Coating synthetic materials with zinc oxide nanoparticles acting as a UV filter

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SUMMARY

Zinc oxide (ZnO) is one of physical filters that effectively absorb ultraviolet light in the UV-A range. ZnO produced at the Laboratory of Nanostructures was characterised by nanometric particle size of 28±4 nm (SSA BET). By coating the surface of a transparent film of polyethylene terephthalate (PET) with ZnO nanoparticles, the authors aimed at obtaining a coating that absorbs UV-A radiation. The coating process took place in a water suspension of ZnO, in which the phenomenon of acoustic cavitation was triggered, where the implosion of cavitation bubbles led to deposition of ZnO nanoparticles on the PET film surface. As part of the work, optimum parameters of the PET film coating process were developed, thus obtaining a filter in the form of a ZnO coating that effectively absorbs UV light.

STRESZCZENIE

Pokrywanie materiałów syntetycznych cząstkami nano-tlenku cynku pełniącymi funkcję filtru UV

Tlenek cynku (ZnO) jest zaliczany do filtrów fizycznych skutecznie pochłaniających światło ultrafioletowe w zakresie UV-A. ZnO wytworzony w Laboratorium Nanostruktur charakteryzował się nanometryczną wielkością cząstek 28±4 nm (SSA BET). Pokrywając powierzchnię transparentnej folii z politereftalanu etylenu (PET) nanocząstkami ZnO autorzy mieli na celu uzyskanie warstwy pochłaniającej promieniowanie UV-A. Pokrywanie odbywało się w wodnej zawiesinie ZnO, w której wytworzono zjawisko kawitacji akustycznej, gdzie implozja pęcherzy kawitacyjnych prowadziła do osadzenia się nanocząstek ZnO na powierzchni foli PET. W ramach prac opracowano optymalne parametry procesu pokrywania folii PET uzyskując filtr w postaci warstwy ZnO, skutecznie pochłaniającej światło UV.

SŁOWA KLUCZOWE
nano-tlenek cynku, filtr UV, politereftalanu etylenu (PET), fale ultradźwiękowe

KEYWORDS
nano zinc oxide, UV filter, polyethylene terephthalate (PET), ultrasound

Introduction

The majority of the currently produced film packaging are made of plastics, with PET being one of the most frequently used polymers. The greatest area of application of plastics in Europe is the packaging sector, with a nearly 40% share in the plastics industry in 2013, generating a positive trade balance amounting to EUR 18 billion [1]. PET plastics are not sufficiently resistant to UV radiation, which causes their ageing and degradation [2]. The poor UV-resistance of plastics often leads to quicker spoilage of food and destruction of other everyday use products placed in transparent packaging covers. One of the examples is milk, where UV radiation leads to decomposition of vitamin A and oxidation of milk fat. UV radiation also adversely affects the packaging aesthetic qualities, i.e. discoloration and colour fading. Efficient methods of plastics surface modification are being sought, in combination with a material that would absorb UV-A light effectively, preserving the aesthetic qualities of the material at the same time, among others the colour or transparency scale.

One of generally available materials protecting against UV radiation (10–400 nm) is zinc oxide, characterised by a broad range of UV-A (315–400 nm) and UV-B (280–315 nm) radiation scattering, band gap of 3.37 eV and high photostability [3]. It is categorised as a compound that does not cause skin damage, eye irritation as well as is not toxic or carcinogenic. It also has matting, covering and antibacterial properties [4], [5]. Zinc oxide in the nanometric form effectively scatters UV-A radiation due to the more developed specific surface area of the particles in comparison with zinc oxide in the micro form [6]. This feature becomes evident when using nanoparticles that are smaller than a certain threshold value usually amounting to below 100 nm [7].

Creation of a nano-coating of ZnO nanoparticles on a PET film will enable obtaining a transparent filter that absorbs UV radiation. In addition, the antibacterial and antifungal action [8] of nano-ZnO might postpone the expiration date of packaged food if the coating is present on the inner side of packaging. Coating the outer surface of materials with nanoparticles is one of the most important fields of nanotechnology, and the market value of ZnO nano-coatings alone is worth over USD 8 billion [9].

The proposed ultrasound coating method provides for immersing the material in water suspension. The cavitation phenomenon is triggered by the interaction of ultrasound waves with water, using titanium horn. The stresses emerging at that moment result in the formation of steam bubbles, which grow in line with the oscillation, until they reach a critical state, in which implosion takes place [10]. The imploding bubbles produce large amounts of energy, i.e.: in water up to 5000°C and 1000 bar and generate "micro jet" impact waves, which can reach the speed of 100 m/s^{-1} [11]. If nanoparticles are suspended in the liquid near the solid surface, the impact wave gives them sufficient kinetic energy to drive them into or deposit them on the material surface, forming a coating. The effectiveness of the ultrasound method for obtaining thin nanoparticle coatings was confirmed on glass, metal, fibre or polymer substrates [12], [13], [14]. This technology was called "throwing stone technology" for creating thin active coatings of metal oxides [15]. The versatility and at the same time the uniqueness of this method enables developing it for many fields of industry, in which nanoparticle coatings can be of great significance for improving the quality of products as well as the efficiency and costs of production.

The object of the work was to employ the ultrasound method and to evaluate its effectiveness for generating coatings of ZnO nanoparticles on PET film substrates, thereby obtaining a filter absorbing UV-A radiation. As part of the works carried out, optimum parameters of the coating process were selected, with the optimised factor being nanoparticle content in water.

1. Test method

ZnO NPs ware obtained by microwave solvothermal synthesis. The materials used for the ZnO NPs synthesis were zinc acetate dihydrate and ethylene glycol (both pure for analysis, CHEMPUR, Poland). Synthesis reaction was conducted in the microwave reactor (MSS2, 2.45 GHz, 3kW) [16]. The duration of the reaction was 12 min under constant pressure of 4 bar. After the reaction, the suspension was sedimented and washed three times with deionized water. ZnO was characterised by a narrow particle size distribution, i.e.: average ZnO particle size of 28±4 nm, specific surface area of 40±3 m^2/g, skeletal density of 5.24±0.05 g/cm^3 [17], [18]. ZnO powder was dispersed in the beaker in deionised water, forming suspensions with selected concentrations, i.e.: 200 mg/L (PET1); 350 mg/L (PET2); 500 mg/L (PET3) and 1000 mg/L (PET4). A PET sample in the form of transparent plate sized 2×1 cm was placed in the obtained suspensions in a 50 ml beaker, 2 cm away from the face surface of the ultrasonic head (Ti horn, 20 kHz). The following were constant parameters of the coating process: temperature 25±2°C, coating duration 15 minutes and amplitude 57 μm (50% of generator efficiency). The coated samples were rinsed by deionised water and dried in the laminar flow cabinet, and subsequently handed over for further analyses.

The morphology of ZnO coatings on the film surface was determined using the scanning electron microscope (SEM) (Zeiss, Ultra Plus, Germany). The samples of coated films were covered with a thin carbon layer using the sputter coater (SCD 005/CEA 035, BAL-TEC, Switzerland). The aim of the microscopic tests was to take photographs of ZnO coatings to determine their morphology. Based on the obtained images an analysis of the degree of coverage was carried out using ImageJ software based on contrast from the substrate and ZnO particles.

Measurements of UV light absorbance of PET film were carried out using a UV/VIS spectrophotometer (Spectra Academy SV2100, South Korea). The tested sample in the measurement chamber was positioned with the coated surface square to the light source and subsequently the spectrophotometric measurement was performed. The test consisted in comparing the intensity of the light beam incident on and penetrating the tested sample, based on the Beer-Lambert law [19]. The results were analysed for the wavelength of 340 nm, i.e. one characteristic of UV-A radiation range.

2. Test results

Images in Fig. 1 are representative SEM images of a coated surface in ZnO suspension with concentration of 500 mg/L, which proved best due to coating uniformity. Ultrasound cavitation causes deposition or driving of ZnO nanoparticles into film surface. When comparing ZnO powder with a coating composed of these nanoparticles, it was not found that their morphology had changed under the cavitation energy. In addition, it was confirmed that the obtained ZnO coatings were stable at room conditions and were not flushed away by the simple procedure of water rinsing.

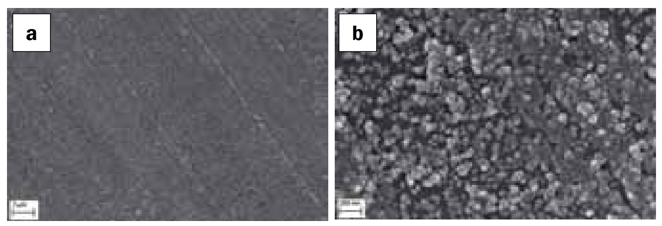

Fig. 1. SEM photographs of the PET surface coated with ZnO particles; enlargement: A: 10 000× B: 100 000×.
Source: Own work.

The analysis of the degree of surface coverage using ImageJ software revealed that for individual concentrations of ZnO suspensions in which samples were coated, the degree of surface coverage amounted to: PET1 – 61%, PET2 – 54%, PET3 – 69% and PET4 – 64%, respectively (Table 1). PET3 sample corresponding to concentration of 500 mg/L of the suspension proved to be the most uniformly coated sample.

Table 1. Degree of surface coverage of individual Zamples.

Sample type	Non-coated	PET1	PET2	PET3	PET4	Coated three times
Degree of surface coverage [%]	-	61%	54%	69%	64%	76%
Absorption [%]	33%	39%	40%	52%	44%	66%

Source: Own work.

One of the considered factors determining the effectiveness of UV-A light absorption was the uniformity of surface coverage with ZnO nanoparticles. It was assumed that the most uniformly covered sample would indicate the greatest absorption of UV light.

As presumed, it was indicated that the best UV-A light absorption coefficient was displayed by a PET3 film coated in a suspension with concentration of 500 mg/L of ZnO (Fig. 2), with absorptivity greater by 19% than a film that was not coated. During the research work, best process parameters were selected (i.e.: 500 mg/L, plus constant parameters of the process), thanks to which an experiment consisting in repeated coating of films was carried out in order to enhance the absorption effect. It was proved that a film coated three times in separate processes was characterised by twice as high absorptivity than a clean film and by 14% higher absorptivity than in the case of a single coating of PET surface (Table 1). The spectrum of the absorbance diagram of individual samples for the wavelength range of 330–400 nm is reflected in Figure no. 3.

The authors conclude that the coating becomes denser with

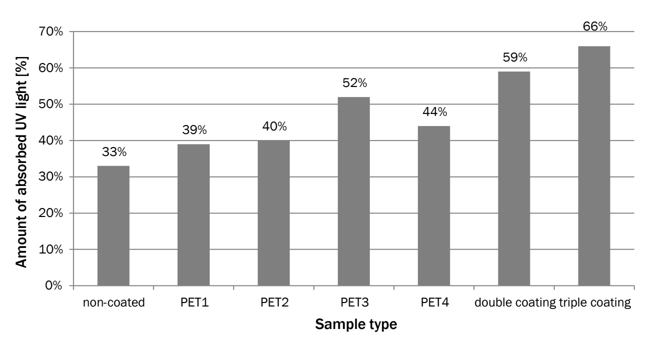

Fig. 2. UV light absorptivity of tested samples for UV wavelength: 340 nm.
Source: Own work

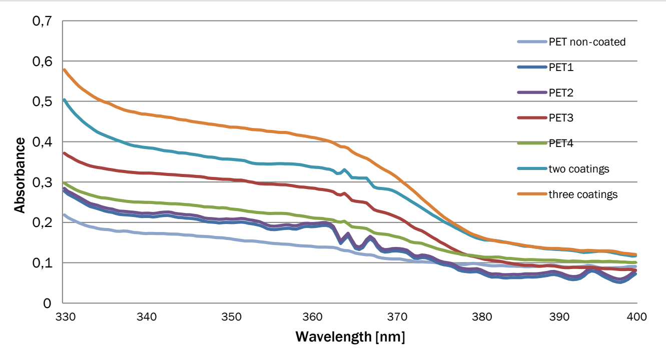

Fig. 3. Diagram of absorbance of the tested samples for wavelength range of UV 330–400 nm.
Source: Own work

each successive coating process, which results also in a greater coating thickness and more effective light absorptivity. The modification of PET film surface does not change the colour or transmittance of visible light. No change of original transparency of the coated sample was noticed with the naked eye (Fig. 4).

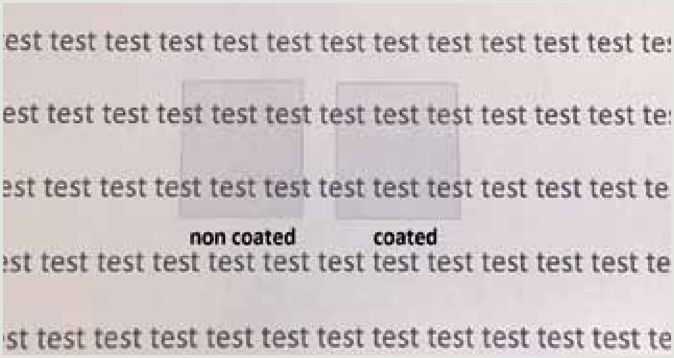

Fig. 4. Comparison of transparency of non-coated PET film and one coated with nano zinc oxide.
Source: Own work

As part of the works, promising attempts to coat PET films with ZnO nanoparticles were made, thereby obtaining an effective UV-A filter. The cavitation energy enabled creation of an active coating of ZnO particles that preserved their initial morphology. Due to the nanometric thickness of the coating, the coated samples preserve their transparency. The described method is a promising coating technology thanks to efficient process capabilities, i.e.: short duration, small nanoparticle contents in the suspension and low process temperature which permits coating such materials that are particularly sensitive to increased temperatures. It was found that the ultrasound method permits creating a UV filter with a possible control of UV light absorptivity if process parameters are selected appropriately. This technology is also characterised by mild process conditions, i.e. those which do not give out hazardous compounds to the environment, thanks to which it can be qualified as "green technology." In the industrial version, this technology can be used for production of polymer UV-resistance packaging with possible biocidal properties, especially packaging for food products with short-expiration date. Additionally, potential applications of this technology and ZnO NPs can be extended for different substrates like glass, for improving their optical properties as well as surface wettability.

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