Bulgarian Chemical Communications, Volume 49, Special Issue L (pp. 85-91) 2017

Printing quality of chitosan-rice starch coated packaging paper

U. Vrabič Brodnjak*, D. Muck

University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Graphic Arts and Design, Snežniška 5, SI-1000 Ljubljana, Slovenia

Submitted October 26 , 2016; Accepted January 25, 2017

Biopolymers used as coatings on packaging paper can provide sufficient barriers (water, gas, etc.). Increased environmental concerns, synthetic packaging and coatings are nowadays getting replaced with bio based materials. Therefore thermoplastic starch and chitosan can be good replacements of petroleum based products in packaging industry. In our research chitosan and rice starch were used as coatings on packaging paper. The aim of the research was to determine printing quality on coated paper, which could be used for further applications. The influence of coated thickness on the printing quality was also investigated. Paper was coated with two different coating mixtures. The first was only chitosan coating and the other one was mixture of chitosan and rice starch (ratio 50:50). Coating was applied with two different bars to achieve two different thickness of the coating: 40µm and 80µm. The ink rub test was proceeded using rub tester and the procedure was made according to standard TAPPI T830. Dry rub test showed that all coated samples achieved better results (optical density), in comparison to uncoated paper. In our research two stroke (Rubbing Times) were determined: 25 and 50 cycles, at rubbing speed 106cpm. After 25 cycles sample paper coated with chitosan and rice starch achieved the best quality, according to uncoated and chitosan coated paper. After 50 cycles, the chitosan and rice starch coating still had better abrasion resistance, but it could not be sufficient for further use. The research has proven increased printing quality of coated paper, especially the coating with mixture of chitosan and rice starch.

Key words: chitosan, rice starch, coatings, packaging paper, printing quality

INTRODUCTION

Bio based polymers are in recent years used in many fields, especially at packaging. Packaging research is focused to develop the use of bio plastics which are useful in reducing waste disposal and are good replaces of petroleum and a non-renewable resource with diminishing quantities [1]. Paper, board and cardboard are widely used packaging materials in many shapes and products (boxes, folding cartons, corrugated boxes, paper bags, cups etc.) and their biodegradability, barrier and mechanical properties are of prime importance. Its main components are the renewable materials and used paper can be unfenced in natural conditions if it's not being used again for the production of recycled paper or some other method [2]. In recent years there has been a research focus on renewable biopolymers used as edible films and coatings [3-5]. Bio based coatings, such as starch, proteins and polysaccharides are extracted directly from the biomass. Their advantage is that they are non-toxic, environmentally friendly and have great grease, gas and aroma barrier properties [5-7]. Chitosan exhibits good moisture properties, but it is not sufficient for food applications, because of its hydrophilic nature which attracts moisture [8]. To improve the moisture properties and functional properties of chitosan coatings, blending it with other biopolymers, hydrophobic substances have been proposed [8, 9]. In previous research numerous of chitosan films and chitosan blends with other natural polymers have been made [10, 11]. Because of high amount of amylase, rice starch is attractive for food packaging as a film barrier or coatings [12]. It has been used also to replace plastic film barriers due to good mechanical properties [12-14]. Based on the literature findings, there has not been done analysis of printing quality of chitosan and/or rice starch coatings on paper.

Inkjet printing is still a growing printing business area, also in the field of packaging. At the same time this printing technique has been used in office and home applications. The properties of coating layer of paper are effecting the inkjet process [15]. The material properties, coatings, capillary structure, temperature and moisture content are important for the topography of the surface [16]. The spreading, penetration and final printing quality are affected by porosity, permeability, thickness, fibre type, moisture content and capillary structure [17, 18]. The printing machine variables can also affect the final droplet setting, but those variables have not been defined in our research.

The goal of our research was to determine printing quality on coated paper with different bio

*) To whom all correspondence should be sent:
E-mail: urska.vrabic@ntf.uni-lj.si

© 2017 Bulgarian Academy of Sciences, Union of Chemists in Bulgaria

based polymers, which could be used for further applications.

EXPERIMENTAL

Materials

Uncoated, unglazed paper, with grammage 80 g/m^2, chitosan with molecular weight 20kDa (purchased from Sigma Aldrich, Austria), 98% malic acid (purchased from Sigma Aldrich, Austria), glycerol as plasticizer (purchased from Sigma Aldrich, Austria) and rice starch (purchased from Farmalabor Srl, Italy) have been used in this study.

Preparation of blend coating solutions

Preparation of chitosan coating solution. The chitosan solution was prepared by dissolving 2g of chitosan in 100 ml of 98% malic acid and 40% w/w of glycerol was added. The solution was mixed at 90°C for 5 minutes until chitosan was not dispersed. Coating solution was after cooling filtered through a polyester screen (mesh no. 140 with mesh opening 160μm) and aspirated in order to remove small lumps in the solution.

Preparation of blend solution with chitosan and rice starch

Firstly solutions of each compound (chitosan and rice starch) have been prepared. The chitosan solution was prepared by dissolving 2g of chitosan in 100 ml of 98% malic acid. The solution was mixed at 90°C for 5 minutes until chitosan was not dispersed. Before cooling down, coating solution was filtered through a polyester screen (mesh no. 140 with mesh opening 160μm), by aspiration to remove small lumps in the solution.

Separately rice starch was prepared by dissolving 2g of rice starch in 100 ml of distilled water. The solution was mixed until it gelatinized (85°C for 20 min) and then cooling to the room temperature. After that chitosan and rice starch solutions were mixed together and glycerol as plasticizer (40% w/w of total solid weight in the solution) was added.

Coatings on paper

After the solutions were prepared, the coating with a coater proceeded. Paper was coated with hand coater, at ambient temperature, using bars with 2 different wire diameters: 0.51mm (with 40μm of wet film deposit) and bar with wire diameter 1.00mm (with 80μm of wet film deposit). On each paper 5 g/m^2 and 10 g/m^2 were applied. The coated papers were dried at 50°RH and 23°C.

Printing

Printing was proceeded on inkjet printer HP Officejet Pro at ambient conditions (T=22±2°C; RH=45±3%) by a drop-on-demand mode with replaceable cartridges. All samples, uncoated and coated were printed with this technique.

Analysis methods

Grammage, thickness, density, moisture, smoothness and porosity. The grammage was determined in accordance with ISO 536 standard. Density was calculated from the grammage and thickness, according to standard ISO 534. The thickness of sample papers was measured with a precision digital micrometre (Mitutoyo Corporation, Japan), to the nearest 0.0001 μm at 10 random locations on each paper. Moisture of paper samples was determined according to ISO 287. Smoothness is an indirect measure and it was analysed according to Bendtsen method (ISO 8791-2). The same as smoothness, porosity was analysed with the Bendtsen method.

Abrasion resistance of printed and coated papers. The abrasion resistance of uncoated, coated and printed papers were made on rub tester Labthink (China), according to TAPPI T830 standard. The test was proceeded on dry samples and two of each paper samples were tested. The procedure was carried out on dual stations with arc movement. In our research two stroke (Rubbing Times) were determined: 25 and 50 cycles, at rubbing speed 106cpm and rub pressure 8.9N. For determination of print abrasion, optical density was measured before and after rubbing.

Surface and image segmentation. The pictures of uncoated and coated paper surfaces were taken with the digital camera Cannon. After that image segmentation and surface analysis with the ImageJ program has been done.

RESULTS AND DISCUSSION

Basic paper properties

Grammage and thickness influence the physical, optical, water barriers. The thickness has an effect on stiffness of the paper. Table 1 presents determined properties of uncoated and coated paper, but not printed (with 2 different coating bars: 40μm and 80μm).

From Table 1 it can be seen that 5 g/m^2 and 10 g/m^2 of blend coating solution was applied onto the paper surface. As expected, the thickness increased at 80μm bar, for 5% more than at 40μm bar. With 40μm bar 5g/m^2 of coating has been applied onto the paper surface and with 80μm 10 g/m^2. Therefore also changes in density were detected.

Moisture content of papers varies depending on used pulp, relative humidity, degree of refining, types of coating and additives used. It has one of the biggest effects on mechanical properties as well as on other properties (printing quality, gloss etc.). The different effect of biopolymer coating on moisture of the paper, depended on the type of paper, which reflected the difference of interaction between the bio-based coating and cellulose fibres of the paper. From the results presented in Table 1 it can be seen that uncoated paper had the highest moisture content (6.7%), compared to all coated samples, but not significantly. Less moisture had papers, which were coated only with chitosan solution, as well as coatings which were applied with 80µm bar. Smoothness is important parameter for printing paper, which controls the contact between the paper, printing form and thus the transfer of the ink. It determines roughness, levelness and compressibility. As expected, coated papers (between 370 and 420 ml/min) have higher smoothness, compared to uncoated (510 ml/min) paper. There is difference between chitosan coated and blend coated papers, using different bars. Coating with chitosan is less smooth then blend coating. The results showed that rice starch in mixture with chitosan improved the surface properties of coated paper. From the results it can be obtained that coating generally improved smoothness, which also had further effect on abrasion resistance.

Table 1. Determination of grammage, thickness, density, moisture and smoothness of uncoated and coated paper with 2 different coating bars (CH-chitosan, CHR-blend solution of chitosan and rice starch).

Sample	Grammage [g/m^2]	Thickness [µm]	Density [g/m^3]	Moisture [%]	Smoothness [ml/min]	Porosity [ml/min]
Uncoated	80	122	655.74	6.7	510	1300
Coated CH-40µm bar	85	132	643.94	6.3	460	0
Coated CH-80µm bar	90	140	642.86	6.1	420	0
Coated CHR-40µm bar	85	133	639.10	6.5	380	0
Coated CHR-80µm bar	90	140	642.86	6.3	370	0

It is known that paper is composed of a felted layer of fibres and therefore the structure has a varying degree of porosity. Paper is highly porous material and this property has important influence of printing quality as well. Porosity of paper is an indicator of absorptivity to absorb or water and it is also important in a vacuum feeding process during printing. Results of porosity has shown that uncoated sample had the highest porosity (1300 ml/min), but on coated papers it was unable to measure it. The surface of the coated papers was even and filled, therefore the porosity showed that the porosity in ml per minutes was 0 at all coated samples.

Abrasion resistance of printed and coated papers

The abrasion resistance was used to evaluate the resistance of printed surfaces to rubbing abrasion. Coating failures or damages on paper are related to coating-substrate adhesion, coating thickness and internal stress in coating. It should be noted that there are several methods that can characterize other aspects of imaging materials degradation as result of frictional contact with various surfaces under different conditions. Therefore the use of specific methods are depending on end-user applications, such as type of packaging materials and coatings, requirements for coating barriers, etc. In our study TAPPI standard was used as standard method for determination of printing quality of rubbed coated papers.

Dry rub test showed that all coated samples achieved better results (optical density), in comparison to uncoated paper. In our research two stroke (Rubbing Times) were determined: 25 and 50 cycles, at rubbing speed 106cpm. After 25 cycles (Figure 1) sample paper coated with chitosan and rice starch achieved better quality, according to uncoated and chitosan coated paper. Before rubbing, the highest optical density (1.49) had sample, which was coated with blend coating (chitosan and rice starch) and where 10g/m^2 coating was applied to the paper. At uncoated paper smaller amount of colour has been applied and fixed to the surface and after rubbing, the optical density was the lowest (1.13), compared to other treated samples after 25 cycles. Paper, where only chitosan was used as coating, achieved lower results before and after rubbing, of the optical density (before 1.43 and after 1.14) in comparison to blend coating, but the difference was not so major. From this part it can be concluded that rice starch as coating component influences on more stable and durable coating. However, only chitosan coating had worse abrasion resistance.

After 50 cycles (Figure 2), the chitosan and rice starch coating still had better abrasion resistance (optical density was 1.23) according to other analysed samples, but it could not be sufficient for further use. The difference between 25 and 50 cycles showed that blend coating, which was applied to the paper surface with two different bars, achieved almost the same values at both rubbing times. As expected, the rubbing abrasion has worsen after 50 cycles at uncoated paper. At chitosan coated paper also the optical density decreased.

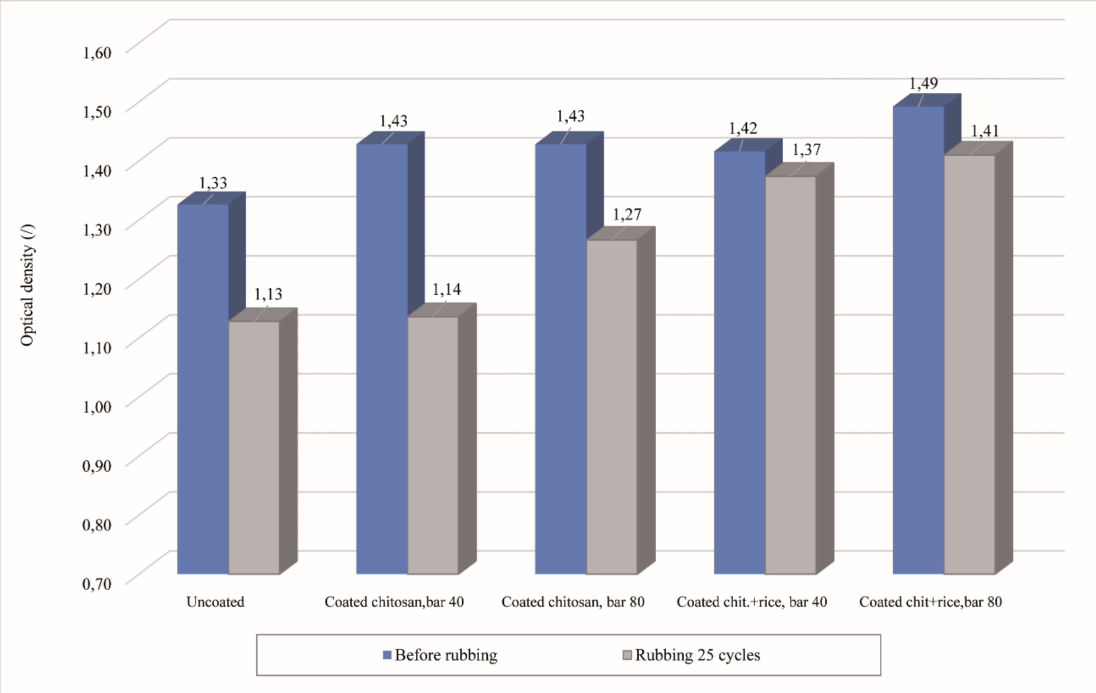


Figure 1. Optical density of uncoated and coated paper samples after rubbing 25 cycles

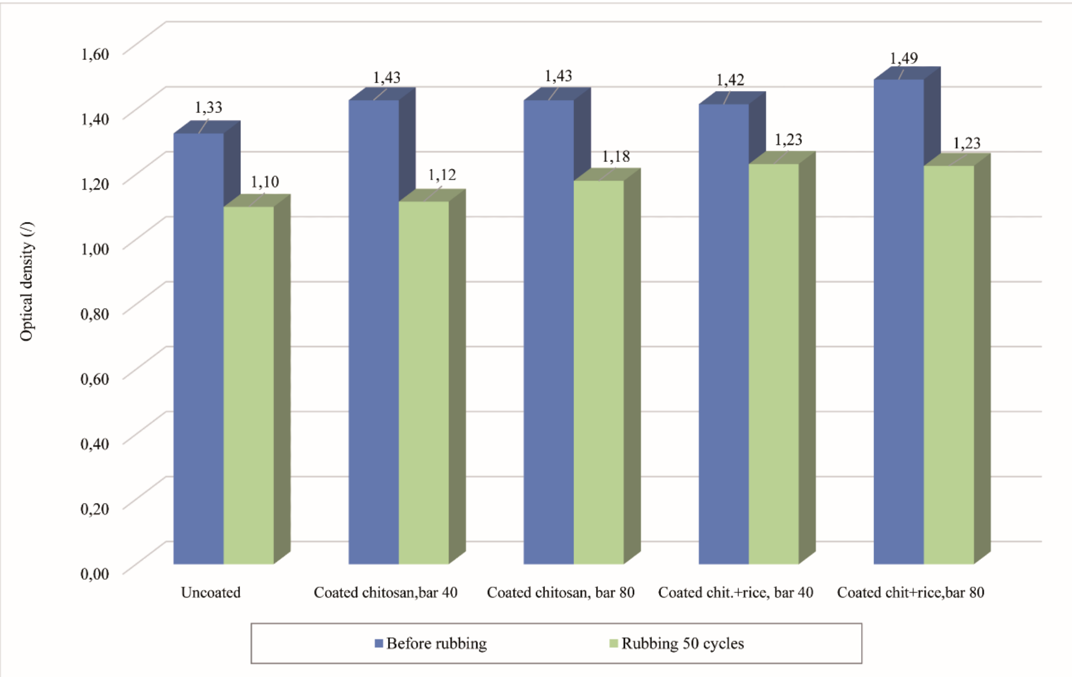


Figure 2. Optical density of uncoated and coated paper samples after rubbing 50 cycles

Surface

All pictures present paper surface after 25 (Figure 3) and 50 cycles (Figure 4). As expected, the surface of coated paper revealed smoother surface, compared to uncoated paper as seen at both figures. After 25 cycles at uncoated paper more damages could be seen, compared to coated paper, which was also proven with determination of optical density. In comparison between coated papers, the best results achieved paper, which was coated with blend solution and the coting has been applied with 80 µm bar.

As expected, all samples rubbed for 50 cycles revealed more damaged surface. At both rubbing times, uncoated sample had the worse surface (more white dots, scraped surface), compared to other tested papers. The best results at both rubbing times achieved paper, which was coated with blend solution and where 10g/m^2 of coating was applied. The research has proven increased printing quality of coated paper, especially at the coating with mixture of chitosan and rice starch.

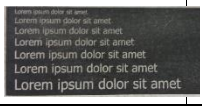
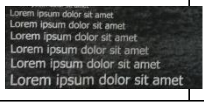
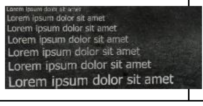
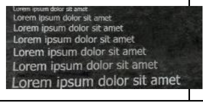
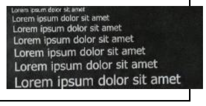
UNCOATED	COATED chitosan, 25 cycles, 40µm	COATED chitosan, 25 cycles, 80µm	COATED chitosan+rice, 25 cycles, 40µm	COATED chitosan+rice, 25 cycles, 80µm
				

Figure 3. Paper printed surface after 25 cycles

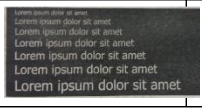
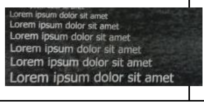
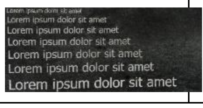
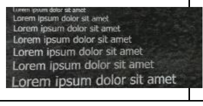
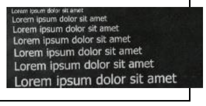
UNCOATED	COATED chitosan, 50 cycles, 40µm	COATED chitosan, 50 cycles, 80µm	COATED chitosan+rice, 50 cycles, 40µm	COATED chitosan+rice, 50 cycles, 80µm
				

Figure 4. Paper printed surface after 50 cycles

Image segmentation

Image segmentation is one of the most common techniques to process a separating an image into different areas on various features of the analysed image.

Figures 5 and 6 present a histograms of Grey-Scale image-printed surface of each paper sample with different coatings and rubbing cycles. At analysed papers the pixels of foreground had different grey value compared to pixels belonging to the background. The image segmentation technique assumes that pixels above certain threshold on grey level (0-255), belong to the analysed object-image foreground and pixels below that threshold are belonging to the background [19]. At our study images have similar grey levels, as seen in both presented figures. According to that the changes at all presented histograms were detected. Grey level histograms from papers analysed at 25 cycles (Figure 5) showed that uncoated paper had more damages on the surface and less colour was on it after rubbing. On the other hand more pixels were detected at grey level between 50 and 80. Less damages had paper, which was coated with blend solution (chitosan and rice starch) with 80µm bar. At this sample the most pixels detected were between 15 and 60 of grey level, meaning that more colour was still applied at the surface, compared to other tested papers. Papers which had coatings of only chitosan and blend coatings showed that had less colour and they were more rubbed after 25 cycles, compared to blend coating with used 80µm bar.

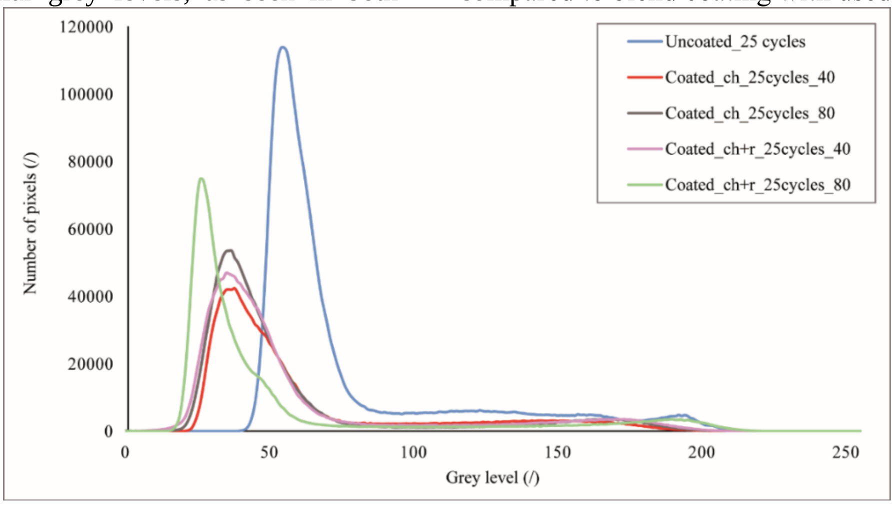


Figure 5. Grey level histograms for paper surface of uncoated and coated samples after 25 cycles of rubbing and 2 different blades (40µm and 80µm).

Figure 6 presents histograms of paper surface for all tested papers at rubbing time 50 cycles. The results have shown similar trend as at 25 cycles. The most damaged surface was again at uncoated paper, where the damages were also confirmed with determination of optical density. The most durable paper surface was again at paper, which was coated with 80µm bar with blend solution. Thus differences between surface damages for each paper between 25 and 50 cycles did not show significant difference, according to image segmentation with this method. For future findings different thresholding methods should be defined, in order to find the most suitable image segmentation for this kind of coatings. Despite this, it can be stated that the analysis has shown differences at uncoated and coated papers, where 2 different bars were used.

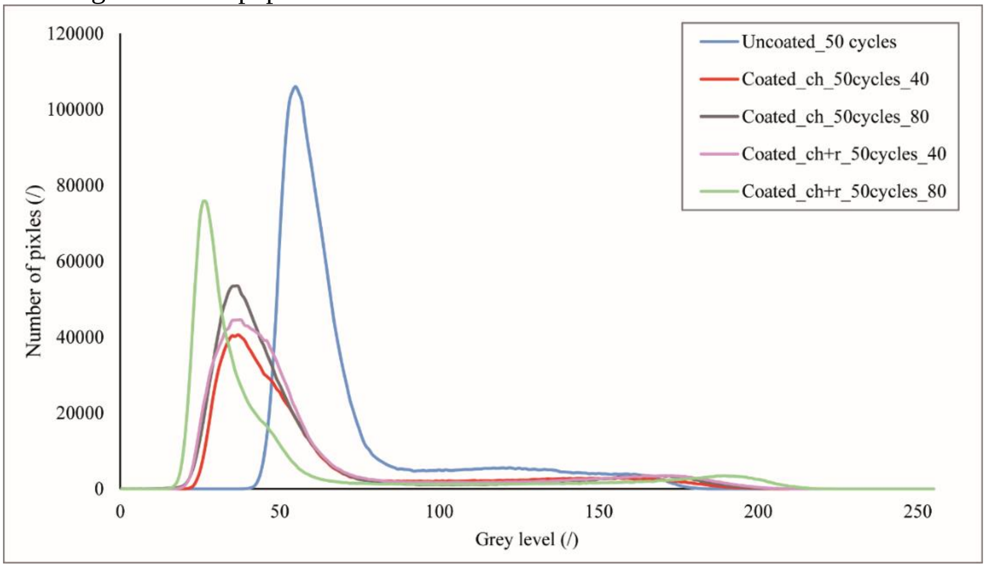


Figure 6. Grey level histograms for paper surface of uncoated and coated samples after 50 cycles of rubbing and 2 different blades (40µm and 80µm).

CONCLUSIONS

In this research different coatings, concerning also the different amount of it, its durability and printing quality were prepared. Coatings were successfully prepared and the results have shown that with coatings paper surface properties have improved. Dry rub test showed that all coated papers achieved better results in comparison to uncoated paper. After 25 cycles paper, which was coated with blend solution of chitosan and rice starch achieved the best printing quality (smoothness, porosity, abrasion resistance), according to uncoated and only chitosan coated paper. This was also confirmed with determination of optical density and image segmentation. After 50 cycles, the chitosan and rice starch coating still had better abrasion resistance compared to other analysed samples. For further use the coatings (chitosan and rice starch) should be modified and then they will have a potential for the use in packaging. It was proven, that the properties of ink and printed surface influenced the interactions between coating and ink, which could be seen from presented results. On the other hand pore surface, the pore size, permeability, together with material, ink components and printing process (pressure, speed, etc.) are important coating properties, for achieving good printing quality.

As a subject of a further paper to enhance coatings for better abrasion resistance is to prepare coatings with different ratios of analysed components or to include other biopolymers, which will have better rubbing resistance.

REFERENCES

1. D.A. Todorova, S.P. Bencheva, *Bul. Chem. Commun.*, **47**, 45 (2015).
2. U. Vrabič Brodnjak, *J. Compos.Biodegrad. Polymers*, **4**, 32 (2016).
3. J. M. Krochta, C. De Mulder-Johnston, *Food Technol*, **51**, 61 (1997).
4. M.S. Rao, S.R. Kanatt, S.P. Chawla, A. Sharma, *Carbohyd Polym*, **82**, 1243 (2010).
5. P. Saym, *J Mater Sci*, **48**, 6455 (2013).
6. N. Bordenave, S. Grelier, V. Coma, *Biomacromol.*, **11**, 88 (2010).
7. S. Wang, Y. Jing, *BioResources*, **11**, 1868 (2016).
8. M.B. Vásconez, S.K Flores, C.A. Campos, J. Alvarado, L.N. Gerschenson, *Food Res Int*, **42**, 762 (2009).
9. J.W. Rhim, C. L. Weller, K. S. Ham, *Food Sci. Biotechnol.*, **7**, 263 (1998).
10. T. Bourtoom, M.S. Chinnan, *Food Sci. Technol.*, **41**, 1633 (2008).
11. M. Jaworska, K. Sakurai, P. Gaudon, E. Guibal, *Polym Int*, **2,** 198 (2003).
12. Z. Zhou, K. Robards, S. Helliwell, C. Blanchard, *Int J. Food Sci Tech*, **37**, 849 (2002).

13. H. Dai, P. R. Chang, F. Geng, J. Yu, X. Ma, *Carbohyd Polym*, **79**, 306 (2010).
14. N. Follain, C. Joly, P. Dole, C. Bliard, *Carbohyd Polym*, **60**, 185 (2005).
15. R. Bollström, A. Määttänen, P. Ihalainen, J. Peltonen, M. Toivakka, *Patent application PCT/FI2010/050056*, (2009).
16. R. Bollström, A. Määttänen, D. Tobjörk, P. Ihalainen, N. Kaihovirta, R. Österbacka, J. Peltonen, M. Toivakka, *Org. Electron*., **10**, 1020 (2009).
17. M. von Bahr, F. Tiberg, B. Zhmud, *Langmuir*, **15**, 7069 (1999).
18. J. Kettle, T. Lamminmäki, P. Gane, *Surf Coat Tech*, **204**, 2103 (2010).
19. A. Drobchenko, J. K. Kamarainen, L. Lensu, J. Vartiainen, H. Kälviäinen, T. Eerola, *Frontiers Electr. Electron. Eng. China*, **6**, 328 (2011).

ПЕЧАТАРСКИ КАЧЕСТВА НА ОПАКОВЪЧНА ХАРТИЯ, ПОКРИТА С ХИТОЗАН И ОРИЗОВА СКОРБЯЛА

У. Врабич Бродняк*, Д. Мук

Департамент по текстил, графика и дизайн, Факултет по природни науки и инженерство, Университет в Любляна, Словения

Постъпила на 26 октомври, 2016 г.; приета на 25 януари, 2017 г.

(Резюме)

Биополимерите, използвани като покрития на опаковъчна хартия, могат да осигурят значителна защита от влага, газове и пр. Поради екологични съображения синтетичните опаковки сега се заменят с материяли на биологична основа. Термопластичната скорбяла и хитозанът могат да бъдат добър заместител на опаковките, базирани на петрола като суровина при опаковките. В това изследване се използват оризова скорбяла и хитозан като покритие на опаковъчна хартия. Цел на изследването е да се определи печатарското качество на така покритата хартия. Изследвано е и влиянието на дебелината на покритието върху печатарското качество.
Хартията е покривана с две различни смеси. Първата е само с хитозан, а втората е смес от хитозан и оризова скорбяла в отношение 50:50. Покритията са правени при различни налягания, за да се постигне различна дебелина на покритието: 40μm и 80μm. Извършено е изпитание за изтриване по стандарта TAPPI T830. Тестът на сухо триене показва, че всички образци с покритие дават по-добри резултати (по оптична плътност) в сравнение с не-покритите проби. В нашите изследвания две серии (по време на триене) са определени: 25 и 50 цикъла при скорост на триене 106 cpm. След 25 цикъла пробата, покрита с хитозан и оризова скорбяла показва по-добри резултати спрямо необработената хартия или обработена само с хитозанов разтвор. След 50 цикъла покритието от хитозан и оризова скорбяла още има по-добро съпротивление на изтриване, но не достатъчно за по-дълга употреба. Изследването показва повишено печатарско качество на покритата хартия, особено при покрития от смес на хитозан и оризова скорбяла..