Article

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Polymeric Chitosan/Poly (Vinyl Alcohol) Hybrid Doped with Zinc Oxide Nanoparticles Synthesized and Characterized Using the Electrospun Method

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بوليمر شيتوزان / بولي (كحول فينيل) مع جزيئات نانوية من أكسيد الزنك تم تصنيعها وتوصيفها باستخدام طريقة الغزل الكهربائي

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ABSTRACT

Background:

Because of their portability and flexibility in altering surface properties, nanofibers have attracted more attention in recent years, particularly in biological applications. The development of affordable antibacterial base agents for wound healing capabilities and other medical technologies is still in high demand. Porosity, ease of forming into different sizes, and high surface area are just a few of the benefits of nanofibers.

Materials and Methods:

A 90% deacetylated (average 200,000 MW) poly(vinyl alcohol) chitosan with a life of 72000 MW was bought.

Results:

Through the samples of the electronic scanner, electrospinning rates, flow of 0.6 ml / sec, voltage of 10 kV, distance between the collector and the needle of 8 cm, and the ratio of PVA / CS / ZnO to the polymer with the addition of nanoparticles ratio 0.4% 65 / 35.

Conclusion:

In this study, the nanofiber compound PVA / CS / ZnO proved to have medical and biological compatibility. There is no toxicity in this compound. It has therapeutic properties against microbes and is good in healing wounds, as in previous studies.

Key words:

polymer blends, Nanofibers, Nanotechnology, Nanocomposite

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INTRODUCTION

Because of their portability and flexibility in altering surface properties, nanofibers have attracted more attention in recent years, particularly in biological applications [1],[2]. This topic takes into account the creation of environmentally friendly materials that can suit medicinal goals such as improving antibacterial activity, cell migration and proliferation, and permeability to both water and oxygen, without modifying or negatively affecting the mechanical properties[3],[4],[5]. Intriguing benefits that set chitosan apart from other polymers include its capacity to adhere to negatively charged surfaces like mucous membranes and gels, as well as its antibacterial and wound-healing characteristics [6]. Chitosan is employed in the pharmaceutical industry and its preparations. Chitosan is a natural and renewable polymer characterized by unique properties, including degradability and biocompatibility, and it is non-toxic. It can interact with proteins, amino acids, metal ions, and other features [7],[8]. This polymer is chitosan which has many natural Chitosan, and one of its properties is also that it is characterized by being antibacterial, germs and viruses [9],[10],[11]. Chitosan in general is subject to antibacterial activity, temperature, degree of deacetylation, and pH of the solution [12],[13],[14]. PVA is characterized by its solubility in water and its high ability to form nanofibers, as well as its ability to biodegrade, [15]. When mixing PVA polymer, it enhances mechanical and thermal stability [16]. ZnO due to the broad activity that characterizes these nanoparticles in medical and biological applications has many properties, including non-toxic and antibacterial [17]. Chitosan and chitosan derivatives play a vital role in antimicrobial activities. adhesion to the negatively charged cell surface and the positive charge of (CS and ZnO) due to electrostatic interactions [18],[19],[20]. The electrical insulation process remains, thanks to an electric force, on the liquid polymer with a high viscosity. The voltage that is applied to the polymer solution ranges from 5 to 50 kilovolts. In the beginning, the viscosity of the polymer solution and the basic viscosity is observed in the formation of nanofibers, after that, the surface tension is observed on the drop leaving the needle, taking into account The parameters of the device are the distance between the collected needles, the diameter of the needle and the flow rate. These parameters are the basic parameters in forming the final nanofibers [21], [22]. The CS/PVA/ZnO nanocomposite was prepared by preparing a mixture of CS/PVA through the process of intermolecular hydrogen bonding and the aggregation of hydrophobic side chains. Then the ZnO nanoparticles were added to the CS/PVA. Among the important characteristics that distinguish it, nanoparticles and chitosan can be used as adsorbents due to their environmental friendliness, effective nature, and easy modification by chemical reaction [23],[24],[25]. Our study aims in this research to examine this CS / PVA / ZnO fiber nanocomposite And the extent of its interaction in terms of inhibiting bacteria, eliminating germs, and aiding in wound healing. This substance is more efficient in medical and biological applications through X-ray diffraction (XRD), spectroscopy (FTIR) and SEM.

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MATERIALS AND METHODS

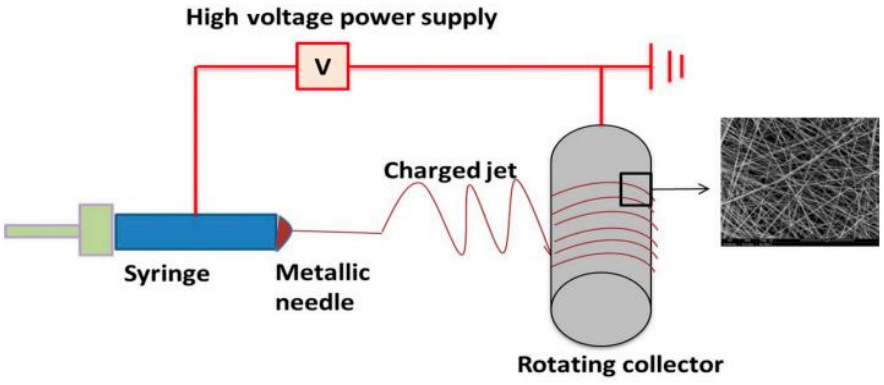
A 90% deacetylated (average 200,000 MW) poly(vinyl alcohol) chitosan with a life of 72000 MW was bought. The local market in Baghdad supplied analytical-grade chemicals and reagents for all applications. Zn, HNO3, and HCl (Ac2). In addition, the University of Baghdad's College of Science donated 2H2O, glacial acetic acid, and NaOH.

Electrospun PVA/CS/ZnO nanofiber synthesis and fabrication.

Initially, 2% by weight of the CS solution was dissolved in acetic acid and 7% by weight of PVA was dissolved in distilled water at an 80 °C temperature for 3 hours with magnetic stirring. The solutions are well-prepared to make electrospinning straightforward . as the Table demonstrates, distinct. 1. To determine the desired CS/PVA ratio, ZnO was dissolved separately from the polymers. CS was then added, along with 30 mL of a 3- weight percent glacial acetic acid solution. A pure fibre PVA (7 weight percent) duplicate of these cases was created for comparison. Processes for electrospinning are shown in figure (1).

Table-1:Polymers used in proportions and electrospinning processes in the formation of nanofibers and their fibers

CS/PVA (v/v) nanofiber	Flow rate (ml/h)	Voltage (kV)	collector distance (cm)
75:25	0.6	10	8
65:35	0.6	10	8
50:50	0.6	10	8
25:75	0.6	10	8
35:65	0.6	10	8



Figure(1):Electrospinning system with a rotating collector shown schematically

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Surface morphological analysis.

To examine the surface morphologies, a field emission electron scanner (FESEM, SIGMAVP, Carl Zeiss, Germany) was employed. Most of the shapes have a thin layer of gold-palladium (SC7620, Emitech) plating in a vacuum depression, according to a SEM test.

Diffraction of X-rays.

For the measured structural analysis by X-ray diffraction of the samples in an X-ray diffract meter, Bruker D8 Advance, the voltage is 42 kV, the current used is 42 mA and the radiation Cu Ka (l ¼ 1.5406 a).

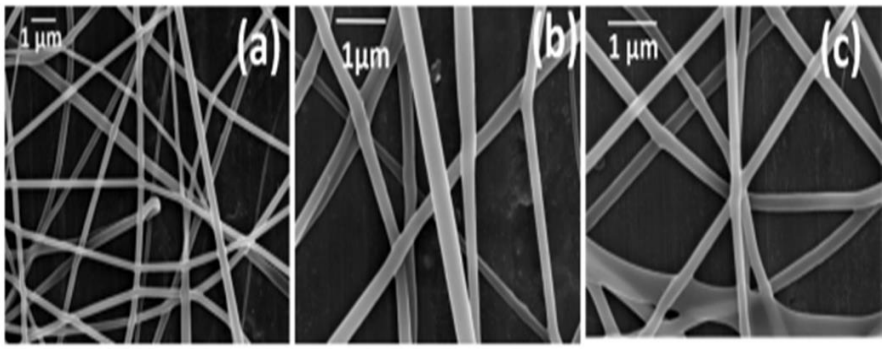
IR spectroscopy with Fourier transforms.

Nanofibers and chemical composition of CS/PVA/ZnO mats were diagnosed by spectroscopy (IRPrestige21, Shimadzu Corporation, Japan). Spectra Samples were recorded in the range of 500 -4000 cm^{-1} .

RESULTS AND DISCUSSION

1.SEM

Through the samples of the electronic scanner, electrospinning rates, flow of 0.6 ml / sec, voltage of 10 kV, distance between the collector and the needle of 8 cm, and the ratio of PVA / CS / ZnO to the polymer with the addition of nanoparticles ratio 0.4% 65 / 35. figure (2). shows the morphologies of the fibrous composite Electrospun nanocomposites. Having a uniform diameter of 128±322 nm and a smooth surface, nanofibers appear to have these characteristics. The interactions between ZnO and CS create a hybrid molecule that enhances the hydrogen bonds between the hydroxymethyl groups in CS and the amine while also making it easier to reach the hydroxyl groups in PVA[26]



Figure(2):PVA, CS, and ZnO nanofibers in SEM images

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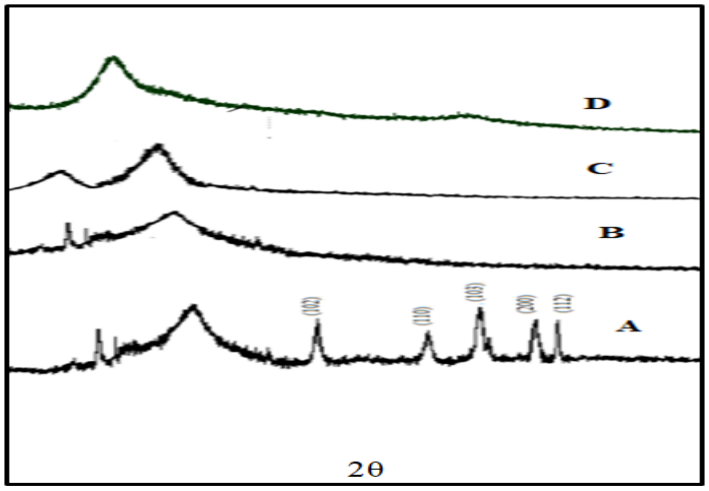
XRD analysis

Concerning the XRD spectrum, we notice the appearance of sharp peaks in the PVA / CS / ZnO nanofiber composite as shown in figure(3A), due to the ZnO nanoparticles that have a good crystalline nature ((102), (110), (103), (200) and (112)). We note the appearance of a low peak in the nanocomposite formed from CS / PVA polymers, appearing at 2θ = 19.7, as shown in Fig. 3B. We also note the appearance of two peaks in the fibers formed from pure CS at 2θ = 10 and 20, as shown in Figure (3C). We also notice the appearance of a peak in the pure PVA matrix 2θ = 19.4 as in figure(3D).

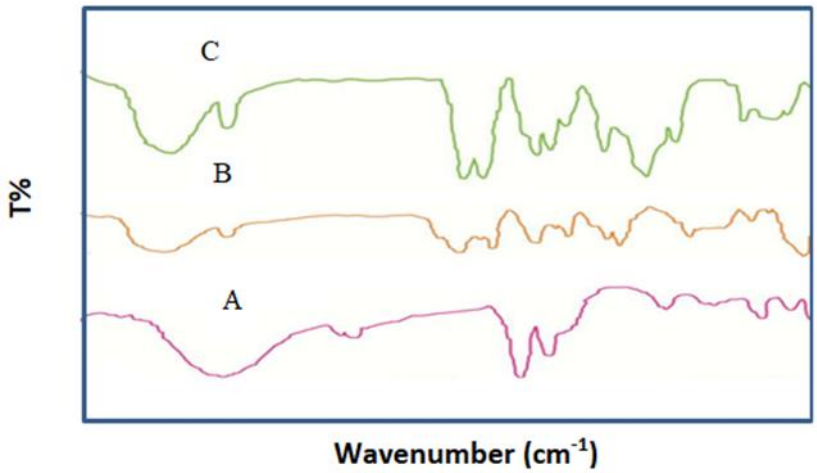


Figure(3):XRD spectrum of A=ZnO/CS/PVA nanofiber composite samples, B= CS/PVA and pure natural polymer C= CS, also pure D=PVA.

FT-IR analysis.

The CS/PVA/ZnO nanofiber composite in figure (A4) showed that most of the properties of the apparent peaks of CS, PVA, and ZnO were exposed to some minor changes from these peaks of the amino and hydroxyl groups of CS, according to the FTIR spectral test. Due to the presence of ZnO nanoparticles, the formation of peaks at 1596, 1404 and 453 cm^{-1} peaks suggests the presence of CS/PVA/ZnO. The appearance of peaks between 520 and 750 cm^{-1} is another proof of the extremely evident vibration and expansion of the ZnO expansion, and this shows that the nanoparticles are present and thoroughly mixed with the polymers. A broad and distinct band from 3100 to 3500 cm^{-1} that appears as peaks at CS/PVA figure(4B) indicates the presence of -OH from potential overlapped -NH vibrations of amide and amine. As further evidence of vibration and

bending at -OH and -NH, we also detect the appearance of peaks at 1642 and 1577 cm^{-1}. The presence of C-O - vibrational expansion is indicated by the PVA/CS and the emergence of a peak at 1085 cm^{-1}. Additionally, in pure chitosan [27] figure (4C), the emergence of a peak at 3443cm^{-1} indicates the presence of vibrational expansion to -OH groups. Indicators of NH2 and CH group expansion can be seen at 2924 cm^{-1}, and a peak can be seen at 1652 cm^{-1}, indicating the presence of secondary amide expansion



Figure(4): shows the FTIR spectra

CONCLUSION

In this study, the nanofiber compound PVA / CS / ZnO proved to have medical and biological compatibility. There is no toxicity in this compound. It has therapeutic properties against microbes and is good in healing wounds, as in previous studies. Through X-ray diffraction, FTIR and SEM analysis.

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Conflict of interests

There are non-conflicts of interest.

References

[1] K. Kalantari, A.M. Afifi, H. Jahangirian, and T.J. Webster, "Biomedical applications of chitosan electrospun nanofibers as a green polymer–Review. Carbohydrate polymers, vol.20,no.7, pp.588-600.2019.doi.org/10.1016/j.carbpol.2018.12.011.

[2] A. N. Erfan, A.M. Nasser, Barakat, and J.M. Barbara. "Preparation and characterization of ß-lactoglobulin/poly (ethylene oxide) magnetic nanofibers for biomedical applications." Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol.57,no.6, pp.63-72.2019. doi.org/10.1016/j.colsurfa.2019.05.035.

[3] Q.S. Kahdim, N. Abdelmoula, H. Al-Karagoly, S. Albukhaty, and J. Al-Saaidi, Fabrication of a polycaprolactone/Chitosan nanofibrous scaffold loaded with nigella sativa extract for biomedical applications. BioTech,vol. 12,no.1, pp.19. 2023.doi.org/10.3390/biotech12010019.

[4] M. Liu, X.P. Duan, Y.M. Li, D.P. Yang, and Y.Z. Long,"Electrospun nanofibers for wound healing." Materials Science and Engineering,vol.7,no.6, pp.1413-1423.2017.doi.org/10.1016/j.msec.2017.03.034.

[5] Y.Wang, J. Qian, T. Liu, W. Xu, N. Zhao, and A. Suo, "Electrospun PBLG/PLA nanofiber membrane for constructing in vitro 3D model of melanoma." Materials Science and Engineering,vol.7,no.6, pp.313-318.2017. doi.org/10.1016/j.msec.2017.03.098.

[6] S. Rimdusit, K. Somsaeng, P. Kewsuwan, C. Jubsilp, and S. Tiptipakorn, "Comparison of gamma radiation crosslinking and chemical crosslinking on properties of methylcellulose hydrogel." Engineering Journal, 16,no.4, pp.15-28.2012doi: https://doi.org/10.4186/ej.2012.16.4.15

[7] A.C. Chao, S.S. Shyu, Y.C. Lin, and F.L. Mi, F.L.,"Enzymatic grafting of carboxyl groups on to chitosan—to confer on chitosan the property of a cationic dye adsorbent Bioresource technology, vol.91,no.2, pp.157-162.2014. doi.org/10.1016/S0960-8524(03)00171-8.

[8] N.R. Sudarshan, D. G. Hoover, and D. Knorr. "Antibacterial action of chitosan." Food biotechnology, vol.6,no.3, pp.257-272.1992. doi.org/10.1080/08905439209549838.

[9] S. Kahdim, N. Abdelmoula, H. Al-Karagoly, S. Albukhaty, and J. Al-Saaidi, Fabrication of a polycaprolactone/Chitosan nanofibrous scaffold loaded with nigella sativa extract for biomedical applications. BioTech, vol.12,no.1, pp.19. 2023.doi.org/10.3390/biotech12010019.

[10] S.G. Hu, C.H. Jou, and M.C. Yang. "Biocompatibility and antibacterial activity of chitosan and collagen immobilized poly (3-hydroxybutyric acid-co-3-hydroxyvaleric acid)." Carbohydrate polymers, vol.58,no.2, pp.173-179.2004. doi.org/10.1016/j.carbpol.2004.06.039.

[11] S.A.A. Alsaati, Q.S. Kadhim, M.H. Rashid, M.H. and T.M.J. Abd UlKadhim, 2021. Hydrodynamics and Warmth Trade in Cycles of Cooling of an Attractive Plate in an Attractive Fluid in the Attractive Field. NeuroQuantology, vol.19,no.11, pp.32. doi:10.14704/nq.2021.19.11.NQ21173.

[12] X.Fei Liu, Y. Lin Guan, D. Zhi Yang, Z. Li, and K. De Yao, "Antibacterial action of chitosan and carboxymethylated chitosan." Journal of applied polymer science ,vol.79,no.7, pp. 1324-1335. 2021.doi.org/10.1002/1097-4628(20010214)79:7<1324::AID-APP210>3.0.CO;2-L.

[13] G.J. Tsai, and S.W. Huey "Antibacterial activity of shrimp chitosan against Escherichia coli." Journal of food protection ,vol.62,no.3, pp. 239-243.1999. doi.org/10.4315/0362-028X-62.3.239.

[14] D.J. Sanchez-Alvarado, J. Guzmán-Pantoja, U. Páramo-García, A. Maciel-Cerda, R.D. Martínez-Orozco, and R. Vera-Graziano, "Morphological study of Chitosan/Poly (vinyl alcohol) nanofibers prepared by electrospinning, collected on reticulated vitreous carbon." International journal of molecular sciences, vol.19,no.6,pp. 1718.2018.doi.org/10.3390/ijms19061718.

[15] A.M. Ahmed, Q.S. Kadhim, and I.A. Ali, 2021. The Debye Method is Used to Create 3D Structure Models of Electroactively Transformed Microcrystalline Cellulose. NeuroQuantology, vol.19,no.6, pp.1.2021. doi: 10.14704/nq.2021.19.6.NQ21059.

[16] Y. Liu, and K. Hyung, "Characterization and antibacterial properties of genipin-crosslinked chitosan/poly (ethylene glycol)/ZnO/Ag nanocomposites." Carbohydrate polymers, vol.89,no.1,pp. 111-116.2012. doi.org/10.1016/j.carbpol.2012.02.058.

[17] W.L. Du, S.S. Niu, Y.L. Xu, Z.R. Xu, and C.L. Fan, "Antibacterial activity of chitosan tripolyphosphate nanoparticles loaded with various metal ions." Carbohydrate polymers,vol.75,no.3 (2009),pp. 385-389.2009.doi.org/10.1016/j.carbpol.2008.07.039.

[18] Y. Gutha, J.L. Pathak, W. Zhang, Y. Zhang, and X. Jiao, "Antibacterial and wound healing properties of chitosan/poly (vinyl alcohol)/zinc oxide beads (CS/PVA/ZnO)." International journal of biological macromolecules, vol.10,no.3 ,pp. 234-241.2017 doi.org/10.1016/j.ijbiomac.2017.05.020.

[19] W.L. Du, Y.L. Xu, Z.R. Xu, and C.L. Fan, "Preparation, characterization and antibacterial properties against E. coli K88 of chitosan nanoparticle loaded copper ions." Nanotechnology, vol.19,no.8 ,pp. 085707.2008. doi:10.1088/0957-4484/19/8/085707.

[20] S. Chakraborty, I.C. Liao, A. Adler, and K.W. Leong, "Electrohydrodynamics: A facile technique to fabricate drug delivery systems." Advanced drug delivery reviews ,vol.61,no.12 ,pp.1043-1054.2009. doi.org/10.1016/j.addr.2009.07.013

[21] T.H. Rodríguez, M. Graciela, and G. Daniel, "Comprehensive review on electrospinning techniques as versatile approaches toward antimicrobial biopolymeric composite fibers." Materials Science and Engineering: vol.10,no.1,pp.306-322.2009. doi.org/10.1016/j.msec.2019.03.099.

[22] V.K. Gupta, M.L. Yola, T. Eren, F. Kartal, M.O. Çağlayan, and N. Atar, "Catalytic activity of Fe@ Ag nanoparticle involved calcium alginate beads for the reduction of nitrophenols." Journal of Molecular Liquids ,vol.1,no.90, pp. 133-138.2014 doi.org/10.1016/j.molliq.2013.10.022.

[23] V.K. Gupta, N. Atar, M.L. Yola, C. Darcan, Ö. İdil, and Z. Üstündağ, "Biosynthesis of silver nanoparticles using chitosan immobilized Bacillus cereus: nanocatalytic studies." Journal of Molecular Liquids ,vol.18,no.8 pp.81-88, 2013. doi.org/10.1016/j.molliq.2013.09.021.

[24] A.L. Alfalluji, and F.O. Essa, 2023.Microcapsules of Protein-Polysaccharide Complexes Produced on a Variety of Matrices .Journal of Medicinal and Chemical Sciences, vol. 6,no.9, pp. 2228–2233.2.23. doi.org/10.26655/JMCHEMSCI.2023.9.27..

[25] L. Altomare, I. Bonetti, C.E. Campiglio, L. De Nardo, L. Draghi, F. Tana, and S. Farè, "Biopolymer-based strategies in the design of smart medical devices and artificial organs." The International Journal of Artificial Organs ,vol.41,no.6, pp. 337-359.2018 doi.org/10.1177/0391398818765323.

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[26] S. Agarwal, H. Sadegh, M. Monajjemi, A.S. Hamdy, G.A. Ali, A.O. Memar, "Efficient removal of toxic bromothymol blue and methylene blue from wastewater by polyvinyl alcohol." Journal of Molecular Liquids, vol. 21,no.8, pp. 191-197.2016. doi.org/10.1016/j.molliq.2016.02.060.

[27] X. Jiao, Y. Gutha, and W. Zhang, "Application of chitosan/poly (vinyl alcohol)/CuO (CS/PVA/CuO) beads as an adsorbent material for the removal of Pb (II) from aqueous environment." Colloids and Surfaces B: Biointerfaces ,vol.14,no.9, pp. 184-195.2017. doi.org/10.1016/j.colsurfb.2016.10.024.

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الخلاصة

المقدمة:

بسبب قابليتها للنقل والمرونة في تغيير خصائص السطح، جذبت الألياف النانوية المزيد من الاهتمام في السنوات الأخيرة، وخاصة في التطبيقات البيولوجية. لا يزال الطلب مرتفعًا على تطوير عوامل أساسية مضادة للجراثيم وبأسعار معقولة لقدرات التئام الجروح والتقنيات الطبية الأخرى. المسامية، وسهولة التشكيل في أحجام مختلفة، ومساحة السطح العالية ليست سوى عدد قليل من فوائد الألياف النانوية.

طرق العمل:

تم شراء شيتوزان بولي (كحول فينيل) منزوع الأسيتيل بنسبة 90٪ (متوسط MW 200000) بعمر MW 72000.

النتائج :

من خلال عينات الماسح الإلكتروني معدلات الغزل الكهربائي تدفق 0.6 مل / ثانية والجهد 10 كيلو فولت والمسافة بين المجمع والإبرة 8 سم ونسبة PVA / CS / ZnO إلى البوليمر مع إضافة نسبة الجسيمات النانوية 0.4% 65 / 35.

الاستنتاجات:

من خلال عينات الماسح الإلكتروني ، ومعدلات الغزل الكهربائي ، وتدفق 0.6 مل / ثانية ، والجهد 10 كيلو فولت ، والمسافة بين المجمع والإبرة 8 سم ، ونسبة PVA / CS / ZnO إلى البوليمر مع إضافة نسبة الجسيمات النانوية 0.4٪ 35/65.

الكلمات المفتاحية:

مزيج البوليمر ، الألياف النانوية ، تقنية النانو ، مركب النانو