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Preparation and characterization of CH/PVA/ZnO-FA nanocomposite

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ABSTRACT

Herein the Chitosan (CH) / Polyvinyl Alcohol (PVA) polymers were added to the ZnO nanoparticles and the folic acid drug (FA). The synthesized sample boasts great potential for application in controlled and targeted drug delivery. The sample was characterized using Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible Spectroscopy and thermal analysis by Differential Scanning Calorimetry (DSC) to identify the structural and morphological changes along with thermal transition and Scanning Electron Microscopy Energy Dispersing X-ray Spectroscopy SEM / EDX. The results exhibit that the samples have sufficient stability and there was mostly no interaction between drug-nanoparticles and polymers that took place.

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1. Introduction

Nanocomposites are made by loading nanoparticles such as metal or metal oxide nanoparticles on polymer substrates. Recent scientific advancements in nanotechnology have been assimilated into all aspects of life, industrial, agriculture and medicine [1]. This study was directed to formulate an improvement of drug delivery system using a polymer nanoparticle composite that can selectively target defective cells without affecting healthy cells. Research forwards the insight that co-processing natural polymers with synthetic polymers will result in a copolymer with the advantages of both polymers combined. Chitosan (CH) is used for its high biocompatibility, nontoxicity, nature and its ability to combine with other polymers and its ability to combine with other natural polymers. Its uses for encapsulating suitable entities of protecting conjugated quantum dots quantum composite material properties [2]. Polyvinyl Alcohol (PVA) is a water solvent, nontoxic, synthetic polymer which has good chemical, physical and mechanical properties, while capable of combining with other natural polymers and by using a synthetic polymer combined with a natural polymer allows the modified polymer to obtain desirable properties to overcome lesser properties [3]. Important components such as, Zn, Cu and Fe are trace metals [4]. Zinc quantum dots absorb energy near

infrared reign therefore, it has potential therapeutic applications. This fact was suggested in photon physical studies [5]. The inorganic nanoparticle materials are displayed in the polymer medium to enhance the material such as, performances physical and chemical characterization. Among the various inorganic nanoparticles, ZnO nanoparticles could improve the properties of polymer matrix, prepare (ZnO / polymers) with nanocomposites are necessary to prevent the formation of agglomerated nanoparticles [6]. Recently, the biological efficacy of ZnO nanoparticles were extensively examined [7] and there were a few studies that had shown Chitosan preparation PVA / ZnO nanoparticles [8]. One of the main problems associated with cancer therapy is its unwanted side effects towards normal cells along with cancer cells. Further investigation has shown the improvement of the therapeutic efficacy of drugs and reduced side effects [9]. Certain types of cancer cells are known to over express folic acid receptors as they require folic acid for their function [10]. In this study synthesis (CH/PVA), (CH/PVA/ZnO), (CH/PVA/ZnO-FA) sample and their characterization to serve as a viable component of drug.

2. Materials and methods

Polyvinyl Alcohol (PVA) polymers and ZnO nanoparticles 20–30 nm were purchased from Sigma-Aldrich and used as received. The FT-IR spectra recorded IR spectra (KBr discs) on a JASCO FT/IR 4200, with a wavenumber range of 400–4000 cm⁻¹.

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Differential scanning calorimetric (DSC), measures the physical nature of the sample, were made for the, all Samples prepared within temperatures (0–200) °C. The absorption spectra were measured in the range of 200–1100 nm for 10^{-3} by using UV-Visible spectrophotometer type Shimadzu UV-160A, available at the Polymer Research Centre, at the University of Basrah, Iraq. The FESEM images, and EXD analysis were obtained using Leo-Supra 50VP (Carl Zeiss, Germany) equipped with EXD system.

2.1. Chitosan extraction

Chitosan was extracted from shrimp shells according to the method used in [11].

2.2. Preparation of hydrogel polymers for standard chitosan

Chitosan is chemically intertwined to prepare polymers, in general meaning that it forms many bonds. Whereby (80 mg/ml) of the cross-agent (Glutaraldehyde) is added to the solution consisting of (2% weight/volume) of Chitosan dissolved in 0.1 M acetic acid. Next, added to it were a few drops of 0.1 Molar of NaOH to neutralize the solution, ensuring the acidity by using litmus paper, then the mixture is left for a period of (15 min) until the polymer is formed, then the mixture is filtered and the sediment is washed several times in distilled water and left to dry [12].

2.3. Sample Chitosan/ Poly (Vinyl alcohol)/PVA/ZnO-FA

Polymer blend film was synthesized according to the following procedure: Equal weight of CH / PVA and ZnO (1:1:1) weight ratio% which dissolved in 0.1 acetic acid aqueous solution with the continuous stirrer. The two solutions were then mixed. The mixture was stirred at high speed and constant temperature of 30 °C and after adding 10 mg FA into the solution [13].

3. Results and discussion

3.1. FT-IR studies

The Fourier Transform Infrared Spectra scope techniques are one of the most powerful analytical techniques which provide useful information about the characteristic band for the function group. Moreover, FT-IR provides a very fast method to identify chemical structures especially those of the organic ones. FT-IR spectra were recorded for the Chitosan / Polyvinyl Alcohol, Chitosan / Polyvinyl Alcohol / Zinc Oxide nanocomposites and Zinc Oxide / Chitosan / Polyvinyl Alcohol-FA which are shown in Fig. 1. In Fig. 1a there is evidence of an active compound link frequency in the Chitosan / Polyvinyl Alcohol blend as the active group in 3492 cm^{-1} O–H bound stretching vibrations and peaked at 2925 cm^{-1} indicated C–H stretching vibrations; the peak 1654 cm^{-1} indicated the C–H vibrations, at 1562 cm^{-1} assigned to N–H bending vibrations from both a mind group [14], peak at 1381 cm^{-1} indicated O–H vibrations and peak at 1317 cm^{-1} indicated the N–H vibrations; peak observed in the range of ($1075\text{--}1026\text{ cm}^{-1}$) are known to arise from C–O stretching vibrations [15]. In Fig. 1b shows that under the FT-IR spectra, the Chitosan / Poly Vinyl Alcohol / Zinc Oxide nanocomposites experience a shift in the peak which was detected with the N–H stretching vibrations at 3475 cm^{-1} , a slight shift of peak at 2928 cm^{-1} indicated by the C–H vibrations, the shift of peak at 1628 cm^{-1} due to the C–H vibrations, the shift of peak at 1028 cm^{-1} was observed due to the C–O stretching vibrations. By adding ZnO to the polymers blend shows a new active group in the range of ($632.213\text{--}601.1901, 477.208$) cm^{-1} whereby it reflected the presence of

Nano-ZnO vibrational groups [16]. Fig. 1c shows the FT-IR spectra of the product synthesis, where the reaction of Chitosan / Polyvinyl, ZnO nanocomposites and folic acid show peaks within a range of $3432\text{--}3000\text{ cm}^{-1}$ due to the N–H and O–H.

Shifts were observed in the Chitosan / Polyvinyl Alcohol / ZnO-FA in comparison to the Chitosan / Polyvinyl Alcohol and the Chitosan / Polyvinyl Alcohol / ZnO nanocomposites, keeping in mind that the peak at 1557 cm^{-1} exhibit C–H vibrations in a range of between 1049 cm^{-1} and 884 cm^{-1} , indicating that a change has occurred after a reaction with the folic acid. A new peak of the N–H bending vibration was observed at 1712 cm^{-1} due to addition of the N–H group from the folic acid. The peak at 1400 cm^{-1} due to the O–H range vibration was observed in the Chitosan / Polyvinyl Alcohol / ZnO-FA spectrum; this peak was observed due to the peak at 1396 cm^{-1} from the C–H vibrations which shifted from the previous C–H vibrations from the related peaks observed in Chitosan / Polyvinyl Alcohol and Chitosan / Polyvinyl Alcohol / ZnO nanocomposites at 1381 cm^{-1} and at 1377 cm^{-1} respectively; as an active group in ($667.26, 616.142, 540.123, 490.795, 459.938, 424.263$) cm^{-1} shows that these were results of adding in ZnO-FA [17].

3.2. UV-Visible spectroscopy

When light propagates through matter, it decreases the direction of wave propagation. Here, there are two types of attenuation, absorption and scattering, as both lead to a loss in the intensity of light in the direction of propagation. The loss in the power of the electromagnetic wave propagating upon absorption results from the transformation of light energy into other types of energy such as retinal vibrations (heat) through the polarization of particles in the medium; ions and electron excitation from the valance band to the conduction band [18]. The absorbance spectra were recorded at room temperature in the range of 200–900 nm as shown in Fig. 2. In that figure the absorbance spectra increased when adding (ZnO nanoparticles and folic acid) into the solution of polymer blend (Chitosan / PVA). It formed a spectrum range of (0.5–2.5 atomic/pre) in Chitosan / PVA, Chitosan / PVA / ZnO and Chitosan / PVA / ZnO-FA. The peak positioned 280–340 nm may be due to $\pi \rightarrow \pi^*$ (K-band) and $n \rightarrow \pi^*$ (R-band) electronic transitions respectively [18]. As deduced in Fig. 2, the peak located in the range of 380–430 nm was due to the adding of the ZnO-FA into the polymer blend [19].

3.3. Thermal analysis DSC

The DSC offers a good thermal analysis method for detecting changes in the physical and chemical properties of the materials as a function of temperature by measuring the heat changes absorption of heat (endothermic reaction) reaction or release of heat (exothermic reaction). Figure (CH/PVA) shows the (DSC) curve of the CH / PVA polymers where the composition exhibited a broad endothermic althat was assigned to T_g (glass transitions which were previously reported at lower positions than that of (CH) Polymers which have the broad endothermic peak at 79 °C; whereas, (PVA) polymers exhibit a smaller endothermic peak at 89 °C [20]. The smaller peak of the melting transition temperature appeared in the DSC curve of the (CH / PVA) polymers at 134.81. This endothermic peak is often termed as dehydration temperature (T_d), due to the evaporation of water associated with the hydrophilic group of the polymers [21] and is responsible for the strength of the interaction [22]. Thus, the melting depression in the CH / PVA polymers may be due to some interaction between two polymers. Figure (CH / PVA / ZnO) shows the DSC curve where ZnO nanoparticles were doped into the (CH / PVA) polymers which have a peak at 122.77 °C. This position of T_d peak shifted to lower temperatures

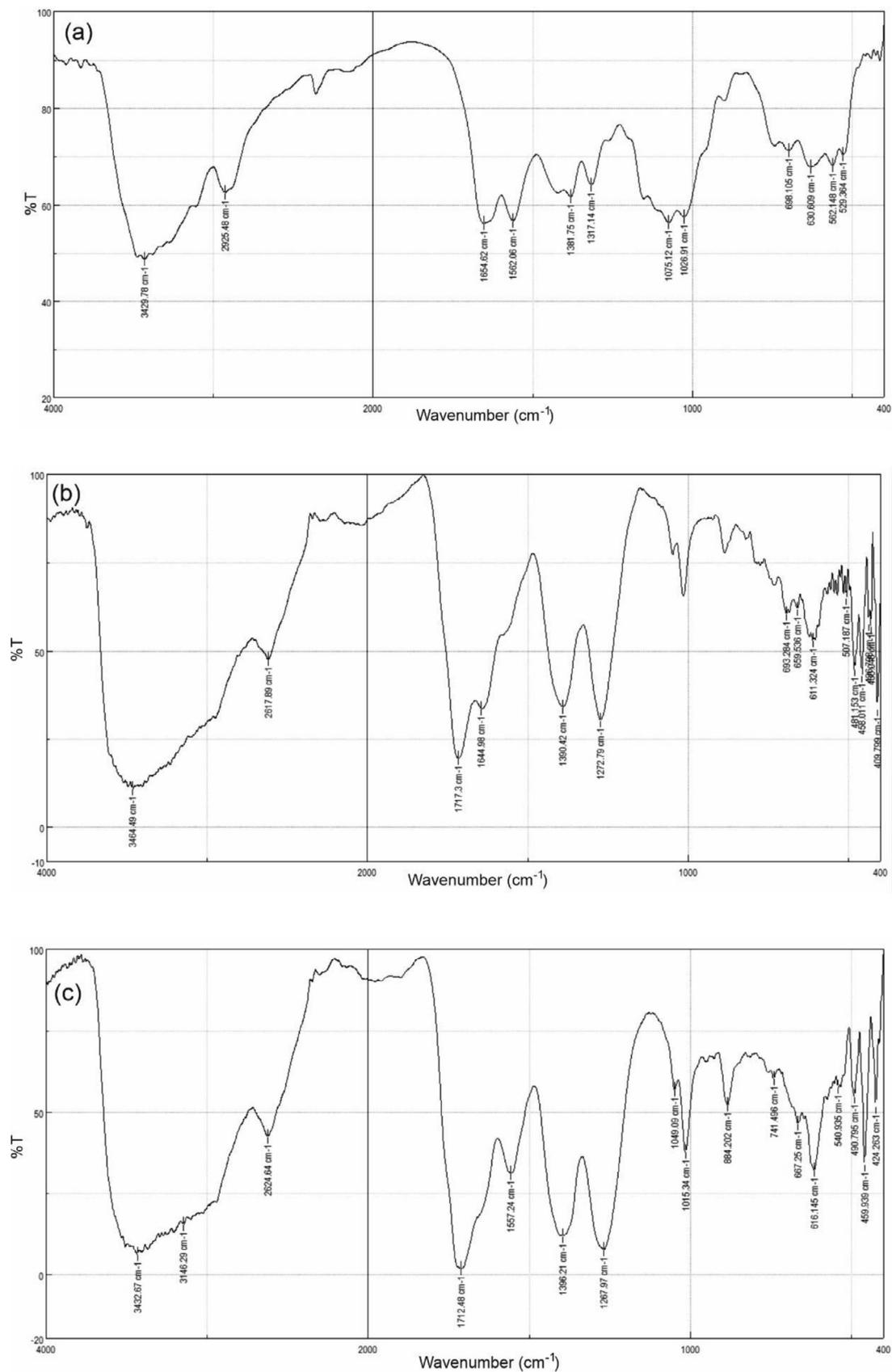


Fig. 1. The FTIR spectra of thin films, CH/PVA (a) and CH/PVA/ZnO (b) CH/PVA/ZnO-FA (c).

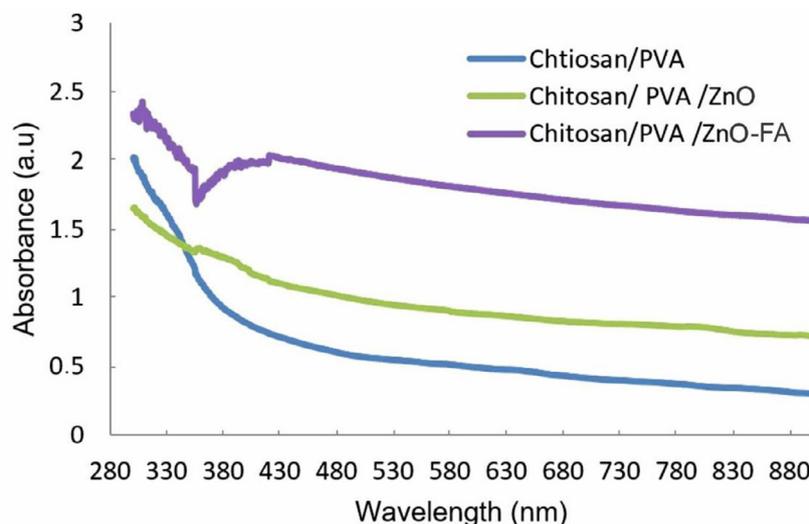


Fig. 2. The absorbance versus wavelength.

as a result of the added ZnO nanoparticles that blended into the sample, exhibiting decreased stability and weakening of the bond strength. Therefore, there are decreases in the crystallinity after the adding of the ZnO nanoparticles with the sample which reflects that addition of ZnO nanoparticles to the CH / PVA polymers sample decreases the intermolecular interaction and crosslink CH and PVA polymers. In the present case, the blend sample of the CH / PVA undoped and doped with the ZnO nanoparticles are immiscible. The DSC Thermal analysis was used to identify any possible chemical interaction between the drug and other compounds in the sample. Figure (CH / PVA / ZnO-FA) (Fig 3) shows the curve of DSC thermograms of the (CH / PVA / ZnO-FA) which have a sharp endothermic signature at 115.48 °C that was observed for the drug-loaded (CH / PVA / ZnO) sample corresponding to the melting point of malformation hydrochloride [23]. There is neither formation of a new peak signature in the DSC thermograms indicating that the drug has not undergone any chemical interaction with the other components of the sample during the process of microns capsulation [24]. Thus, DSC thermograms prove no interaction between the drug and the CH / PVA / ZnO nanoparticles.

3.4. Scanning Electron Microscopy (SEM) AND energy dispersing X-ray spectroscopy (EDX)

Scanning Electron Microscopy (SEM) images were taken at random positions of the films. The FESEM micrographs of the polymer blend was magnified by 50 Kx and 100 Kx times. Scanning Electron Microscopy (SEM) observations were carried out to get a better insight into the homogeneity and the microstructure of the blend film. SEM images of the surface of the polymer blend reveal that. The SEM image of the CH / PVA polymers sample as referenced in Fig. 4a shows that the surface is quite rough and dense in nature which provides the maximum surface area of adsorption of ZnO nanoparticles and the FA drug. The appearance of CH / PVA polymers sample is aligned with result from previous studies [25]. The SEM image of the CH / PVA / ZnO nanoparticles sample in

Fig. 4 shows the agglomeration of ZnO particles and the average diameter of ZnO nanoparticles is 69.43 nm in accordance with the previous reported studies [26]. After the reaction with folic acid, the surface of the sample bead-like structure as, shown in Fig. 4c which is that indicating a change has occurred. Further evidence for the presence of ZnO nanoparticles in Chitosan/PVA/ZnO and Chitosan/PVA/ZnO-FA sample was seen EDX studies which is represented in Tables 1–3), revealing, which reveal the presence of ZnO, O, C and N elements in composite results. While not observed in Chitosan/PVA sample show Table 1, thus, the result of Chitosan/PVA /ZnO Chitosan/PVA /ZnO-FA sample indicates that ZnO nanoparticles are encapsulated into the polymers matrix, hence can significantly improve the compactness of the polymers. However, the presence of Mg, Na and Fe element Chitosan/PVA/ZnO-FA sample as shown in Table 3, but absence in Chitosan/PVA/ZnO and Chitosan/PVA sample as shown in Tables 2 and 1 respectively, thus confirming the formation of final product.

4. Conclusion

Chitosan/ Poly Vinyl alcohol, Chitosan/ Poly Vinyl alcohol /ZnO Nano composite and Chitosan/ Poly Vinyl alcohol /ZnO -FA were successfully prepared in this work, characteristic bands of Chitosan, PVA, ZnO Nps and FA drug were identified by FTIR and UV-Vis, spectroscopy and confirming the interaction between ZnO nanoparticles and FA with Chitosan /PVA polymers matrix. FESEM observations reveal chitosan /PVA polymers are fully covered by ZnO nanoparticles and FA drug. Edx result indicates that presence of ZnO nanoparticles and FA drug in the final product the results obtained from Dsc thermal analysis shows structural and morphological changes along with thermal transition of Chitosan/ PVA, Chitosan/ Poly Vinyl alcohol /ZnO Nano composite and ZnO / Chitosan/ Poly Vinyl alcohol/ZnO -FA, sample have sufficient stability.

The results indicates that the synthesized sample having a great potential for application in drug delivery system.

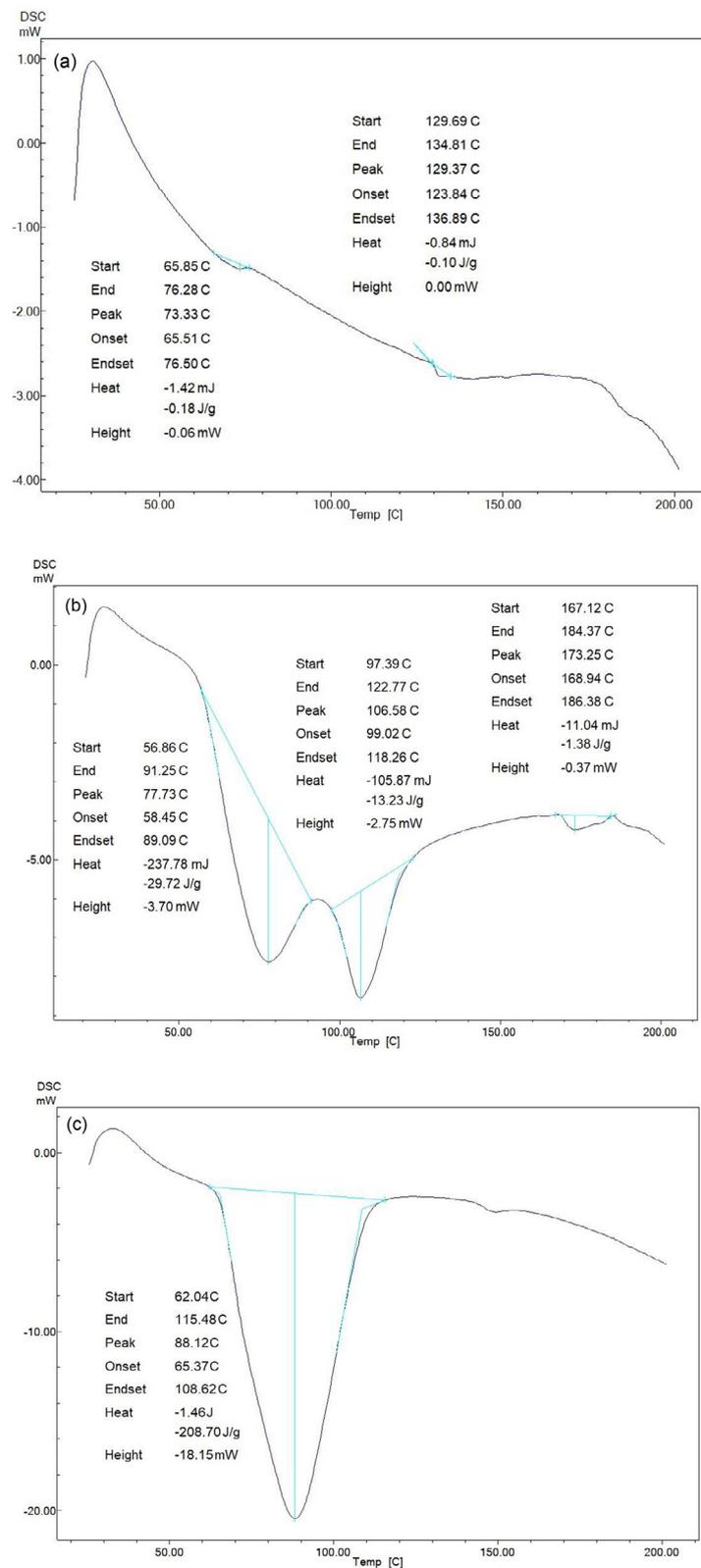


Fig. 3. DSC behavior of CH/PVA (a), CH/PVA/ZnO (b), and CH/PVA/ZnO-FA (c).

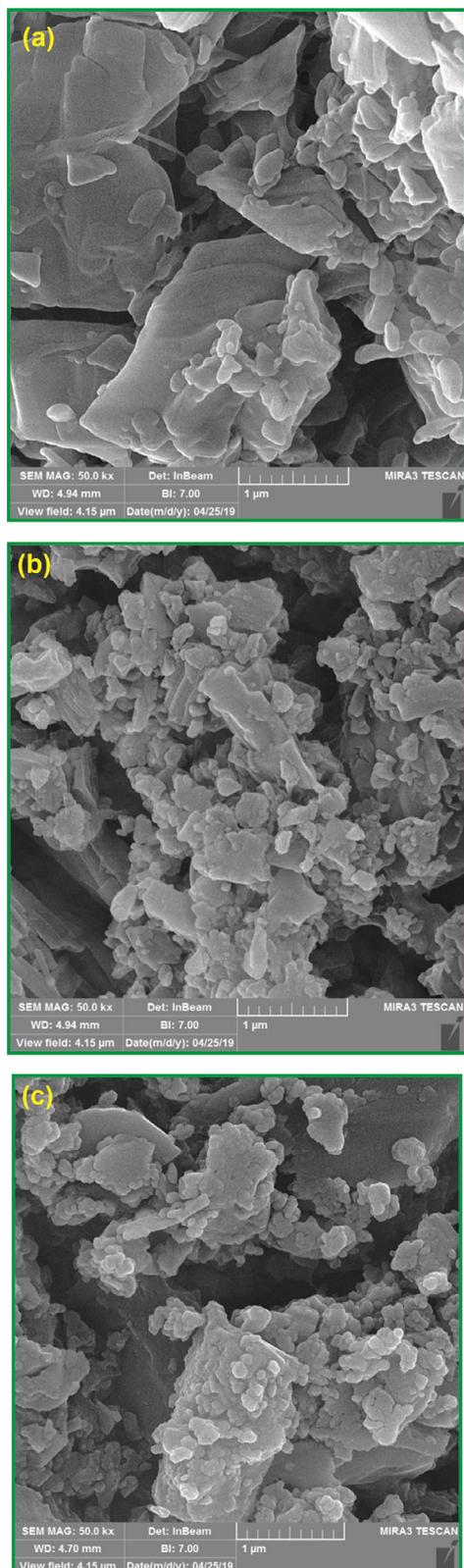


Fig. 4. SEM images of CH/PVA (a), CH/PVA/ZnO (b), and CH/PVA/ZnO-FA (c).

Declaration of Competing Interest

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

Table 1
Element in Chitosan / Poly Vinyl alcohol PVA.

Elt	W%	A%
C	41.96	48.65
N	11.18	11.12
O	45.77	39.85
Ca	1.09	0.38
	100.00	100.00

Table 2
Element in Chitosan / Poly Vinyl alcohol PVA/Zno nanoparticles.

Elt	W%	A%
C	28.37	47.56
N	1.91	2.75
O	29.69	37.36
Zn	40.03	12.33
	100.00	100.00

Table 3
Element in Chitosan / Poly Vinyl alcohol PVA/Zno -FA.

Elt	W%	A%
C	35.40	45.94
N	4.25	4.73
O	44.32	43.18
Na	0.48	0.33
Mg	0.70	0.45
Ca	12.03	4.68
Fe	0.75	0.21
Zn	2.07	0.49
	100.00	100.00

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Further Reading

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