsorption chemistry of the composite films [26]. It is worth noting that the observed surface morphology has important implications for the overall properties and potential applications of the reinforced polymeric films.

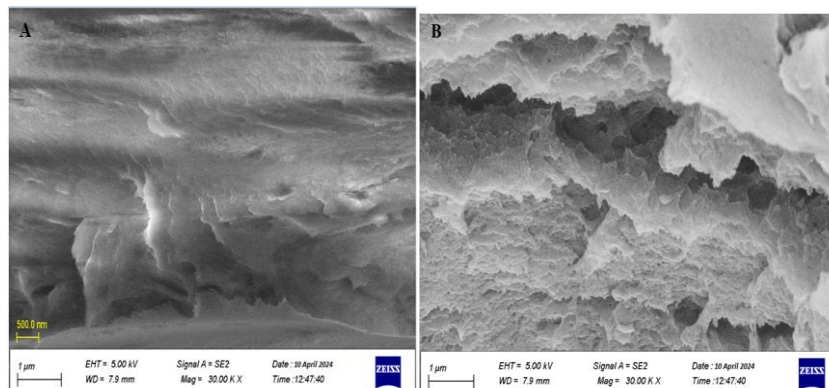


Fig 2. FE-SEM for the Samples A- CMC:PVA Pure and B - PVP: CMC- MnO_3 Nanocomposite.

3.3 Optical Properties

The presence of MnO_3 nanoparticles in the (PVP: CMC) blend can significantly alter the transmittance and reflectance properties of the material, Adding MnO_3 nanoparticles to the blend reduces the amount of light transmitted in the visible and near-infrared regions, This is because more light is reflected from the material's surface when nanoparticles are present since they are more capable of scattering and absorbing light than the polymer blend [28, 27], The influence of MnO_3 nanoparticles on transmittance and reflectance depends on the wavelength of the light and Greater dispersion and absorption are attributed to higher nanoparticle concentrations [29, 30], causing more pronounced changes in (T %) and (R), as depicted in Figure (3).

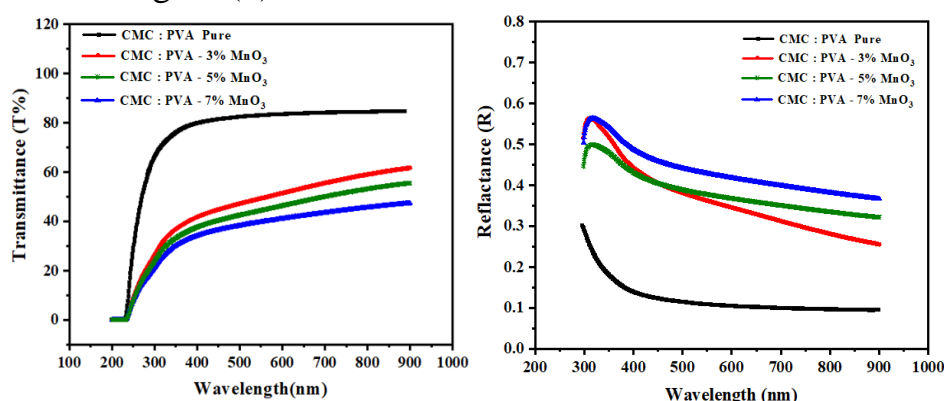


Fig 3. Transmittance (T %) and Reflectance (R) for the Samples.

Figure (4) illustrates the energy gap values of the pure (PVP:CMC) film and the reinforced films with varying concentrations of manganese oxide (MnO_3) nanoparticles. The energy gap of the pure film was measured at 4.43 (eV). As the content of MnO_3 nanoparticles increased, the energy gap (E_g) values of the reinforced films decreased. Specifically, for reinforcement ratios of 3%, 5%, and 7%, the energy gap values were recorded as 4.33 (eV), 4.27 (eV), and 3.89 (eV), respectively. This decrease in energy gap values can be attributed to the presence of MnO_3 nanoparticles, which introduce defects in the films. These defects create localized states within the optical energy gap, leading to a reduction in the overall energy gap values as the concentration of nanoparticles in the polymer substrate increases [31]. As in equation (1) [32,33] :

$$\alpha h\nu = A(h\nu - E_g) \quad (1)$$

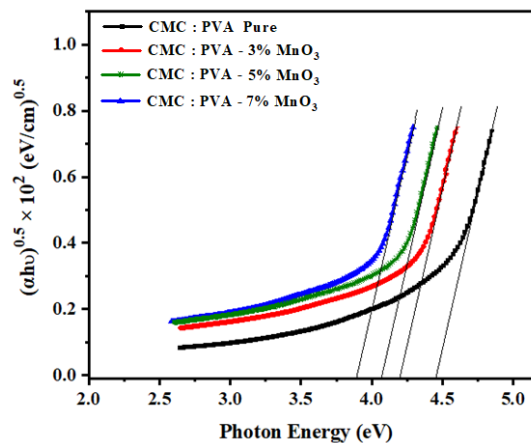


Fig 4. Energy Gap for the Samples .

3.3 A.C. Electrical Conductivity

Figure (5) illustrates the electrical conductivity of the Samples, The presence of MnO_3 nanoparticles increases the conductivity due to the introduction of additional free charge carriers, The size of the nanoparticles also plays a role in determining the impact on conductivity [34]. Moreover, the electrical conductivity of MnO_3 -doped PVP: CMC is influenced by the frequency of the applied AC electric field, Depending on the frequency range, the conductivity can either increase or decrease [35].

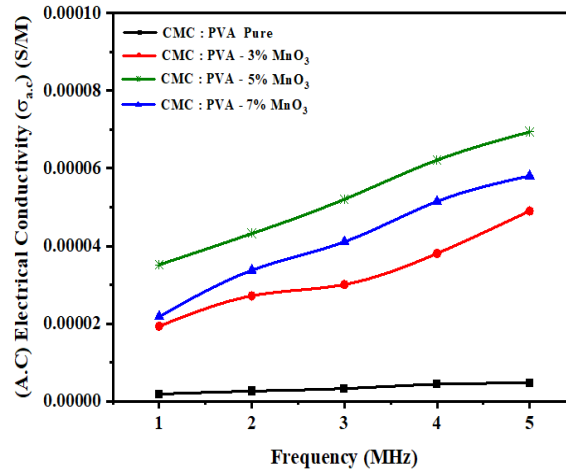


Fig 5. Dissipation Factor for the Samples.

3.4 Dielectric Constant

In Figure (6), the incorporation of MnO₃ nanoparticles into (PVP: CMC) blend polymers increases the dielectric constant of the material, This increase can be attributed to the additional polarizability introduced by the nanomaterial. The effect of MnO₃ NPs on the dielectric constant is also dependent on the shape and size of the nanoparticles, leading to more pronounced changes in the dielectric constant [36]. The dielectric constant of the Samples exhibits dependence on the frequency of the electric field [37]. Additionally, the temperature of the material can influence the dielectric constant, as higher temperatures can induce changes in polarizability and subsequently affect the dielectric constant [38].

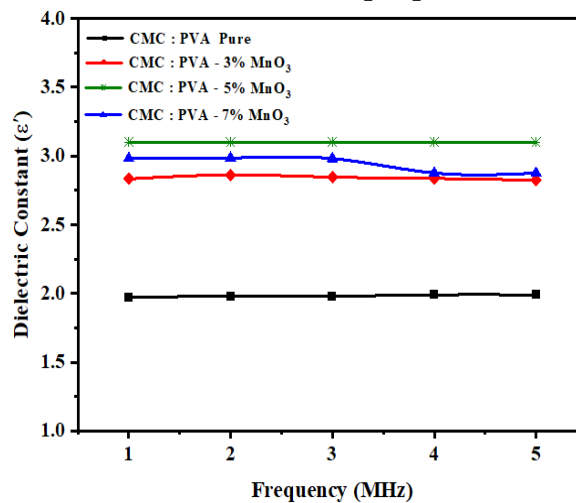


Fig 6. Dielectric Constant for the Samples.

3.5 Dissipation Factor

The addition of MnO_3 NPs to (PVP: CMC) blend leads to a decrease in the dissipation factor of the Samples, Figure (7) illustrates that the dissipation factor tends to decrease as the concentration of nanoparticles increases. The effect of MnO_3 nanoparticles on the dissipation factor of PVP: CMC blend also depends on the size of the nanoparticles [39]. Additionally, the dissipation factor of MnO_3 -doped PVP: CMC blend can vary with the frequency of the applied electric field. Moreover, the temperature of the material influences the dissipation factor. At higher temperatures, changes in the polarizability of the material can lead to alterations in the dissipation factor. It is important to consider various factors such as nanoparticle size, frequency and temperature when assessing the effect of MnO_3 NPs on the dissipation factor of (PVP: CMC) blend. These electrical properties have potential applications like sensors, and capacitors [40].

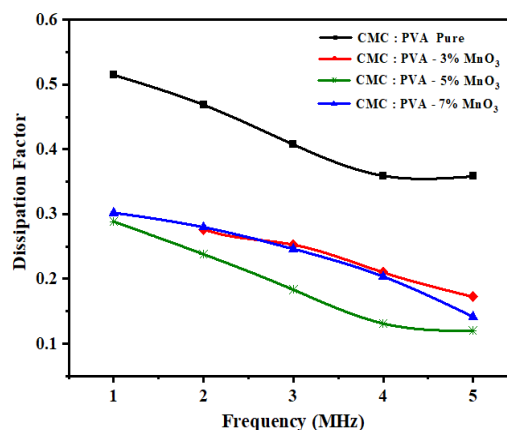


Fig 7. Dissipation Factor ($\tan\delta$) for the Samples .

4. Conclusions

The addition of MnO_3 nanoparticle at concentrations of 3%, 5%, and 7% for (PVP : CMC) blend can enhance the structural properties of the material by using the casting method. the optical properties of the blend can be improved, resulting in better light transmission also The energy gap (E_g), initially measured at 4.48 eV for the (PVA: CMC) blend , decreases to 3.89 eV when the MnO_3 NPs concentration is increased to 7%. The electrical properties of the blend can be enhanced by increasing its conductivity, This makes the blend suitable for various applications like sensors, and capacitor devices.

References

- [1] Jawad, Y. M., & Al-Kadhemy, M. F. H. (2021). Enhancement optical properties of CMC/PAA polymer blend by MgO, SiO₂ and bacteriocin for antimicrobial packaging application. *Journal of Global Scientific Research* (ISSN: 2523-9376), 6(9), 1715-1725. <https://www.example.edu/paper.pdf>
- [2] T.-P. Nguyen, "Polymer-based nanocomposites for organic optoelectronic devices. A review," *Surf. Coatings Technol.*, vol. 206, no. 4, pp. 742–752, 2011. <https://doi.org/10.1016/j.surfcoat.2011.07.010>
- [3] N. N. Nazmi, M. I. N. Isa, and N. M. Sarbon, "Preparation and characterization of chicken skin gelatin/CMC composite film as compared to bovine gelatin film," *Food Biosocial.*, vol. 19, pp. 149–155, 2017. <https://doi.org/10.1016/j.fbio.2017.07.002>
- [4] Almasi, H., Ghanbarzadeh, B., & Entezami, A. A. (2010). Physicochemical properties of starch–CMC–nanoclay biodegradable films. *International journal of biological macromolecules*, 46(1), 1-5. <https://doi.org/10.1016/j.ijbiomac.2009.10.001>
- [5] Nayef, M. J. (2011). Structure rheology of carboxymethyl cellulose (CMC) solutions. *B. Sc. in Chemical Engineering*, 1, 1-103. <https://www.example.edu/paper.pdf>
- [6] M. Teodorescu, and M. Bercea, "Poly (vinylpyrrolidone)–a versatile polymer for biomedical and beyond medical applications," *Polymer-Plastics Technology and Engineering*, 54(9), 923-943 (2015). <https://doi.org/10.1080/03602559.2014.979506>
- [7] P. Franco, and I. De Marco, "The Use of Poly (N-vinyl pyrrolidone) in the Delivery of Drugs: A Review." *Polymers*, 12(5), 1114 (2020). <https://doi.org/10.3390/polym12051114>
- [8] S. Gono, Doctoral thesis, African University of Science and Technology, 2020. <http://repository.aust.edu.ng/xmlui/handle/123456789/5007>
- [9] Mohammed, A. A., Ahmed, A. R., & Al-Timimi, M. H. (2022). Structural, Optical and Thermal Properties of (PEG/PAA: MnO₂) Nano Composites. *Technium BioChemMed*, 3(2), 107-119. <https://doi.org/10.47577/biochemmed.v3i2.7116>
- [10] S.S. Chiad, N.F. Habubi, S.F. Oboudi, and M.H. Abdul-Allah, "Effect of Thickness on the Optical Parameters of PVA: Ag," *Diyala Journal for Pure Sciences*, 7, 153-161 (2011). <https://www.iasj.net/iasj/pdf/4b03ea1b233568b1>

- [11] M.S. Rahman, M.S. Hasan, A.S. Nitai, S. Nam, A.K. Karmakar, M.S. Ahsan, et al., "Recent developments of carboxymethyl cellulose," *Polymers*, 13(8), 1345 (2021). <https://doi.org/10.3390/polym13081345>
- [12] A.H. Saputra, L. Qadhayna, and A.B. Pitaloka, "Synthesis and characterization of carboxymethyl cellulose (CMC) from water hyacinth using ethanol-isobutyl alcohol mixture as the solvents," *International Journal of Chemical Engineering and Applications*, 5(1), 36 (2014). <http://dx.doi.org/10.7763/IJCEA.2014.V5.347>
- [13] H.M. Hussein, M.H. Al-Timimi, and Y.M. Jawad, "The Properties, Preparation and Applications for Carboxymethyl Cellulose (CMC) Polymer: A Review," *Diyala Journal for Pure Science*, 18(4), (2022). <https://djfps.uodiyala.edu.iq/index.php/Home/article/view/37/36>
- [14] T. Franca, D. Goncalves, and C. Cena, "ATR-FTIR spectroscopy combined with machine learning for classification of PVA/PVP blends in low concentration," *Vibrational Spectroscopy*, 120, 103378 (2022). <https://doi.org/10.1016/j.vibspec.2022.103378>
- [15] S.S.H. Almgrs, and M.H. Al-Timimi, "(CMC-PVP) Films Filled with SnO₂ Nanoparticles Synthesized by (Solution-Gel) Method," *Journal of the college of basic education*, 27(113), (2021). <https://www.iasj.net/iasj/pdf/d05159f9f9bc79f1>
- [16] A. Jalali, A. Shockravi, V. Vatanpour, and M. Hajibeygi, "Preparation and characterization of novel microporous ultrafiltration PES membranes using synthesized hydrophilic polysulfide-amide copolymer as an additive in the casting solution," *Microporous and Mesoporous Materials*, 228, 1-13 (2016). <https://doi.org/10.1016/j.micromeso.2016.03.024>
- [17] G. Balakrishnan, R. Velavan, K.M. Batoo, and E.H. Raslan, "Microstructure, optical and photocatalytic properties of MgO nanoparticles," *Results in Physics*, 16, 103013 (2020). <https://doi.org/10.1016/j.rinp.2020.103013>
- [18] F.R. Saeed, M.H.A.A. Al-Timimi, W.H.A. Al-Banda, M.Z. Abdullah, I. Stamatina, S. Voinea, et al., "Thermal Properties of Paraffin/Nano-Magnetite/tetraphenylsilane Phase Change Materials," *Journal of Ovonic Research*, 14(5). (2018). <https://scholar.google.com/scholar?oi=bibs&cluster=14895011915883851214&btnI=1&hl=en>
- [19] A.A. Mohammed, A.R. Ahmed, and M.H. Al-Timimi, Structural, "Optical and Thermal Properties of (PEG/PAA: MnO₂) Nano Composites,"

Technium BioChemMed, 3(2), 107-119 (2022).

<https://doi.org/10.47577/biochemmed.v3i2.7116>

[20] A. Khan, A. Naeem, T. Mahmood, B. Ahmad, Z. Ahmad, M. Farooq, and T. Saeed, "Mechanistic study on methyl orange and congo red adsorption onto polyvinyl pyrrolidone modified magnesium oxide," Int. J. Environ. Sci. Technol. 19, 2515–2528 (2022). <https://doi.org/10.1007/s13762-021-03308-z>

[21] M.Z. Abdullah, M.H. Al-Timimi, W.H. Albanda, M. Dumitru, A.E. Balan, C. Ceaus, et al., "Structural and Electrochemical Properties of P3-Na0.67Mn0.3Co0.7O2 Nanostructures Prepared by Citric-Urea Self-Combustion Route as Cathode for Sodium Ion Battery," Digest Journal of Nanomaterials and Biostructures, 14(4), 1179-1193 (2019).

https://chalcogen.ro/1179_AbdullahMZ.pdf

[22] S.S. Sainudeen, L.B. Asok, A. Varghese, A.S. Nair, and G. Krishnan, "Surfactant-driven direct synthesis of a hierarchical hollow MgO nanofiber–nanoparticle composite by electrospinning," RSC advances, 7(56), 35160-35168 (2017). <https://doi.org/10.1039/C7RA05812H>

[23] H.M. Ragab, "Optical, thermal and electrical characterization of PEO/CMC incorporated with ZnO/TiO2 NPs for advanced flexible optoelectronic technologies," Ceramics International, 49(8), 12563-12569 (2023). <https://doi.org/10.1016/j.ceramint.2022.12.118>

[24] A.J. Mawat, M.H. Al-Timimi, W.H. Albanda, and M.Z. Abdullah, "Morphological and optical properties of Mg1-xCdSx nanostructured thin films," AIP Conference Proceedings, 2475(1), 090019 (2023).

<https://doi.org/10.1063/5.0103955>

[25] Y.M. Jawad, M.F.H. Al-Kadhemy, and J.A.S. Salman, "Synthesis structural and optical properties of CMC/MgO nanocomposites," Materials Science Forum, 1039, 104-114 (2021).

<https://doi.org/10.4028/www.scientific.net/MSF.1039.104>

[26] M. Habeeb, and R.S.A. Hamza, "Synthesis of (Polymer blend-MgO) nanocomposites and studying electrical properties for piezoelectric application," Indonesian Journal of Electrical Engineering and Informatics, 6(4), 428-435 (2018). <http://dx.doi.org/10.52549/ijeei.v6i4.511>

[27] S.A. Salman, M.H. Abdu-allah, and N.A. Bakr, "Optical characterization of red methyl doped poly (vinyl alcohol) films," International Journal of Engineering and Technical Research, 2(4), 126-128 (2014).

[28] D.H. Wang, D.Y. Kim, K.W. Choi, J.H. Seo, S.H. Im, J.H. Park, et al., "Enhancement of donor–acceptor polymer bulk heterojunction solar cell

- power conversion efficiencies by addition of Au nanoparticles,” *Angewandte Chemie*, 123(24), 5633-5637 (2011). <https://doi.org/10.1002/ange.201101021>
- [29] S. Biswas, S.S. Panja, and S. Bose, “Tailored distribution of nanoparticles in bi-phasic polymeric blends as emerging materials for suppressing electromagnetic radiation: challenges and prospects,” *Journal of Materials Chemistry C*, 6(13), 3120-3142 (2018).
<https://doi.org/10.1039/C8TC00002F>
- [30] J. Al-Zanganawee, M. Al-Timimi, A. Pantazi, O. Brincoveanu, C. Moise, R. Mesterca, et al., “Morphological and optical properties of functionalized SWCNTs: P3OT nanocomposite thin films, prepared by spincoating,” *Journal of Ovonic Research*, 12(4), 201-207 (2016).
https://chalcogen.ro/201_AlzanganaweeJ.pdf
- [31] Hashim, A., & Hadi, Q. (2018). Structural, electrical and optical properties of (biopolymer blend/titanium carbide) nanocomposites for low cost humidity sensors. *Journal of Materials Science: Materials in Electronics*, 29(13), 11598-11604.
- [32] A. Hashim, and M.A. Habeeb, “Synthesis and characterization of polymer blend-CoFe₂O₄ nanoparticles as a humidity sensors for different temperatures,” *Transactions on Electrical and Electronic Materials*, 20, 107-112 (2019). <https://doi.org/10.1007/s42341-018-0081-1>
- [33] A.T. Abood, O.A.A. Hussein, M.H. Al-Timimi, M.Z. Abdullah, H.M.S. Al-Aani, and W.H. Albanda, “Structural and optical properties of nanocrystalline SnO₂ thin films growth by electron beam evaporation,” *AIP Conference Proceedings*, 2213(1), 020036 (2020).
<https://doi.org/10.1063/5.0000454>
- [34] S. El-Gamal, and A.M. El-Sayed, “Physical properties of the organic polymeric blend (PVA/PAM) modified with MgO nanofillers,” *Journal of Composite Materials*, 53(20), 2831-2847 (2019).
<https://doi.org/10.1177/0021998319840802>
- [35] S.T. Hameed, T.F. Qahtan, A.M. Abdelghany, and A.H. Oraby, “Structural, optical, and dielectric characteristics of copper oxide nanoparticles loaded CMC/PEO matrix,” *Journal of Materials Science*, 57(15), 7556-7569 (2022). <https://doi.org/10.1007/s10853-022-07134-7>
- [36] N.S. Alghunaim, “Effect of CuO nanofiller on the spectroscopic properties, dielectric permittivity and dielectric modulus of CMC/PVP nanocomposites,” *Journal of Materials Research and Technology*, 8(4), 3596-3602 (2019). <https://doi.org/10.1016/j.jmrt.2019.05.022>



- [37] M.A. Morsi, R.A. Pashameah, K. Sharma, E. Alzahrani, M.O. Farea, and A.A. Al-Muntaser, "Hybrid MWCNTs/Ag nanofiller reinforced PVP/CMC blend-based polymer nanocomposites for multifunctional optoelectronic and nanodielectric applications," *Journal of Polymers and the Environment*, 31(2), 664-676 (2023). <https://doi.org/10.1007/s10924-022-02656-2>
- [38] A. Hashim, F.L. Rashid, Z. Al-Ramadan, and M.H. Abdul-Allah, "Characterization of (PVA-BaSO₄ 5H₂O) Composites," *Diyala Journal for Pure Science*, 8, 296-302 (2012).
<https://www.iasj.net/iasj/pdf/a5577c17b8b8e701>
- [39] S.S. Chiad, N.F. Habubi, S.F. Oboudi, and M.H. Abdul-Allah, "Effect of Thickness on the Optical Parameters of PVA: Ag". *Diyala Journal for Pure Sciences*, 7, 153-161(2011).
<https://www.iasj.net/iasj/download/4b03ea1b233568b1>
- [40] A.A. Al-Muntaser, R.A. Pashameah, E. Alzahrani, S.A. Al-Subhi, S.T. Hameed, and M.A. Morsi, "Graphene Nanoplatelets/TiO₂ Hybrid Nanofiller Boosted PVA/CMC Blend Based High Performance Nanocomposites for Flexible Energy Storage Applications," *J. Polym. Environ.* 31, 2534-2548 (2023). <https://doi.org/10.1007/s10924-022-02748-z>