RESEARCH ARTICLE

Designing a new active nanocomposite packaging film based on zein biopolymer and titanium dioxide containing essential oil

Elham Karami¹, Shadab Shahsavari^{2*}, Ali Vaziri Yazdi¹, Azadeh Hemmati¹

¹ Chemical Engineering Department, Oil and Chemical Engineering Campus, Science and Research Branch, Islamic Azad University, Tehran, Iran

² Chemical Engineering Department, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

ARTICLE INFO	ABSTRACT			
Article History: Received 21 Jan 2023 Accepted 09 Apr 2023 Published 01 May 2023	One of the categories of antimicrobial substances are medicinal plants, which are technically categorized as a relatively new method in active packaging due to the presence of phenolic compounds, in addition to solving the mechanical and physical issues with packaging films. In this study, the weight-to-weight ratio of nano-titanium dioxide to zein (X1), the weight-to-weight ratio of rosemary to zein (X2) and the solution feeding rate (X3) were examined for their effects on the			
Keywords: Biodegradable packaging Rosemary Zein Nanofiber Nano titanium dioxide	A2, and the solution receiving rate (x5) were examined for their energies of the dependent variables of nanofiber diameter (Y1) and solution viscosity (Y2). The electrospinning procedure was then carried out in the following circumstance applying the ideal voltage of 12 kV; placing a 150 mm gap between the needle tip and the collector; feeding the solution at a variable pace; and operating room temperature and pressure. The ideal nanofibers had a size of 88.69 nr a consistent structure, no flaws, and a viscosity of 0.62 pascal-second. Zein, biodegradable and biocompatible biopolymer, rosemary essential oil, which he antibacterial qualities, and nano titanium dioxide are three ingredients that mal an excellent combination for active food packaging.			

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INTRODUCTION

Today, the advancement of technology and development in the food industry, on the one hand, and the desire for easy access to all kinds of food, on the other hand, have turned the society's tendency towards the use of ready-made food in various packages with a suitable appearance. Cases have led to an increasing evolution in food packaging technology (1).

The materials currently used in food packaging are often non-degradable and have many environmental problems. Therefore, finding a suitable alternative to synthetic plastics, so that it leaves less environmental pollution, has attracted the attention of researchers. Biodegradable packages that are edible and can be consumed with food are divided into two categories: films and edible coatings (2 and 3). Edible films are produced in the form of thin layers before being used in food packaging, and then they are used for packaging like synthetic polymers (4). One of the most important advantages of edible films and coatings compared to synthetic polymers is that these types of coatings can act as a carrier for various additives and compounds such as antimicrobial substances, antioxidants, etc., which in this case They are called active packaging (5).

Among the various methods used to produce nanofibers, the electrospinning method is considered as one of the newest methods. In this method, by applying electric current to the polymer solution and by evaporating the solvent in it, structures without texture are produced (6).

Structured polymer fibers with a diameter of several micrometers to several nanometers have attracted considerable attention in various sciences. Compared to the usual spinning methods,

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^{*} Corresponding Author Email: Sh.shahsavari@srbiau.ac.ir

the electrospinning method creates fibers with a smaller and nanometer diameter (7). The layers obtained from electrospun nanofibers have unique properties such as specific surface area and high porosity, which provides the basis for their use in various applications, including food packaging industries. Therefore, electrospinning is considered a promising method for producing active packaging materials (8).

Zein is a type of prolamin or the main storage protein in corn, which makes up about 45 to 50% of the protein content of corn (9). This protein has many applications in the food industry, food coating and packaging. Nanofibers created by zein solution electrospinning have unique characteristics that distinguish them from other fibrous nanostructures produced by other nanotechnology methods (10). Meanwhile, the biodegradability and biocompatibility of zein are key parameters for its use in the fields of food, biomedical and pharmaceutical packaging (11).

Antimicrobial packaging is a type of active packaging that provides the continuous transfer of antimicrobial compounds to the surface of the food, so that the continuous release of antimicrobial compounds will not allow the growth of restored microbial cells. Therefore, antimicrobial packaging can be used to increase safety and improve food quality (12).

One of the types of antimicrobial compounds are medicinal plants, which have received a lot of attention due to their minimal side effects and various applications in therapeutic fields. Rosemary plant is one of the most important medicinal plants that has different medical uses, among them its antibacterial and antioxidant properties. Its anti-mutagenic property is also known (13). It is worth mentioning that the presence of phenolic compounds, in addition to solving the physical and mechanical problems of packaging films, can technically be classified as a relatively new process in active packaging (14).

Also, among the materials with antimicrobial properties are particles in the form of nanoparticles. Today, these materials have found a special place in health and industry (15). Nanoparticles refer to particles that have dimensions less than 100 nm in at least one dimension. Nanoparticles, in addition to increasing the inhibitory (mechanical, thermal, chemical, microbial), improving mechanical properties and heat resistance, developing antimicrobial activity and antifungal levels and biochemical changes (16). They show good antimicrobial properties due to their high surface-to-volume ratio (17). Adding antimicrobial compounds to the packaging covers gives them antimicrobial activity, and therefore the packaging film can be effective in controlling the growth of microbes and spoilage-causing microorganisms (18).

Among the nanoparticles used in the food industry, we can mention titanium dioxide. Nanoparticles of titanium dioxide is an inexpensive material with high efficiency, which preserves nutrients and freshness, as well as reduces the microbial load in packaged food (19).

Therefore, in this study, two materials, nanotitanium dioxide and rosemary essential oil, have been used simultaneously as antibacterial materials to produce nanofibers by electrolysis method.

MATERIALS AND METHODS

Corn protein and glacial acetic acid with a purity of 5.99 were purchased from Merck (Germany), nano titanium dioxide from Degosa (Germany) and rosemary essential oil from Barij Essence Company.

Experiment design

Based on the research, the statistical method offers several advantages over the classical method; It helps to understand the relationships between parameters in different values, it is reliable, it reduces the number of tests and saves time, time and manpower. For this reason, experiment design using experiment design software to investigate the effects of three independent variables including the ratio of nano titanium dioxide to zein (X1) and the ratio of rosemary to zein (X2) and solution feeding rate (X3), on dependent variables including nanofiber diameter (Y1) and solution viscosity (Y2), in three levels and based on di-optimal array, and optimization was done by response surface method. Table 1 shows the levels of independent and dependent variables in the electrospinning process.

Preparation of electrospinning solution

In order to carry out the electrospinning process, zein protein solutions with different concentrations were prepared along with acetic acid solvent and certain amounts of nano titanium dioxide and rosemary essential oil according to Table 2, the experimental design table. In order to homogenize, the solutions were placed on a magnetic stirrer at E. Karami et al. / Designing a new active nanocomposite packaging film

Variables	Range	
Independent Variables		
(X1) Ratio of nano titanium dioxide to zein	0-1.8	
(X ₂) Ratio of rosemary to zein	0-1.6	
(X ₃) Solution feeding rate (ml/h)	0.1-1	
Dependent Variables		
(Y1) Nanofiber diameter (nm)	min	
(Y2) Solution viscosity (pa.s)		

Table 1. The levels of independent and dependent variables

Run	Dette of more Tite stress direction to	Detie of Decomposite Zain	Feeding rate	Viscosity	Nanofiber
	Ratio of nano 1 itanium dioxide to	Ratio of Rosemary to Zein			diameter
	Zein %(w/w)	%(W/W)	(mi/n)	(pa.s)	(nm)
1	0.1	0.6	0.10	0.27	89.02
2	0.8	0.6	1.00	0.35	71.73
3	0.8	0.6	0.42	0.35	63.82
4	0.1	0.1	0.55	0.62	78.42
5	0.1	0.1	1.00	0.62	93.94
6	0.35	0.6	1.00	0.31	80.37
7	0.1	0.4	0.64	0.41	70.26
8	0.8	0.6	0.42	0.35	63.81
9	0.52	0.4	0.10	0.48	102.64
10	0.8	0.3	1.00	0.38	75.32
11	0.1	0.6	0.10	0.27	89.04
12	0.1	0.1	1.00	0.62	93.93
13	0.8	0.1	0.10	0.75	72.94
14	0.17	0.35	0.17	0.51	79.75
15	0.1	0.1	0.10	0.62	68.04
16	0.53	0.4	0.66	0.60	96.52
17	0.35	0.6	1.00	0.31	80.38
18	0.52	0.1	0.64	0.55	116.74
19	0.8	0.1	0.10	0.75	72.93
20	0.45	0.1	0.14	0.60	79.13

Table 2. Experimental design

200 rpm for one day and night.

Optimization of electrospinning voltage

For this purpose, experiments were conducted with different voltages and the optimal voltage of 12 kV was obtained experimentally and then by examining the results of the scanning electron microscope.

Measure solution viscosity

To measure the viscosity of polymer solutions, Anton Paar MCR 302 plate and cone rheometer, located in Zakaria Razi Complex, Science and Research Unit, was used. For this purpose, a certain amount of each of the solutions was placed on the spindle of the machine and the viscosity of each of the solutions was measured at room temperature using a CP-50 model spindle under a shear speed of 100/s and a cone and plane angle of 1 radian.

Measuring the diameter of nanofibers

To check the diameter of electrospun nanofibers, a scanning electron microscope, model XL-30, manufactured by Philips, located in Amirkabir University, Faculty of Mining and Metallurgy, was used. The resulting nanofibers were cut into 1x1cm dimensions on the foil and then coated with gold nanoparticles in a vacuum chamber, and then the surface morphology of the nanofibers was observed using a scanning electron microscope. Photos of the nanofibers were determined at different magnifications under a voltage of 25 kV from each image. Then Measurement software was used to measure the diameter of nanofibers was calculated by Excel software.

Formulation optimization

After conducting the designed experiments and analyzing the results and obtaining all the dependent variables, optimization was done based on the dioptimal level response method.

RESULTS AND DISCUSSION

Optimization of electrospinning voltage

order to determine the optimal In electrospinning voltage, various tests were performed at two voltages of 12 and 18 kV at a constant feeding rate, and the obtained nanofiber diameter results were checked (20). The results of the scanning electron microscope showed that the nanofibers obtained under the voltage of 12 kV were smaller in diameter. The diameter of nanofibers with voltage of 12 and 18 kV was reported as 68.04 and 74.97 nm, respectively. Figure 1 shows the scanning electron microscope images of nanofibers with two voltages of 12 and 18 kV.

Viscosity measurement

After preparing each of the solutions based on the test design table and at the optimal voltage of 12 kV, the viscosity of the nanofiber solution was analyzed at room temperature, and the results of the test design table are shown in Table 2.

Measuring the diameter of nanofibers

Also, in order to measure the diameter of nano fibers from each of the solutions, photographs with different magnifications were taken under a voltage of 25 kV. Measurement software was used to measure the diameter of nanofibers and the average diameter of nanofibers was calculated by Excel software, the results of which are shown in Table (2).

Examining response surface diagrams

To show the effect of independent variables on dependent variables, three-dimensional response surface curves were drawn to provide a better understanding of the interaction of two independent variables on dependent factors.

The response surface diagram showing the effects of independent variables on dependent variables including 1) nanofiber diameter and 2) viscosity is shown in Figure 2.

As can be seen in the response surface diagram of Figure 1-2, with the increase in the ratio of rosemary essential oil to zein, the diameter of nanofibers decreases, which is due to the decrease in the ratio of polymer to essential oil and the decrease in concentration, resulting in the formation of particles with a smaller diameter (21).

Also, according to the response surface diagram in Figure 2-2, it can be seen that increasing the ratio of rosemary essential oil to zein viscosity decreases and increasing the ratio of nano titanium dioxide to zein viscosity increases. This decrease in viscosity is a result of the decrease in concentration due to the increase in the proportion of essential oil in the solution, but on the contrary, with the increase in the ratio of nano titanium dioxide to zein and the sticking of nanoparticles of titanium dioxide to the polymer, the concentration of the solution increases and the viscosity increases.

Formulation optimization

After carrying out the experiments designed using the results of viscosity and scanning electron microscopy, the optimal nanofiber was determined with the experiment design software and based on the response surface method. The electrospinning



Fig. 1. Scanning electron microscope images of nanofibers with two voltages of 1) 12 and 2) 18 kV.



Fig. 2. Response surface diagram of 1) nanofiber diameter and 2) viscosity

Table 3. Optimal nanofiber formulation

Ratio of nano Titanium dioxide	Ratio of Rosemary to	Feeding rate	Voltage	Nanofiber	Viscosity
to Zein %(W/W)	Zein %(W/W)	(ml/h)	(Kv)	diameter (nm)	(pa.s)
0.1	0.1	0.97	12	88.69	0.62

process was performed on the optimized nanofibers, and the results of the optimal nanofiber formulation can be seen in Table 3.

Scanning Electron Microscope (SEM)

The analysis of the scanning electron microscope image obtained from the optimal nanofibers, which can be seen in Figure 3, shows that the resulting nanofibers have a uniform structure and no defects with a diameter of nano dimensions.

Infrared spectroscopy (IR)

In this study, infrared spectroscopic analysis has been used to investigate the chemical structure and optimal formulation of active nanocomposite based on zein, containing rosemary essential oil and nano titanium dioxide. This analysis was performed on pure samples including nano titanium dioxide, rosemary essential oil and zein as well as optimized nano fibers, the results of which are depicted in Figure 4.

As seen in Figure (4-4), a new peak at the wavelength of 3763.53cm-1 is observed in the spectrum obtained from nanofibers, which indicates the acidic O-H group, which is caused by stretching vibrations. Also, the peak at the wavelength of 3315/61 cm-1 indicates the N-H and O-H groups, which can be caused by the stretching

vibrations of the O-H group on the nano titanium dioxide surface and the N-H and O-H groups on the pure zein surface. Another new peak has been obtained at the wavelength of 3064/54 cm-1 with C-H group, which is caused by aromatic stretching vibrations and the peak in the wavelength region of 2874/89-2955 cm-1 is caused by aliphatic stretching vibrations (23).

The resulting peak at a wavelength of 1664.56 cm-1 is caused by the C=O bonds present in pure zein and rosemary essential oil and is caused by stretching vibrations, the peak at a wavelength of 1536.28 cm-1 is caused by the N-H group present in pure zein and is caused by Bending vibrations, the peak at the wavelength of 1451/18 cm-1 is caused by the C-H group in rosemary essential oil and caused by bending vibrations. Also, the C-N group in pure zein, which is caused by stretching vibrations, is observed at the wavelength of 1262.57 cm-1 in optimal nanofibers.

Finally, by comparing the graph related to the optimal nanofibers with other graphs, we conclude that links between nanomaterials have been established and the components have been combined and a nanocomposite has been formed.

X-ray diffraction study (XRD)

This device has very high accuracy and power of

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Fig. 3. Scanning electron microscope image of optimal nanofibers



Fig. 4. infrared spectroscopic analysis of 1) nano titanium dioxide, 2) rosemary essential oil, 3) zein and 4) optimized nano fibers

analysis, and in the field of recognition of crystals, pressure and stress analysis to control rolling and pressing operations, qualitative and quantitative analysis of phases has very high application and capabilities. The results of the X-ray diffraction analysis of optimal nanofibers can be seen in Figure 5.

The diagram obtained from X-ray diffraction analysis of optimal nanofibers shows the structure of anatase. Anatase crystal phase is tetragonal and its photocatalytic activity is far higher than other phases (24).

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Fig. 5. X-ray diffraction analysis of optimal nanofibers



Fig.6. Differential scanning thermometric analysis of 1) nano titanium dioxide, 2) rosemary essential oil, 3) zein and 4) optimized nano fibers

X-ray fluorescence spectroscopy

This device has the ability to analyze samples in solid form (tablets) with a diameter of 3-4 cm and can reveal the elements of the periodic table from element number 11 (sodium) to element number 92 (uranium).

X-ray fluorescence spectroscopic analysis was performed on pure samples as well as optimized nanofibers, and the analysis results are as follows:

The polymer sample (Zein) contains elements of copper, iron, titanium, calcium and zinc, all of which were observed in small amounts. The titanium dioxide nanoparticle sample contained a large amount of titanium element and a small amount of vanadium element. The rosemary essential oil sample contained a large amount of calcium and a moderate amount of iron and scandium elements and a small amount of strontium and rubidium elements as well as very small amounts of copper, cobalt, potassium, silicon and zinc elements (25).

Also, the optimal nanofiber sample showed that the sample contained elements of titanium, zinc, copper, cobalt, scandium, calcium and a large amount of iron.

Differential scanning thermometric analysis (DSC)

Using this analysis, it is possible to check the thermal stability of the material and also check the glass transition temperature. Therefore, this analysis was performed on pure samples and optimal nanofibers, and the glass transition temperature and enthalpy of the samples were determined from the temperature curves, the results and graphs of which are shown in Figure 6. Based on the results of calorimetric analysis (Figure 6), the glass transition temperature of pure components of zein, nano titanium dioxide, and rosemary essential oil were 154.32, 152.32, and 178.89 °C, respectively. The optimal nanofiber glass transition temperature was obtained at 136.78°C, which had a lower transition temperature compared to the single polymer component (zein).

The endothermic peak in the range of 328.02 to 353.34 °C has appeared in the nano-titanium dioxide calorimetry diagram, which is related to the melting phenomenon of the substance and the area below the peak shows the enthalpy changes of the sample. As seen in Figure 1-6, the enthalpy changes of the sample is 30.1246J/g.

In the thermometric diagram obtained from rosemary essential oil in Figure 2-6, the endothermic peak in the cooling stage is in the region of 97.21 to 124.01 C and another endothermic peak in the region is 370.81 to 373.42 in the secondary heating stage. become The enthalpy changes of the sample are 43.1178 and 1.8945 J/g respectively (26).

In the thermometric diagram of Zein polymer in Figure 6-3, an endothermic peak is observed in the area of 345.76-337.96 °C with enthalpy changes of 5419.5 J/g.

In the calorimetric graph obtained from the optimal nanofibers in Figure 6-4, the calorific value peak is observed in the region of 314.01 to 315.02 °C with enthalpy changes of 1.2655 J/g.

CONCLUSION

The results of this research showed that zein can be used as a protein carrier for antimicrobial compounds such as nano titanium dioxide and rosemary essential oil in food packaging or coating. Also, according to the need of the industry to replace biodegradable packaging with plastic packaging, Zein biodegradable polymer, which is odorless, tasteless, insoluble in water and edible, is a suitable choice for use in food and pharmaceutical industries. The results obtained from the response surface graph showed that with the increase in the ratio of rosemary essential oil to zein, the diameter of nanofibers and also the viscosity of the solution decreases. By increasing the ratio of nano-titanium dioxide to zein, the viscosity increases and the diameter of the nanofibers first increases and then decreases. According to the studies conducted on the structure of optimal nanofibers, it was determined that all nanofibers with a diameter less than nanometers have a uniform structure. Optimum nanoparticle with the characteristics of titanium dioxide to zein ratio of 0.1, rosemary essential oil to zein ratio of 0.1, feeding rate of 0.97 mL/hr, diameter size of 88.69 nm and viscosity of 0.62 pascal-second. was achieved.

CONFLICT OF INTEREST

There is no conflict of interest.

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