ANTIMICROBIAL PROPERTIES OF TiO_2 NANOCOMPOSITE COATING

[1]Tomislav HUDIKA, [1]Tomislav CIGULA, [1]Marina VUKOJE

[1]*Univesity of Zagreb, Faculty of Graphic arts, Zagreb, Croatia, EU, thudika@grf.hr*

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Abstract

Packaging plays important part of the visual communication and in consumer's choice of purchasing goods. To enhance visual appearance, packaging material is often coated. Beside enhancement of visual appearance, additional coating often improves other packaging properties. The COVID-19 pandemic stressed the importance of the antimicrobial properties of goods that encounter consumers. During purchasing, consumer first meets the packaging making it significant in the consumer's protection. The aim of this research is to determine antimicrobial properties of nanocomposite coating which includes nanosized TiO_2. For the purpose of the research a set of offset cardboard prints was coated with nanocomposite coating composed of water-based varnish (WD) and nanoscale TiO_2 particles. The prepared samples were characterized by determining *CIE L*a*b** coordinates of primary colours (CMYK), detecting colour fading after the accelerated ageing process by density measurements and by determining inhibition of microorganisms' growth by using smear test.

The change in chroma affected by UV radiation (accelerated ageing) is most visible on yellow samples while both, cyan and magenta proved to be more resistant to UV radiation. UV radiation did not cause significant change on the *L** coordinate of black, although its values were affected with initial varnishing as TiO_2 is also used as a white pigment. Although increase of the TiO_2 concentration in nanocomposite causes increase of the colour change, only the one with the highest concentration (2%) proved to be unacceptable. On the other hand, as the beneficial effects of nanocomposites increase with increase of the TiO_2 concentration, the nanocomposite with 1% of TiO_2 should be the choice.

Keywords: Cardboard packaging, nanoparticles, titan dioxide, functional coating, antimicrobial properties

1. INTRODUCTION

The packaging sector is the part of printing industry that connects protection of the goods and packaging as well as the visual communications [1]. To achieve this role some packaging materials are coated. To enhance inclusion of the coating process in the packaging production it is beneficial if the coating can provide more then one advantage i.e., to protect printed surface from colour degradation, to help with the barrier properties, to have antimicrobial potential, to be sustainable, etc. To upgrade existing varnish benefits, it is possible to introduce certain compounds into the composition, which are known to have protective potential. Those kinds of compounds are mostly nanosized (<100 nm) and could be added in the commercial varnishes [2]. Recent studies show that metal oxides such as titanium dioxide (TiO_2) and zink oxide (ZnO) demonstrate strong antifungal and antibacterial potential against wide range of known bacteria [3][4][5][6]. Moreover, the TiO_2 has the ability when UV exposed, to develop photocatalyst state in which oxygen free radicals (OFRs) develop. Those OFRs can affect the bacteria/fungus cell wall and help stop its growth [7]. Due to overuse of antibiotics, humans are more vulnerable to bacterial and fungus [8]. Even more, it is not uncommon for the customers to wear the gloves during shopping as a means of protection against COVID19 and other microbes which also leads to human's lower immunity against microbes [9][10]. In the light of the recent pandemic COVID19, consumers have become more aware of microbial threat in general [10]. Although, microbes are all around us and help maintain the natural balance, not all of them are desirable [8]. The printing industry and its packaging sector has a new challenge; how to provide antimicrobial properties on the packaging surface while maintaining the quality of visual communications. On the other hand, this is also significant market opportunity as it is projected that packaging alone is to have growth of 2.85% and reach 1.05 trillion US dollars (2019-2024) [11]. The antimicrobial packaging alone is projected 5.89% (2021-2026), mostly attributed with previously mentioned pandemic [12]. The aim of this research is to determine antimicrobial properties and diminished colour fading of the prepared cardboard prints due to the applied with TiO_2 nanocomposites.

2. MATERIALS AND METHODS

For this research, the gloss art print paper (coated) with production name UPM Finesse gloss paper (300g/m^2) was used as a printing substrate. The samples were printed via sheetfed offset printing technique using quickset process inks (Novavit Supreme Bio by Flintgroup) in compliance with FOGRA PSO 2016, i.e., ISO 12647-2:2013 [13].

Nanocomposite coatings were prepared by dispersing nano sized TiO_2 (Sigma Aldrich TiO_2, rutile) in commercial water-based varnish (TerraWet High Gloss Coating G9/285, ACTEGA, NY) further denominated as WD. Nanoparticles were added in designated weight ratios 0.25%, 0.5%, 1% and 2%.

The homogenisation process of nanoparticles into the WD varnish was done using ultrasound dispenser Hielscher UP100H for 30 minutes at 100% amplitude and 100% power [14]. The samples were cooled during the homogenisation by immersing containers containing the mixtures into a cooled water at 7 °C. Following the process, nanocomposites were applied onto printed samples using K202 Control Coater in compliance with ISO 187:1990, using coating bar 1 which leads to approx. 6 µm of wet film thickness [15].

After drying and characterization the samples were exposed to an artificial ageing process in the Cofomegra Solarbox 1500e Xenon Test chamber for 30 hours period at irradiation energy of 550 W/m^2 and 50 °C. The indoor filter was used for the simulation of internal environment i.e. sunrays filtered through a window pane [16].

To analyse and characterize prepared samples, optical density and colour coordinates were determined at three stages: original (uncoated) prints, coated prints and aged coated prints. The colorimetric measurements were conducted using Techckon SpectroDens spectrophotometer with colorimetric measurements' settings: D50 illuminant, 2° standardized observer, M1 filter, no polarisation filter and calibrated before measurements on absolute white. Instrument settings for density measurements were density status E, illuminant D50, no polarization filter and calibrated on plain paper (original print).

The influence of TiO_2 nanoparticles in varnish on growth of microorganisms was evaluated by examination of the total number of microorganisms of on coated samples (S2) and artificially aged samples (S3). For the microbiological testing of samples by smear method, the procedure described by Guzińska et. al was used [17]. The microorganisms were isolated (washed) from the samples surface by horizontal sampling method by means of a swab wetted in 9% saline solution. The swab was then transferred to a 9% saline solution and shaken, after which that solution was used for the preparation of series of dilutions from 10^{-1} - 10^{-5}. Petri dishes were inoculated with 1 mL of the prepared dilutions and flooded with nutrient agar (NA) medium. Incubation of the Petri dishes was made at 37 °C for 48 to 72 hours and at 30 ± 1 °C. The number of microorganisms per 1 mL of the tested cardboard surface was calculated.

3. RESULTS AND DISCUSSION

3.1. Results and discussion

To check the printing process, the ΔE_{ab} colour difference of the printed sample in relation to ISO 12674-2:2013 standard (Fogra PSO 2016) by was calculated. The measured values of Cyan (ΔE_{ab} = 1,5) show that is the closes to the standard of all presented samples, while Black (ΔE_{ab} = 3,1) and Magenta (ΔE_{ab} = 3,7) and Yellow (ΔE_{ab} = 4,2) are within the tolerance. Yelow is closest to allowed tolerance (ΔE_{ab}<5). To determine the influence of the coating process on the colour's perception between two sets of prints (*printed samples (S1), coated samples (S2)*) colour difference ΔE_{00} was calculated from measured *L*a*b** values (**Table 1**). The black ink is sensitive to change as the ink is dark, so contrast is easy to spot. The biggest change occurred on the black coated with nanocomposite including 2% TiO_2 (*ΔE_{00}=4,32*). This result could be attributed to the fact that the TiO_2 is used as white pigment [18].

Table1 ΔE_{00} calculated difference

	C	M	Y	K
S1-S2 wd	0,54	0,84	0,40	2,47
S1-S2 0.25%	0,68	1,36	0,26	1,58
S1-S2 0.5%	0,83	1,18	0,32	1,55
S1-S2 1%	0,86	1,52	0,21	1,60
S1-S2 2%	1,18	3,13	1,60	4,32

3.2. Influence of accelerated ageing on prints' colour

Chroma in colours is mostly connected with intensity of colour, meaning that the low chroma colour can appear dull to the human eye. In order to detect behaviour of the colour intensity C_{ab}, was calculated using formula (1):

$$C_{ab} = \sqrt{a^2 * b^2} \quad (1)$$

where: *a – is a* coordinate from CIE L*a*b** and *b – is b* coordinate from CIE L*a*b**

In the **Figure 1**, Croma (C_{ab}) is presented for cyan (right) and magenta (left). The cyan samples (**Figure 1 left**) show insignificant change after accelerated ageing. The increment in the WD (varnished samples without TiO_2) can be attributed to the spectrophotometer measurements error since the change is so small. The magenta (**Figure 1 right**) shows very similar behaviour on all samples after except 2% TiO_2 where the values are lower, but the trend is similar. It could be noted that on both colours the accelerated ageing is causing diminishing of the colour chroma, i.e. colour intensity.

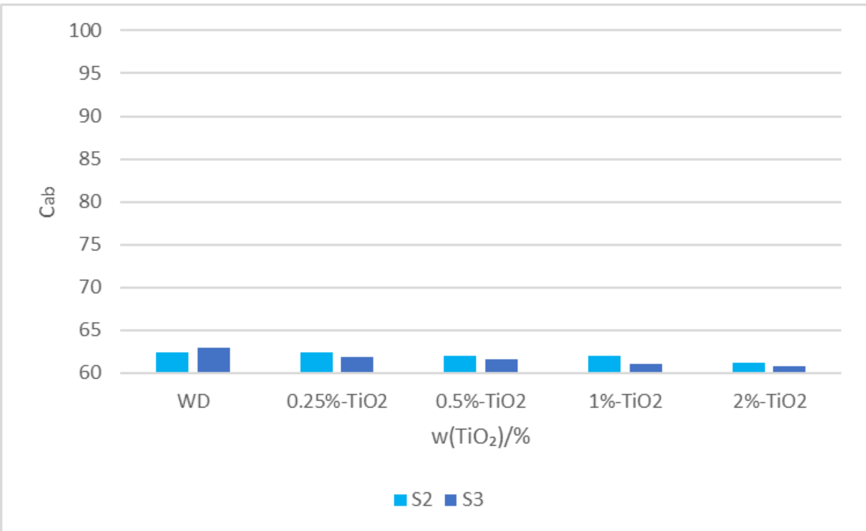

Figure 1/1 Cyan (up) and magenta (down) C_{ab} values

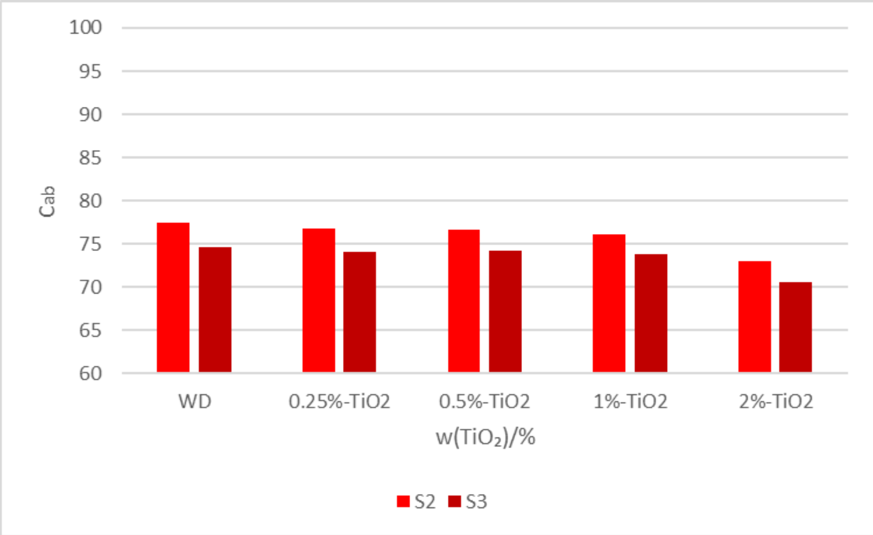

Figure 1/2 Cyan (up) and magenta (down) C_{ab} values

Chroma of yellow printed samples (**Figure 2**) is most affected with the UV radiation exposure (*ageing process*). Although it appears that nanocomposite coatings are keeping chroma at the same level, please note that increasing the weight ratio of the TiO_2 is decreasing chroma of coated samples (before accelerated ageing process). The chroma decrease with increase of the TiO_2 could be attributed to the addition of achromatic (TiO_2 is used as a white pigment) while one the other hand, it is preserving pigment from degradation by absorbing part of the UV light.

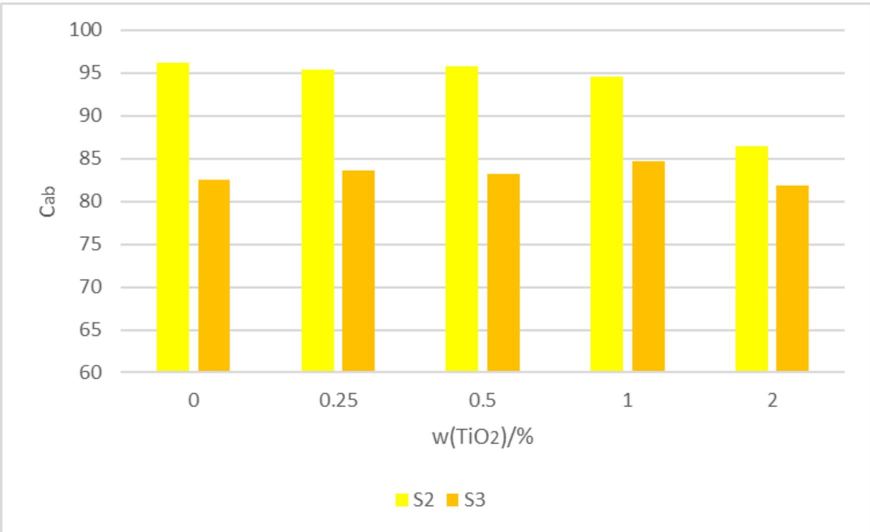

Figure 2 Yellow (left) C_{ab} values

The change that occurs with the black samples can be best observed via *L** coordinate due to fact that black is achromatic and therefore change in *a** and *b** is less visible. In the **Figure 3**, measured lightness (L* coordinate) values can be seen. It can be noted that with the increase of TiO_2 weight ratio, the lightness increases since the TiO_2 is also used as a white pigment. The change from S2 to S3 is below 0,5 meaning it is insignificant. This shows that although TiO_2 rises initial values after coating it does protect the ink from additional fading.

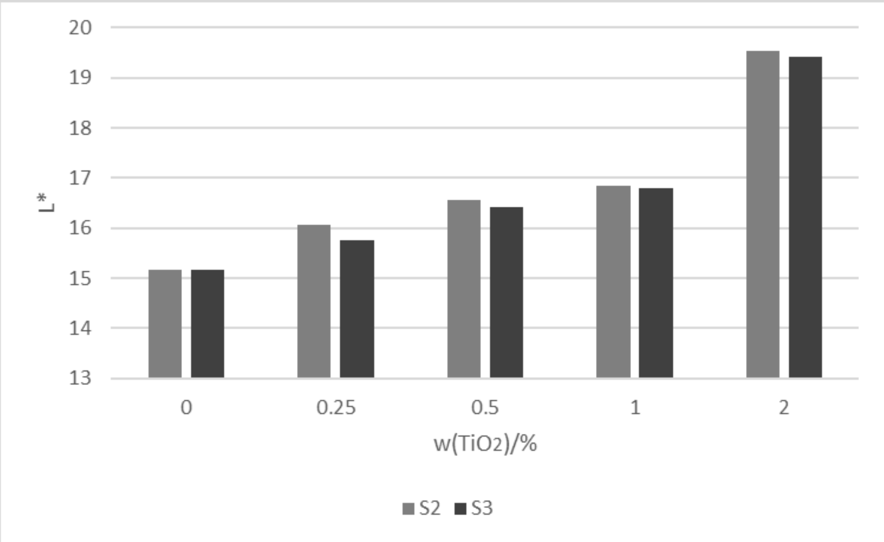

Figure 3 Black *L'* values

To further assess the influence of UV exposure during accelerated ageing, ink' density was measured. To enable better image of the coating and aging influence, In **Figures 4**, one can see diagrams for density change (*D'*). The cyan (*left*) and magenta (*right*) samples are presented. As the colours are printed to match colorimetric expectation, printing is performed in different densities. Therefore, to enable comparison between inks, density change (*D'*) was intorduced. The density change is calculated using Equation (3) :

$$D' = \frac{D_0}{D_i} \tag{3}$$

where, D_o – density value of coated samples(*S2*), D_i – density value of coated samples after aging(*S3*).

Observing **Figure 4**, it can be noted that cyan's and black's density is constant and nearly 1 which means it was unchanged after accelerated aging. Magenta is also almost unchanged in the 0-1% weight ratio, where a growing trend can be spotted in the higher ratios. This can be attributed to the TiO_2 photoluminescence which occurs both in polymorphs (*rutile and anatase*)[19]. Yellow, as the most sensitive one show that increase of the TiO_2 weight ratio in nanocomposite lead to the increased UV resistance (the lowest D' is at 2% of TiO_2).

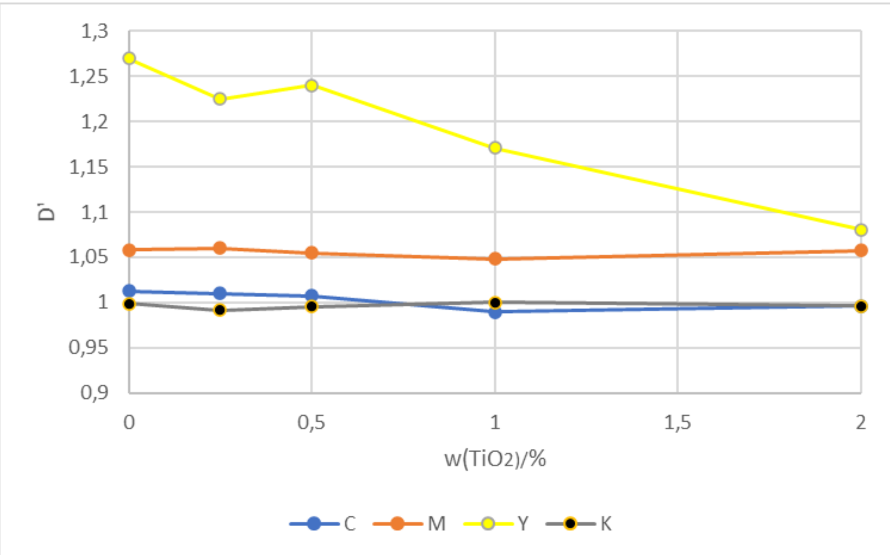

Figure 4 Ink density change (D') – magenta (left) and yellow (right)

3.3. Antimicrobial properties of prepared samples

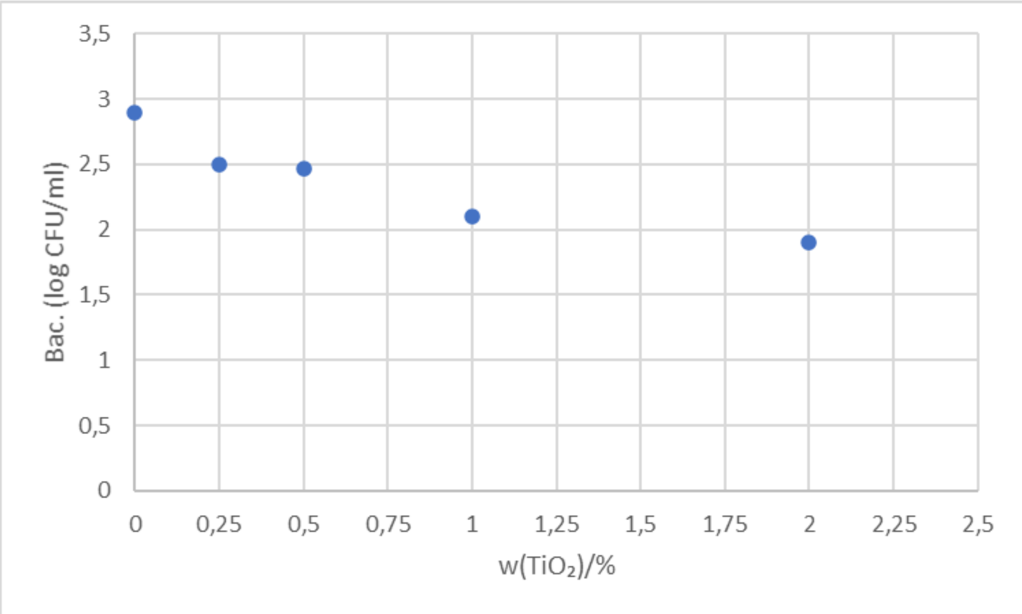

Figure 5 Total number of bacteria in the tested aged samples

The applied smear method did not reveal the bacterial contamination of the unaged uncoated and coated samples surface probably due to the presence of antibacterial additives in varnish or by the presence of the bacteria in the deeper layer [17]. The problem related to the growth of various microorganisms occurs in almost all water-based inks. Since water-based varnishes used in printing have similar composition as printing inks, only without pigment, this problem can be related to them as well. In order to prevent or inhibit microbial growth, different biocides and fungicides can be added in their formulation [20]. When it comes to printing inks, additives in a function of biocides/fungicides are added in proportion of <0.5%, based on the total quantity of the ink formulation. For this reason, on the unaged samples no bacteria occurred. On the contrary, bacterial growth was obtained on aged samples. This leads to a conclusion that UV irradiation most probably caused the breakdown of biocide composition. On the aged samples, it can be seen that by increasing the content of TiO_2 in varnish, the total number of bacteria decreases which may lead to a conclusion that nanoparticles have antibacterial effect (**Figure 5**), i.e. higher share of TiO_2 nanoparticles has higher antimicrobial effect.

4. CONCLUSION

The growing packaging market demands new solutions that can cope with numerous challenges at the same time. The change in the colour during product storage and sales and, due to the recent pandemic of Covid19, antimicrobial behaviour are, among other, two factors that can be a powerful tool in demanding market. The aim of this research was to investigate how does application of nanocomposites composed of commercial water based varnish and nanoscale TiO_2 is replying to those challenges.

To summarize, although increase of the TiO_2 concentration in nanocomposite causes increase of the colour change, only the one with the highest concentration (2%) proved to be unacceptable. On the other hand, as the beneficial effects of nanocomposites increase with increase of the TiO_2 concentration, the nanocomposite with 1% of TiO_2 should be the choice. Nevertheless, to further evaluate application of the proposed nanocomposites, future research will be focused on the coating process, barrier properties, adhesion on the substrate etc.

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