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Investigation of synergistic effect of nano sized Ag/TiO_2 particles on antibacterial, physical and mechanical properties of UV-curable clear coatings by experimental design

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ABSTRACT

The synergistic effect of nano titanium dioxide (10 and 30 nm) and nano silver (10 nm) as antibacterial agents were investigated on UV curable clear coating. Antibacterial and physical–mechanical properties of coating were optimized using experimental design in response surface method. Twenty different samples of nano Ag and nano TiO_2 were prepared in this method. Antibacterial properties on Gram-negative bacteria (*Escherichia coli*) were investigated. The results revealed that using equal amounts of two sizes of nano TiO_2 promote the antibacterial activity of nano Ag. So, the coating shows strong activity against *E. coli*. Physical–mechanical properties such as surface hardness, abrasion resistance, scratch resistance and gloss of the coating were evaluated. The results depicted appropriate physical–mechanical properties. Also, scanning electron microscope (SEM), atomic force microscope (AFM) and Fourier transform infrared (FT-IR) spectroscopy were used to study the effect of nano particles on coating properties.

1. Introduction

Coatings have been used to protect surfaces from biodegradation and environmental degradation [1]. UV curable coatings are known as environmentally friendly with excellent mechanical properties and chemical resistance [2,3]. Moreover, they have numerous advantages such as low curing time [4] high cross linked networks [5] and low energy consumption [6].

In this regard, many studies have been conducted on properties of UV curable coatings. Among different resins, UV curable polyurethane offers properties such as: excellent hardness [5], high gloss [7], good chemical and weather resistance [8], good adhesion and film forming performance [9].

Antibacterial coatings are a kind of functional coatings that have wide range of applications in clothing, textiles, floor and medical instruments. Anti-microbial agents such as Ag, TiO_2, ZnO, Au, chitosan, SiO_2, $Mg(OH)_2$ and carbon nanotubes have been used to prevent microbial infection in coating [1,10]. Among these materials, nano-sized Ag has received considerable attention because of its greater efficacy and durability [11].

The antimicrobial mechanism of the silver nanoparticles has not yet been fully understood. It is believed that silver nano particles release Ag^+ ions which band to sulphur, oxygen or nitrogen in proteins, DNA and RNA molecules and disrupt their functions. For example, Ag^+ ions affect the replication of DNA by interacting with the thiol groups in bacteria proteins [12,13].

Furthermore, the ability of TiO_2 to improve the antibacterial performance of coatings has been proven [14]. Titanium dioxide can create electron–hole pairs as a result of UV radiation. The electron–hole pairs in this reaction with the available water and oxygen molecules can generate reactive oxygen species such as hydroxyl and superoxide radicals. The oxidation of all organic compounds in the microorganisms by these reactive oxygen species leads to cell death [15].

Recently, researchers have been used Ag–TiO_2 nanocomposite to expand antibacterial function to a broader range of working conditions [16,17].

Various methods have been presented to synthesis of Ag/TiO_2 nano composites [18,19]. Likewise, anti-bacterial efficiency of Ag/TiO_2 in different kinds of fabrics such as polypropylene [20], polyester [21] has been reported. The antibacterial activity of Ag/TiO_2 in thin solid films has been also investigated [22–25].

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Table 1
The range of nanoparticles.

Nano particles	Range of particle size (nm)	Surface area (m^2/g)	Bulk density (g/m^3)	Purity (%)	Shape
TiO_2	<10	150	0.24	99	Spherical
TiO_2	<30	60	0.7	99.9	Spherical
Ag	<14	–	–	99.9	Spherical

The synergistic effect of nano silver and nano titanium dioxide on organic coating especially UV curable coating has not yet been studied.

This work intends to study the synergistic effect of nano silver and nano titanium dioxide on antibacterial and subsequently mechanical properties of UV curable polyurethane acrylate coating. For this purpose, the software experimental design was used to optimize the amount of nano particles.

2. Experimental

2.1. Materials

Trimethylolpropanetriacrylate (TMPTA), 1,6 hexanediol diacrylate (HDDA) and dipentaerythritol pentaacrylate (DIPEPA) as monomers, also Eterphoto PI BP and Etermer 641 as photoinitiator and amine respectively were obtained from Taiwan Eternal Company. Aliphatic urethane triacrylate oligomer (Ebecryl 204) was purchased from Cytec – UV/EB curable resins and additives. Buthyl acetate was purchased from Merck. Dispersant and leveling agent were obtained from BYK and EFKA, respectively.

Nano titanium dioxide (anatase) in two different sizes (10 nm and 30 nm) and colloidal nano silver (10 nm) were obtained from Iran Pars Lima Co. Some of the physical and chemical properties of the nano particles are reported in Table 1.

2.2. Experimental design

The Design-Expert software (Version 7) in response surface method is used to achieve the optimum properties. The software was used for graphical analysis of the obtained data. The main goal of response surface is hunt efficiently for the optimum values of the variables such that the response is maximized [26].

The input parameters of the software were selected experimentally with regard to antibacterial performance of the coating.

Preliminary trials were enabled to determining the range of nano particles as the inputs. Three samples were prepared as samples a, b and c with a: 100 ppm, b: 170 ppm and c: 240 ppm of nano silver. The antibacterial test of the cured samples showed 58%, 73% and 100% reductions of CFU, respectively. Therefore, the range of nano silver was selected from 100 to 240 ppm. In addition, the range of nano TiO_2 was selected from 0 to 2400 ppm because the appropriate amount of TiO_2 to Ag was reported 10:1 [27]. The input parameters are summarized in Table 2.

Table 3 presents weight of the nanoparticles in ppm for preparation of samples according to the experimental design.

Table 2
The range of nanoparticles (the input parameters).

Factor	A: Ag (10 nm)	B: TiO_2 (30 nm)	C: TiO_2 (30 nm)
Range of nanoparticles (ppm)	100–240	0–2400	0–2400

The associated *p*-value for all the models were selected lower than 0.05 (i.e. $\alpha = 0.05$, or 95% confidence) which indicated that the models were considered to be statistically significant. Therefore, according to sequential model sum of squares and analysis of variance tables, the significant model was selected for each test. For analysis the data, the checking of goodness of fit of the model is very much required. The model adequacy checking includes test for significance of the regression model, test for significance on model coefficients and test for lack of fit [28]. For this purpose, analysis of variance (ANOVA) is performed.

2.3. Preparation of coating formulation

For preparing 20 g of final formulation, defined amount of nano TiO_2 powder (according to Table 3) was added to the n-butyl acetate (4 ml) and a kind of dispersant (BYK 110, 0.12 content of total TiO_2) then ultrasonicated for 15 min. Subsequently, nano Ag and HDDA monomer (37 wt.%) were sonicated for 15 min. Exterior cooling was employed by surrounding the samples container in an ice and water bath to avoid heat rising during sonication process. TMPTA (4.5 wt.%), DIPEPA (4.5 wt.%), Ebecryl 204 (46 wt.%), PI (3.7 wt.%), amine (3.7 wt.%) and leveling agent (EFKA 3033, 0.3 wt.%) were added to the nano Ag suspension and stirred at 1000 rpm for 30 min. Then, nano TiO_2 suspension was added to the mixture and pearled at 1000 rpm for 45 min.

Prepared formulation was applied on glass, metal and polycarbonate plates. The coatings were applied using 30 μm bar coater (Model 352, Erichsen Co.) on the panels.

A UV lamp with radiation intensity equal to 25 mW/cm^2 and a high pressure mercury lamp (RW-UV.2BP Shenzhen Runwing) were used to cure samples. These plates were cured with a belt speed of 0.5 m/min and intensity 120 W in ambient temperature (range from 10 to 365 nm).

Table 3
Concentration of nano materials (ppm) in each sample.

Experimental no.	Ag	TiO_2 (30 nm)	TiO_2 (10 nm)
1	100	0	2400
2	100	2400	0
3	100	0	0
4	240	0	0
5	240	0	2400
6	240	2400	0
7	170	0	1200
8	170	1200	0
9	240	800	800
10	170	1200	1200
11	170	109	109
12	100	598	1200
13	115	1500	602
14	170	0	2400
15	223	1500	266
16	131	634	300
17	137	378	1800
18	224	150	1470
19	166	600	600
20	170	240	0