

Evaluation of viscosity and printing quality of chitosan-based flexographic inks: The effect of chitosan molecular weight

Hongxia Wang, Ting Guo, Houbin Li

School of Printing and Packaging, Wuhan University, 299, Bayi Road, Wuchang District, Wuhan, Hubei 430072, People's Republic of China

Correspondence to: H. Li (E-mail: lhb@whu.edu.cn)

ABSTRACT: Inks composed of renewable resources are important for the environment protection. We report preparation of a new type of edible chitosan-based flexographic ink. The performance of three inks, containing three different molecular weight (MW) chitosan, was analyzed by the different experimental techniques. The Ink viscosity was investigated from the parameters shear rate, time, temperature, and flexographic printing simulation. The printing quality on coated paper was studied by the scratch resistance, contact angle, print fastness, chromatic aberration, and dot gain. Viscosity recovery rate reached 69% after 6 s, and the print fastness was up to 91%. The experimental ΔE is 0.97, the dot gain is 23%, and contact angle is 69° for the best ink. Experimental results indicate that the developed ink is suitable for the flexographic printing with good application prospects. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43997.

KEYWORDS: coatings; composites; biomaterials; optical properties; rheology

Received 30 March 2016; accepted 1 June 2016

DOI: 10.1002/app.43997

INTRODUCTION

Inks composed of renewable resources are increasingly introduced to the market to meet the requirements of environmental protection, safety, and hygiene, which enjoy great popularity.¹ The edible ink is a polymer-dispersing system, among which the resin is of vital importance for protecting the pigment and forming the ink coating. Currently there are edible inks using environmentally safe materials, such as propanediol, maltose, corn starch, gumarabic, sucrose, and glucose as resins.^{2–4} They were mostly used in lithographic printing and inkjet printing.^{5,6} However, types of resin used in edible inks are small.

Chitosan can act as the resin for edible inks, because it possesses the film-forming ability, mechanical strength, edibility, nontoxicity, biodegradability, and high biocompatibility.^{7–11} Also, it is the second largest natural biological organic resource in nature after cellulose and is used in many fields at present.^{12,13}

Though there were some similar reports about inks containing chitosan, these seldom studied viscosity properties and the detailed printing quality.¹⁴ Nowadays, although flexographic printing (Figure 1) is one of the fastest growing printing ways worldwide with characteristics of no pollution, high efficiency, and high yield,^{15–17} the edible flexographic ink is rare in our life and research. In this article, we report preparation of environment friendly, edible flexographic ink containing different

amount of chitosan with different MWs as resin, evaluation of viscosity properties, and printing qualities.

EXPERIMENTAL

Materials

Molecular weights (MWs) of chitosan-1, chitosan-2, and chitosan-3 are 30, 80, and 230 kDa, respectively, with their deacetylation degree being 85% (Shanghai Ruji Biotechnology Development Corporation, Shanghai, China). Pigment Red 101 (Fe_2O_3 , diameter $<45 \mu\text{m}$) (Cathay Pigments (China) Ltd, Shanghai, China) was adopted. Polysorbate 80 (Aladdin, Shanghai, China) served as the surfactant to promote the stability of inks.¹⁸ Soybean oil was the antifoaming agent. The ordinary standard ink was purchased in supermarket (Tianjin Enterprising Xin Trading Corporation, Hebei, China).

Ink Preparation

The ink preparation involved in three formulations (Table I). The process: the chitosan ($(\text{C}_6\text{H}_{11}\text{NO}_4)_n$) acid solution was added with the quantitative pigment (Fe_2O_3), polysorbate ($\text{C}_{24}\text{H}_{44}\text{O}_6(\text{C}_2\text{H}_4\text{O})_n$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and soybean oil and stirred together at the speed of 1500 rpm. As resin, chitosan could protect the pigment, sustain the stability and dispersity of ink system with surfactant, and form into the compact ink coating (Figure 2). During the process, Weissenberg effect could be seen and should be taken into account. Then it was placed in

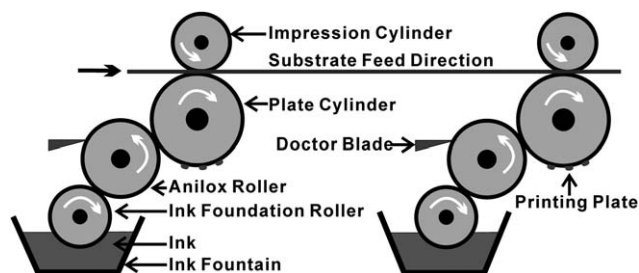


Figure 1. The flexographic printing process.

the horizontal planetary ball mill (XQM-0.4) (Changsha Tencan Powder Technology Co., Ltd, Hunan, China) to grind for 4 h. Finally, samples were obtained, i.e., ink A, ink B, and ink C.

Viscosity under Shear Rate Ramp

The rheometer (KINEXUS PRO; Malvern, Shanghai, China) would be operated similarly to the way in the study of Payne *et al.*, Hussain *et al.*, and Faddoul *et al.*^{19–21} The shear rate range was from 0.01 to 10000 s⁻¹. All the procedures were performed at 25 °C with 50% relative humidity (RH). Also, samples for each formulation were put in storage at 0, 25, and 65 °C of which the viscosity was measured every 5 days. The relationship between viscosity and shear rate is in accordance with the following equation:

$$\eta_a(\dot{\gamma}) = \tau(\dot{\gamma}) / \dot{\gamma} \quad (1)$$

where $\eta_a(\dot{\gamma})$ is viscosity, $\tau(\dot{\gamma})$ is shear stress, and $\dot{\gamma}$ is shear rate.

Viscosity during the Simulation of Printing Process

To clarify the rheological properties during the flexographic printing, the process was simulated.²¹ There were three processes at 25 °C with 50% RH. First, the viscosity was evaluated at the shear rate 0.1 s⁻¹ for 3 s, which was close to the ink state in the ink fountain reservoir before flexographic printing. Second, shear rate was increased to 500 s⁻¹ for 3 s, which was almost equal to the printing speed during flexographic printing. Third, the shear rate was dropped to 0.1 s⁻¹ for simulation of the viscosity recovery after flexographic printing, which kept for 9 s.

Flexographic Printing

The developed inks were applied to the flexographic press (Shanghai Modern Environmental Engineering Technology Corporation, Shanghai, China) on the 80 g m⁻² coated paper.

Scratch Resistance

At 25 °C with 50% RH, the pencil hardness tester (JISK5401 ASTMD2197; Shenzhen Suderui Technology Corporation,

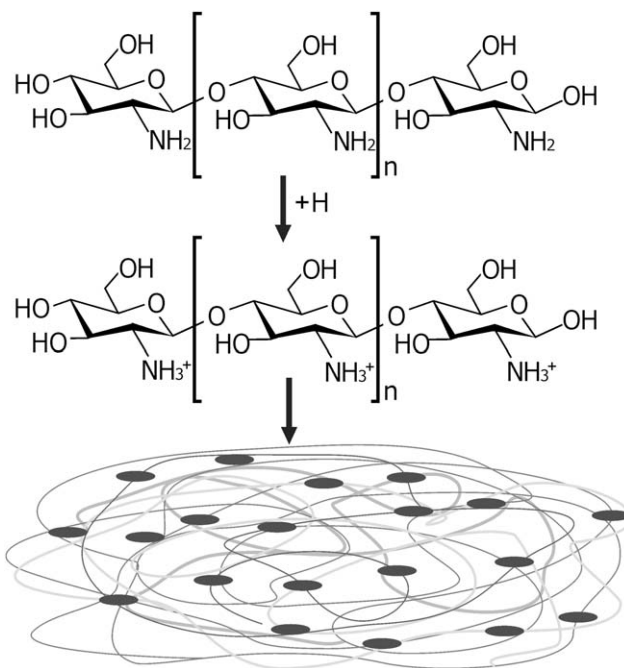


Figure 2. Chitosan acid solution development and its sustainability for ink components.

Guangdong, China) was used for the scratch resistance,²² which was in accord with ISO 15184:2012.

Contact Angle

The contact angle of water on prints was measured by contact angle measurement instrument JC2000DF with digital camera (Beijing Zhongyikexin Technology Corporation, Beijing, China) at 25 °C with 50% RH. At least eight samples of each formulation were tested, and the relative standard deviation should be less than 5%.²³

Optical Density and Print Fastness

At 25 °C with 50% RH, X-rite SpectroEye (Shenzhen Sanenchi Technology Corporation) was used to investigate the optical density of prints and then measure again the density of the print after being rubbed by the MCJ-01A friction machine, indicating the colorant retention.^{24,25} The fastness could be calculated according to the following equation on the basis of the regulation of China national standard GB/T 17497.1-2012:

$$A_s = (D_2 / D_1) \times 100\% \quad (2)$$

where A_s is the print fastness, D_1 is the optical density values measured on coated paper before rubs, and D_2 is the optical density values measured on coated paper after rubs.

Table I. The Formulations of Edible Inks (Mass %)

	Chitosan	Pigment (%)	Acetic acid (%)	Deionized water (%)	Ethanol (%)	Polysorbate 80 (%)	Soybean oil (%)
Ink A	Chitosan-1, 2%	27.5	0.81	39.69	29.8	0.1	0.1
Ink B	Chitosan-2, 2%	27.5	0.81	39.69	29.8	0.1	0.1
Ink C	Chitosan-3, 2%	27.5	0.81	39.69	29.8	0.1	0.1

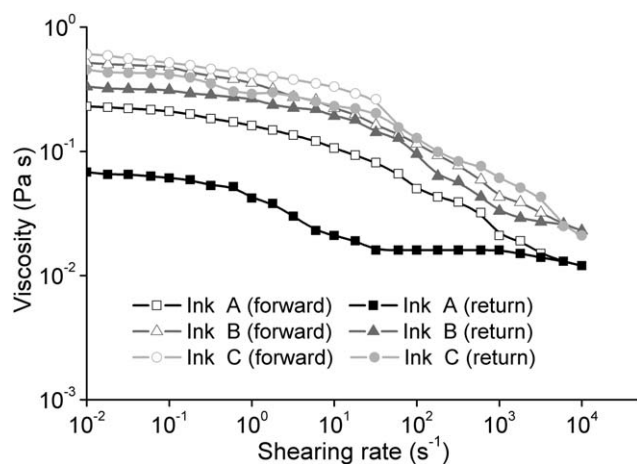


Figure 3. The relationship between viscosity and shear rate.

Chromatic Aberration

Under the illuminant D50 (simulated sunlight, color temperature: 5000 K) (ISO 13655:2009) with a viewing angle of 2° at 25°C with 50% RH, the color measurement instrument NS820 (Shenzhen Sanenchi Technology Corporation) was used to measure L^* , a^* , and b^* of prints. Then ΔL (positive values indicate bright and negative values indicate dark), Δa (positive values indicate red and negative values indicate green), Δb (positive values indicate yellow and negative values indicate blue), and ΔE (chromatic aberration) could be calculated by the following equations^{26–28}:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (3)$$

$$\Delta L = L^* - L_p^*, \quad \Delta a = a^* - a_p^*, \quad \Delta b = b^* - b_p^* \quad (4)$$

where L^* , a^* , and b^* are values of prints of the developed inks and L_p^* , a_p^* , and b_p^* are values of prints of the ordinary standard inks.

Dot Gain

X-rite SpectroEye (Shenzhen Sanenchi Technology Corporation) was used to test the dot area rate of grade blocks (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100%) at 25°C with 50% RH. The dot gain, a vital factor for the printing quality,²⁹ was calculated via the following equation:

$$Z = a - F \quad (5)$$

where Z is the dot gain value, a is the dot area rate on the print, and F is the dot area rate on the original corresponding printing plate.

RESULTS AND DISCUSSION

Viscosity under Shear Rate Ramp

Shear rate range from 0.01 to 10,000 s^{-1} was realized by the rheometer (KINEXUS PRO), during which viscosity of all inks changed. The shear thinning thixotropic behavior and pseudo-plastic property were obvious in developed inks (Figure 3), which were conducive to leveling, draining and pumping.^{30,31}

Viscosity decreased with an increase in shear rate and recovered with the decrease in shear rate. The structure recovery of ink A was poor with the lowest viscosity reaching 1.2×10^{-2} Pa s,

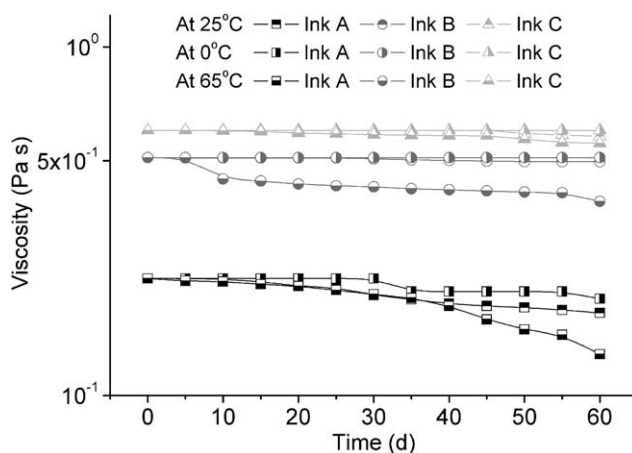


Figure 4. Viscosity under different temperature and time.

which might cause the phenomenon of pigment sinking and unfavorable transferring. With the lowest viscosity of 2.9×10^{-2} Pa s, ink C possessed the ability to rebuild the structure when the shear rate decreased, exhibiting good thixotropic behavior, ensuring the ink to transfer continuously during printing.

During the printing, the developed inks should own thixotropy that will benefit the process. The ink viscosity will decrease with the liquidity enhanced because of the shearing of the roller. This will help ink to transfer smoothly and uniformly. After the ink is transferred onto the paper, the physical shearing disappears. Then viscosity increases, and the liquidity decreases, ensuring the fixing of ink on the coated paper.

Influence of Temperature and Time on Viscosity

After storage for 60 days at 0°C , the viscosity of ink B and ink C changed little, while that of ink A decreased slightly in the later process (Figure 4). At 25°C , the viscosity of the ink C almost had no change and that of ink A and ink B kept decreasing after 30 days. At 65°C , the viscosity of ink A and ink B dropped obviously by 9.5×10^{-2} and 1.25×10^{-1} Pa·s, respectively, while that of ink C only descended by 4.7×10^{-2} Pa·s. The viscosity change process was similar to study of Hicks *et al.*³² At the same temperature, the chitosan

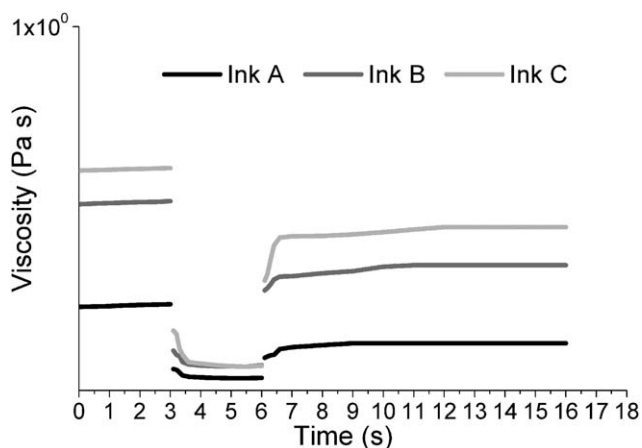


Figure 5. Viscosity of developed inks during simulation.

Table II. The viscosity values during the printing simulation (Pa s)

	0.1 s ⁻¹ (before printing)	500 s ⁻¹ (during printing)	0.1 s ⁻¹ (after printing)	Recovery time (s)	Recovery rate (%)
Ink A	0.229 ± 0.021	0.036 ± 0.008	0.118 ± 0.015	3	51
Ink B	0.511 ± 0.033	0.078 ± 0.011	0.312 ± 0.027	5	61
Ink C	0.601 ± 0.032	0.080 ± 0.015	0.420 ± 0.030	6	69

Table III. Contact angle

	Contact angle	
	Contact angle θ (°)	The relative standard deviation (%)
Ink A	61°	2.7
Ink B	65	1.9
Ink C	69	3.3

with larger MW had longer molecular chains, and the relative movement resistance between molecules was larger, so the viscosity was relatively higher (ink C > ink B > ink A). At the same time, high temperature accelerated the degradation of chitosan,^{33–35} which resulted in the viscosity of developed inks to decline.

Viscosity during the Simulation of Printing Process

Ink viscosity that is decreased obviously during printing will allow the ink to pass quickly among the fountain roller, anilox roller, plate cylinder, and impression cylinder. During the printing simulation, the viscosity decreased when the shear rate rose from 0.1 to 500 s⁻¹, increased when the shear rate went back to 0.1 s⁻¹ and then remained stable at the later process (Figure 5), which was similar to the study of Faddoul *et al.*²¹ The viscosity of the ink A recovered only 51% with 3 s (Table II). This time was too short for ink to level and dry. The recovery rates of ink B and ink C were 61% (5 s) and 69% (6 s), respectively, which could give the ink on substrates enough time to level, permeate, and dry with high recovery rate. It is likely due the reason that higher molecular-weight chitosan contains long molecular chains, which require more time to restore the original structure.

Scratch Resistance and Contact Angle

The pencil hardness of the prints of ink A, ink B, and ink C reached 2B, HB, and F, respectively. It may be due to that chitosan with large MW intersperses and crosses with each other

closely, and the print coating is compact after drying. So the pencil tip could not scratch the coating easily.

The smaller contact angle θ shows that the print coating is more hydrophilic with good wetting ability.³⁶ Also, chitosan in different states owns different hydrophilicity. The contact angles of water on all print coatings were smaller than 90°, so all prints had certain hydrophilicity (Table III). Contact angle of water on the ink A print coating was the minimum (61°), so the print coating was easy to wet with the strongest hydrophilicity, which would result in poor water resistance.

Optical Density and Print Fastness

The optical density can be used to describe the print quality and the thickness of the dried ink coating. The optical density values of each formulation were relatively stable, which indicated that the thickness of the ink coatings was uniform with good color rendering (Table IV). According to China national standard GB/T 17497.1-2012, the fastness should be greater than 70.0%. So the developed inks satisfied the printing requirements on the coated paper. The fastness of the ink C print was 91%, and that of the ink A print was 80%. The reason may be that the long molecular chains of the chitosan interspersed and crossed with each other, forming into the compact coating after drying. When rubbed, the loss of pigment was small under protection of the compact coating, so the fastness of the ink C print was high.

Chromatic Aberration

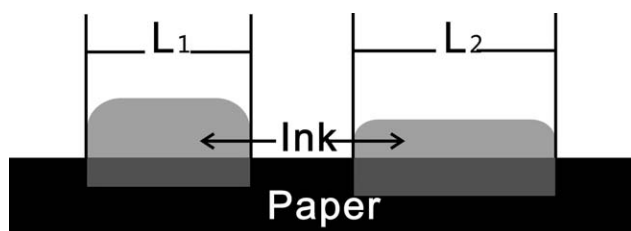
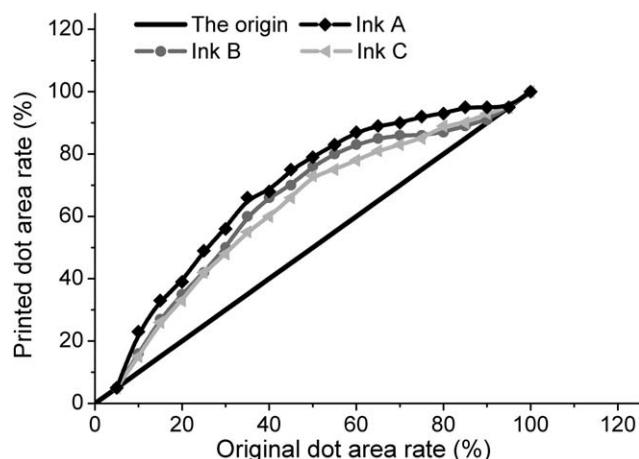
During printing, the ink is the key to the print color, and the slight change of ink composition can generate the variation of absorption and reflection of light, thus causing the change of the print color. CIE L^* , a^* , b^* is a direct measurement of visual effect for the human eye, reflecting the color vision and psychological effect of the people and influencing consumer preferences.^{22,26,37–40} L values on prints of developed inks were higher than that of ordinary standard ink (Table V), so the print colors of developed inks were relatively bright. Δa values of developed inks were all negative, which exhibited that red intensity was weak. Δa of the ink C print was the highest showed the red

Table IV. Optical density and fastness of prints

	Optical density before rubs						Optical density after rubs (average)	Fastness (%)
	1	2	3	4	5	Average		
Ink A	0.95	0.94	0.95	0.95	0.95	0.95	0.76	80
Ink B	0.93	0.93	0.93	0.93	0.93	0.93	0.76	82
Ink C	0.96	0.96	0.97	0.96	0.96	0.96	0.87	91

Table V. Chromatic aberration

	Chromatic value						
	L	a	b	ΔL	Δa	Δb	ΔE
Ink A	52.21	61.55	31.66	2.98	-2.00	1.55	3.91
Ink B	51.47	61.96	31.26	2.14	-1.59	1.15	2.90
Ink C	50.52	62.35	31.01	0.63	-0.51	0.53	0.97
Ordinary standard ink	49.23	63.55	30.11	—	—	—	—

**Figure 6.** The shape of dot gain.**Figure 7.** Dot area rate of prints.

intensity was the strongest in all developed inks. ΔE values of the ink A print and the ink B print were higher than 1, but lower than 4, which demonstrated that color difference could be observed by the naked eye.²² However, the color difference between the ink C print and the standard ink print was small, conforming with the China national standard GB/T 17497.1-2012.

Dot Gain

During printing, the dot area may change and the dot edge may expand around (Figure 6), forming into dot gain, darker color, and chaos.⁴¹ The ink with greater liquidity is relatively more easy to permeate the paper, causing the more serious dot gain.⁴²

The optical dot gain, related closely to the printing press, ink-transfer, and ink-paper interaction, actually demonstrates the fact that practical dot area is bigger than the dot area on the original corresponding printing plate.^{43–45} The maximum dot gain value of the ink A print was up to 29% (Figure 7), which

would influence the printing effect, generating the fuzzy color. This is presumably due to that the ink with small-molecular-weight chitosan has good liquidity and is easy to penetrate the paper, causing the dot gain. The dot gain of prints of ink B and ink C was 25 and 23%, respectively. The reason may be that inks with large molecular weight chitosan are not easy to penetrate the paper when printing. Therefore, the relatively smaller value of dot gain (23%) observed for the Ink C shows that it is more satisfactory.

CONCLUSIONS

We prepared a new type of edible, renewable, chitosan-based flexographic ink and evaluated its properties and application. The performance of three inks containing three different MWs of chitosan was analyzed by the different experimental techniques. We found that viscosity and the printing quality were closely connected with the relative molecular mass of chitosan, thus causing the viscosity differences and the printing quality differences between developed inks.

REFERENCES

- Robert, T. *Prog. Org. Coat.* **2015**, *78*, 287.
- Baydo, R. A.; Bogomolny, M.; Lee, C. L. U.S. Pat. 7247199 B2 (2007).
- Caiger, N. A.; Balch, A. R.; Williams, S. R. U.S. Pat 2010/0166934 A1 (2010).
- Shastry, A. V.; Ben-Yoseph, E. M.; Walters, M.; Willcocks, N. A.; Collins, T. M.; Suttle, J. M. Eur. Pat. 1,551,930 B1 (2003).
- Russell, J. R.; Candler, A. M.; Wright, A. WO Pat 2006/028847 A1 (2006).
- Wen, L.; Lanner, D. A.; Lin, P. Y. T. U.S. Pat 2006/0038866 A1 (2006).
- Chen, X.; Xia, N.; Guo, K.; Qi, C. *Bioresources* **2015**, *10*, 7038.
- Genskowsky, E.; Puente, L. A.; Pérez-Ivarez, J. A.; Fernandez-Lopez, J.; Muñoz, L. A.; Viuda-Martos, M. *LWT Food Sci. Technol.* **2015**, *64*, 1057.
- Madhuprakash, J.; El Gueddari, N. E.; Moerschbacher, B. M.; Podile, A. R. *Bioresource Technol.* **2015**, *198*, 503.
- Anaya, P.; Cardenas, G.; Lavayen, V.; Garcia, A.; Odwyer, C. *J. Appl. Polym. Sci.* **2012**, *128*, 3939.
- Hassan, M. L.; Fadel, S. M.; El-Wakil, N. A.; Oksman, K. J. *Appl. Polym. Sci.* **2012**, *125*, E216.

12. Prasanna, K.; Sailaja, R. R. N. *J. Appl. Polym. Sci.* **2012**, *124*, 3264.
13. Rogovina, S. Z.; Alexanyan, C. V.; Prut, E. V. *J. Appl. Polym. Sci.* **2011**, *121*, 1850.
14. Zhang, Y.; Li, X.; Mou, X.; Li, N. *Lect. Notes Electric. Eng.* **2016**, *369*, 977.
15. Bois, C.; Dumont, P. J. J.; Blayo, A.; Vincent, R.; Nayoze, C.; Chaussy, D. *Fuel Cells* **2014**, *14*, 614.
16. Preis, M.; Breikreutz, J.; Sandler, N. *Int. J. Pharm.* **2015**, *494*, 578.
17. Wang, Z.; Winslow, R.; Madan, D.; Wright, P. K.; Evans, J. W.; Keif, M.; Rong, X. *J. Power Sources* **2014**, *268*, 246.
18. Todosijevic, M. N.; Savic, M. M.; Batinic, B. B.; Markovic, B. D.; Gasperlin, M.; Randelovic, D. V.; Lukic, M. Z.; Savic, S. D. *Int. J. Pharm.* **2015**, *496*, 931.
19. Payne, C.; Methven, L.; Fairfield, C.; Gosney, M.; Bell, A. E. *J. Texture Stud.* **2012**, *43*, 95.
20. Hussain, M.; Bakalis, S.; Gouseti, O.; Zahoor, T.; Anjum, F. M.; Shahid, M. *Int. J. Biol. Macromol.* **2015**, *72*, 687.
21. Faddoul, R.; Reverdy-Bruas, N.; Blayo, A. *Mater. Sci. Eng. B* **2012**, *177*, 1053.
22. Żółek-Tryznowska, Z.; Izdebska, J.; Tryznowski, M. *Prog. Org. Coat.* **2015**, *78*, 334.
23. Zvonkina, I. J.; Gkountara, P.; Hilt, M.; Franz, M. *Prog. Org. Coat.* **2014**, *77*, 646.
24. Zhang, Y.; Liu, Z.; Cao, Y.; Li, R. A.; Jing, Y. *Bioresources* **2015**, *10*, 1462.
25. Li, R.; Zhang, Y.; Cao, Y.; Liu, Z. *Bioresources* **2015**, *10*, 8135.
26. Calvo, C.; Salvador, A.; Fiszman, S. *Eur. Food. Res. Technol.* **2001**, *213*, 99.
27. Zhang, Y.; Luo, S.; Wang, W. *J. Food Process. Preserv.* **2014**, *38*, 1259.
28. Gerhardt, J.; Hardeberg, J. Y. *COLOR Res. Appl.* **2008**, *33*, 494.
29. Li, X. Z. *Teh. Vjesn.* **2015**, *22*, 845.
30. Wang, Y.; Ju, B.; Zhang, S. *Carbohydr. Polym.* **2012**, *90*, 696.
31. Fijan, R.; Basile, M.; Lapasin, R.; Šostar-Turk, S. *Carbohydr. Polym.* **2009**, *78*, 25.
32. Hicks, C. R.; Carlson, B. E.; Mallick, P. K. *Int. J. Adhes. Adhes.* **2015**, *63*, 108.
33. Huang, Y.; Wang, P.; Yuan, Y.; Ren, X.; Yang, F. *Ultrason. Sonochem.* **2015**, *27*, 592.
34. Corazzari, I.; Nisticò, R.; Turci, F.; Faga, M. G.; Franzoso, F.; Tabasso, S.; Magnacca, G. *Polym. Degrad. Stabil.* **2015**, *112*, 1.
35. Nguyen, T. T. B.; Hein, S.; Ng, C. H.; Stevens, W. F. *J. Appl. Polym. Sci.* **2008**, *107*, 2588.
36. Park, J.; Moon, J. *Langmuir* **2006**, *22*, 3506.
37. Rodríguez-Pulido, F. J.; Gordillo, B.; Lourdes González-Miret, M.; Heredia, F. J. *Comput. Electron. Agric.* **2013**, *99*, 108.
38. Shaili, T.; Abdorreza, M. N.; Fariborz, N. *Carbohydr. Polym.* **2015**, *134*, 726.
39. León, K.; Mery, D.; Pedreschi, F.; León, J. *Food Res. Int.* **2006**, *39*, 1084.
40. Saeed Sel, S.; El-Molla, M. M.; Hassan, M. L.; Bakir, E.; Abdel-Mottaleb, M. M.; Abdel-Mottaleb, M. S. *Carbohydr. Polym.* **2014**, *99*, 817.
41. Yang, L.; Lenz, R.; Kruse, B. *J. Opt. Soc. Am. A* **2001**, *18*, 360.
42. Hersch, R. D.; Crété, F. In Proceedings of SPIE-IS&T Electronic Imaging, **2005**; Vol. 5667; p 434.
43. Bates, I.; Zjakic, I.; Budimir, I. *Imaging Sci. J.* **2014**, *63*, 103.
44. Nemedanian, M.; Gooran, S. *J. Imaging Sci. Technol.* **2013**, *48*, 48.
45. Liu, H.; Wang, Y.; Yuan, Z.; Zou, X.; Zhou, Y.; Ni, Y. *Colloid Surf. A* **2014**, *452*, 154.