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ORIGINAL ARTICLE

# High-Barrier and Light–protective Bionanocomposite Film Based on Rye Starch/nanorod-ZnO for Food Packaging Applications

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**KEYWORDS**

Bionanocomposite film;
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**ABSTRACT:** Improving food quality, nutritional value and biodegradability are the reasons for developing edible films. Fine-dispersed starch-based nanobiocomposites were provided by adding nanorod-ZnO as fillers to aqueous starch. In this work, the impact of ZnO nanorod (ZnO-N) filler on the barrier properties and UV transmission of biofilms based on rye starch was studied.The solutions containing nanoadditives were homogenized by ultrasound waves and embedded in rye starch at various levels(1 - 5% w/w dried solid). Starch films were prepared by casting method with nanoparticles and plasticizers. Biofilms containing 5% ZnO-N had 0% UV transmittance. Active films were able to absorb Near Infrared spectra. After applying ZnO-N to the bionanocomposite film no new bond has emerged. Regarding barrier characterization, rye starch film with 5% ZnO-N showed better barrier properties than neat films, mainly by the gravimetric method, starch films containing 5% ZnO-N and control samples were 1.6 ± 0.02 and 1.18± 0.01 g/mPah, respectively.

## INTRODUCTION

In the last decades, polysaccharide biopolymers have been used in the food industry area [1]. Numerous studies have recently focused on finding solutions to the issues caused by plastic waste to produce environmentally friendly substances. To this purpose, various studies investigate the potential of replacing petroleum-based plastics with biodegradable, inexpensive materials that have comparable properties [2]. Biodegradable films provide an alternative to conventional packaging that does not cause pollution and is made from renewable resources [3, 4]. Since starch can form a continuous matrix and has a low oxygen penetration, it is one of the polysaccharides applied to fabricate biofilms.[5, 6]. Incorporation of nanoparticles into composite materials enhances polymer properties such as thermal, gas barrier, and mechanical [7]. Green materials currently used in food packaging are from renewable resources, which intend to reduce the human impact on the environment. Synthetic plastic has a high adverse effect on the environment than green materials.

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In comparison these natural polymers have advantages over petroleum or synthetic polymers; natural polymers are biodegradable and renewable materials. On the other hand, high permeability to water vapor and poor mechanical properties are two main disadvantages of natural polymers that nanoscience helps to solve these problems[8, 9]. Bionanocomposites-based packaging materials have great potential for enhancing food quality, stability and, safety, as an innovative packaging, and processing technology[10]. Bionanocomposite is defined as a combination of polymers with organic or inorganic nanofillers with particular size, surface chemistry and, geometry properties [11]. Because of their resistance in extreme conditions and safety for both humans and animals, inorganic materials including ZnO, MgO, and metal oxides have special attention [12].

Nanocomposite substances have attracted a significant amount of attention due to their catalytic characterization and their use in a wide range of fields, including biomedical, bioengineering, electronics, protection of the environment, biotechnology sector, etc.[13, 14]. Nanostructures have been widely used as fillers, to improve water vapor permeability, heat resistance, transparency and, mechanical properties [15].

Zinc oxide is used as a food additive also is currently listed as GRAS material by the Food and Drug Administration [16]. Also, Zinc oxide nanoparticles, which are nontoxic and biocompatible, have been utilized as drug carriers and medical filling materials[17]. Zinc oxide nanostructure is incorporated into various polymers to fabricate nanocomposite production, characterized by different properties such as enhancing tensile strength, UV shielding, antibacterial, barrier behavior against water and oxygen molecules, etc.) [18, 19].

In the presentation paper, ZnO-Ns were applied as fillers to fabricate rye starch bionanocomposit film. The active films were evaluated for their UV absorption, chemical and barrier properties.

Based on our knowledge, few papers have been reported to estimate the effectiveness of biofilms containing nanorod-ZnO. There are no reported data on the properties of rye films containing nanorod-ZnO. This work purposed to introduce a novel biofilm based on rey starch/zinc oxide nanorod film through casting method; to investigate their effect on the relevant characterizations to estimate the films' barrier, UV absorption, and chemical properties as food packaging:

## MATERIALS AND METHODS

### *Materials*

Rye Starch powder was purchased from Glucosan Co (Ghazvin, Iran). Glycerol and liquid sorbitol were obtained from Liang Traco (Penang, Malaysia). nano-ZnO was provided from University Sains Malaysia.

### *Film preparation*

Zinc oxide nanofillers with 1- 5%, w/w were embedded in water and stirred for 1 h. The dispersion was exposed to ultrasound wavelengths for 1 h to perform homogenization. Rye starch was mixed with nano-dispersion at a ratio of 4% (w/w) of total solid [20]. Sorbitol and glycerol with 40% of starch powder(w/w)were added to films as a plasticizer according [21]. Nano-suspension was heated at 90°C for 50 min to perform gelatinization. Finally, the Nano-suspensions were cooled at 25°C. Amount specific of solution (85g) was applied on casting special plate (16cm×16cm). Biofilms were dried in a desiccator at 50% and RH 25°C. Specimen samples without nanoparticles were prepared in the same way. Nano-biofilms were removed and conditioned in a glass container containing saturated salt at 50 relative humidity (RH) and 25°C.

### *Characterization of bionanocomposite film*

### *Water vapor permeability (WVP)*

The evaluation of the WVP of the starch/ZnO-N films was applied according to the standard method E96-05 with some modifications [22].

The biodegradable film was sealed in a cup test (S=0.00196) that stored in a desiccator at 30°C and silica gel was used in the desiccator. Water vapor travel was evaluated from the weight gained on the cup test. Seven weight determinations were taken during 14 h.

A linear equation of cup weight versus represents time was obtained to calculate water vapor transmission rate (WVTR). WVP of the biofilms was computed as follows:

$$wvp = WVTR \times T / A(P1-P2)$$

where t is the thickness of biofilm(m), A is the area of the film($m^2$), and p is signifies the partial pressure difference of the gas across the biofilm (Pa) at 30°C.

### *UV–visible*

UV transmittance of samples was detected at wavelengths rang UV, visible, and infrared (200-1100nm) using UV–visible spectrophotometer model specord 250 (Analytik Jena, Jena, Germany).

### *FTIR spectra*

The FTIR spectra (4000-500 $cm^{-1}$) of the biofilms were performed based on the ATR method using FTIR spectrometers (IRTracer-100, Shimadzu, Tokyo, Japan) at 4 $cm^{-1}$ resolution with 64 scans. The samples were assayed as biofilm at 25°C.

### *Statistical analysis*

One-way analysis of variance (ANOVA) was applied to compare data of water vapor permeability of biodegradable films at 95% confidence level. Data from water vapor permeability measurements were analyzed by Minitab 21.2.0 (MiniTab, State College, PA).

## RESULTS AND DISCUSSION

### *Water vapor permeability (WVP)*

The results of water vapor permeability are presented in Table 1. Barrier property significantly decreased by incorporation of ZnO-N. Since the incorporation of ZnO-Ns into the film create tortuous pathway for gas molecules to pass through the decrease in WVP after nanoadditive insertion may be attributed to Nano-higher ZnO's water resistance than that of the biopolymer[23]. Decreasing penetration of Nano-films against water vapor can be described according to the Nielsen model [24]. Each layer of nanoadditive is said to be perpendicular to the diffusion path, demonstrating that for the permeability index to reduce, water vapor molecules to travel through a longer diffusive pathway [25-27].

**Table 1.** WVP of rye starch nanocomposites.

| ZnO-N (%) | WVP×$10^{-7}$ [g/mPah] |
|---|---|
| **0** | 1.6±0.01a |
| **1** | 1.56±0.01ab |
| **2** | 1.52±0.0.02b |
| **3** | 1.36±0.03c |
| **5** | 1.18±0.02d |

WVP data are mean ± standard deviation. Different superscripts in WVP column values show significant difference at $p<0.05$ among rye films

### *UV–visible spectra*

The transmission of the rye starch bionanocomposites at 200-1100 nm is indicated in Figure 1. In Nano-biofilms, by increasing nanofiller, UV transmittance decreased. The control films indicated high level transmission in the UV range of 290 to 400 nm. UV transmittance decreased with the addition of 3% nano-ZnO to the biopolymer matrix, thus showing that bionanocomposite films had higher absorption in the UV range. These findings of UV transmittance are in agreement with others studies on biofilms [28-30]. Recently report indicated that the incorporation of ZnO-N (4 w/w %) into edible film resulted in the transmission of 3.4% UV light [31]. Jafarzadeh, et al. [32] Stated that adding 3% zinc oxide nanorod into biofilm based on semolina reduces UV light transmission.

Likewise, the transmission of visible to IR (>400 nm) spectra decreased after the addition of ZnO-N. The difference between edible films in electromagnetic properties may have an attributed to shape of the nanostructure since; the best figure for UV light absorption is nanorod. The results suggest that bionocomposite films could be used as UV-shielding films in food packaging.

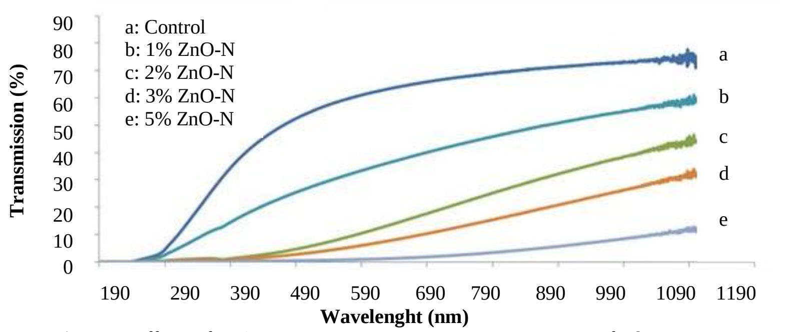


**Figure 1.** Effects of ZnO-N contents on UV-vis transmission spectra for bionanocomposites films.

### *FTIR spectra*

The FTIR spectra of the bionanocomposite films incorporated with ZnO-N at selected concentrations are shown in Figure 2. Three peaks (1000 and 1200cm$^{-1}$) in the biofilm were related to C—O bond stretching of starch. After the incorporation of nanoadditive, no new bond arises, demonstrating that the biomolecules and nanoadditive engaged in physical interaction. Marvizadeh, et al. [29]incorporated Nano-ZnO into tapioca starch/bovine gelatin film and found that physical interaction has occurred between nanoadditive and biopolymer. These findings of FTIR spectra are in agreement with another study on biopolymers [33].

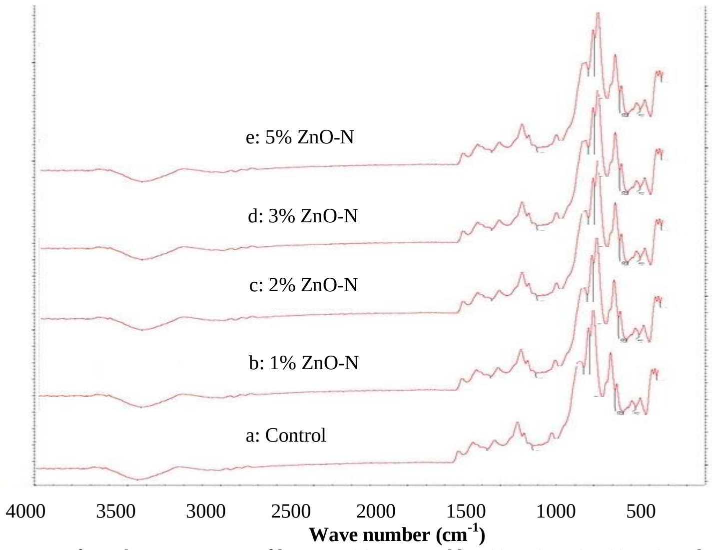


**Figure 2.** FTIR spectra of starch nanocomposite films at 25°C a: control b; 1% ZnO-N C; 2% ZnO-N d; 3% ZnO-N e; 5% ZnO-N.

## CONCLUSIONS

In the presentation work, the ZnO nanostructure was added into the biofilms based on rye starch at different levels (1% to 5%, w/w). ZnO-N played an important role in changing the barrier properties of rye starch-based biocomposites. Barrier properties against water vapor molecules are significantly increased by the incorporation of nanoadditive. The electromagnetic properties of bionanocomposites showed that the UV absorption becomes almost 100% with the addition of ZnO-N to the biodegradable film. FTIR spectra of the films indicated the physical contact between the biomolecules and nanoadditives. In summary, ZnO-N improves the functional characterizations of biofilms and these results indicated that bionanocomposite films containing ZnO nanorods had great potential for applications in food and pharmaceutical industries.

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***Conflict of interests***

The authors declare that there is no conflict of interest.

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