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INFLUENCE OF LIGHT INDUCED ACCELERATED AGEING ON SURFACE PROPERTIES OF CARDBOARD PACKAGING COATED BY TIO_2 NANOCOMPOSITES

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Abstract: *Although the primary role of packaging is to protect its content, it also acts as the carrier of both relevant information and visual identity. To enhance its properties, packaging materials are often coated with material which could provide barrier against chemicals, atmospheric conditions, or electromagnetic radiation. This paper focuses on the change of surface properties, i.e., wetting of a coated cardboard surface when packaging material is exposed to light induced accelerated ageing.*
Prepared printed cardboard was coated with nanocomposites composed of commercial water-based varnish and defined mass concentration of nanosized TiO_2. The prepared samples were subjected to accelerated ageing in a light chamber equipped with Xenon lamp. The characterization of the samples included determining contact angles with liquids of known surface tension and calculating surface free energy, determining water vapour transfer rate and performing burst resistance tests (Mullen burst test).
It can be concluded that the UV radiation influenced the cardboard substrate and varnished samples where AcA made some changes in the polar component due to forming of new oxidation products, which are less polar from its -OH group. However, with the introduction of nanoparticles, the UV influence was lowered in terms of surface parameters. The smallest TiO_2 weight ratio (0.25%) lowers the WVTR by 56%. Moreover, with increase of TiO_2 nanoparticles weight ratio, water permeability decreases significantly where the 0.5% TI/NC provided the best result (decrease of63%). Regarding the mechanical properties, although bursting strength of samples coated with nanocomposites is higher than the one coated by WB, there is no visible dependence between mechanical properties and weight ratio of nanoparticles.
This research showed that addition of TiO_2 nanoparticles will improve commercial varnish and will increase protection against UV radiation in terms of adhesion to the substrate and water vapour barrier.

Keywords: Coating, Nanocomposite, Packaging, Titanium dioxide (TiO_2), Accelerated ageing

1. INTRODUCTION

The global packaging industry grew from 843 billion US to 914 billion US from 2015 up to 2019, which is approx. 2%. Due to Covid-19 pandemic in 2020, the industry had a drop of approx. 6% (to 859 billion US), but according to forecasts, the "new dawn" of packaging is yet to come where in period of 2020-2030 is estimated that the industry will reach 1.13 trillion US (Smithers, n.d.). To have the continuous growth and to follow new trends, industry must develop more resistant and more sustainable packaging. In terms of secondary printed packaging application of these concepts must not degenerate its basic purpose and requirements. The basic purposes of the packaging are product protection and aesthetics (Makower, n.d.). Paper and its derivatives are ecologically acceptable materials since the use of single-use plastic is at its final (European Commision, 2021). On the other hand, paper as such, also has some issues, for example relative low resistance to outer influences like UV radiation, moisture or simply the weather in general. With this in mind, some quality factors of printed packaging can be reduced by an outer influence such as UV induced degradation, i.e., UV radiation causes the change in surface morphology and structural properties leading to the overall degradation of material (Hudika, 2022).
To diminish that setback, one of the solutions is to laminate protective layer or coat the printed packaging surface (*The Importance of Secondary Packaging*, n.d.; Soroka, 1999). Due to the limited protective properties of varnishes, further step in enhancing protection is to upgrade the existing varnish by modifying it to meet specific needs (Cigula, Hudika & Vukoje, 2021; Hudika, Cigula & Vukoje, 2021; Hudika, 2022). The water-based varnish (denominated as WB) is the most "eco-friendly" coating type on the market that has the industrial, technological, and commercial capability since it does not create hazardous vaporization when handling or curing, but WB varnish has some downsides when compared to

UV varnish for instance in terms of lightfastness, barrier properties etc. (Kipphan, 2001a; Yam, 2010; *3 Oak News - Why are water based lacquers becoming so popular*, 2015; Moreira *et al.*, 2018). Some research has been made with incorporation of nano sized compounds in commercial varnishes that improved packaging properties (Zvekic *et al.*, 2011; Salla, Pandey & Srinivas, 2012; Cigula, Hudika & Vukoje, 2021; Hudika, Cigula & Vukoje, 2021; Hudika, 2022). One of those compounds is a metal oxide, titanium-dioxide (TiO_2), well known for its ability to absorb UV radiation and commonly used as part of inks, colours, coatings, sunscreens, etc. (Kumar, Verma & Singla, 2012; Hudika *et al.*, 2020; Pfaff, 2021).
The aim of this research was to compose a nanocomposite coating containing TiO_2 (denoted as TI/NC) which will upgrade existing varnish in terms of preservation of printed packaging under influence of UV radiation, therefore preserving the function of the packaging throughout the assumed product's lifespan. In the same time, to implement those particles into a commercially available varnish enables easier implementation of newly formed composite to production workflow.

2. MATERIALS AND METHODS

For this research, lithographic offset printed samples were coated with prepared nanocomposites in various nanoparticle's weight ratios, where the base of nanocoating was commercial water-based varnish while chosen nanoparticle was titanium dioxide (TiO_2).
The printing of the samples for the purpose of this research was done in accordance with the ISO 12647-2:2013 standard, i.e., FOGRA PSO (ISO/TC 130 Graphic technology, 2013). The sheetfed offset printing was conducted using industrial printing press KBA 105 PRO-5+L FAPC. The prints were made in four colour process (CMYK). The printing inks used were Novavit F918 Supreme Bio inks made by Flint Group (*Flintgrp, n.d)*. The printing substrate was UPM Finesse white gloss cardboard WFC (Woodfree coated) grade with gloss coating and grammage of 300g/m^2. Cardboard was conditioned and stored in environment at temperature of (23 ± 1) °C and (50–55) % relative humidity for 48 hours before the printing process.
The nanocomposite's base was water-based varnish (denoted as WB) with production name Terra High Gloss Coating G9/285 by Actega USA. The varnish is to be used in a varnishing unit at lithographic printing press (a flexographic unit) (*TERRAWET®, n.d.*). The nanoparticles were TiO_2 from Sigma Aldrich with the production code EC 2015-282-2 (Titan dioxide, Sigma A., 2012). To determine weight ratios, compounds (base and nanoparticles) were weighed using Mettler Toledo XS205DU Dual range Analytic Scale. Preliminary showed that adding NPs increases viscosity of the composite above boundaries set by coating technology. In flexography, viscosity should not excide 0.7 Pa*s (Kipphan, 2001b). To counter that, initial WB was diluted by adding 5% wt. of demineralized water. The nanocomposites were prepared by homogenization of nanoparticles into water-based varnish using ultrasound dispenser Hielscher UP100H from 20 to 40 minutes depending on the nanoparticles weight ratio (%), as presented in Table 1.

Table 1: Homogenisation time for preparing nanocomposites

Weight ratio of TiO_2 (%)	Homogenization time (min.)
0.25	20
0.5	30
1	35

Time-to-weight ratio of homogenization process derived from previous testing and proved to be the most optimal one using this setup. During the course of homogenization process the mixture was cooled down in cooling bath filled with water at temperature of 5°C.
To apply the prepared nanocomposite coating onto the prepared prints, IGT F1 printability tester for flexography was used (IGT, n.d.). For the coating process, IGT 402-258 anilox roller with 90 l/cm screen line and 18 ml/m^2 cell volume was used. The coating was transferred by the usage of Kodak Flexcel NX with DigiCap NX patterning flexographic polymer printing plate. The printing plate had 100% TV coverage (*Workflowhelp, n.d.*).

To investigate the influence of lightfastness of the prepared samples (packaging material), accelerated aging (AcA) by Xenon lamp chamber was used. To create those conditions Solarbox 1500 e chamber was used. As the packaging is not exposed to the Sunlight, an indoor filter S208/S408 (artificial daylight) was used. Irradiation in the chamber was set to 550 W/m^2 and the temperature of 50 °C (30h of AcA, i.e., to electromagnetic energy of 59 MJ/m^2). The experiment was done in accordance with the ISO 4892-2 standard (International Organization for Standardization, 2013).

To characterise the surface properties before and after 30h AcA, surface free energy (SFE) and adhesion parameters were calculated. The SFE can be also referred to as the surface tension of a solid. The SFE is presented in mN/m in the SI system or dynes/cm in the metric system. In terms of physics, the interaction in the solid-liquid system is important as it determines the adhesion force. This is an important feature in the printing industry as well, as paints, varnishes and must adhere on the printing substrate surface To calculate SFE of solid surfaces, contact angles (CA) of reference liquids (liquids with known surface tension) must be measured.

For the purposes of this paper, contact angles were measured using sessile drop method and Laplace-Young fitting, ten times per sample, at different sample positions. The droplet shape was a spherical cap, and the volume was set to 1µl. The measurements of the contact angles were performed 2 seconds after the initial contact between liquid and the surface. From the CA results, SFE was calculated. When SFE is high, the solid is easily wetted. To obtain the optimal approximation of the SFE in the Owens, Wendt, Rabel and Kaelble (OWRK) method with the use of Equation 1 (Owens and Wendt, 1969). For this method a minimum of three liquids with known SFE values have to be applied. In order to diminish possible errors, we measured CA of four liquids with known properties: water, diiodomethane, formamide and glycerol. The Surface tension and its dispersive and polar part of known liquids is presented in *Table 2*.

Table 2: Liquids used for contact angle measurements

Liquid	SFT (total)	SFT (disp.)	SFT (polar)
Water (Ström et al.)	72.80	21.80	51.00
Diiodomethane (Ström et al.)	50.80	50.80	0.00
Glycerol (Ström et al.)	63.40	37.00	26.40
Formamide (Van Oss et al.)	58.00	39.00	19.00

The equation used for the calculation of SFE using the OWKR method:

$$\frac{(1+\cos\theta)*\sigma_s}{2\sqrt{\sigma_l^D}} = \sqrt{\sigma_s^P}\sqrt{\frac{\sigma_l^P}{\sigma_l^D}} + \sqrt{\sigma_s^D} \quad (1)$$

Where are: γ_s – surface tension of the solid, γ_l – surface tension of the liquid, γ^d– dispersive part of surface tension, γ^p– polar phase of surface tension, Θ- contact angle.

To determine adhesion between applied coatings and the printing substrate, adhesion parameters were determined. The thermodynamic work of adhesion W_{12} between two phases was calculated using equation (2):

$$W_{12} = \gamma_1 + \gamma_2 + \gamma_{12} \quad (2)$$

Where are: γ_1 – refers to SFE of the first layer, γ_2 – refers to SFE of the second layer, i.e., printed sample and coating, γ_{12} – refers to interfacial tension between first and second solid.

Using the Owens-Wendt model, the SFE of the interface was determined according to the equation (3):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\sqrt{\gamma_1^d * \gamma_2^d} + \sqrt{\gamma_1^p * \gamma_2^p}\right) \quad (3)$$

Where are: γ^d– dispersive component of surface tension, γ^p– polar component of surface tension, while indexes 1 and 2 mean first and second material.

The adhesion parameter of wetting S_{12} was calculated using equation (4):

$$S_{12} = \gamma_1 - \gamma_2 - \gamma_{12} \quad (4)$$

Optimal adhesion is achieved if the following conditions of the adhesion parameters are fulfilled: thermodynamic work of adhesion must be maximal, interfacial tension must be minimal and close to zero, and wetting must be equal to or greater than zero (Petković *et al.*, 2019). The SFE calculation and CA measurements were performed using the Data Physics OCA 30 goniometer, with the support of Dataphysics SCA 20 software (*Dataphysics-instruments, n.d.*).

The barrier to the water vapour of the prepared samples was determining by calculating water transfer rate (WVTR). The WVTR test was done via permeability cups made by TQC Sheen with the production name VF 2201 in accordance the ASTM D1653 standard (American Society for Testing and Materials, 2021). Test cup consists of a cup, seal and a cover ring. The seal is designed to prevent turning when closing the cup while the cover ring secures the sample in place. The cup is filled with 25 ml of demineralized water, sealed weighted with analytic weight (the same used as for the weighing of the coatings components). The WVTR was calculated using equation (5):

$$WVTR = \frac{\Delta m}{\Delta t * A} \quad (5)$$

Where are: Δm - change of the container mass in grams, Δt - time between sample weighing given in days, A - area of the sample in m^2.

The settings for this test were: surroundings temperature 22 ± 1 °C and RH of 60 ± 2%. Weighting of samples was performed at beginning and after 24, 48 and 72 hours after test began.

The bursting strength measurements for this test were conducted by means of Lorentzen & Wettre Bursting Strength Tester. The tested samples were cut to ø=100 mm, while the testing area was ø=50 mm. The rubber diaphragm is ø=33.1 mm. Under the diaphragm, the pressure in the Lorentzen & Wettre burst tester rises from 70 kPa up to 1400 kPa in accordance to the ISO 2759-2001 standard (International Organization for Standardization, 2014).

3. RESULTS AND DISCUSSION

Table 3 presents all calculated SFE values (total/disp./polar) of prepared samples. As mentioned before, for this research four liquids (Table 2), with know SFT were applied onto the solid surface to obtain CAs which were used for SFE calculations. The SFE calculations were conducted using average values of measured CAs.

The presented results indicate that at plain cardboard and ink without any coating the SFE decreases with the AcA. At the cardboard substrate this is due to the increase of the dispersive part of SFE while at the ink the polar part of SFE increases. It can be noted that the plain cardboard after 30h AcA has some change in the polar component due to forming of new oxidation products, which are less polar from its -OH group. Kaolin, also one of the ingredients of the cardboard is a very hydrophilic substance as well (Bundy and Ishley, 1991). The ink contains vegetable oil in its composition, which is influenced by the UV radiation, therefore the ester bounds are destroyed, and the polarity has risen (Erhan &Bagby, 1995).

Table 3: Calculated SFE of samples before and after 30h AcA

Sample	*Before AcA*			*After 30 h AcA*		
	SFE (Total) / (γ)	Dispersive SFE /(γ^d)	Polar SFE/ (γ^p)	SFE (Total) / (γ)	Dispersive SFE /(γ^d)	Polar SFE/ (γ^p)
Cardboard	27.06	20.27	6.81	28.01	22.32	5.69
Ink	32.41	30.83	1.57	35.03	30.58	4.45
WB	33.68	28.61	5.08	30.85	26.45	4.41
0.25% TiO_2	33.59	29.15	4.45	28.82	22.69	6.13
0.5% TiO_2	37.03	34.94	2.09	36.18	33.24	2.94
1% TiO_2	38.08	37.07	1	34.55	28.66	5.89

On the other hand, it is visible that coated samples decreased their SFE due to the AcA mainly due to the change of the dispersive part of SFE. In addition, the SFE of coated samples is higher than of the uncoated ones. The addition of the TiO_2 to the coatings will increase the SFE.

WB samples, after 30h AcA have lower polar component but higher total SFE values. This can be attributed to the acrylic resin that is a common ingredient in water based varnishes and it tends to become more hydrophobic after exposure to UV or ozone (Dou *et al.*, 2021). On the other hand, with the increase of TiO_2 nanoparticle weight ratio (%), the wettability of TiO_2 coated samples also increases but after the AcA it lowers. According to the Stevens et al., with UV exposure, the surface properties in terms of SFE change, increasing the hydrophilic properties of TiO_2 (Stevens *et al.*, 2003).

In Table 4 values of calculated adhesion parameters are presented. To evaluate results, all three parameters (γ_{12},, *and* S_{12}) should be observed together as a whole. From the presented, the best adhesion was achieved adding 0.25% of TiO_2 in the nanocomposite coating.

The highest work of the adhesion was achieved between the print and the coating with 1% TI/NC (70.12 mJ/m^2). Furthermore, the increased concentration of resulted with the increased work of adhesion, pointing to the increased work necessary to separate the two layers and improved adhesion. From SFE of the interphase and wetting coefficients one can also note that SFE of interphase generally lowers as the wetting coefficient increase 0.25% TI/NC / 1% TI/NC (S_1 = - 1.94 mJ/m^2 / S_1 = - 6.04 mJ/m^2). However, SFE of the interphase is close to zero for all samples, which is favourable for the optimal adhesion.

Table 4: Adhesion parameters between the plain print and - nanocomposite coatings

	Adhesion parameters (mJm^{-2})		
Sample	γ_{12}	W_{12}	S_{12}
WB	1.13	66.64	-2.71
0.25% TiO_2	0.75	65.24	-1.94
0.5% TiO_2	0.17	69.26	-4.80
1% TiO_2	0.36	70.12	-6.04

As mentioned before, barrier properties of substrates can be upgraded by lamination or by coating, where introduction of various compounds that could improve surface impregnation is beneficial. Increase of TiO_2 nanoparticles weight ratio, water permeability decreases significantly (Figure 1). The *WVTR* results of 0h remained more or the less unchanged regardless of the NPs weigh ratio (%). After 30h AcA the water permeability lowers for WB, but slightly increases for samples coated with nanocomposites. The TiO_2 is a metal oxide, which is a compound that is found to have good water permeability features in various bulk studies (Nazari & Riahi, 2011; Benkoula *et al.*, 2015; Hegyi *et al.*, 2020).

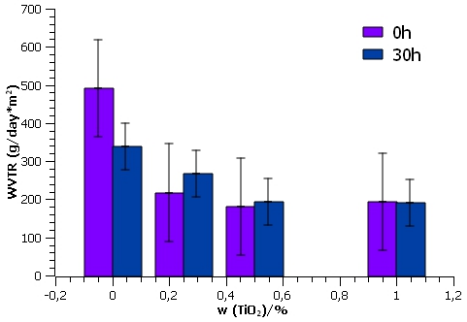

Figure 1: WWTR in dependence to the added TiO_2 in the nanocomposite

In the Figure 2, bursting strength diagram for TI/NC samples is presented. It can be noted that the highest value was achieved on sample coated with nanocomposite containing 0.25% TiO_2 (283.20 kPa) while other samples coated with nanocomposites samples have slightly higher values than the WB in the start (266.25 kPa). The results after 30h AcA show that lower change was noted by samples coated with nanocomposites containing higher weight ratios of TiO_2, which can be attributed to the TiO_2 ability to absorb the UV radiation. The increase of the TiO_2 nanoparticle's weight ratio did not show any significant upgrade to the sample performance. On the 0.25% TI/NC sample, the change is notable before and after 30h AcA (approx. 32 kPa).

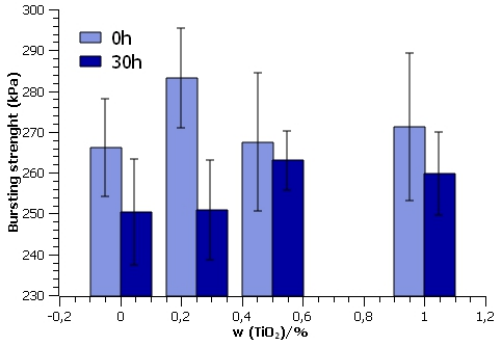

Figure 2: Bursting strength in dependence to the added TiO_2 in the nanocomposite

4. CONCLUSION

The aim of this research was to compose a nanocomposite coating which will upgrade properties of existing varnish in terms of preservation of printed packaging under influence of UV radiation (Sunlight), i.e., preserving the function of the packaging throughout the product's lifespan. To do so, the newly formed nanocomposite compositions were created with commercially available water-based varnish as a base that was enriched with TiO_2 nanoparticles in various weight ratios.

The results showed that SFE of samples coated with nanocomposites will decrease with weight ratio of added TiO_2 due to the increase of the dispersive part of the SFE. The highest work of the adhesion was achieved between the print and the coating with nanocomposite containing 1% TiO_2, but it is visible that even lower weight ratios of the nanoparticles will result in similar values (with exception of the 0.25%), which are higher than the one achieved at WB. Observing all adhesion parameters, it is clear that although adding TiO_2 will increase S_{12} (with the exception of 0.25% TiO_2), the interface tension decreases to 0 and work of adhesion increasing could mean that adhesion will not decrease. The smallest TiO_2 weight ratio (0.25%) lowers the WVTR by 56%. Moreover, with increase of TiO_2 weight ratio, water permeability decreases significantly where the nanocomposite with added 0.5% wt. of TiO_2 provided the best result (63% decrease). Regarding the mechanical properties, although bursting strength of samples coated with nanocomposites is higher than the one coated by WB, there is no visible dependence between mechanical properties and weight ratio of nanoparticles.

This research showed that adding TiO_2 nanoparticles will improve commercial varnish and will provide increased protective benefits against outer environmental influence such as UV radiation in terms of adhesion to the substrate and barrier to the water vapour.

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