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Changes in Color and Drying Time of Modified Polyvinyl Acetate Adhesive with Nanoparticles

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Abstract

Adhesive bookbinding is growing in popularity due to advancements in adhesive binding technology, shorter delivery time and the introduction of innovative materials. It is suitable for medium volume books and enables the production of durable and flexible end-products in accordance with today's market needs, such as smaller product volumes and personalized consumer requirements. Polyvinyl acetate (PVAc) adhesives are widely used adhesives in the printing industry for paper, board, leather and cloth. In addition, water-based PVAc adhesives are more environmentally acceptable, compared to used hotmelts. In order to improve PVAc limiting and retain its existing positive properties, numerous studies dealing with modification of PVAc adhesives have been carried out. The aim of this research was to investigate the impact of PVAc modification with SiO_2 and TiO_2 nanoparticles on the end-product appearance and the productivity of the production process, more precisely change in color and drying time. Colorimetric values of dried PVAc and nano-modified PVAc adhesive films were measured on five different paper substrates, according to ISO 11475:2017 standard, in order to calculate the total color difference ($CIEDE_{2000}$). Results showed that the color difference between dried PVAc and nano-modified PVAc films is not recognizable by a standard observer, but it is slightly larger with TiO_2. The drying time of PVAc and nano-modified PVAc adhesive films was observed over a period of 60 minutes. Adhesives were applied on transparent foil and observed under UV light in a Judge II X-rite lightbox. Results showed that nano-TiO_2 PVAc adhesive has much shorter drying time. According to obtained results it can be concluded that both types of nano-modified PVAc adhesives, as well as the original PVAc, are suitable for the production of end-products with a visible adhesive line. By adding TiO_2 nanoparticles the productivity of the production process can be improved due to reduced drying time.

Key words

Adhesive color, Adhesive drying time, Nanoparticles, Polyvinyl acetate, Short-run

1. INTRODUCTION

Graphic production, especially post press bookbinding processes, include various types of bonding and adhesives. Currently, the most common adhesives used in bookbinding can be divided into three main categories: water-based emulsions (e.g. polyvinyl acetate), hot melts (e.g. ethylene vinyl acetate) and reactive hot melts (e.g. polyurethane). Polyvinyl acetate adhesives (PVAc) are customized for the short runs of graphic production or production of personalized products on demand [1]. Current guidelines for the development of adhesive technology are focused on replacing solvent–based adhesives with water-based [2], and therefore PVAc is much more environmentally acceptable compared to the other two. Polyvinyl acetate (PVAc) is a clear, water-white, thermoplastic synthetic resin produced from its monomer by emulsion polymerization. PVAc is a good adhesive for paper, plastics, metal foil, leather, cloth and wood, but it is also used as a general building adhesive [3]–[5]. PVAc sets through evaporation and diffusion of the water into the substrate, and at the same time, by polymerization of polymer particles as the water evaporates [3], [6]. In order to improve PVAc limits and retain its existing positive properties, numerous studies dealing with modification of PVAc adhesives have been carried out. In previous studies, most researchers have been using nano clay (NC) [7], [8], cellulose nanofibrils (CNFs) [9], silica (SiO_2) [10]–[13] or titanium dioxide (TiO_2) [10], [11], [14] nanoparticles for the improvement of PVAc properties. The modification of PVAc adhesive with nanoparticles is successful if the adhesive retains its existing positive properties, such as satisfactory adhesive joint strength and invisibility of the dry adhesive film, with a positive effect of nanoparticles on its limiting properties, such as long drying time and low resistance to temperature and humidity changes [3], [6], [15]–[18].

In our previous research a significant increase in adhesive joint strength [19] and positive effect on the increase of the adhesive joints resistance to temperature and humidity changes [20] by addition of 1% SiO_2 or 1% of TiO_2 nanoparticles in the PVAc adhesive was demonstrated. In addition, the optimum nanoparticle concentration in PVAc adhesive was defined by determination of the surface free energy and by analysis of the paper-adhesive samples morphological structure using scanning electron microscopy and Fourier transform infrared spectroscopy [21]. The aim of this research was to investigate the impact of PVAc modification with SiO_2 and TiO_2 nanoparticles on the end-product appearance and the productivity of the production process, more precisely changes in color and drying time.

2. MATERIALS AND METHODES

2.1. Adhesive

Used polyvinyl acetate adhesive (Signokol L) is water dispersion of vinyl acetate homopolymers with polyvinyl alcohol and addition of plasticizers. Properties of the used adhesive are listed in Table 1.

Table 1. Properties of Signokol L adhesive given by the producer [22]

PROPERTY	APPEARANCE / VALUE:
State of Matter:	liquid
Main Purpose:	paper, board
Color:	white
Dry Film Color:	transparent
Density (20 °C):	1.0776 g/cm^3
Viscosity (20 °C):	8-10 Pa s
pH Value:	6 ± 0.5
Solid Content:	45 ± 2%

2.2. Nanoparticles

Silica (SiO_2) (Aerosil R 8200) and titanium dioxide (TiO_2) (Aeroxide P25) nanoparticles were used for PVAc adhesive modifications. Both are odorless, solid, white powders with approximately the same temped density (140 g/L), but a different BET surface area (135–185 m^2/g SiO_2; 35–65 m^2/g TiO_2) and assay based on ignited material (≥99.8% SiO_2; ≥99.5% TiO_2) [23], [24].

2.3. Substrates Used for Application of Adhesive Film

PVAc and nano-modified PVAc adhesives were applied on different papers described in Table 2. All of them belong to a different paper type group, based on fiber composition. After drying of adhesive films on the paper surfaces, changes in color of PVAc and nano-modified PVAc adhesives were observed.

Table 2. List of used papers and their properties

TRADE NAME	TYPE	GRAMMAGE [g/m^2]	ABBREVIATION
Amber Graphics	woodfree uncoated	100	WFU
Garda Gloss	woodfree coated	115	WFC
Munken White	containing wood (bulky)	90	CW
Navigator Universal	woodfree, office	80	WF office[1]
Recy Office	containing recycled (100%), office	80	CR office

In addition, adhesives were applied on transparent polyvinyl chloride (PVC) foil, with thickness of 180 μm, to observe changes in adhesive drying time.

2.4. Adhesive Preparation

Three types of adhesives were used – neat PVAc adhesive and PVAc adhesive modified with 1% of SiO_2 and 1% of TiO_2 nanoparticles. After adding 1% of nanoparticles to neat PVAc adhesive, IKA T 25 digital ULTRA-TURRAX disperser was used for mixing and adhesive homogenization. Adhesive was stirred for 15 minutes, firstly 5 minutes at lower stirring speed (from 3500 to 7000 rpm) and then 10 minutes at 7000 rpm. The same mixing procedure was used for both nano-modified adhesives.

2.5. Determination of Changes in Adhesive Color

Preparation of samples, for the evaluation of adhesives color changes, involved manual application of adhesive (with a brush) on pre-cut sheets of paper (210 x 99 mm), 48 hours of drying (18° C – 20° C, 60% - 70% RH), measuring of dry adhesive thickness in order to select five samples from each sample group (75 samples in total) and cutting selected samples on smaller dimensions 40 x 20 mm. Changes in color for selected papers with PVAc adhesive and those same papers with nano-modified PVAc adhesives, were evaluated in accordance with ISO 11475:2017 standard [25], using X-Rite SP62 Sphere spectrophotometer (D65/10°). After determination of the colorimetric parameters (L^*, a^* and b^*), the total color differences between the papers with PVAc adhesive and the papers with nano-modified PVAc adhesives ($CIEDE_{2000}$) were calculated.

2.6. Determination of Changes in Adhesive Drying Time

The drying time of PVAc and nano-modified PVAc adhesive films was observed over a period of 60 minutes. For testing purposes, it was necessary to construct the auxiliary steel tool shown in Figure 1.

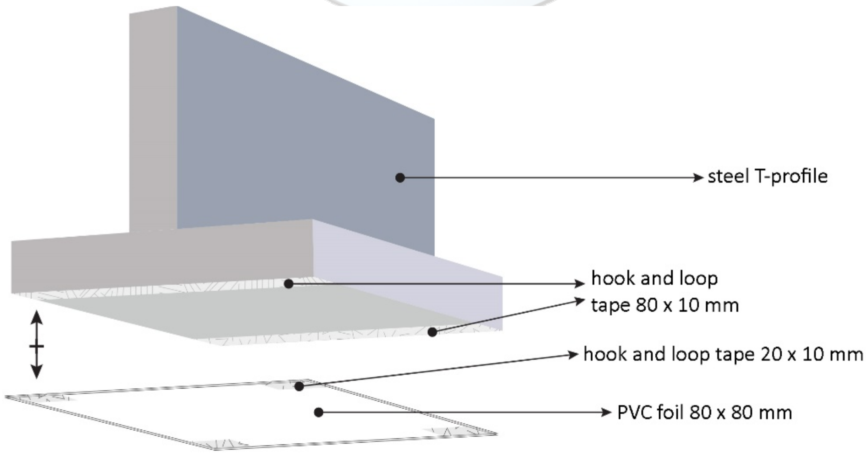

Figure 1. The auxiliary steel T-tool

Adhesives were applied with a brush on non-absorbent transparent PVC foil (80 x 80 mm). As defined period of time (1, 2, 4, 8, 16, 20, 30, 40, 50 or 60 min) has expired, the pressure was applied with another PVC foil fastened with self-adhesive “hook and loop” tape to the T-tool. Immediately after the application of pressure, PVC foils from the T-tool were left at room temperature (18° C – 20° C) allowing the accepted adhesive to dry completely. After 48 hours of drying, the final samples for the evaluation of the drying time were cut from the middle of foil sheets to 40 x 40 mm. Conclusions on the changes in drying time of adhesives were made based on the amount of adhesive accepted on the PVC foils from the T-tool. Samples were observed under UV light in a Macbeth Judge II X-Rite lightbox due to the adhesive color (transparent, white, yellowish) which is not visible enough in daylight and after drying is almost completely transparent.

3. RESULTS AND DISCUSSION

3.1. Changes in Adhesive Color

The values of colorimetric parameters (*L**, *a** and *b**) of papers with PVAc and papers with nano-modified PVAc adhesives are given in Table 3, along with the results of the total color difference between dried PVAc and dried nano-modified PVAc adhesive films on selected papers ($CIEDE_{2000}$[nano-SiO_2 PVAc], $CIEDE_{2000}$[nano-TiO_2 PVAc]).

Table 3. Colorimetric values (L, a*, b*) of papers with PVAc and papers with nano-modified PVAc adhesives, the total color difference ($CIEDE_{2000}$[nano-SiO_2 PVAc], $CIEDE_{2000}$[nano-TiO_2 PVAc])*

	WFU			WFC			CW			WF_{office}^1			CR_{office}		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
PVAc	93.20	1.51	-4.76	93.53	0.85	-1.25	93.18	0.91	1.05	92.32	2.65	-8.66	86.90	0.04	6.42
PVAc + 1 % SiO_2	93.51	1.49	-5.07	93.77	0.94	-1.82	93.80	0.93	0.74	92.71	2.56	-8.56	87.67	0.03	5.64
PVAc + 1 % TiO_2	93.35	0.98	-3.14	93.32	0.66	-0.57	93.35	0.62	1.76	91.89	2.22	-7.49	87.37	-0.11	5.89
$CIEDE_{2000}$ (nano-SiO_2 PVAc)	0.33			0.57			0.49			0.27			0.79		
$CIEDE_{2000}$ (nano-TiO_2 PVAc)	1.51			0.71			0.82			0.99			0.56		

Based on the calculated total color differences ($CIEDE_{2000}$), it is evident that the color change of the adhesive is slightly larger when TiO_2 nanoparticles are added, but also that the difference between the color of PVAc adhesive and nano-modified PVAc adhesives applied to selected papers, after drying, is not recognizable by a standard observer (Figure 2) according to ISO 11475:2017 standard.

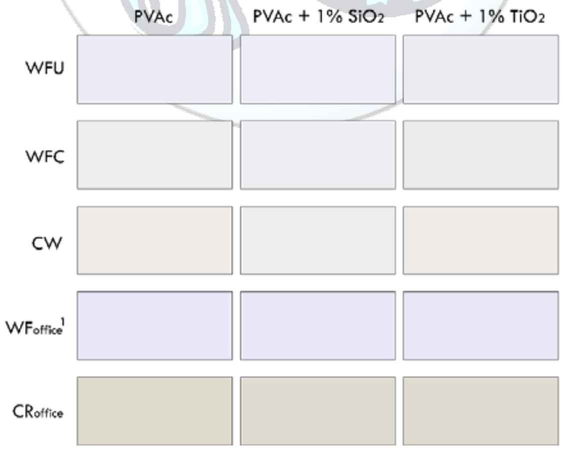

Figure 2. Color of tested papers with PVAc and nano-modified PVAc adhesives

The results of total color difference for nano-SiO_2 PVAc adhesive are 0.27 – 0.79, while the total color differences of nano-TiO_2 adhesive are 0.56 – 1.51, respectively. Given the obtained results, it can be concluded that nano-modified PVAc adhesives, as well as the original PVAc adhesive, are suitable for making graphic products with visible adhesive line, i.e. that the color of adhesive will not affect the appearance of the end-product.

3.2. Changes in Adhesive Drying Time

Ten different drying time intervals of the tested adhesives, observed under UV light, are shown in Figure 3. Figure 3 clearly shows that the drying of nano-TiO_2 PVAc adhesive is faster compared to PVAc adhesive, but also that nano-SiO_2 PVAc adhesive has a prolonged drying time. Areas without adhesive, made after a short contact with another PVC adhesive foil, represent drying of the observed adhesive sample. In order to notice the differences easier, areas without adhesive are marked in Figure 4.

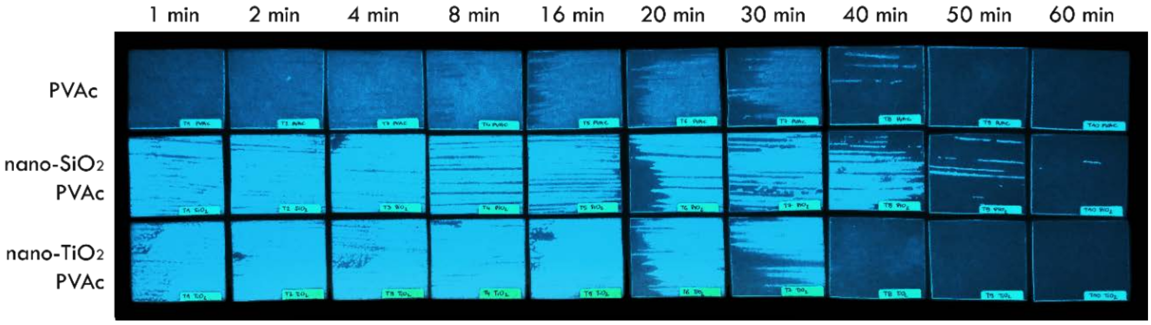

Figure 3. Adhesive samples accepted on transparent PVC foils after ten different time intervals (1-60 min)

Figure 4 (a) shows that after 1 minute only nano-TiO_2 adhesive started to dry. After 20 minutes a significant drying of all types of adhesives was noticed. After 30 minutes nano-TiO_2 adhesive continued to dry faster compared to other adhesives, but nano-SiO_2 PVAc adhesive was drying slower than the original PVAc adhesive. Figure 4 (b) shows complete drying of nano-TiO_2 adhesive after 40 minutes. The original PVAc adhesive was dried completely after 50 minutes, while nano-SiO_2 PVAc adhesive was not dry even after 60 minutes.

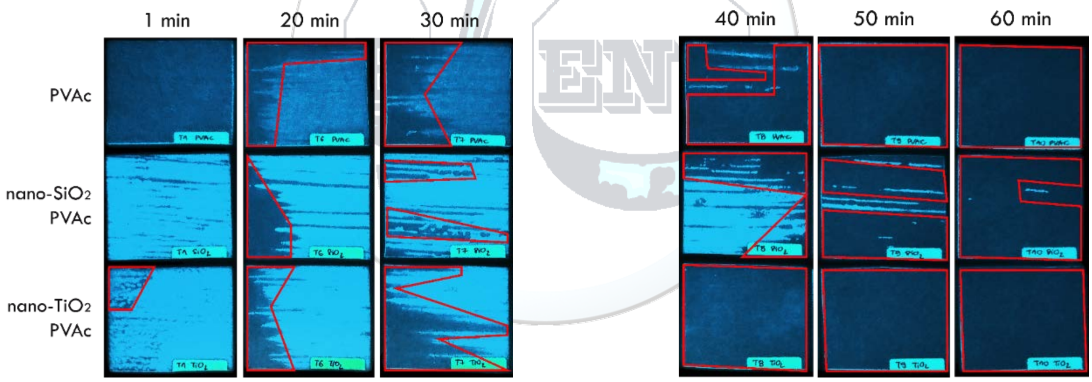

Figure 4. (a) Adhesive drying after 1, 20 and 30 minutes (b) Adhesive drying after 40, 50 and 60 minutes

4. CONCLUSIONS

In this research PVAc adhesive was modified with SiO_2 and TiO_2 nanoparticles in order to improve its certain properties. Unfortunately, during adhesive modification it is not possible to selectively change only one desired property, such as the strength of the adhesive joint, thus it is necessary to test, observe and compare changes in all key properties.

The invisibility of the dry adhesive film stands out as one of PVAc's main advantages. The change in color, i.e. decrease in transparency after modification with SiO_2 and TiO_2 nanoparticles, was noticed during the application of the adhesive – on tool and protective equipment. Therefore, it was necessary to perform colorimetric determination of the dry adhesive films in order to test the suitability of nano-modified PVAc adhesives for the production of graphic products with visible adhesive lines. Based on the presented results, it can be concluded that the color difference between PVAc and nano-modified PVAc films after drying is not recognizable by a standard observer and will not affect the appearance of the end-product. However, the highest total color difference had nano-TiO_2 PVAc adhesive film on woodfree uncoated paper.

Sometimes long drying time of PVAc adhesives can be a limiting factor for the fast delivery of personalized graphic products on demand, and thus drying time can become one of the key factors in the productivity of the production process. Based on the presented observation of adhesives drying time, it can be concluded that nano-TiO_2 PVAc adhesive had a much shorter drying time and that by adding TiO_2 nanoparticles the productivity of the production process can be improved. Unfortunately, by adding SiO_2 nanoparticles drying time was insignificantly prolonged.

In addition to already investigated PVAc performance improvements with SiO_2 and TiO_2 nano-modification, this study reconfirm the positive impact of selected nanoparticles on the quality of the end graphic products.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest.

REFERENCES

[1]. M. Bigianti and A. Lanter, "Digital Printing Leads to Print Finishing Opportunities," 2014. [Online]. Available: https://postpressmag.com/uncategorized/2014/digital-printing-leads-to-print-finishing-opportunities/
[2]. M. Jović, Z. Buhin, I. Krobot, and S. Lučić Blagojević, "Analiza okolišne održivosti tehnologije adheziva," *Kemija u industriji*, vol. 60, no. 5, pp. 269–276, 2011.
[3]. S. Ebnesajjad, Ed., *Adhesives Technology Handbook*, 2nd ed. Norwich, NY, US: William Andrew, 2008.
[4]. A. Pizzi and K. L. Mittal, Eds., *Handbook of Adhesive Technology*, 2nd ed. New York, NY, US: Marcel Dekker, Inc., 2003.
[5]. M. T. Roberts and D. Etherington, *Bookbinding and the conservation of books: A dictionary of descriptive terminology*. Washington, NY, US: Library of Congress, 1982.
[6]. D. E. Packham, Ed., *Handbook of Adhesion*, 2nd ed. Bath, UK: John Wiley & Sons, Ltd, 2005.
[7]. D. Aydemir, G. Gündüz, N. Aşık, and A. Wang, "The Effects of Poly(vinyl acetate) Filled with Nanoclay and Cellulose Nanofibrils on Adhesion Strength of Poplar and Scots Pine Wood," *Drvna industrija*, vol. 67, no. 1, pp. 17–24, 2016, doi: 10.5552/drind.2016.1441.
[8]. R. Moya, A. Rodríguez-Zúñiga, J. Vega-Baudrit, and V. Álvarez, "Effects of adding nano-clay (montmorillonite) on performance of polyvinyl acetate (PVAc) and urea-formaldehyde (UF) adhesives in Carapa guianensis, a tropical species," *International Journal of Adhesion and Adhesives*, vol. 59, pp. 62–70, 2015, doi: 10.1016/j.ijadhadh.2015.02.004.
[9]. O. Chaabouni and S. Boufi, "Cellulose nanofibrils/polyvinyl acetate nanocomposite adhesives with improved mechanical properties," *Carbohydrate Polymers*, vol. 156, pp. 64–70, 2017, doi: 10.1016/j.carbpol.2016.09.016.
[10]. T. Bardak, A. N. Tankut, N. Tankut, E. Sozen, and D. Aydemir, "The effect of nano-TiO2 and SiO2 on bonding strength and structural properties of poly (vinyl acetate) composites," *Measurement*, vol. 93, pp. 80–85, 2016, doi: 10.1016/j.measurement.2016.07.004.
[11]. N. Tankut, T. Bardak, E. Sozen, and A. N. Tankut, "The effect of different nanoparticles and open time on bonding strength of poly (vinyl acetate) adhesive," *Measurement*, vol. 81, pp. 80–84, 2016, doi: 10.1016/j.measurement.2015.12.003.
[12]. N. Wen, Q. Tang, M. Chen, and L. Wu, "Synthesis of PVAc/SiO2 latices stabilized by silica nanoparticles," *Journal of colloid and interface science*, vol. 320, pp. 152–158, 2008, doi: 10.1016/j.jcis.2007.11.059.
[13]. A. Bonnefond et al., "Effect of the Incorporation of Modified Silicas on the Final Properties of Wood Adhesives," *Macromolecular Reaction Engineering*, vol. 7, pp. 527–537, 2013, doi: 10.1002/mren.201300117.
[14]. J. Ahmad, K. Deshmukh, M. Habib, and M. B. Hägg, "Influence of TiO2 Nanoparticles on the Morphological, Thermal and Solution Properties of PVA/TiO2 Nanocomposite Membranes," *Arabian Journal for Science and Engineering*, vol. 39, pp. 6805–6814, 2014, doi: 10.1007/s13369-014-1287-0.
[15]. A. Salvini, L. M. Saija, S. Finocchiaro, G. Gianni, C. Giannelli, and G. Tondi, "A new methodology in the study of PVAc-based adhesive formulations," *Journal of Applied Polymer Science*, vol. 114, no. 6, pp. 3841–3854, 2009, doi: 10.1002/app.31032.

[16]. IBookBinding, “Book Binding Tutorial : Glues - Tips , Techniques , Types & Recipes,” 2014. [Online]. Available: https://www.ibookbinding.com/blog/bookbinding-gluing-tips-techniques-types-info/.
[17]. P. Šedivka, J. Bomba, M. Böhm, and P. Boška, “Influence of Temperature on the Strength of Bonded Joints,” *BioResources*, vol. 10, no. 3, pp. 3999–4010, 2015, doi: 10.15376/biores.10.3.3999-4010.
[18]. S. Kim, H. Kim, Y. M. Choi, and S. Jang, “Characteristics of Non-plasticizer PVAc Resin for Wood Products,” *Mokchae Konghak*, vol. 35, no. 2, pp. 61–68, 2007.
[19]. G. Petković, S. Pasanec Preprotić, and M. Vukoje, “The Quality Assessment of Bookbinding Strength for Polyvinyl Acetate Adhesive (PVAc) and Nano-modified PVAc Adhesives,” in *Proc. 9th International Symposium on Graphic Engineering and Design – GRID*, 2018, pp. 109–119, doi: 10.24867/GRID-2018-p13.
[20]. G. Petković, I. Bolanča Mirković, and S. Pasanec Preprotić, “Čvrstoća adhezijskih nano-modificiranih polivinil-acetatnih spojeva uslijed promjene temperature i vlage,” in *Proc. 20th International Conference on Materials - MATRIB*, 2019, pp. 247–256.
[21]. G. Petković, M. Vukoje, J. Bota, and S. P. Preprotić, “Enhancement of polyvinyl acetate (PVAc) adhesion performance by SiO_2 and TiO_2 nanoparticles,” *Coatings*, vol. 9, no. 11, 2019, doi: 10.3390/coatings9110707.
[22]. Signoplast, “Sigurnosno-tehnički list za kemijske proizvode: Signokol L,” 2011.
[23]. Evonik Industries, “Product information AEROXIDE P25,” 2017.
[24]. Evonik Industries, “Product information AEROSIL R 8200,” 2013.
[25]. Paper and board – Determination of CIE whiteness, D65/degrees (outdoor daylight). ISO 11475:2017, 2017.