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Formation and photoluminescent properties of nanophotonic elements with nanosized ZnO for smart packaging, deposited by screen printing

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Abstract

Smart food packaging (active and intelligent packaging), which indicates and/or prevents changes in the packaged food product, traces the history of its storage etc., is becoming more popular due to the fact that it enhances safety of packaged food storage, transportation and consumption. It is convenient to use printing techniques to produce active elements of smart packaging, including the elements which respond to the changes in packaged food, which occur as the result of food spoilage or aging. However, issues concerning technological aspects arise when the compositions are printed onto materials such as paper or polymer films, especially if these compositions contain functional nanoparticles with luminescent properties. There has been conducted technological research of formation of luminescent coatings containing nano-sized ZnO, for active and intelligent packaging, using screen printing. Photoluminescent properties of the obtained nanophotonic elements are studied and the factors that affect their properties are defined. It was determined that by manipulating coating thickness, molecular weight of the polymer and the concentration of nanophotonic component in the composition it is possible to increase photoluminescent intensity of the screen-printed coatings and obtain different colors of photoluminescence.

Keywords: screen printing, nanophotonics, photoluminescence, nanomaterial, zinc oxide

1. Introduction

In respect to the global trend of increasing requirements for food safety, increasing the functionality and environmental safety, packaging containing nanoscale materials and nanotechnology in food packaging seems to be perspective to provide special properties, that is to create active and intelligent packaging. Achievements of nanotechnology are beginning to be used in all areas of production, including printing and packaging printing.

Active and intelligent packaging are able to respond to the changes in condition of packaged product in various ways: the first ones ensure the safety of content of a packaging for a longer time without increasing heat treatment parameters or other processing procedures for the product, the second ones monitor the status of a product or the environment in which the product is stored and inform consumers about the safety of consumption of the product (Suppakul et al., 2003; Sekhon, 2010). Informing consumers may be carried out by changing certain properties of packaging elements such as optical, electrical, geometrical properties and so on (Yam, Takhistov and Miltz, 2005). Therefore, the use of luminescent tags or sensors that respond to changes in the packaged product by changing the intensity of photoluminescence is quite promising. These elements,

for instance, based on nanosized zinc oxide (ZnO), are an example of the use of nanophotonic systems for printed active and intelligent packaging.

The use of ZnO nanoparticles has several advantages over the use of other luminescent compounds as nano-ZnO is primarily a safe, possess antimicrobial properties, absorbs UV radiation (Li et al., 2010; Seo et al., 2011) and changes the intensity of luminescence in contact with decomposition products of organic matter: carbon dioxide, organic acids (lactic, acetic acid), alcohols (ethanol), aldehydes, hydrogen sulfide, ammonia, biogenic amines formed by the interaction of ammonia with carboxylic acids and amino acid decarboxylation in result of bacteria (cadaverine, lysine, histamine) due to destruction of nano-ZnO crystals and the formation of aggregates without luminescent properties (Emamifar et al., 2010). Experimental studies showed that ZnO nanocrystals in polymers react to the presence of decomposition products of organic matter almost the same way as without polymer, presumably due to migration of such substances into the upper layers of the composition. This enables the use of printed layers of nano-ZnO with polymers for application to smart packaging. Yet as a result of introduction of ZnO nanoparticles in

a solvent for the purpose of printing application onto a packaging material there is often a loss of luminescent properties of nano-ZnO, so the selection of polymers that can serve as a matrix for nanoparticles of ZnO is necessary. We have determined that the introduction of colloidal solution of ZnO nanocrystals in ethanol to polyvinylpyrrolidone (PVP) (safe for consumption polymer) leads to no considerable loss of nano-ZnO photoluminescence intensity. However, in the process of manufacturing compositions and applying coatings there is a number of factors that affect the luminescent properties of the obtained printed labels which should be considered when producing photoactive printed packaging elements.

Despite a rather extensive research of the process of incorporating ZnO nanoparticles in polymeric materials,

2. Methods

Colloidal solution of ZnO nanoparticles in ethanol was prepared from zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), sodium hydroxide (NaOH), and 100 % ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Shvalagin, Stroyuk and Kuchmii, 2004). Polyvinylpyrrolidone (PVP) was added to the colloidal solution of ZnO in ethanol (concentration of $2 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ mol/L) at room temperature and intensive stirring (molar weight 10 000, 40 000 and 360 000 g/mol).

The coatings were obtained using screen printing of the produced nanophotonic compositions on polypropylene substrates. For the depositions of layers, hand screen printing was used under standard press conditions with controlled room temperature. The mesh #21 (52 tpi) with the thickness of the thread 144 μm was used to print 20×20 mm areas. The layers with thickness of 20 μm were printed onto each other several times (up to

3. Results

There was investigated the formation of coatings containing ZnO nanoparticles in PVP using screen printing and the influence of several factors on the intensity of photoluminescence of the obtained films.

It was found that with the inclusion of ZnO nanoparticles in PVP and subsequent application of the coating films two peaks in the luminescence spectra are displayed: one at 400 nm and the other at 530 nm (Figure 1, curve 2). Peak at 530 nm is typical for ZnO nanoparticles (Figure 1, curve 1) and a small peak at 400 nm is observed when irradiating PVP (Figure 1, curve 3).

By increasing the molar mass of PVP, the luminescence intensity of the samples increases (Figure 2). The peak

the issues of producing compositions for printed photoactive elements of smart packaging with nanoscale substances, such as ZnO, is practically not disclosed in the literature. Given this, the study of the features of printing production of photoactive elements for novel packaging with nanoscale luminescent substances is an important and urgent task, which is to enable the use of varnish and ink compositions based on nano-ZnO for production of printed smart packaging that respond to the state of packaged food by changing the luminescent properties.

The aim of this work is to study the factors and parameters of manufacturing process of photoluminescent coatings based on nanosized zinc oxide applied by screen printing onto the surfaces for producing active and intelligent packaging.

5 times to obtain layer thicknesses up to 100 μm). The layer thicknesses were measured with a thickness gauge based on the use of profilogram, measuring the increase in thickness with each print and calculating the average for 15–20 printed impressions. The printed impressions were cured under room temperature conditions without special equipment.

Photoluminescence spectra were recorded using luminescence spectrometer (Perkin Elmer, LS 55) and excited by light with a wavelength of 330 nm (λ_{ex}). The results for photoluminescence intensity in arbitrary units are obtained with the luminescence spectrometer with the same conditions of the measurements – spectral width of apertures (15 nm and 2.5 nm), speed of measurement (600 nm/min), filters (at 350 nm). The absorption spectra (optical density) were recorded using a spectrophotometer (Analytic Jena, Specord 210).

at 400 nm, which is typical for the polymer, increases most likely as a result of the participation of functional groups at the ends of the polymer chains of PVP in emissive processes in the polymer, and efficient capture of electronic excitation of ending groups of ZnO nanoparticles, followed by the emission in the natural region of the polymer. The number of functional groups increases with the decrease of molecular weight of the polymer and leads to a decrease of the luminescence band of nano-ZnO and an increase of the luminescence intensity of PVP.

Therefore, for maximum luminescence intensity of the films in the long-wave region (typical for nanocrystalline ZnO), it is optimal to use PVP with the highest

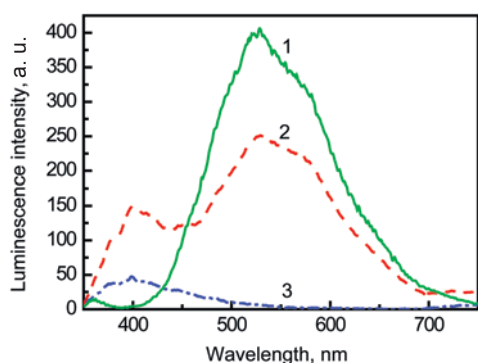


Figure 1: Luminescence spectra of colloidal solution of ZnO nanoparticles (1), coatings of ZnO nanoparticles in PVP (2) and PVP without ZnO nanoparticles (3);
 $M(\text{PVP}) = 360\,000 \text{ g/mol}$, $[\text{ZnO}] = 2 \cdot 10^{-2} \text{ mol/l}$,
 $\lambda_{\text{ex}} = 330 \text{ nm}$

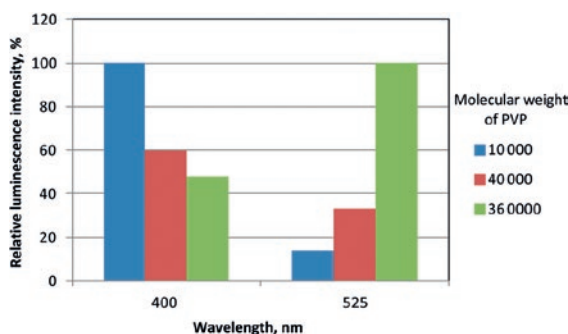


Figure 2: Influence of molecular weight of PVP on the height of the luminescence peaks of the coatings (400 and 525 nm)

molecular weight ($M = 360\,000 \text{ g/mol}$). However, the change in molecular weight of PVP allows changing the color of luminescence from blue to green and yellow, which might be useful for creation of various colors of luminescent emission for active and intelligent packaging. That is, with the increase of molecular weight of PVP the peak at 400 nm decreases and the peak at 525 nm increases. Consequently, if for higher luminescence intensity at 525 nm zone, PVP with a molecular weight of $360\,000 \text{ g/mol}$ should be used; if peaks need to be about the same, PVP with a molecular weight of $40\,000$ should be used; and for a more distinguished peak at 400 nm, PVP with a molecular weight of $10\,000 \text{ g/mol}$ should be used.

The study of the influence of the film thickness of PVP containing nano-ZnO on the intensity of luminescence of films is important for film deposition on the surface by printing techniques. Figure 3 shows that in order to increase total luminescence intensity the thickness of the coating layer should be increased. It is possible to use different printing techniques (screen printing, flexography, inkjet, pad printing, etc.). By increasing the layer thickness, the peak at 400 nm can be increased to the level of the peak at 525 nm. In this case, the peak

at 525 nm (a concentration of ZnO is $2 \cdot 10^{-2} \text{ mol/L}$) is always higher than the peak at 400 nm (Figure 4).

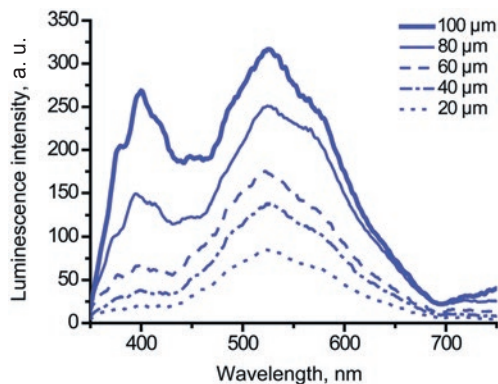


Figure 3: Luminescence spectra of the coatings depending on the thickness; $M(\text{PVP}) = 360\,000 \text{ g/mol}$,
 $[\text{ZnO}] = 2 \cdot 10^{-2} \text{ mol/L}$, $\lambda_{\text{ex}} = 330 \text{ nm}$

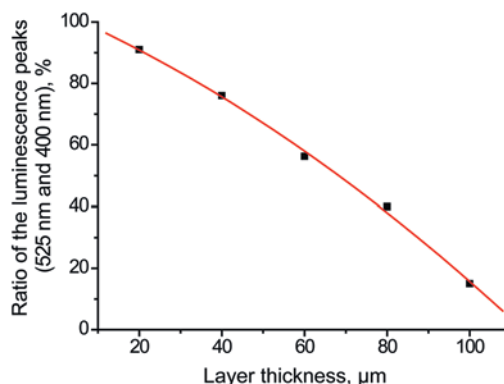


Figure 4: Effect of layer thickness on the ratio of the luminescence peaks (400 and 525 nm); $M(\text{PVP}) = 360\,000 \text{ g/mol}$, $[\text{ZnO}] = 2 \cdot 10^{-2} \text{ mol/L}$, $\lambda_{\text{ex}} = 330 \text{ nm}$

Figure 5 shows the relative change in luminescence intensity depending on the thickness of the coating layer. Relative luminescence intensity is calculated dividing the luminescence intensity of the analyzed sample by the primary luminescence intensity (or the luminescence intensity of the basic sample). Thus, in the Figure 5, the last sample (with layer thickness of $100 \mu\text{m}$) has the luminescence intensity (in the short-wave region – 400 nm) about 7 times higher than the first sample (with layer thickness of $20 \mu\text{m}$) does.

For different concentrations of nano-ZnO, relative change in luminescence intensity with the thickness of the coating layer is almost the same. With the increase of thickness of the coating layers, the increase of the peak at 400 nm (typical for the polymer) is more significant than the increase of the peak at 525 nm. Total luminescence intensity increases with the increase of coating layer thickness, therefore for the highest total luminescence of the films it is appropriate to use the highest technologically achievable thickness of the coating layer.

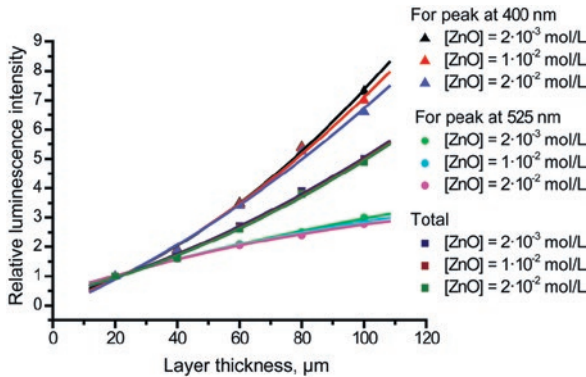


Figure 5: Effect of layer thickness on the luminescence intensity of coatings with different concentrations of nano-ZnO; $M(PVP) = 360\,000\text{ g/mol}$, $\lambda_{ex} = 330\text{ nm}$

The observed pattern is related to the fact that the increase of the thickness of the layer takes place due to the polymer component, as shown in Figure 6.

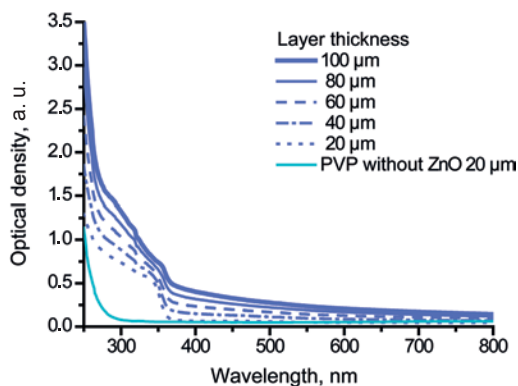


Figure 6: Absorbance spectra of the coatings depending on the thickness; $M(PVP) = 360\,000\text{ g/mol}$, $[ZnO] = 2 \cdot 10^{-2}\text{ mol/L}$

This phenomenon can be explained by the processes of luminescence quenching caused by the presence of oxygen in the deposited layers. With the increase of thickness of a coating layer, the intensity of absorption of

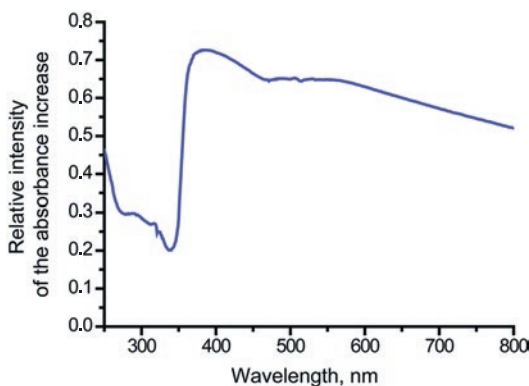


Figure 7: The relative intensity of the absorbance increase with increasing coating thickness of the layer 4 times; $M(PVP) = 360\,000\text{ g/mol}$, $[ZnO] = 2 \cdot 10^{-2}\text{ mol/L}$

the layer in the region of nano-ZnO absorption (250–350 nm) increases less significantly than in the region of absorption of the polymer (350–800 nm) – on average of 30 % and 60 %, respectively, with the thickness 4 times higher (Figure 7).

The increase in absorbance depending on the thickness of the coating layer in the shortwave (300 nm) and longwave (500 nm) regions of the spectrum is linear (Figure 8). Relative optical density is calculated dividing the optical density of the analyzed sample by the primary optical density (or the optical density of the basic sample). Thus, in the Figure 8, the last sample (with layer thickness of 100 μm) has the optical density (in the longwave region – 500 nm) almost 5 times higher than the first sample (with layer thickness of 20 μm) does.

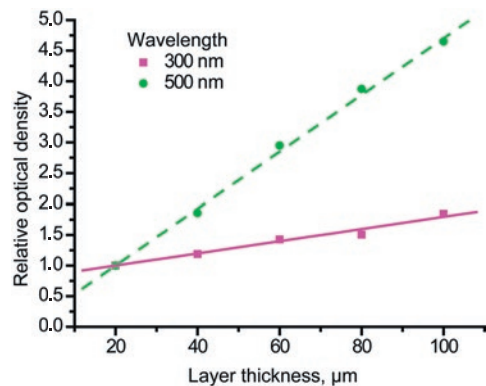


Figure 8: The influence of layer thickness on the change of the optical density of the coatings; $M(PVP) = 360\,000\text{ g/mol}$, $[ZnO] = 2 \cdot 10^{-2}\text{ mol/L}$

The influence of the concentration of ZnO nanoparticles on the luminescent properties of PVP films was also studied (Figure 9).

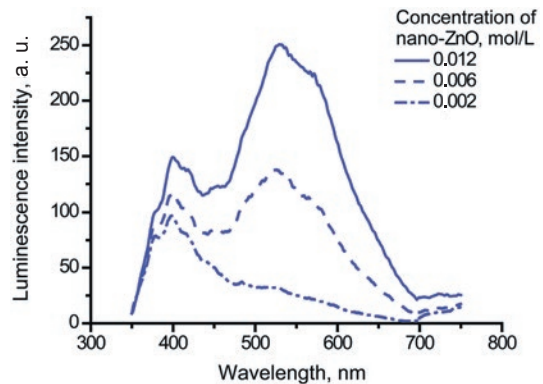


Figure 9: Luminescence spectra of the coatings depending on the concentration of ZnO nanoparticles; $M(PVP) = 360\,000\text{ g/mol}$, $\lambda_{ex} = 330\text{ nm}$

Figure 10 shows that with the increase of concentration of nano-ZnO in the composition the luminescence peak at 525 nm can be reduced to the level of peak at

400 nm and lower or the peak at 525 nm can be raised above the peak at 400 nm. Thus the peak at 525 nm may be lower than the peak of 400 nm, in contrast to the case of changing the thickness of the coatings.

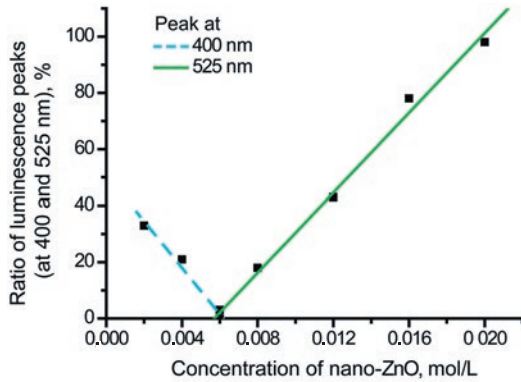


Figure 10: The influence of the concentration of ZnO nanoparticles on the ratio of luminescence peaks (at 400 and 525 nm); $M(\text{PVP}) = 360\,000 \text{ g/mol}$, $\lambda_{\text{ex}} = 330 \text{ nm}$

The integrated luminescence intensity of coatings increases with the increase of concentration of ZnO nanoparticles (Figure 11). Therefore, for the highest total luminescence intensity it is appropriate to use the highest concentration of ZnO nanocrystals in ethanol, which is limited to $2 \cdot 10^{-2} \text{ mol/L}$ (Shvalagin, Stroyuk and Kuchmii, 2004). Figure 11 also shows that with the increase of concentration of nano-ZnO in the composition the luminescence peak at 525 nm increases more significantly than the peak at 400 nm. It allows the manipulation of the ratio of luminescence peaks and, consequently, its color not only by the initial choice of molecular weight of the polymer and change of the layer thickness, but also by changing the concentration of the luminescent component in the composition.

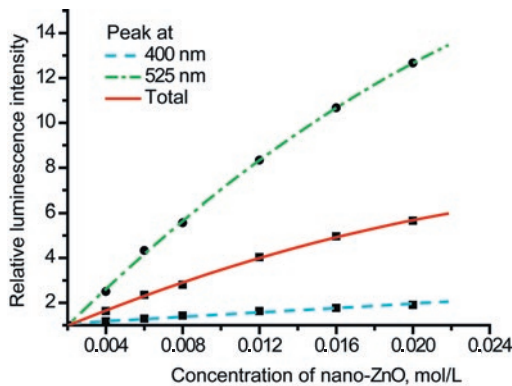


Figure 11: Effect of the concentration of ZnO nanoparticles on the luminescence intensity of the coatings; $M(\text{PVP}) = 360\,000 \text{ g/mol}$, $\lambda_{\text{ex}} = 330 \text{ nm}$

The rapid growth of the luminescence peak at 530 nm, typical for nano-ZnO, can be explained by the increased concentration of ZnO nanoparticles and, consequently,

the optical density in the UV area of the spectrum, as shown in Figure 12. A slight increase of the peak at 400 nm, typical for the polymer, can be explained by the capture of increased emission of ZnO nanocrystals by functional groups at the ends of the polymer chains.

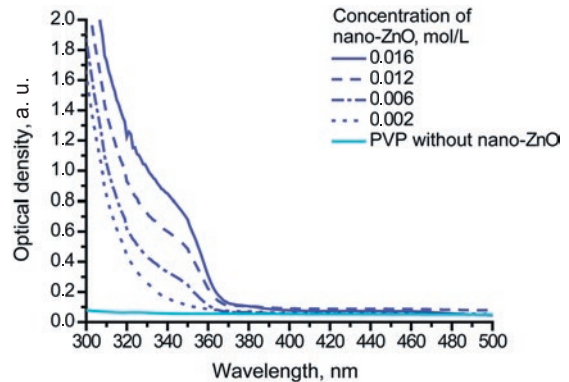


Figure 12: Absorbance spectra of coatings depending on the concentration of ZnO nanoparticles; $M(\text{PVP}) = 360\,000 \text{ g/mol}$

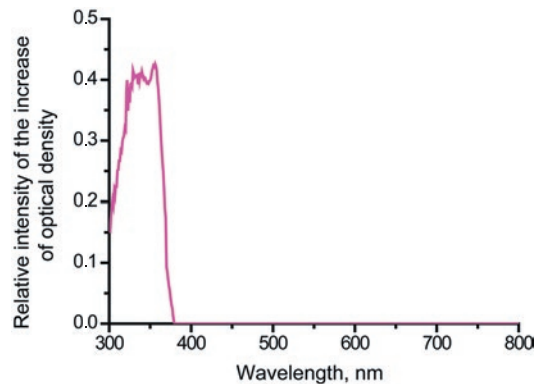


Figure 13: The relative intensity of the increase of optical density of the coatings with the twice increase of concentration of ZnO nanoparticles; $M(\text{PVP}) = 360\,000 \text{ g/mol}$

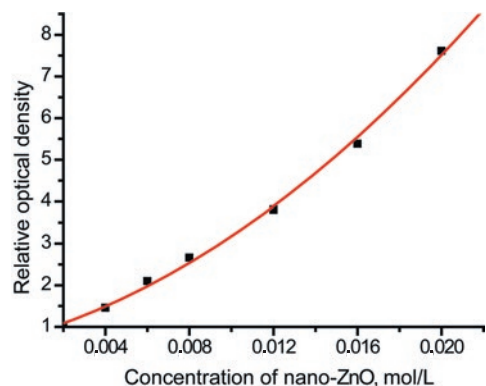


Figure 14: Influence of the concentration of ZnO nanoparticles on the change of optical density in the shortwave region of the spectrum; $M(\text{PVP}) = 360\,000 \text{ g/mol}$

Figure 13 shows that the intensity of absorption in the region of absorption of nano-ZnO (250–350 nm) increases significantly, while in the region of polymer absorption (250–800 nm) it is virtually unchanged. Figure 14 shows that with the increase of concentra-

4. Discussion

In the presented research work the factors and parameters of manufacturing process of photoluminescent coatings based on nanosized ZnO and PVP applied by screen printing onto the surfaces for producing active and intelligent (smart) packaging has been studied.

It was found that the highest intensity of photoluminescence of the coatings can be obtained by increasing thickness of the coatings (up to 100 μm), molecular weight of PVP (up to 360 000 g/mol) and concentration of ZnO nanoparticles (up to 0,02 mol/L) in the initial composition.

The developed compositions based on nano-ZnO and PVP displays two peaks of luminescence in different regions of the visible spectra, which allows controlled changes in luminescent color by manipulation of the peaks ratio. The research has shown that such manipulation is possible by changing the molecular weight of PVP in the composition.

It was determined that for higher luminescence intensity at 525 nm zone (yellow color of luminescence) PVP with a molecular weight of 360 000 g/mol should be used; if peaks need to be about the same (green color of luminescence), PVP with a molecular weight of 40 000

5. Conclusions

As a result of the study, the formation of luminescent coatings by screen printing on polypropylene films was carried out, the parameters of the process of film deposition were defined and the photoluminescence properties of obtained coatings were studied. Optimum parameters of applying the luminescent compositions based on nano-ZnO to the surfaces of smart packaging by screen printing were defined to maximize total luminescence intensity. The possibility to manipulate color of the luminescence by changing molecular weight of the polymer (PVP), concentration of nano-ZnO and layer thickness was studied in detail.

tion of ZnO nanoparticles the absorption intensity of PVP films in the UV region of the spectrum increases proportionally. The relative change in optical density is exponential due to the changes in the concentration of ZnO nanoparticles.

should be used and for a more distinguished peak at 400 nm (blue color of luminescence) PVP with a molecular weight of 10 000 g/mol should be used.

The manipulation of color is also possible by changing film thickness. It was shown that with the increase of the layer thickness the peak at 400 nm can be increased to the level of the peak at 525 nm. Therefore, for relatively thin layer thicknesses (20 μm), blue shades of luminescence color could be obtained. With the increase of layer thickness the color of luminescence gradually changes to green.

The experiments showed that manipulation of color is also possible by changing concentration of nano-ZnO in the composition. It was determined that with the increase of concentration of nano-ZnO in the composition the luminescence peak at 525 nm can be reduced to the level of the peak at 400 nm and lower; or the peak at 525 nm can be raised above the peak at 400 nm. Therefore, for low concentration of nano-ZnO (0,002 mol/L), blue color of luminescence could be obtained, and with the increase of concentration of nano-ZnO up to the maximum possible 0,02 mol/L the color of luminescence gradually changes to green and then to yellow.

The study contributes to the development of smart packaging – a novel method to inform consumers, producers and distributors about various changes in the food packaging during transportation and storage. Smart food packaging is able to notify customers whether the product is safe for consumption. Resulting signal is based on the analysis of chemical content – due to the presence of substances which reveal the degradation and aging processes taking place in packaged foodstuffs. The study will allow the use of existing equipment and technological lines of printing companies to produce the new product – smart packaging with printed nanophotonic elements.

Acknowledgements

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