

available online @ www.pccc.icrc.ac.ir Prog. Color Colorants Coat. 14 (2021), 129-138



# **Direct Sublimation Inkjet Printing as a New Environmentally Friendly Approach for Printing on Polyester Textiles**

## M. R. Alihoseini<sup>1</sup>, M. R. Khani<sup>1</sup>, M. Jalili<sup>\*2</sup>, B. Shokri<sup>3</sup>

<sup>1</sup> Laser and Plasma Research Institute, Shahid Beheshti University, P. O. Box: 19839-4716, Tehran, Iran

<sup>2</sup> Department of Printing Ink, Institute for Color Science and Technology, P. O. Box: 16765-654, Tehran, Iran

<sup>3</sup> Department of Physics, Shahid Beheshti University, P. O. Box: 19839-4716, Tehran, Iran

#### ARTICLE INFO

Article history: Received: 27 Mar 2020 Final Revised: 19 Jul 2020 Accepted: 20 Jul 2020 Available online: 23 Sept 2020 Keywords: Direct sublimation printing Inkjet Atmospheric-pressure plasma Polyester K/S value

# ABSTRACT

olyester is one of the most important synthetic fibers extensively used in textile industry. Inkjet printing on polyester textile is performed either by direct or transfer approaches. The first method needs chemical surface treatment, while the latter uses transfer paper. In this article, direct sublimation inkjet printing (DSIP) on polyester textile has been studied to overcome the natural resource limitations and environmental problems by eliminating the need for transfer paper and chemical surface treatment. Polyester textile was surface treated using atmospheric-pressure plasma under air atmosphere. The effects of different factors including plasma speed, plasma power, and the number of treatments on the contact angle and K/S value have been investigated via experimental design method. Scanning electron microscopy (SEM), attenuated total reflection-fourier transform infrared (ATR-FTIR), and bleeding test showed that plasma power has the least effect on both K/S value and contact angle. The K/S values increased while the contact angle decreased by increasing the number of treatments and decreasing the plasma speed. Optical and scanning electron microscopy images also revealed that the treated textile using constant plasma power of 350 W, 60 plasma treatments and the plasma speed of 3 m/min showed the most printing thickness and the highest image resolution. Prog. Color Colorants Coat. 14 (2021), 129-138© Institute for Color Science and Technology.

# 1. Introduction

The most widely used printing method in textile industry is screen printing which is performed via three approaches including rotary screen printing, flat (bed) screen printing and conventional screen printing. 58% of the printed textiles are produced by rotary screen printing while 28% of worldwide output belongs to flat (bed) screen printing. In rotary screen printing, a cylindrical screen is used that rotates in a fixed position. Other printing methods such as handheld screen printing (6%), intaglio printing (3%) and transfer printing (5%) are also applicable in traditional printing industry [1]. In screen printing, the dye is squeezed across the screen with a blade (known as squeegee) to fill the open mesh apertures with ink and transfer them onto the surface of the textile.

However, rotary screen printing suffers from the following limitations. Changing the color and pattern is done slowly and expensively because the set-up process is time-consuming (up to 6-8 weeks). Screen

printing machines have low durability and need more storage and operation space compared to digital printing machines [2].

By further development of textile industry and the increasing need for rapid style change, it is necessary to use new textile printing technologies in which style and color changes are performed rapidly. One solution is digital inkjet printing in which the desired design is transferred directly onto the textile from a computer file without using screens or heavy-duty machinery [3].

Inkjet printing has some disadvantages compared to screen printing. It produces thin films with low color strength and durability. The transparency and color strength of the printed film strongly depend on the textile surface treatment. The color gamut in inkjet printing is more limited and it is not suitable for spot color printing. Inkjet technology is commonly used in low-volume productions because its low printing rate limits its use in massive production. Physical properties of the ink (e.g. rheology and surface tension) also significantly affect the ink performance and the final printing quality. So, they should be compatible with the printer head. Nozzle clogging (especially in the case of pigment-based inks) and ink drying on the nozzle plate are other challenges in inkjet printing [1, 4–6].

Inkjet printing on polyester textiles is performed either by direct or transfer approaches. In direct inkjet printing, polyester textile is treated with proper chemicals before printing and the color is stabilized by using steam after printing. The drawbacks of this method are the need for chemical surface treatment, after-steam washing, and low color lightness. The printed film, however, has high color strength as well as high fastness to washing and temperature. Transfer inkjet printing, also called transfer sublimation inkjet printing, and does not need surface chemical treatment. In this case, printing is first done on the transfer paper and then the dye molecules are sublimated from the surface of the paper by heating under pressure. Under such conditions, dye molecules penetrate into the textile and create the desired printing pattern. Although the printed film has high lightness, it shows low fastness to washing and temperature due to the presence of dye materials [7].

Nowadays, direct printing is rapidly developing due to its high speed and quality, lower manpower, and promising environmental aspects. However, if printing is directly performed on raw polyester textile, the obtained printed film has weak color and physical

properties due to its low surface energy and hydrophobicity. Therefore, it is necessary to treat the surface before printing in order to increase the surface energy and hydrophilicity [8]. One of the methods for surface treatment, known as chemical method, is the use of chemicals and a variety of surface active agents. Many researchers have used this method for the surface treatment. Chen et al. [9] investigated the effect of polyester surface treatment with cyclodextrin on color strength and print quality. They showed that the print quality improves and the color strength increases by 47%. Polyurethane and acrylic resins were used to modify the surface of polyester textiles. It was found that the printed lines on the surface treated with acrylic resin showed higher resolution [10]. In order to increase the color gamut and prevent ink from bleeding during printing with inkjet ink on polyester, commercial surface treatment agents were used. As a result, the color gamut, color intensity, and print quality were improved [11, 12]. In addition to environmental pollution, chemical surface treatment methods also need post-printing washing operations. So, physical surface treatment methods have attracted considerable attention.

Plasma is one of the most promising physical surface treatment methods which, in comparison with chemical methods, benefits from low processing temperature in the case of temperature-sensitive polymers, higher safety, lack of chemical materials, no need for water cleansing, and environmental compatibility [13, 14].

Several studies have been reported on the application of plasma for printing in textile industries. Zhang et al. [15] investigated the surface modification of polyester textile using oxygen and helium plasma to increase the color and adhesion strength. They obtained a high printing resolution by developing functional groups on the surface of the substrate. In another study [16], surface properties and printing quality were improved by using atmospheric plasma containing air/helium gas mixture. Fang et al. [17] studied the physical and chemical effects of atmospheric plasma containing air/argon mixture on polyester textile. They reported that using gas mixture instead of pure gas results in more oxygen-containing functional groups on the surface. Some research works have also reported the use of plasma method for the treatment of polyester textile surface at low [18, 19] and atmospheric [20, 21] pressures before printing with

pigment-based digital inks.

Sublimation digital printing on polyester textiles is usually performed via transfer approach by using transfer paper. In this study, high-quality direct sublimation inkjet printing (DSIP) method is performed on polyester textile for the first time. To this end, plasma method has been applied rather than chemical surface treatment which is conventionally used in dispersed-ink digital printing on polyester textile. This led to the less water consumption and the elimination of environmentally hazard chemical materials. On the other hand, the environmental performance and sustainable development have been improved by replacing the transfer paper by direct printing.

#### 2. Experimental

#### 2.1. Materials and equipment

100% polyester textile with the surface density of 36  $g/m^2$  was purchased from Seyyed-o-Shohada textile Co., Yazd. Sublimation digital ink was supplied from Next Co. In the present work, atmospheric plasma system (Corona Print) was used for the processing of polyester textile, as shown in Figure 1. This system consisted of a stainless steel roll of 50 cm in length and 18 cm in diameter. Five metal electrodes coated with alumina (50 cm in length and 8 cm in diameter) were also used as high-voltage electrodes. The plasma speed, plasma power, and the number of treatments were

adjustable.

Epson Stylus T10 was used to print the ink on the treated substrate. The contact angle was measured using Hamilton Microliter syringe, CCD camera, Image J software, distilled water and diiodomethane at room temperature. The measurements were performed at four points and the average value is reported. The surface energies of the samples were measured according to the Fowkes theory (Eq. 1) [15]:

$$\gamma_L (1 + \cos \theta) = 2(\gamma_S^P \gamma_L^P)^{1/2} + 2(\gamma_S^d \gamma_L^d)^{1/2}$$
(1)

Where  $\theta$  is the contact angle,  $\gamma_L$  is the liquid surface tension,  $\gamma_L^P$  is the polar component of the liquid surface tension,  $\gamma_L^d$  is the disperse component of the liquid surface tension,  $\gamma_S^P$  is the polar component of the solid surface tension, and  $\gamma_S^d$  is the disperse component of the solid surface tension.

Spectrophotometer (IHARA S900, Japan) was used to measure the K/S values of the printed samples according to Kubelka- Munk equation (Eq. 2):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{2}$$

Where K is the absorption coefficient, S is the emission coefficient, and R is the reflection percentage. The printing quality and the ink bleeding were investigated using Dino-Lite digital optical microscopy (AM-314TS, ANMO Electronic, Taiwan).



Figure 1: (a) Normal error distribution and (b) fitting model results to experimental data.

## 2.2. Design of experiments

Design Expert v. 11 was used to study the influence of processing factors and their interactions on the response. Response surface methodology was used for experimental design in which power, speed, and the number of treatments were considered as variables. The

factors and their levels are presented in Table 1.

Twenty experiments were suggested by the software, as shown in Table 2. The K/S value and the contact angle presented in Table 2 were considered as the response.

#### Table 1: Processing factors and their levels considered in experimental design.

Factor	Name	Unit	level 1	level 2	level 3
А	Power	W	350	385	420
В	Speed	m/min	3	9	15
С	The number of treatments	n	2	31	60

Table 2: Experimental design factors (A, B, and C), K/S and contact angle values.

Experiment No.	plasma power: A (w)	plasma speed: B (m/min)	the number of treatments: C	Contact angle (degrees)	K/S
1	385	9	60	89.02	3.705
2	385	9	31	98	3.126
3	420	9	31	112.6	2.723
4	385	9	31	97.3	3.282
5	350	15	2	140.65	2.90
6	385	3	31	63.1	3.552
7	385	9	2	139.76	2.908
8	350	15	60	107.35	2.964
9	385	9	31	92	3.383
10	385	9	31	101.1	3.357
11	420	15	2	134.96	2.636
12	385	9	31	95	3.129
13	385	9	31	100	3.028
14	350	9	31	107.95	3.285
15	350	3	2	130.23	2.765
16	350	3	60	0	4.564
17	420	3	60	0	4.203
18	385	15	31	128.6	2.964
19	420	3	2	124.7	2.546
20	420	15	60	134.96	2.681

#### 3. Results and Discussion

#### 3.1. Contact angle

In the experiments,  $\alpha$  value was considered as 0.05. So, the effect of a factor on the response or effectiveness of a model is higher when the p values are lower than the  $\alpha$  value (the least  $\alpha$  value by which the null hypothesis can be rejected).

Table 3 shows the effect of factors A, B, and C on the response and the effectiveness of the proposed model predictions. It can be observed that the number of treatments and the speed, as well as the interactions between the speed and the number of treatments significantly affect the contact angle, while the plasma power showed negligible effect on the contact angle (p value of 0.52 which is much higher than 0.05). The p value of the proposed model is also much lower than  $\alpha$ value. Since the model parameters were close to unity  $(R^2 = 0.95, R^2_{adjusted} = 0.94 \text{ and } R^2_{predicted} = 0.90)$  and showed a high signal to noise ratio (Adeq. Precision= 27.28), the proposed model can be considered effective in explaining the variation of the response with the considered factors. Figure 1a shows the normal error distribution, while Figure 1b represents the correlation between the experimental values and the modelpredicted values. So, the model effectiveness can be confirmed based on the normal distribution of the errors and the good conformity between predicted and experimental results. Figure 1. (a) Normal error distribution, (b) fitting model results to experimental data

According to the variance analysis results presented in Table 3 and the plots in Figure 2a, plasma power has negligible effect on the contact angle in comparison with the two other factors. So, in 3D representation of the response variation, factors B and C can be varied while keeping factor A constant at 350 W, as shown in Figure 2b.

It can be seen that reducing the speed or increasing the number of the plasma treatments result in a slight decrease in the contact angle, while a significant decrease occurs by simultaneously reducing the plasma speed and increasing the number of treatments. According to Figure 2b, zero contact angle was obtained for 60 plasma treatments and the plasma speed of 3 m/min. In other words, the nonpolar surface of the polyester turned into a high surface energy polar surface after plasma treatment. FTIR analysis was performed to further investigate the effect of factors A, B, and C on the contact angle.

#### **3.2. Surface chemistry**

ATR-FTIR analysis is a suitable method to identify surface functional groups [22–24]. Figure 3 shows the ATR-FTIR spectra of the treated and untreated samples. The peaks in Figure 6a are attributed to the functional groups in polyester [25]. As it can be seen, the peaks related to polar functional groups of C=O (1713 cm<sup>-1</sup>), NH (3310-3340 cm<sup>-1</sup>), and OH (3400-360 cm<sup>-1</sup>) have more intensities in the treated sample relative to the untreated one (Figures 3a and 3b). This is an indicative of more functional groups per unit surface area and higher surface energy. So, the surface becomes more hydrophilic, resulting in lower contact angle and better surface wetting by the ink.

Source	Sum of Squares	df	Mean Square	F value	p value	
model	28464.90	4	7116.22	69.73	< 0.0001	
А	44.27	1	44.27	4344.00	<0.52	
В	10790.57	1	10790.57	105.88	< 0.0001	
С	11490.07	1	11490.07	112.74	< 0.0001	
BC	6140.00	1	6140.00	60.25	< 0.0001	
Model parameters	$R^2 = 0.95$ , $R^2_{adjusted} = 094$ , $R^2_{predicted} = 0.90$ , Adeq. Precision= 27.28					

Tahlo	3.	Variance	analysis	roculte	for	contact	anala
rapie	<b>J</b> :	variance	analysis	results	101	contact	angle.



Figure 2: (a) Effect of factors A, B, and C on the response, and (b) response variations in the experimental space.

As shown in Figure 3b, the peaks obtained for constant plasma power of 350 W are more intense than those obtained for 420 W at wavelengths related to OH, NH, and C=O groups. This indicates that, by increasing the plasma power, the number of functional groups does not necessarily increase; so there might be an optimum value for the plasma power. The reason can be explained as follows. By increasing the plasma power, electron energy increases, resulting in the increase in the number of impacts. Therefore, as most of atmosphere is composed of nitrogen, these impacts excite nitrogen molecules by increasing their kinetic energy, and finally they release their energy as light. These impacts can also break the surface bonds (according to the decrease in peak intensity of CH

bonds in Figure 3a).

#### **3.3.** Effect of factors on the color strength

The variance analysis results showed that although plasma power is important, the plasma speed and the number of treatments are more effective. Also, the interaction between these two factors is of high importance. It is worth noting that other interactions did not reveal considerable effects, so they were omitted from the model ( $\alpha$  was considered as 0.05). Table 4 shows that the model fits well with the experimental results, since p value (<0.0001) is far less than 0.05 and the model parameters were very close to unity. The signal to noise ratio was also within an acceptable range.



Figure 3: a) ATR-FTIR spectra of treated and untreated samples, and b) developed OH and NH polar groups.

Source	Sum of Squares	df	Mean Square	F value	p value
model	4.8	4	1.19	81.8	< 0.0001
А	0.25	1	0.252	17.3	< 0.0008
В	1.21	1	1.21	83.3	< 0.0001
C	1.90	1	1.9	131	< 0.0001
BC	1.40	1	1.4	59.9	< 0.0001
Model parameters	$R^2 = 0.956$ , $R^2_{adjusted} = 0945$ , $R^2_{predicted} = 0.937$ , Adeq. Precision= 33.57				

Table 4: Variance analysis results for color strength.

It is observed in Figure 4a that the errors have normal distribution. Also, Figure 4b shows that there is a good correlation between the experimental data and the model results, confirming the model effectiveness.

Figure 5a shows the influence of factors A, B, and C on K/S value. It can be seen from the Figure that factors B and C have more influence on K/S value. So, in 3D representation of the response variation, factors B and C can be varied while keeping factor A constant (350 W), as shown in Figure 5b. It is evident that the number of treatments has more influence on increasing the color strength than plasma speed reduction. The maximum color strength is obtained by simultaneously

reducing the plasma speed and increasing the number of treatments. The same results were obtained for the contact angle.

As mentioned above, plasma treatment increases the number of polar groups on the surface of the textile, hence enhances the surface energy and hydrophilicity. So, the ink adhesion to the surface is improved by increasing the ink wettability on the textile. As a result, a uniform and thick ink film is formed on the surface, enhancing the color strength. SEM and bleeding tests were also performed to further investigate these observations.



Figure 4: (a) Normal error distribution and (b) fitting the model results to experimental results.



Figure 5: (a) Effect of factors A, B, and C on the response, and (b) response variations at constant power of 350 W.

#### 3.4. Effect of plasma on the printing quality

SEM analysis was performed to investigate the ink film thickness and its homogeneity on plasma-treated and untreated textiles [26]. The treated sample with the highest K/S value and the lowest contact angle (according to experiment 16 in Table 2) was called "Sam" and the untreated sample was called "Bulk". Figure 6 shows that the ink film on the Sam sample (6b) is thicker and more uniform than that on the Bulk

sample (6a). This is mainly due to the formation of polar groups and the improvement of surface hydrophilicity after plasma treatment which in turn increases the surface wettability. On the contrary, the ink does not form a uniform film on the surface of the untreated sample due to the surface intrinsic hydrophobicity and lack of polar functional groups. This is also confirmed by the results of bleeding test, as shown in Figure 6.







Figure 7: Optical microscopy images of Sam and Bulk printed samples showing the effect of plasma on the bleeding and resolution.

#### 3.5. Effect of plasma on bleeding

Black color bleeding is one of the challenges in inkjet printing which occurs mainly due to the improper viscosity, surface tension, or low surface energy of the substrate. The effect of plasma on black color bleeding in blue region was investigated for both Sam and Bulk printed samples. As can be seen from Bulk 1 image in Figure 7, black ink bleeding in blue region is apparent and completely fades the blue color in horizontal direction. The black ink has also diffused into the blue region in the vertical direction. The Bulk 2 image in Figure 7 also shows that the boundaries of the printed black strips have low resolution with "feathering" morphology. In addition, the printed area has diffused into the blue region and shows low color strength. On the contrary, inkjet printing on Sam sample yields high resolution and color strength without bleeding, as shown in Sam 1 and Sam 2 images in Figure 7.

### 4. Conclusion

The results obtained from the experimental design showed that not only the plasma speed and the number of treatments but also the interaction between these two factors have significant effect on color strength and surface energy in comparison with plasma power. It was also revealed that by simultaneously reducing the plasma speed and increasing the number of treatments at a constant plasma power of 350 W, the color strength increases while the contact angle diminishes significantly (the maximum color strength of 4.564 and the zero contact angle were obtained for 60 plasma treatments and the plasma speed of 3 m/min). ATR-FTIR spectra demonstrated that the number of polar groups of hydroxyl, carbonyl, and amine increases after plasma treatment, creating higher surface energy and hydrophilicity. SEM and bleeding tests also confirmed that plasma treatment enhances the surface energy and the interaction between the ink and the substrate. Since water-based inks are used in sublimation inkjet printing, they show excellent interaction with plasmatreated hydrophilic substrates, resulting in higher resolution, less bleeding and enhanced color strength. It can be concluded from the results that direct sublimation inkjet printing on polyester textile is a promising method to preserve natural resources and reduce environmental pollution because it does not need transfer paper, chemical surface treatment, or post-printing washing. In contrast to transfer sublimation printing method in which ink transfer efficiency depends on the transfer conditions (i.e. temperature and pressure), the ink is completely transferred to the substrate in direct sublimation inkjet printing. This advantage is highly beneficial in reducing the concentration of the pigments in the inks, hence reducing the printing cost.

## 5. References

- C. W. Kan, C. W. M. Yuen, Digital Ink-jet Printing on Textiles, *Res. J. Text. Appar.*, 16(2012), 1–24.
- A. Dehghani, F. Jahanshah, D. Borman, K. Dennis, J. Wang, Design and engineering challenges for digital ink-jet printing on textiles, *Int. J. Cloth. Sci. Technol.*, 16(2004), 262–273.
- 3. C. Cie, Inkjet Textile Printing (First Edition)., Woodhead Publishing, Oxford, 2015, 15-34.
- E. Hanson, Recent Progress in Ink Jet Technologies II, Society for Imaging Science and Technology, Newyork, 1999, 555-558.
- S. Kiatkamjornwong, P. Putthimai, H. Noguchi, Comparison of Textile Print Quality between Inkjet and Screen Printings, *Surf. Coatings Int. Part B Coat. Trans.*, 88(2005), 25–34.
- S. K. Malik, S. Kadian, S. Kumar, Advances in ink-jet printing technology of textiles, *Indian J. Fibre Text. Res.*, 30(2005), 99–113.
- W. Zapka, ed., Handbook of Industrial Inkjet Printing (First Edition), Wiley-VCH Verlag, Weinheim, 2018, 179-194.
- 8. C. Cie, Ink Jet Textile Printing (First Edition), Woodhead Publishing, Cambridge, 2015, 125–137.
- L. Chen, C. Wang, A. Tian, M. Wu, An attempt of improving polyester inkjet printing performance by surface modification using β-cyclodextrin, *Surf. Interface Anal.*, 44(2012), 1324–1330.
- H. Park, W.W. Carr, H. ok, S. Park, Image Quality of InkJet Printing on Polyester Fabrics, *Text. Res. J.*, 76(2006), 720–728.
- 11. Y. Ding, L. Parrillo-Chapman, H. S. Freeman, A study of the effects of fabric pretreatment on color gamut from inkjet printing on polyester, *J. Text. Inst.*, 109(2018), 1143–1151.
- Y. Ding, R. Shamey, L. P. Chapman, H. S. Freeman, Pretreatment effects on pigment-based textile inkjet printing – colour gamut and crockfastness properties, *Color. Technol.*, 135(2019), 77–86.
- S. K. Nemani, R. K. Annavarapu, B. Mohammadian, A. Raiyan, J. Heil, M. A. Haque, A. Abdelaal, H. Sojoudi, Surface Modification of Polymers: Methods and Applications, *Adv. Mater. Interfaces*, 5(2018), 1–26.
- A. Vesel, Miran Mozetic, New developments in surface functionalization of polymers using controlled plasma treatments, J. Phys. D. Appl. Phys., 50(2017), 293001.
- C. Zhang, M. Zhao, L. Wang, L. Qu, Y. Men, Surface modification of polyester fabrics by atmosphericpressure air/He plasma for color strength and adhesion enhancement, *Appl. Surf. Sci.*, 400 (2017), 304–311.

#### How to cite this article:

M. R. Alihoseini, M. R. Khani, M. Jalili, B. Shokri, Direct Sublimation Inkjet Printing as a New Environmentally Friendly Approach for Printing on Polyester Textiles., *Prog. Color Colorants Coat.*, 14 (2021), 129-138.



- 16. C. Zhang, M. Zhao, L. Wang, M. Yu, Effect of atmospheric-pressure air/He plasma on the surface properties related to ink-jet printing polyester fabric, *Vacuum*, 137(2017), 42–48.
- 17. K. Fang, C. Zhang, Surface physical-morphological and chemical changes leading to performance enhancement of atmospheric pressure plasma treated polyester fabrics for inkjet printing, *Appl. Surf. Sci.*, 255(2009), 7561–7567.
- 18. C. Wang, C. Wang, Surface pretreatment of polyester fabric for ink jet printing with radio frequency O2 plasma, *Fibers Polym.*, 11(2010), 223–228.
- 19. C. W. M. Yuen, C. W. Kan, Influence of low temperature plasma treatment on the properties of inkjet printed cotton fabric, *Fibers Polym.*, 8(2007), 168–173.
- C. Zhang, K. Fang, Surface modification of polyester fabrics for inkjet printing with atmospheric-pressure air/Ar plasma, *Surf. Coatings Technol.*, 203(2009), 2058–2063.
- Y. Kusano, Atmospheric pressure plasma processing for polymer adhesion: *A review*, *J. Adhes.*, 90(2014), 755–777.
- R. Kumar, V. Sharma, Chemometrics in forensic science, *TrAC - Trends Anal. Chem.*, 105(2018), 191– 201.
- V. Sharma, A. Bharti, R. Kumar, On the spectroscopic investigation of lipstick stains: Forensic trace evidence, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 215(2019), 48–57.
- 24. V. Sharma, R. Kumar, Fourier transform infrared spectroscopy and high performance thin layer chromatography for characterization and multivariate discrimination of blue ballpoint pen ink for forensic applications, *Vib. Spectrosc.*, 92(2017), 96–104.
- 25. M. R. Jung, F. D. Horgen, S. V. Orski, V. Rodriguez C., K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, *Mar. Pollut. Bull.*, 127(2018), 704–716.
- 26. N. Verma, V. Sharma, R. Kumar, R. Sharma, M.C. Joshi, G.R. Umapathy, S. Ohja, S. Chopra, On the spectroscopic examination of printed documents by using a field emission scanning electron microscope with energy-dispersive X-ray spectroscopy (FE-SEM-EDS) and chemometric methods: application in forensic science, *Anal. Bioanal. Chem.*, 411(2019), 3477–3495.