

Structural and mechanical properties of chitosan/PVA composite reinforced by Ag/Au

Huda Razaq Kttafah^{1,*}, Hanaa Shuker Mahmood²

¹Department of Physics, Ministry of Education, Directorate General of Education Rusafa, Baghdad, Iraq.

²Department of Physics, College of Education for Pure Sciences Ibn AlHaitam, University of Baghdad, Baghdad, Iraq.

*Corresponding author: Huda.Razaq2104p@ihcoedu.uobaghdad.edu.iq

Original Research

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Abstract:

The sample was created in two stages, the first stage is preparing a solution of chitosan (CS) powder by adding it gradually to acetic acid placed on the electric magnetic stirrer device with a small magnetic leg in the beaker until we get a homogeneous solution. As for the second stage, preparing a solution of polyvinyl alcohol (PVA) powder by dissolving it with distilled water, and adding it gradually until we get a homogeneous solution. Then the two solutions are mixed with each other and gradually while they remain on the electric magnetic stirrer device. After that, the resulting solution was enriched with gold and silver nanoparticles in different ratios (Au NPs/Ag NPs) using a constant ratio of chitosan solution and polyvinyl alcohol for all samples. The best percentage after conducting the tests was CS/PVA (90:10) blends reinforced with Ag NPs/Au NPs. Nanoparticles of both are (2 mL). Inspection techniques were performed for the resulting structural and mechanical samples using the FTIR, DSC and the tensile test, from which we extracted Young's modulus and the maximum elongation of the sample. It was found through the tests that the results were better with the addition of silver nanoparticles and gold nanoparticles. The values of the young coefficient increase from 1.54 GPa until it reaches its highest value at 2.05 GPa. The highest value of the Young's coefficient was for the (50% AuNPs and 50% AgNPs).

Keywords: Chitosan; PVA; Silver nanoparticles; Gold nanoparticles; Mechanical properties; FTIR and DSC

1. Introduction

Polymers have attracted the world greatly because of their great importance, as they are used in the manufacture of many electrical and non-electrical devices because of their specifications [1]. They are light in weight, flexible, easy to process, and low in cost. Their mechanical strength is high and distinguishes them from other materials. Materials with physical stability [2]. Chitosan is a kind of natural polymer that has excellent biological properties because it is biodegradable, safe, non-toxic and also biocompatible [3]. It dissolves in acids, specifically dilute acids. It has the ability to renew and is abundant in nature. Its availability comes after cellulose [4]. One of the most common uses of chitosan is in the tissues that suffer from damage, repairing and engineering them, as they are used in surgery It has many applications, including medical applications, for several reasons [5]. It has many uses in food preservation containers over a wide range due to its non-toxicity and works against

microbes and fungi [6]. It can be used to preserve food and protect it from atmospheric environmental pollution and at the same time, it is considered a disinfectant [7]. Therefore, it is often preferable to incorporate Ag NPs, which are highly efficient antigens [8]. Polyvinyl alcohol is a multi-use polymer, and its chemical formula is $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is present in the form of white granules and can be dissolved in pure water [3]. PVA is considered a suitable matrix for nanoparticles, including gold and silver, because of its thermal stability, chemical resistance, water solubility, and non-toxicity [1]. The polyvinyl alcohol here was converted into a solution by adding a solution of nanoparticles of gold and silver [9]. When it turns into a solution by mixing it with pure water, its solution is characterized by a transparent color, but when it is mixed with a solution of gold and silver particles at the beginning, the color of the solution is transparent, and then after a period of time, and when it is added to the chitosan solution, its color tends to

red, and the degree of color changes by changing the percentage of adding nanoparticles [10]. Gold nanoparticles have attracted the greatest interest from many researchers because of their distinctive and unique properties, as they are non-toxic. Since they are metals, they possess electrical and thermal properties [11]. As for silver nanoparticles, they have different properties, as they are antibacterial. To improve the properties of the polymer matrix, nanoparticles of metals are added to it [12]. The polymer mixture reinforced with metal nanoparticles has many applications due to its response to the properties and its ability to modify the physical properties of the final product [12]. The modification links the material with each other with link chains. Ag NPs not only have important physical and chemical properties but also have antibacterial activities on a wide range due to their effective biocompatibility [13]. The creation of new polymeric materials that differ from the original material after the addition of mineral reinforcers is to improve structural and mechanical properties [12]. Polymers have multiple uses and their ability to form new materials with good specifications that can be applied in various aspects of life [14]. In our work, chitosan was mixed with polyvinyl alcohol at a constant rate [15]. However, by adding nanoparticles in different proportions using the electric magnetic stirrer device with a small magnetic leg in the beaker mixing techniques and the solution pouring method, samples were prepared through which the structural and mechanical properties were obtained using FTIR technology and tensile technique [5].

2. Experimental

The mixture of CS/PVA was reinforced to a single-weight ratio for all samples synthesized with nanoparticles (Au NPs/Ag NPs). The percentage by weight of chitosan was 90% and the percentage by weight of polyvinyl alcohol was 10%. The amount taken for nanoparticles was (2 mL), but in different proportions for each type of nanoparticles used in the work [13].

A solution of polyvinyl alcohol powder was prepared after being prepared in (Au NPs/Ag NPs) solutions, which were also prepared for each type separately. Silver nanoparticles

were made from a compound of silver nitrate in the liquid phase by chemical reduction, and silver powder was obtained, which was white nanoparticles, after which a silver nanoparticle solution was prepared [5]. Gold nanoparticles, it was prepared from gold chlorides, which after so her solution was prepared [12] and by taking different proportions of each of the nano-silver solution and the gold nano-solution and combining them with each other in a glass beaker and on an electro-magnetic device and using the magnetic leg inside the beaker for good viscosity, PVA powder is gradually added to the nano-solution until the amount ends and the mixing device remains for a period of time until the poly dissolves completely [7].

Then it is added gradually and in the form of droplets to the chitosan powder that has been dissolved in acetic acid and also in another glass flask and on the electrical device to ensure that all particles are dissolved and a homogeneous mixture is obtained [16]. To obtain a good and homogeneous mixture. Special molds made of Teflon polymeric material were used to pour the solution after completing the homogenization process and at room temperature [17]. The mixing period took several hours until a homogeneous mixture was obtained. The sample was extracted from the mold after three to four days, depending on the humidity in the air. The higher the humidity in the atmosphere, the longer the sample needed to be extracted, and then it was kept in special nylon bags [18].

3. Results and discussions

The force applied perpendicular to a unit area is known as stress σ ($\sigma = F/A$), The change in length to the original length can be described as strain ϵ , which is devoid of units ($\epsilon = \Delta L/L$). The ratio between the stress to the relative plasticity when it is within the elastic limits is what is known as the Young's coefficient ($Y = \sigma/\epsilon$) [19].

The Figure 1 shows the stress curves of the superimposed chitosan and polyvinyl alcohol reinforced with gold and silver nanoparticles. Where the enhancement was done by adding a constant ratio to the mixture of gold and silver nanoparticles taken in different proportions for both. Where typical behavior of stress and stress curves were

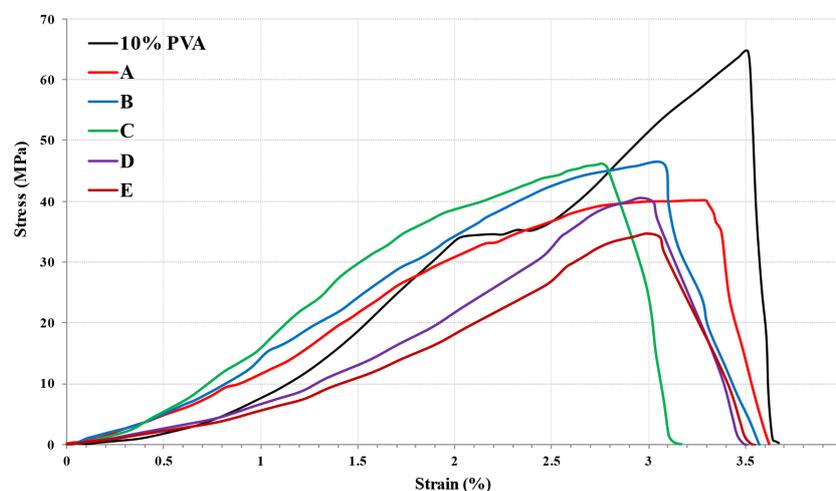


Figure 1. Stress-strain curve for CS/PVA Composite Reinforced by (Au NPs/Ag NPs).

shown [20], [21]. The curve is divided into two regions, the first is the flexibility region, in which the increase is linear within certain limits, and these limits end at a limit called the flexibility limit. As the area subjected to stress within the flexibility limits returns to its original shape after the removal of the effective stress [15].

As for the second region, in which the relationship is non-linear, it is outside the limits of elasticity. After the removal of the effective stress, it does not return to its original position, the sample is exposed to permanent deformation. We get the Young's modulus from the linear slope including the elastic region for each sample. A sample test device was used (H10KT) [22].

The properties of polymers depend on the mechanical properties and their behavior on hydrogen bonds. After loading the nanoparticles on the polymer's mixture, the stress began to increase, but then it decreased. The highest stress value was obtained from the sample that loaded (50% Au NPs and 50% Ag NPs). It is the sample with the symbol C [23]. The stress showed a decrease by loading the nanoparticles on the mixture after the stress was high without the reinforcement with nanoparticles. I agree with the researcher "Danmin Yang, Qun" Liu who explained in his research that whenever the proportion of silver nanoparticles is added, the stress and elongation decrease [24].

The measure of the hardness of the material and knowing the range for it is by measuring Young's modulus. While the softness of the material is measured through the final elongation. The mixture was taken 90:10 with different ratios of gold and silver nanoparticles as in Figure 2. It was shown from the figure that the values of the young coefficient increase from 1.54 GPa until it reaches its highest value at 2.05 GPa, and then it decreases again with the

change of the proportions of the nanoparticles. The highest value of Young's coefficient was for the (50% Au NPs and 50% Ag NPs) sample C in the figure. It is clear from this test that the higher the percentage of silver and gold particles in the composite and in an equal proportion for both, the lower Young's coefficient and tune 0.82 GPa. On the other hand, the elongation decreases from 3.51 to zero. This indicates that flexibility decreases. I agree with a number of researchers that as the percentage of nanoparticles is added, Young's modulus decreases, and the elongation also decreases [13].

To determine the variance in the sample to know the extent of organic compounds and inorganic compounds, we use the spectral analysis tool, which is FTIR spectra. FTIR spectroscopy is based on the IR absorption frequency ($400 - 4000 \text{ cm}^{-1}$). Figure 3 shows the dominant aggregates and interaction ranges of the composite after it was reinforced with nanoparticles of silver and gold, with different concentrations of both. Where the patterns appeared for the polypropylene aggregates. A wide band appeared at 3440 cm^{-1} . This group appeared compatible with hydroxyl. CH₂ vibrating aggregates appeared at 2890 cm^{-1} and 2979 cm^{-1} , respectively. Where this group was corresponding to symmetric and asymmetric expansion [12]. These interactions show that their energy gradually decreased with an increase in the proportion of silver nanoparticles with a decrease in gold nanoparticles, and we also note that their intensity increases relatively [25]. The increase by adding the percentage of silver nanoparticles offset by the decrease in the addition of the percentage of gold nanoparticles led to an expansion in the range of 1490 cm^{-1} , this confirms the interaction between the superimposed and the added nanoparticles (Au NPs/Ag NPs). The methylene group

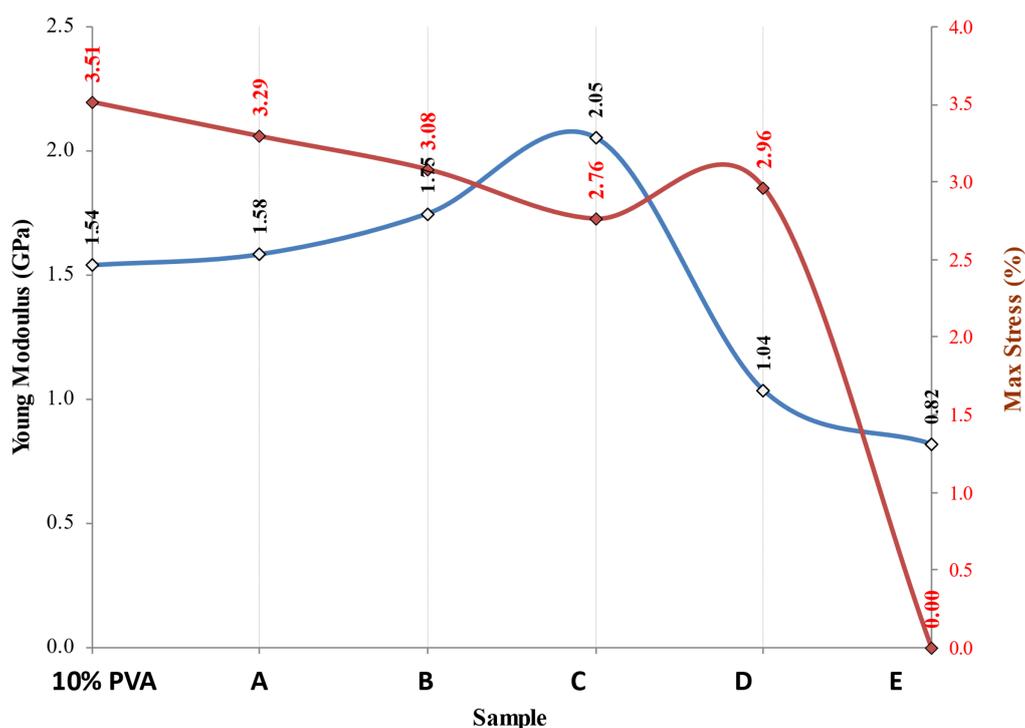


Figure 2. Young Modulus and maximum elongation for CS/PVA Composite Reinforced by (Au NPs/Ag NPs).

arose at 1112 cm^{-1} and expanded to 1175 cm^{-1} . This group was the appearance of C=O, while at 610 cm^{-1} the appearance of C-H. This was the effect of adding nanoparticles, which led to a decrease in some aggregates and an increase in others [26]. The data showed a decrease in the expansion peaks and expansion, which confirms the addition of nanoparticles. Here I agree with the researcher “Jixi Chen” when adding silver nanoparticles and increasing the percentage of their addition leads to a decrease in intensity. Where the scientist explained in his study that by adding nanoparticles, significant changes occurred, decreasing the intensity and a slight shift in the peak [27].

The Figure 4 shows the DSC curves of a sample of a mixture of chitosan and polyvinyl alcohol at a ratio of 90:10, which was reinforced with gold and silver nanoparticles in different proportions. The temperature range used was from zero to 400 degrees Celsius. These curves help us to know and understand the thermal behavior of the mixture of natural

and synthetic polymers. Reinforcement with two types of nanoparticles [28]. We note that the mixture of chitosan and polyvinyl alcohol is absorbent at a temperature of $120\text{ }^{\circ}\text{C}$ and it is at its peak, and by adding gold nanoparticles it is endothermic at a lower temperature of up to $100\text{ }^{\circ}\text{C}$. But by adding silver nanoparticles, we note the stability of its temperature with the sample without Adding any kind of nanoparticles. It also appears that the mixture of chitosan and polyvinyl alcohol is exothermic, which is the point at which the polymer decomposes at $280\text{ }^{\circ}\text{C}$, but the polymer decomposition process reaches $288\text{ }^{\circ}\text{C}$ after the addition of gold and silver nanoparticles by 50% each, and the highest decomposition peak of the polymer, and this applies to the researcher Hana Shukr [12] and with the researcher ESAM A. EL-HEFIAN et al. [29].

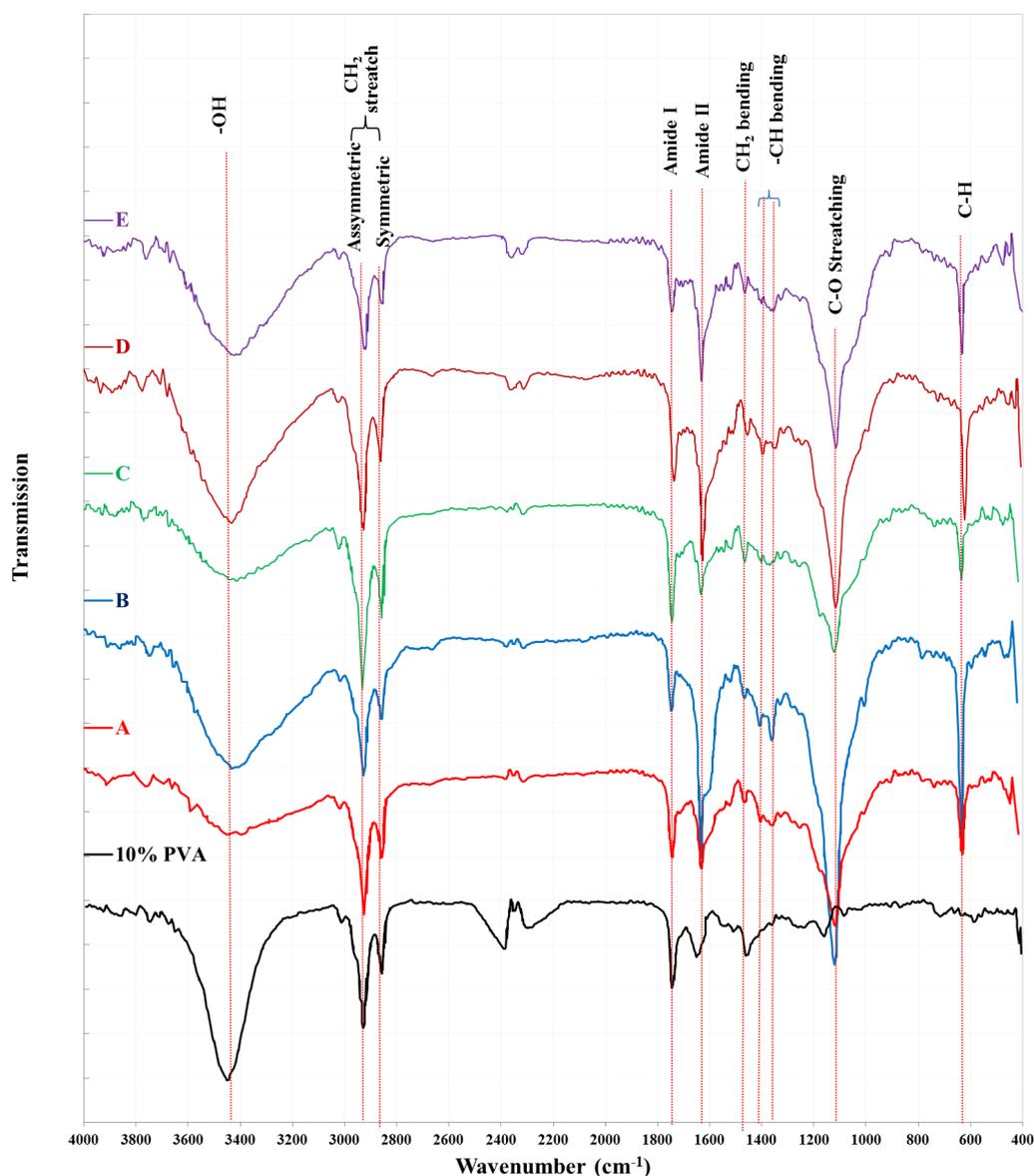


Figure 3. FTIR spectra for CS/PVA Composite Reinforced by (Au NPs/Ag NPs).

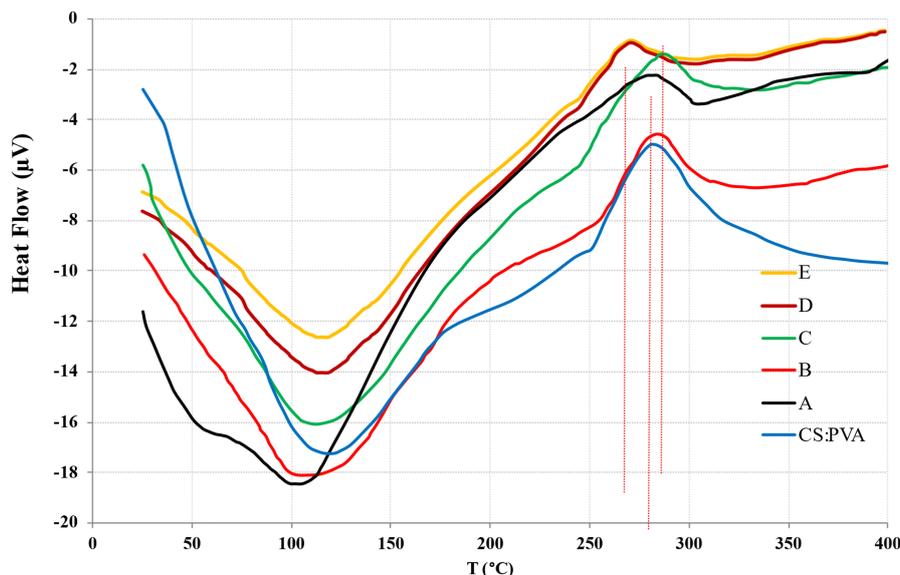


Figure 4. DSC spectra for CS/PVA at 90:10 blend ratio reinforced with different Au NPs/Ag NPs ratios.

4. Conclusion

Prepare a mixture of CS/PVA with a fixed ratio of both, adding different ratios of nanoparticles (Au NPs/Ag NPs). Where brown colors appeared and tended to red in all samples according to the different proportions of adding nanoparticles in the mixture. It was found through the tensile technique that the value of stress and elongation decreased due to the presence of nanoparticles in the polymer matrix. In addition to a decrease in Young's modulus. The highest value of the Young's coefficient was for the (50% Au NPs and 50% Ag NPs) sample C in the figure. It is clear from this test that the higher the percentage of silver particles in the composite, the lower the Young's coefficient and tune $0.82 \mu\text{m}$. As for the peaks in the examination (FTIR) their strength the effect of adding nanoparticles, which led to a decrease in some aggregates and an increase in others.

Ethical approval

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Authors Contributions

All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

Availability of data and materials

The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interests

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] S. A. Maykhan and A. F. Mkhair. "Theoretical study for the calculation of some attenuation parameters of polymeric composites.". *AIP Conference Proceedings*, , 2019.
- [2] M. A. S. Mohammed and A. S. Saleh. "Study the effect of temperature on structural, mechanical and thermal properties of PVC/CaCO₃ composite.". *Iraqi J. Sci.*, **54**:44–56, 2018.
- [3] K. Ibrahim, M. M. Rahman, H. Taha, E. Mohammad-

- pour, Z. Zhou, C. Y. Yin, A. Nikoloski, and Z. T. Jiang. "Structural, morphological, and optical characterizations of Mo, CrN and Mo: CrN sputtered coatings for potential solar selective applications." *Appl. Surf. Sci.*, **440**:1001–1010, 2018.
- [4] R. Fadhil and S. H. Mahdi. "Effect of pistachio husks powder additive on unsaturated polyester composites." *Ibn AL-Haitham J. Pure Appl. Sci.*, **36**:191–200, 2023.
- [5] A. I. Khadim, D. H. Badrri, and Z. S. Abdul-Ridha. "The effect Of phoenix dactylifera L. Pinnae reinforcement on the mechanical and thermal properties of polymer composite." *J. Coll. basic Educ.*, **25**:339–351, 2019.
- [6] S. A. Ebrahiem, F. M. Hady, M. K. Jassim, and H. M. Tawfeek. "Simulation study of sputtering yield of Zn target bombarded by xenon ions." *Ibn AL-Haitham J. Pure Appl. Sci.*, **29**:104–114, 2017.
- [7] N. A. Mohammed and S. A. Ebrahiem. "Study of lung cancer hazard due to radiate radon gas for two factories in industrial region (Shaikh Omar) of Baghdad Governorate." *Ibn AL-Haitham J. Pure Appl. Sci.*, **33**:27–33, 2020.
- [8] S. A. Abbas, S. H. Salman, S. A. Ebrahiem, and H. M. Tawfeek. "Investigation of the nuclear structure of some ni and zn isotopes with Skyrme-Hartree-Fock interaction." *Baghdad Sci. J.*, **19**:914, 2022.
- [9] I. H. Khudayer. "Fabrication of AgInSe₂ heterojunction solar cell." *AIP Conference Proceedings*, , 2018.
- [10] L. A. Mohammed and K. A. Jasim. "Effect of nickel substitution on structural and electrical properties of Hg_{0.5}Pb_{0.5}Ba₂Ca₂Cu_{3-y}NiyO_{8+δ} superconductor composite." *Journal of Physics: Conference Series*, *IOP Publishing*, **100**:12047, 2019.
- [11] Z. A. Abbas and S. H. Aleabi. "Studying some of mechanical properties (tensile, impact, hardness) and thermal conductivity of polymer blend reinforce by magnesium oxide." *AIP Conference Proceedings*, , 2019.
- [12] H. S. Mahmood and N. F. Habubi. "Structural, mechanical and magnetic properties of PVA-PVP: iron oxide nanocomposite." *Appl. Phys. A Mater. Sci. Process.*, **128**:1–6, 2022. DOI: <https://doi.org/10.1007/s00339-022-06107-6>.
- [13] H. S. Mahmood and M. K. Jawad. "Investigation of chitosan/PEO reinforced with Ag NPs for antibacterial activity prepared by solution casting method." *Ann. Trop. Med. Public Heal*, **22**:70–82, 2019.
- [14] H. R. Kttafah and A. I. Khadim. "The effect of dates palm trunk particles as improvement reinforcement material of polymeric composites and sustainable environmental material." *AIP Conference Proceedings*, :20095, 2019.
- [15] Z. W. Ahmed, A. I. Khadim, and A. H. R. ALSarraf. "The effect of doping with some rare earth oxides on electrical features of ZnO varistor." *Energy Procedia*, **157**:909–917, 2019.
- [16] F. K. Arhan, M. A. Thejeel, and S. H. Mahdi. "Preparation and investigation of the structural and mechanical properties of Nanobiomaterial zircFonolite." *Solid State Technol.*, **63**:1949–1961, 2020.
- [17] S. H. Mahdie. "Preparation of unsaturated polyester/nano ceramic composite and study electric, thermal and mechanical properties." *Iraqi J. Phys.*, **15**:188–201, 2017.
- [18] R. Mohammadinejad, S. Pourseyedi, A. Baghizadeh, S. Ranjbar, and G. A. Mansoori. "Synthesis of silver nanoparticles using Silybum marianum seed extract." *Int. J. Nanosci. Nanotechnol.*, **9**:221–226, 2013.
- [19] H. Niragire, T. G. Kebede, S. Dube, M. Maaza, and M. M. Nindi. "Chitosan-based electrospun nanofibers mat for the removal of acidic drugs from influent and effluent." *Chem. Eng. Commun.*, :1–23, 2022.
- [20] A. F. Gouveia, R. A. Roca, N. G. Macedo, L. S. Cavalcante, E. Longo, M. A. San-Miguel, A. Altomare, et al. "Ag₂WO₄ as a multifunctional material: Fundamentals and progress of an extraordinarily versatile semiconductor." *J. Mater. Res. Technol.*, **21**:4023–4051, 2022. DOI: <https://doi.org/10.1016/j.jmrt.2022.11.011>.
- [21] A. Zahir, Z. Aslam, M. S. Kamal, W. Ahmad, A. Abbas, and R. A. Shawabkeh. "Development of novel cross-linked chitosan for the removal of anionic Congo red dye." *J. Mol. Liq.*, **244**:211–218, 2017.
- [22] S. Mohan, O. S. Oluwafemi, S. C. George, V. P. Jayachandran, F. B. Lewu, S. P. Songca, N. Kalarikkal, et al. "Completely green synthesis of dextrose reduced silver nanoparticles, its antimicrobial and sensing properties." *Carbohydr. Polym.*, **106**:469–474, 2014.
- [23] L. T. A. K. Al-Aish. "Analysis and study of the effect of atmospheric turbulence on laser weapon in Iraq." *Baghdad Sci. J.*, **14**:427, 2017.
- [24] I. Younes and M. Rinaudo. "Chitin and chitosan preparation from marine sources. Structure, properties and applications." *Mar. Drugs*, **13**:1133–1174, 2015.
- [25] R. H. Athab and B. H. Hussein. "Growth and characterization of vacuum annealing AgCuInSe₂ thin film." *Ibn AL-Haitham J. Pure Appl. Sci.*, **35**:45–54, 2022.
- [26] S. M. Riyadh, K. D. Khalil, and A. H. Bashal. "Structural properties and catalytic activity of binary poly (Vinyl alcohol)/Al₂O₃ nanocomposite film for synthesis of thiazoles." *Catalysts*, **10**, 2020. DOI: <https://doi.org/10.3390/catal10010100>.

- [27] M. Zahid, A. Rashid, S. Akram, Z. A. Rehan, and W. Razzaq. "A comprehensive review on polymeric nano-composite membranes for water treatment." *J. Membr. Sci. Technol*, **8**:1–20, 2018.
- [28] A. Balde, S.-K. Kim, and N. R. Abdul. "Crab (*Charybdis natator*) exoskeleton derived chitosan nanoparticles for the in vivo delivery of poorly water-soluble drug: Ibuprofen. ". *Int. J. Biol. Macromol.*, **212**:283–293, 2022.
- [29] A. Sajjad, H. Sajjad, S. Hanif, F. Rasheed, and M. Zia. "Fabrication and characterization of wheat-gluten/hematite nanocomposite film with antibacterial and antioxidant properties for biological applications. ". *Biomass Convers. Biorefinery*, :1–13, 2023.