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Research Article

PHYSICOCHEMICAL PROPERTIES OF BIOCOMPOSITE FILMS FROM BIOSYNTHESIZED ZINC OXIDE NANOPARTICLES (ZnONps) FROM KAPPA-CARRAGEENAN (kC)

FLYNDON MARK S. DAGALEA[1*] and KARINA MILAGROS R. CUI-LIM[1,2]

[1]Department of Physical Sciences, College of Science,

[2]University Research and Development Services,

University of Eastern Philippines, University Town, Northern Samar, Philippines 6400

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ABSTRACT

Objective: Kappa-Carrageenan, a natural polymer is a product derived from seaweeds has been gaining vast attention on researches because of its biodegradability and low cost production. On the side, Nanotechnology, the emerging Science of nanoparticles have been indulging the world with its new approaches on improving the characteristics of the medium used. This study differentiated the physicochemical properties of the films without and with the incorporation of Zinc Oxide Nanoparticles to kappa-Carrageenan. ***Materials and methods:*** Incorporation of ZnONps to kC was done. Physicochemical properties, namely: moisture content, degradation time, wavelength spectra, structural composition, and surface morphology was differentiated between biocomposite films with and without the ZnONps.

***Results and conclusion*:** After several tests, Zinc Oxide Nanoparticles incorporated to kappa-Carrageenan exhibited some changes to its physicochemical properties: lower moisture content and longer degradation time was revealed; ZnONps was seen in the surface of the biocomposite film. However, structural composition analysis showed that no new formation of functional group was seen. The biocomposite films could be a substitute with the existing drug capsule because of its longer decomposition, low water content and secured safety of the drug's quality.

KEYWORDS: Zinc Oxide Nanoparticles (ZnONps), biocomposite films, kappa- carrageenan (kC), physicochemical property

INTRODUCTION

Kappa-Carrageenan is a natural polymer product from the extract of seaweeds. Nanotechnology, as an emerging field of Science catered researches with modifications of the characteristics of a substance.

This research targeted the changes on the physicochemical property of the kC biocomposite films packed with ZnONps. Incorporation of metal oxide in polymer based substances modified some of the characteristics based on the research conducted.

The biocomposite film with ZnONps created the new products aligned to the pharmaceutical and packaging industries. Products that can be developed like capsules and packaging plastics with higher degradation time for preserving the medicine and foods. Pharmaceutically produced capsules and industry produced packaging film could be replaced with this developed biocomposite films. With the alteration on the properties, kC/ZnONps will make a debut in the market and could replace the existing products.

***Corresponding Author,**

FLYNDON MARK S. DAGALEA[1*]

and KARINA MILAGROS R. CUI-LIM[1,2]

[1]Department of Physical Sciences, College of Science,

[2]University Research and Development Services, University of Eastern Philippines, University Town,

Northern Samar, Philippines 6400

Email: flyndondagalea@gmail.com

Seaweeds produce a carbohydrate form known as carrageenan. A natural polymer like polysaccharides, as such, it has been receiving great deal of attention by many scientists, because of its biodegradability and availability at low cost. The innate properties and structure of carrageenan may be used for non-food applications.

The wide range of applications is possible as ZnO has key advantages. It is bio- safe, biocompatible and can be used for biomedical applications without coating. With these unique characteristics, ZnO could be one of the most important nanomaterial in future research and applications (Kathirvelu, *et. al*, 2008).

The usage of acidic electrolyzed water in the production of carrageenan and gelatin hydrosols and hydrogels has not caused undesirable changes in their chemical and texture properties. (Brychcy, *et. al*, 2015).

This study focused on the physicochemical properties of biocomposite film from kappa-Carrageenan filled with Zinc Oxide Nanoparticles.

MATERIALS AND METHODS

Preparation of Zinc Oxide from Zinc Nitrate

The preparation was done with the procedure of Rao (2015) with some modification made. Nanorod-rich Zinc oxide was prepared by using Zinc nitrate and sodium hydroxides precursors and starch as a stabilizing agent. Kappa-Carrageenan about 0.1g was dissolved in 500 mL of lukewarm distilled water. Zinc nitrate, 14.874 grams (0.1 mol), was added in the above solution, and then followed by constant stirring for 1 hour using magnetic stirrer to completely dissolve the zinc nitrate. After complete dissolution of zinc nitrate, 0.2 M of NaOH solution was added drop by drop under constant stirring. The reaction was allowed to proceed for 2 hours. After the completion of reaction, the solution was kept overnight and the supernatant solution was kept overnight and the supernatant solution was discarded carefully. Rest of the solution was centrifuged at 10,000 g for 10 min and the supernatant was discarded. Thus, the nanoparticles were obtained and washed thrice using distilled water. Washing was carried out to remove the by-products and the excessive starch bound with the nanoparticles. After washing, the nanoparticles were dried at 80^0C overnight.

Preparation of Biocomposite Films

The preparation was done using Nafchi et. al. (2012) method, with some modification made. Five grams of (5g) ZnONps was dispersed in 95mL water (0.92% ZnONps solution), stir for 1 hour, and then sonicated in an ultrasonic bath (if not available, use the magnetic stirrer as substitute) for 30 minutes. The solution will be used to prepare the aqueous dispersion with 2 g addition of kappa-carrageenan. A mixture of sorbitol and glycerol (3:2) was added as plasticizer. The biocomposite solution was heated to and held for 45 min to allow gelatinization. Upon completion of starch gelatinization, the solution was cooled to room temperature. A portion of the solution was dispersed to a petri dish. Films were dried under controlled conditions in a humidity chamber. Control films were prepared similarly and stored at and relative humidity (RH) until experimentation.

Determination of the Physicochemical Properties of kappa-Carrageenan packed with Zinc Oxide Nanoparticles (kC/ZnONps)

Test for Moisture Content of the Biocomposite Films

Films were conditioned at 58% RH and for 7 days. The weight difference was determined after drying of the equilibrated films in an oven at for 24h (Nafchi, *et. al*, 2012). The formula for moisture content is:

Test for Degradation Time of the Biocomposite Films

In this analysis, a Thermogravimetric analysis was used. Temperature range from 95- 600 was used. TGA determined the degradation time of the sample. The temperature range was based on the degradation of kC and ZnONps.

Test for Wavelength Spectra of the Biocomposite Film Solution

The UV-visible transmission spectra of the biocomposite film solution were recorded from 350 to 550nm using a UV-vis spectrophotometer. The set wavelength was used to know if ZnONps was incorporated to kC, ZnO has a wavelength of 370 nm (Paul and Ban, 2014). Distilled water was used as the blank solution.

Test for Structural Formation of the Biocomposite Films

FTIR spectra was recorded using an attenuated total reflection (ATR) method in Smart Itr. The thin films were applied directly onto the ZnSe ATR cell. For each spectrum, 64 consecutive scans at 500 to 4000 cm^{-1} resolutions.

Test for Surface Morphology of the Biocomposite Films

The conditioned bionanocomposite samples was place in a Scanning Electron Microscope (SEM), the surface microstructure of films was investigated with this machine. Magnifications from 500 to 4000 was used.

Moisture Content

RESULTS AND DISCUSSION

Zinc Oxide was successfully synthesized from Zinc Nitrate, from white chunky bulks to powdery white substance. The biocomposite films exhibited changes in its wavelength spectra, moisture content, degradation time, surface morphology. No new formation of functional group was seen in the structural formation analysis.

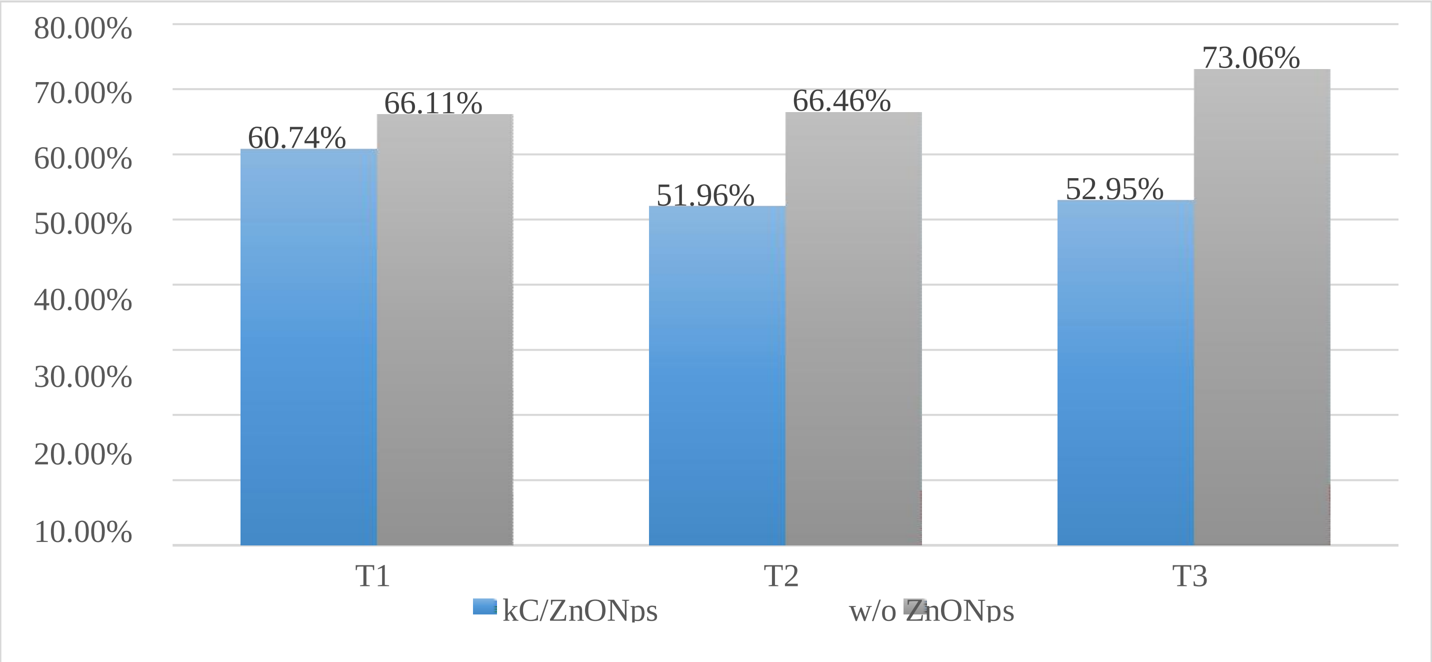


Figure 1. Comparative Chart for the Moisture Content

Moisture content place an important role in this film, greater moisture content indicates that the degradation is rapid because of the high water content. Nafchi (2012) cited in his work that increasing the nanoparticle (ZnO) content of films results in the formation of more hydrogen bonds the ZnO and the matrix components, thus, free water molecules do not interact as strongly with nanocomposite films compared with composite alone. Hence, increased in ZnONps levels leads to decreased moisture content and with high degradation time, products will be preserve in a longer period of time.

Using the t-test, results showed that there was significant difference between the biocomposite film with and without the ZnONps. Thus, the kC/ZnONps films can replace the commercially available drug capsules or the plastic films for the packaging industry.

Degradation Time

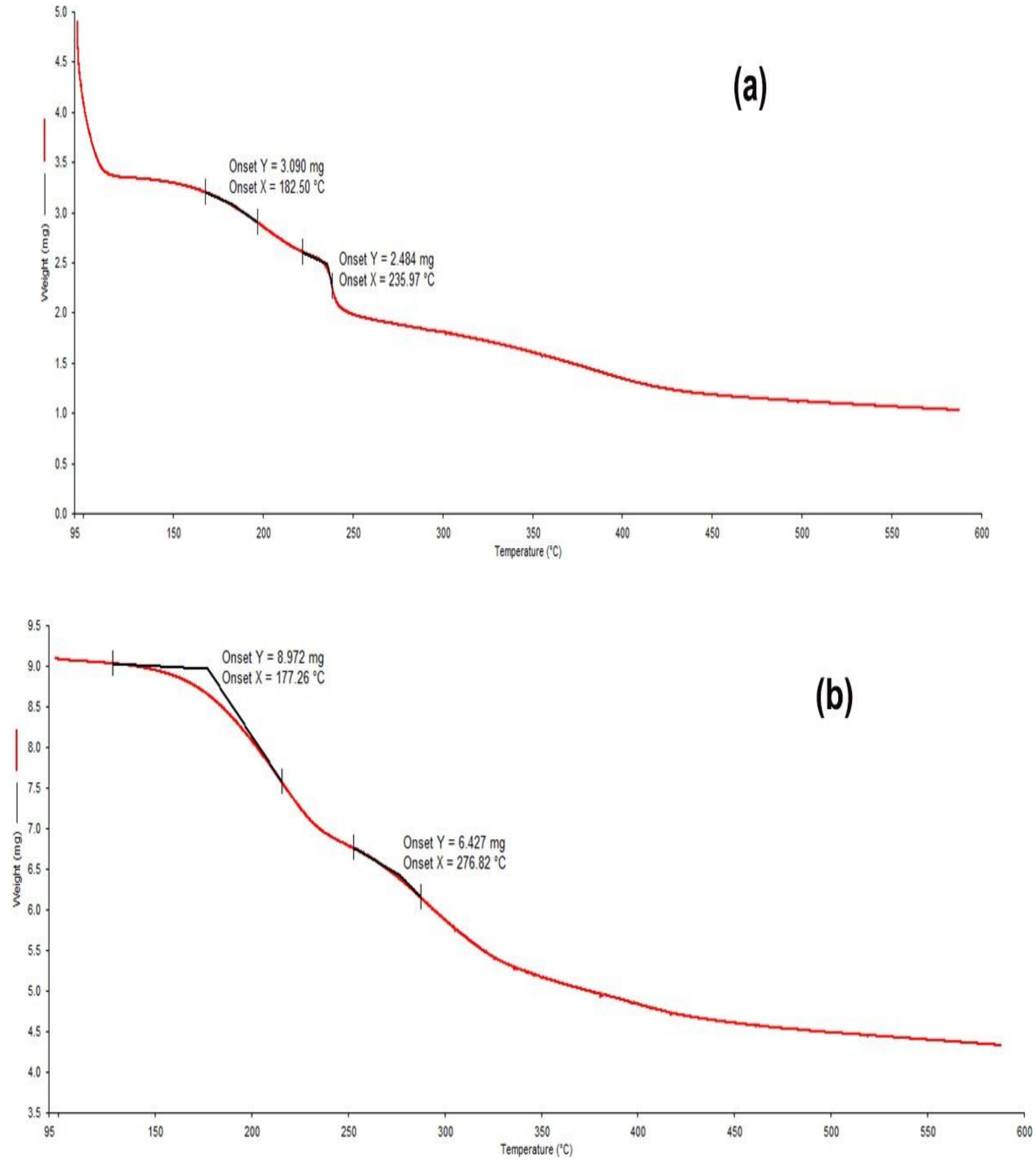


Figure 2. Degradation Time of the Biocomposite Films from kC (a) and kC/ZnONps (b) KC/ZnONps exhibited unique degradation time than the kC alone. Between 95-150 the biocomposite film from kC started to degrade rapidly and lost approximatively 1.5mg of mass and continue as the temperature increases (a). The kC/ZnONps started to degrade at 150-200. This only implies that the incorporated ZnONps to the kC manages to extend the degradation time of the biocomposite film (b). Thus, biocomposite material incorporated with metal oxide gives longer time to degrade. In layman’s term, kC/ZnONps have been upgraded to have a longer shelf life. Products in the market may decompose as it is not consumed by men, but products that uses biocomposite films with metal oxide will have longer time to decompose.

Wavelength Spectra

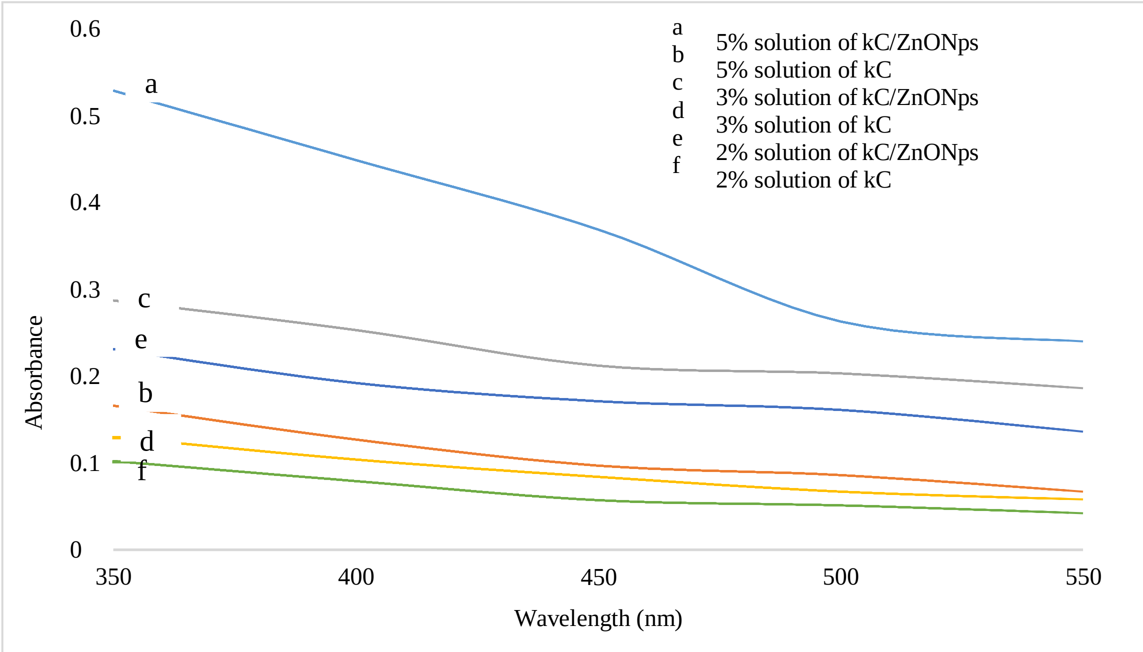
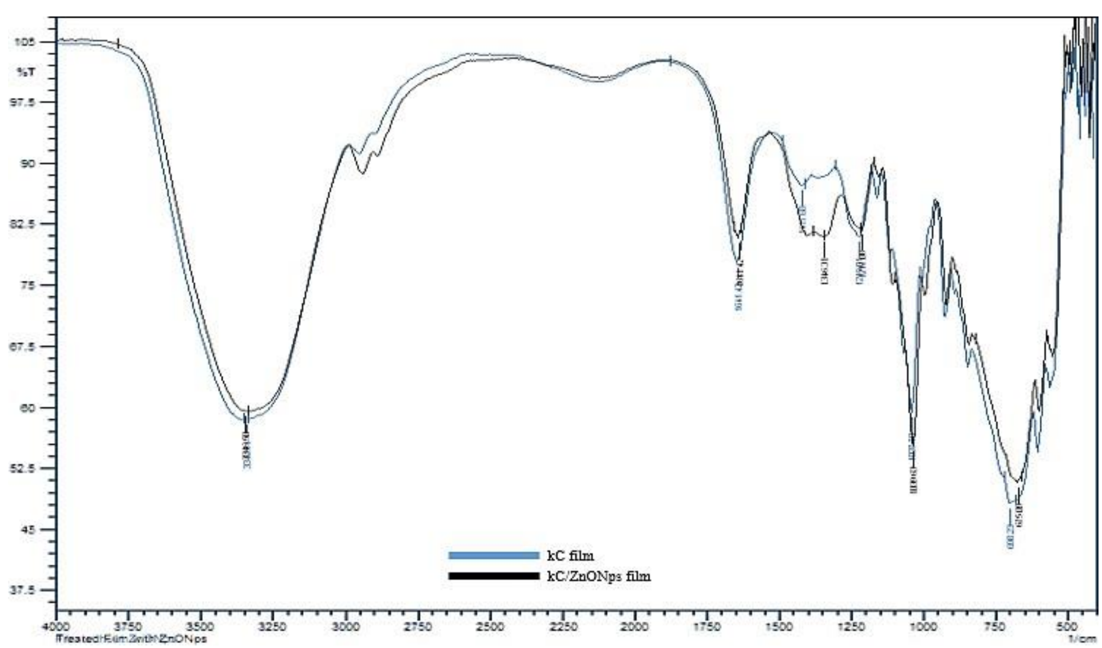


Figure 3. Wavelength Spectra Analysis

Different concentration (5%, 3% and 2%) of the kC filled with ZnONps film and kC film solutions were analyzed. The figure revealed that the biocomposite films incorporated with metal oxides have change its visible spectra. Altered from its previous composition, incorporation of metal oxide to a biocomposite material took place, changes in its property occurs. Nafchi (2012) suggested that biocomposite films incorporated with ZnONps could be used as UV-shielding films and heat insulators in the packing industry because of its capacity absorb UV light. This property is important especially in the application of pharmaceutical capsules since the drug inside the capsules can be protected from unwanted rays that might change its properties or cause damages (Rahman, *et al.*, 2014).

Structural Composition: Figure 4. FTIR result



The structural formation analysis produced by FTIR showed that there were no changes on the peaks of the films. The functional group alcohol (-OH) was present in both film samples. The functional group present in both films are the same but as we can observe, there is a sequence between the peaks observed. This may explain the structural composition of the film, biocomposite films with metal oxide have parallel peaks to kC alone. It was postulated that the ZnONps will only coat the kC following the van der Waals interaction. Thus, the theory of interaction between the kC and ZnONps was seen. It only proves that the biocomposite material, the kappa-Carrageenan, will decompose longer because of the incorporation of Zinc oxide. Nafchi (2012) cited that there was no new functional group appeared after the application of ZnO, indicating that only physical interaction between the ZnONps and the film matrix occurs.

Surface Morphology

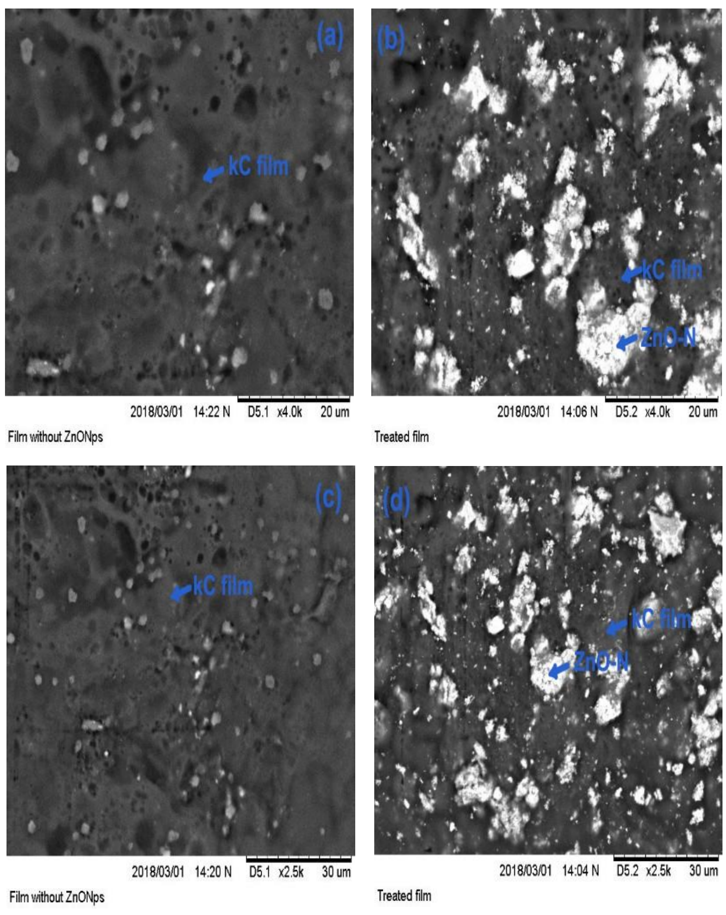


Figure 5. SEM Micrograph of the kC film without ZnONps (a) magnification =4,000,
(c) magnification =2,500. The films with ZnONps (b) magnification = 4,000, and (d) Magnification = 2,500

Using a scanning electron microscope (SEM), the result revealed that films without ZnONps had holes in it at magnification at 4000 with 20 in diameter (a). Furthermore, results for the film with ZnONps revealed that the metal oxide was attached to the surface of the films. Also, it is seen that Zinc Oxide nanoparticles covered some of the holes present in the untreated film (b). This implies that the metal oxide incorporated is in the surface only of the biocomposite film. This simply tells us that the kC remains the same, but there is a presence of a metal oxide that enhanced its physicochemical property. Another, nano-sized ZnO suspension clearly has much higher activity than the micron-sized ZnO (Zhang, *et al.*, 2009).

COMPARATIVE ANALYSIS BETWEEN THE kC/ZnONps FILMS AND kC FILMS

In this area, results between the kC films and kC/ZnONps will be compared.

Table 1. Comparative Data of the Sample films

PARAMETERS	kC FILMS	kC/ZnONps FILMS
Moisture Content	68.54% (high water content)	55.22% (low water content)
Degradation Time	Started between 95-150, rapidly	Started between 150-200, slowly
Wavelength spectra	Low absorbance	High absorbance
Structural composition	No formation of new groups	No formation of new groups
Surface morphology	Holes are seen in the surface of the film	ZnO was present in the surface

The physicochemical properties of the treated film as seen in the table was much better compared to the untreated film. Moisture content was higher in kC film than the kC/ZnONps film which indicates that kC has more water content than the kC/ZnONps. The degradation time proves the claim of the moisture content analysis, kC film degraded and loss weight faster than kC/ZnONps film. Wavelength spectra and structural composition revealed that the film developed no new functional group. Surface morphology tells us the presence of ZnONps in the kC film.

With this, the kC/ZnONps film exhibited unique properties that can be used in the pharmaceutical and packaging industries. In this starting point, this film could replace the existing medicine capsules for better drug protection and resistance to bacterial contamination.

CONCLUSIONS

Biocomposite film from kC/ZnONps has more chances of being substituted in the market as the new drug capsule and as packaging plastic. With its unique and enhanced property compared to kC film, kC/ZnONps developed a longer time of decomposition and moisture content less than the standard.

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