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Research article

APPLICATION OF SOME NOVEL PYRAZOLE DISPERSE DYES TO SYNTHETIC FABRICS

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Abstract

In this study, 8 novel pyrazole disperse dyes were applied to polyethylene terephthalate (PET), poly (lactic acid) (PLA) and polyamide 6.6 (PA 6.6) fiber fabrics and their colorimetric and fastness properties were evaluated. The measured a^*, b^* and hue angle (h^o) values of all dyed fabrics exhibited yellow, orange and red color shades. Quite high color strength values (K/S) were measured particularly for dyes containing substitute groups; p-OCH_3 and o-OCH_3. Shade changes of all fabrics after standard washing and sublimation tests were in the commercially adequate range. All dyed PET, PLA and PA 6.6 fabrics exhibited commercially acceptable fastness staining performances with very good to excellent levels. Synthesized novel disperse dyestuffs led to moderate to high light fastness levels particularly in the case of PLA and PET fabrics.

Keywords: *Poly (lactic acid), Polyethylene terephthalate, Polyamide, Color, fastness.*

1. Introduction

Azo dyestuffs are one of the most widely used groups among dyestuff classes. In particular, disperse azo groups are among the most commonly used groups in the dyeing of synthetic textile materials in the industry. Especially when they are applied to polyamide and polyester group textile materials, its preferability levels are high along with their good to excellent fastness degrees [1-4].
Pyrazole derivative groups, among the dispersed azo dyestuffs, which are the most commonly used group in the dyeing of hydrophobic fibers, have recently become very popular [5-11]. Pyrazole group is characterized by being the most frequently used

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heterocyclic compound in many application fields. Especially because of its chemical structure, it could be used for many different purposes such as pharmacological, antibacterial, antimicrobial, anticancer, antifungal, antiviral, antitubercular, antitumor…etc. in the medical field [12-21]. Besides, it is widely used for dyeing synthetic based fabrics for textile industry due to their wide and different color choices [22-25]. Color and color fastness characteristics of synthetic fibers dyed with these dyes displayed satisfying results [26-31].

In this work, 8 novel pyrazole disperse dyes (A1, B1, C1, A2, C2, A3, B3 and C3) which have been synthesized previously were applied to synthetic fibers [32]. These novel eight disperse dyestuffs were applied at % 2 owf to various synthetic fabrics. Since the yield percentage in obtaining the dyestuff B2 (4-(4′-(m-methoxyphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole) is very low, could not be synthesized in sufficient quantity to dye all fabrics and for this reason couldn't applied to fabrics. Herein we report the dyeing of PET, PLA and PA 6.6 fiber fabrics with these eight novel pyrazole disperse dyes and the examination of colorimetric and color fastness characteristics of these dyed fabrics after scouring, dyeing and reduction clearing operations. The CIE *L*, a*, b*, C*,* and h^o co-ordinates were measured and also K/S values were determined. Moreover, wash, alkaline and acid perspiration, dry and wet rub fastness, sublimation fastness (shade change and staining), water fastness, sea-water fastness and light fastness performances were also explored and reported.

2. Materials and Method

Synthesized 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (A1, B1, C1, A2, C2, A3, B3 and C3), shown at Table 1 [32], were applied to 100% PET, PLA and PA 6.6 fiber fabrics. The characteristics of the dyed fabrics are as follows, respectively; ***PET fabric***: 30/1 Ne staple yarns, single jersey, 100% polyethylene terephthalate (PET) fiber fabric, ***PLA fabric:*** 30/1 Ne staple yarns, single jersey, 100% poly (lactic acid) (PLA) fiber fabric, ***Polyamide 6.6 fabric (PA 6.6)*****:** 78 dtex/68 filament yarn/two folded, single jersey, 100% Polyamide 6.6 fiber fabric. All chemicals used in scouring, dyeing and reduction-clearing operations are provided from BASF company and these chemicals are as follows, respectively; kieralon Jet B conc. (non-ionic surfactant), Setamol BL (anionic dispersing agent for dyes), sodium dithionite, sodium hydroxide and sodium carbonate.

2.1 Solubility Parameter Determination

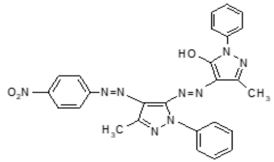
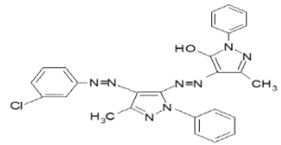
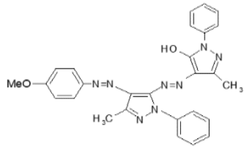
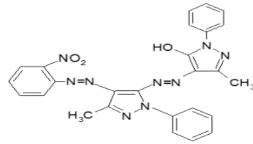
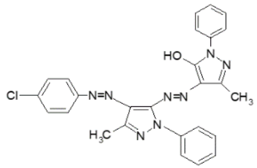
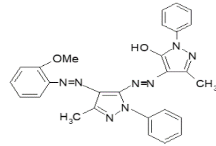
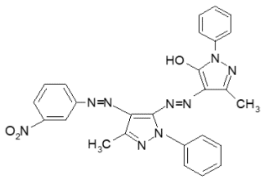
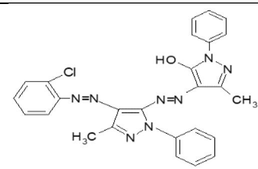
The dye uptake of fibers during dyeing process in the textile industry is related to solubility parameters. Karst and Yang [33] worked on this parameter in their study and developed a formula. According to this formula they developed, dye uptake capacities of synthetic fibers dyed with disperse dyestuffs can be calculated (*Eq.uation 1*) [33].

$$\delta = \sqrt{\frac{\sum E\mathrm{coh}_i}{\sum V\mathrm{m}_i}} \tag{1}$$

In here; **δ** is the "solubility parameter of a molecule ((J/cm^3)$^{0.5}$)", $\mathbf{\Sigma \boldsymbol{E}coh}_i$ is the "cohesive energy for the *i* functional group on the molecule (J/mol)" and $\mathbf{\Sigma \boldsymbol{V}m}_i$ *is* the "molar Volume (cm^3/mol)"

In this study, the effect of fabrics on dye uptake was investigated by calculating the solubility parameters.

Table 1 Dyestuffs used in dyeing [32]

Code	Generic Name	Molecular structure	Code	Generic Name	Molecular structure
A1	"4-(4′-(p-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"		C2	"4-(4′-(m-chlorinephenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"	
B1	"4-(4′-(p-methoxyphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"		A3	"4-(4′-(o-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"	
C1	"4-(4′-(p-chlorinephenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"		B3	"4-(4′-(o-methoxyphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"	
A2	"4-(4′-(m-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"		C3	"4-(4′-(o-chlorinephenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1phenylpyrazole"	

2.2 Scouring, Dyeing and Reduction-Clearing Operations

All raw fabrics were scoured in a bath comprising 1 g/l Kieralon Jet B conc. (non-ionic surfactant from BASF) and 1 g/l sodium carbonate at 60°C for 15 min. After scouring, the fabrics were rinsed with cold water for 10 minutes and dried at ambient conditions.
Dyeing of fabrics was carried out in ATAC lab-dye HT dyeing machine at a liquor ratio of 30:1 and 2% owf. Dyeing profiles of each fiber are given in Figure 1. Herein Setamol BL is the anionic dispersing agent for dyes from BASF. These conditions are taken from the related literatures, commercial scale applications from industry and DyStar [34-38].
After the dyeing process, all fabrics were rinsed with 5 minutes warm and 5 minutes cold water. Afterwards, the fabrics were left to air-flat-dry at room temperature.
After dyeing processes, reduction clearing is applied to all fabrics according to the below conditions respectively; ***PET fiber:*** "3g/l sodium dithionite and 3g/l sodium hydroxide at 70°C for 15 minutes", ***PLA fiber:*** "3g/l sodium dithionite and 3g/l sodium carbonate at 60°C for 15 minutes", ***Polyamide 6.6 fiber:*** "3g/l sodium dithionite and 3g/l sodium carbonate at 40°C for 15 minutes".
All reduction clearing temperatures were selected corresponding with the glass transition temperature (T_g) of the fibers. Since it is known that the cleaning temperature of the fibers should be lower than the glass transition temperatures and the glass transition temperature of each fiber is different, different cleaning temperatures were applied to the fabric in each fiber [39-42].
After reduction clearing, all fabrics were rinsed with 5 minutes warm and 5 minutes cold water. Cleared fabrics were then left to air-flat-dry at ambient conditions.

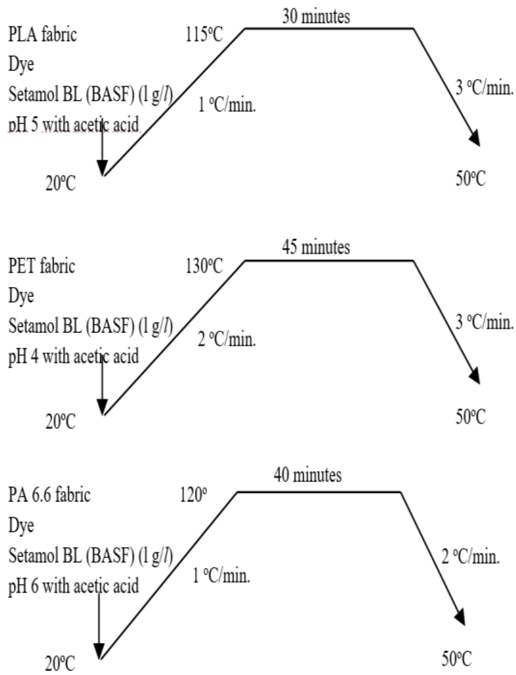


Fig. 1 Dyeing procedures of synthetic fiber fabrics

2.3 Color Properties Determination

After scouring, dyeing and reduction-clearing operations, color properties of each fabric were explored. The CIE *L*, a*, b*, C**, and h^o co-ordinates were acquired and K/S values were found out from the reflectance values at the precise wavelength of maximum absorbance (λ_{max}) for every dyed sample fabric using a Data Color Spectra Flash 600 spectrophotometer (Datacolor International, Lawrenceville, NJ, USA), below illuminant D_{65} through 10º standard observer. The measurements were finished for every fabric in 4 exclusive regions and two times on every side. The common value become acquired and reported.

2.4 Assessment of Color Fastness Properties

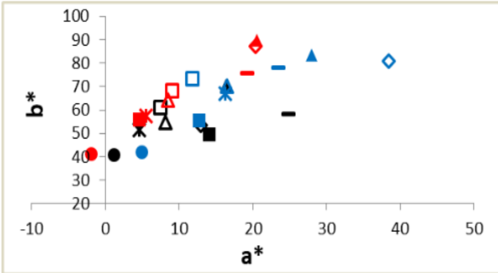
The alkaline and acidic perspiration, dry and wet rub, wash, sublimation, water and sea water, light fastness levels of PET, PLA and PA 6.6 samples dyed with 8 novel dyes were investigated. The utilized test standards are given below.

- Wash-fastness to home laundering (C06) become implemented in line with the ISO 105:C06 Test Standard in a Rotawash machine (SDL ATLAS, UK). This washing test was applied at 50°C with sodium perborate (C06/B2S) for PLA and PET fabrics while, similar test was become accomplished at 40°C with sodium perborate (C06/A2S) for PA 6.6 fabric due to low glass transition temperatures of polyamide fibers (Tg: 40-55°C) [43].
- Both alkaline and acid perspiration fastness become received in keeping with the ISO 105-E04 (Color Fastness to Perspiration) standard.
- Both dry and wet rub fastness tests were done consistent with the ISO 105: X12 standard.
- Sublimation fastness (shade change and staining) were done following ISO 105: P01 protocol using SDL Scorch Tester M247B at 180°C for 30 seconds for PET and PA 6.6 fiber fabrics (for fair comparison) and lower temperature of 130°C for 30 seconds withinside the case of PLA fiber fabrics [44-46].
- The evaluation of water fastness become done in regards to the ISO 105-E01.
- Sea water fastness was received in line with according to the ISO 105-E02.
- Light fastness tests were carried out corresponding with ISO 105-B02: color fastness to artificial light (Xenon arc lamp).
- Color fastness to light was obtained utilizing the blue wool scale control. All other evaluations of the tests were implemented with the utilization of ISO grey scales.

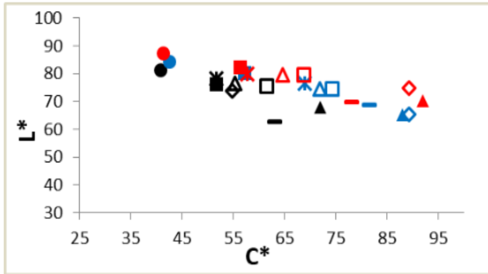
3. Results and discussion

3.1 Colorimetric Properties

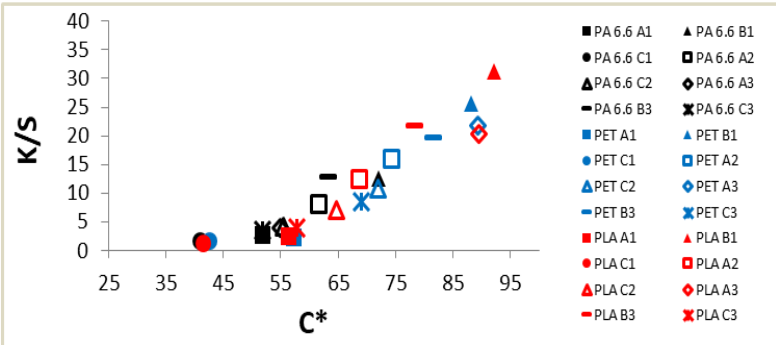
The colorimetric data of PLA, PET and PA 6.6 fiber fabrics dyed with 8 different synthesized disazo disperse dyes (A1, B1, C1, A2, C2, A3, B3 and C3) at 2 % dye concentration are displayed in Table 2, and their related *a*-b**, *L*-C** and *K/S-C** graphics are shown in Figure 2(a-c).



a) *a**- *b**



b) *L**- *C**



c) *K/S*- *C**

Fig. 2 Colorimetric properties of dyed synthetic fiber fabrics **a)** *a**- *b** **b)** *L**- *C** **c)** *K/S*- *C**

As is known, colorants are defined according to their ability to absorb light in the visible region (400nm-700nm). As A1, B1, C1, A2, C2, A3, B3 and C3 dyestuffs dye PET, PLA and PA 6.6 fabrics, the color tones of the fabrics are between +a and +b values, that is, the color tones of the fabrics are yellow and red. There was only one exception, the value of C1 dyestuff dyeing PLA fabric was found at -a. This shows that there is a slight shift to green tone in the color imparted by the dyestuff to the fabric. When the K/S values of the dyed fabrics are examined, the lowest value is 1.42 with C1 dyestuff for PLA and highest is 31.2 WİTH B1 dyestuff for PLA. As it can be understood from here, the λmax (nm) value is between 550 nm and 700 nm for the yellow and red color tone range of dyed fabrics.

As it can be clearly seen from Table 2 and Figure 2, the color properties of dyed fabrics vary according to the type and location of the substituent group. As it is known, a and b indicate the color directions, +a* indicates the red direction, and +b* indicates the yellow direction. As can be seen from Table 2 and Figure 2(a), all of these synthetic fibers dyed with 8 different disperse dyestuffs gave results in yellow, orange and red color tones. This determination can also be seen in Table 2 that hue angle (*h*°) values are below 90 degrees. Figure 2(a) shows that dyed PET fibers displayed significantly more reddish appearance with higher *a** values than PLA and PA 6.6 fiber fabrics. In addition, as it is clearly seen from Figure 2a, C1 dyestuffs containing p-Cl substituent group gave the palest color tones for all three synthetic fiber fabrics.

Table 2 Colorimetric properties of synthetic fiber fabrics dyed with disperse dyes

Fabrics dyed at 2% dye concentration [Fiber type, synthesized dye type (Auxochromes position and substituent group type)]																								
Color parameters	**PA 6.6 A1 (p-NO_2)**	**PA 6.6 B1 (p-OCH_3)**	**PA 6.6 C1 (p-Cl)**	**PA 6.6 A2 (m- NO_2)**	**PA 6.6 C2 (m- Cl)**	**PA 6.6 A3 (o- NO_2)**	**PA 6.6 3 B3 (o- OCH_3)**	**PA 6.6 C3 (o- Cl)**	**PLA A1 (p-NO_2)**	**PLA B1 (p- OCH_3)**	**PLA C1 (p-Cl)**	**PLA A2 (m-NO_2)**	**PLA C2 (m- Cl)**	**PLA A3 (o- NO_2)**	**PLA B3 (o- OCH_3)**	**PLA C3 (o- Cl)**	**PET A1 (p-NO_2)**	**PET B1 (p-OCH_3)**	**PET C1 (p-Cl)**	**PET A2 (m- NO_2)**	**PET C2 (m- Cl)**	**PET A3 (o- NO_2)**	**PET B3 (o- OCH_3)**	**PET C3 (o- Cl)**
L*	76,3	68,1	81,5	75,7	76,4	73,7	62,8	78,1	82,5	70,4	87,3	79,6	79,7	74,7	69,7	79,9	80,5	65,3	84,4	74,4	74,6	65,2	68,6	76,5
a*	14,1	16,3	1,18	7,44	8,15	12,9	24,8	4,66	4,52	20,5	- 1,94	9,05	8,45	20,4	19,2	5,54	12,6	28,0	4,88	11,9	16,5	38,4	23,5	16,3
b*	49,7	70,2	40,8	61,2	54,8	53,4	58,1	51,6	56,1	89,7	41,4	*68,2*	64,1	87,0	75,8	57,5	55,8	83,5	42,2	73,4	70,0	80,7	78,1	67,1
C*	51,7	72,0	40,8	61,6	55,4	54,9	63,2	51,8	56,3	92,0	41,4	68,8	64,6	89,4	78,2	57,8	57,2	88,1	42,5	74,3	72,0	89,4	81,6	69,1
h^o	74,2	76,9	88,3	83,1	81,6	76,4	66,9	84,8	85,4	77,1	92,7	82,4	82,5	76,8	75,8	84,5	77,3	71,5	83,4	80,8	76,7	64,5	73,2	76,3
K/S	2,79	12,6	1,81	8,09	4,14	3,99	12,9	3,42	2,62	31,2	1,42	12,4	7,06	20,4	21,7	4,01	2,42	25,7	1,81	15,9	10,7	21,7	19,8	8,44

As can be seen from Figure 2, *p*-OCH_3 substituent group (B1) resulted mostly the highest C^* levels as compared the other fabrics. In fact, overall, -OCH_3 substituent groups generally led to better results than -NO_2 and -Cl substituent groups. However, it is worth noting that pyrazole disperse dye with an o-NO_2 substituent group (dye A3) also resulted high chroma levels in PLA and PET fabrics (Figure 2b). PA 6.6 fiber fabrics dyed with all 8 dyestuffs showed the lowest color chroma values when compared with dyed PET and dyed PLA fiber fabrics (Figure 2 (b)).

L^* value is the lightness level of the fabric. If the L^* value approaches to zero, the color of the fabric becomes black (darkness increases). On the other hand, if L^* value approaches to 100, this means that the color of the fabric becomes lighter (lightness increases). Table 2 shows that electron accepting -NO_2 and -Cl groups displayed higher lightness values. There is an interesting fact that pyrazole disperse dye having *p*-Cl substituent group (C1) displayed the lightest color in all fiber groups, respectively 81.5 for PA 6.6, 87.3 for PLA, 84.4 for PET. The lowest lightness degree of 62.8 was measured for PA 6.6 fabric dyed with pyrazole disperse dye having *o*-OCH_3 substituent group (B3) (Figure 2(b) and Table 2)

As can be seen from Figure 2c, like Chroma levels, color strength values (*K/S*) of PA 6.6 fabrics dyed with all 8 disazo disperse dyes exhibited again lower values when compared to PET and PLA fabrics. In the color strength evaluation, the examination of the dyed fabrics' color strengths according to the auxochrome types and auxochrome positions in the synthesized pyrazole disperse dyes would be appropriate. Figure 3 shows the effects of auxochrome types and auxochrome placements on the color strength values of fabrics dyed with disazo dispersion dyes. The color strength levels of PLA, PET, PA 6.6 fabrics varied significantly depending on the type (-OCH_3, -NO_2, -Cl) and location (ortho, para, meta) of substituent groups in the synthesized pyrazole disazo disperse dye (Table 2 and Figure 3). On PLA, PET, and PA 6.6 fiber fabrics, rather high color strength values (K/S) were determined, particularly for pyrazole dispersion dyes including p-OCH3 (B1) and o-OCH3 (B3) colors. Indeed, pyrazole disazo dispersion dyes synthesized with electron donor -OCH3 substituent groups at para and ortho locations often exhibited better color intensities when compared to pyrazole disazo disperse dyes synthesized with electron receiver -NO_2 and -Cl groups at the same position. The methoxy group (-OCH3) connected to the aromatic ring in the para and ortho positions increased the aromatic ring's electron density, which normally results in a rise on the color level and improved color strength performance. As an illustration, the highest color strength value of 31.2 (K/S) was measured for poly(lactic) acid fabric dyed with pyrazole disperse dyes containing *p*-OCH_3 substituent group (B1) (Table 2). The same dye type (B1) also led to the highest color strength value with 25.7 (K/S) in the case of PET fiber fabric (Table 2). Moreover, also high color strength values were obtained from pyrazole disperse dyes having *m*-NO_2 (A2) and *o*-NO_2 (A3) substituent groups on all fibers (Table 2 and Figure 2(c)). In contrast, C1 (p-Cl), C2 (m-Cl), and C3 (o-Cl) disazo dispersion dyes with a weak electron receiver -Cl group as an auxochrome produced the lowest color strength levels for PLA, PET, and PA 6.6 fiber fabrics, as predicted (Table 2). When compared to the -OCH3 substituent group, -Cl and -NO2 groups connected to the aromatic ring resulted in a decrease in electron density of the aromatic ring, resulting in typically lesser color intensity. For example, the color intensity of the weak electron receiver -Cl group were low in all locations (para, meta, and ortho) (Figure 3).

Overall, as earlier mentioned, *p*-OCH_3/*o*-OCH_3 substituents and *m*-NO_2 /*o*-NO_2 substituents resulted in high color strength (K/S) for all studied fiber types. Indeed, B1 (*p*-OCH_3), A2 (*m*-NO_2), A3 (*o*-NO_2) and B3 (*o*-OCH_3) disazo disperse dyes resulted in medium to heavy depth of shades for both PET and PLA fiber fabrics, and therefore these 4 dyes could be advised for PET and PLA dyeing operations with regard to the colorimetric properties (Figure 3). As a matter of fact, these four dyes [B1 (*p*-OCH_3), A2 (*m*-NO_2), A3 (*o*-NO_2) and B3 (*o*-OCH_3)] resulted in the lowest lightness (L^*) values, the highest b^*, chroma (C^*) and color strength (*K/S*) values on both PET and PLA fibers (Table 2 and Figures 2-3). Besides, B1 (*p*-OCH_3) and B3 (*o*-OCH_3) disazo disperse dyes led to medium depth of shades for PA 6.6 fiber fabric and therefore can be recommended for PA 6.6 dyeing. Indeed, B1 (*p*-OCH_3) and B3 (*o*-OCH_3) disazo disperse dyes resulted in the lowest lightness (*L**) values, the highest *a**, chroma (*C**) and color strength (*K/S*) values on PA 6.6 fibers (Table 2 and Figures 2-3).

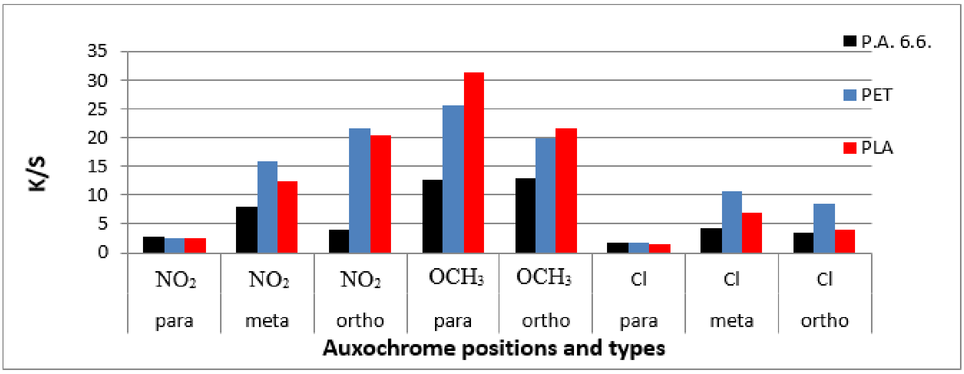


Fig. 3 For 2% dyeing, color yield varies based on location of auxochromes on the dye

3.2 The Effects of Molar Volume and Solubility Parameter Levels of Dye on Color Strength

The molar volume, solubility parameter and color strengths of eight dyes are shown in Table 3. It is the right point to mention that only the auxochrome's kind and its location in the dye structure differs among these studied dyes. The highest molecular volume and the lowest molecular volume were 375 cm^3 for pyrazole disazo disperse dyes containing –OCH_3 substituent group and 358.6 cm^3 for pyrazole disazo disperse dyes containing –NO_2 substituent group, respectively (Table 3). Pyrazole disazo disperse dyes containing –Cl substituent group displayed the molecular volume of 362.7 cm^3. It is very visible that there is no direct distinct correlation determined between molar volume-color strength and solubility parameters-color strength of poly(ethylene terephthalate), poly(lactic acid), and polyamide 6.6 fabrics dyed with 8 dyes.

However, when examined more closely, pyrazole disazo disperse dyes containing -OCH_3 (B1 and B3) substitute group led to quite high color strength for poly(ethylene terephthalate), poly(lactic acid), and polyamide 6.6 fabrics (Table 3). The solubility parameter value of these pyrazole disazo disperse dyes containing -OCH_3 substituent group was 23.57 $(J/cm^3)^{0.5}$, which was the lowest value among the solubility parameter of all generated investigated dyes (Table 3). This value was closest to the solubility values of PLA and PET fibers, which were 20.2 (J/cm3)0.5 and 21.7 (J/cm3)0.5, respectively [33]. As previously indicated, dyes having solubility properties similar to poly(lactic acid) (20.2 (J/cm3)0.5) tend to have greater saturation, and hence stronger color strength, on poly(lactic acid) fiber [33]. Indeed, the lowest solubility parameter levels as well as the closest solubility parameter to the solubility parameters of PLA and PET fibers resulted in relatively high color strength and chroma levels for poly(ethylene terephthalate), poly(lactic acid), and polyamide 6.6 fabrics (Table 3).

Table 3 Solubility parameter, molar volume and color yield of fibers dyed with 8 dyes

Dye	Substituent	Molar volume (cm^3)	Solubility parameter ($(J/cm^3)^{0.5}$)	*K/S*		
				PLA	***PET***	***PA 6.6***
A1	p- NO_2	358.6±7.0	24,22	2,62	2,42	2,79
B1	p- OCH_3	375.0±7.0	23,57	31,2	25,7	12,6
C1	p-Cl	362.7±7.0	24,28	1,42	1,81	1,81
A2	m- NO_2	358.6±7.0	24,22	12,4	15,9	8,09
C2	m-Cl	362.7±7.0	24,28	7,06	10,7	4,14
A3	o- NO_2	358.6±7.0	24,22	20,4	21,7	3,99
B3	o- OCH_3	375.0±7.0	23,57	21,7	19,8	12,9
C3	o-Cl	362.7±7.0	24,28	4,01	8,44	3,42

3.3 Color Fastness Performance

The color fastness performances of dyed fabrics after different color fastness tests are given in Table 4.

***Color fastness to washing*:** According to gray scale evaluation, the shade changes of all fibers dyed with synthetic pyrazole disazo dispersion dyes after standard washing tests were relatively high, at least 4/5 and more, and in the commercially satisfactory level, which was equivalent to 4 or higher (Table 4). In the area of wash fastness staining performance, similar pretty satisfactory findings were obtained. Wool, acrylic, polyester, nylon, cotton, and acetate fibers are known to be included in the multifiber adjacent standard test fabrics for color fastness determination. Among the other fibers (wool, acrylic, polyester, cotton, and acetate) in the multifiber adjacent standard test fabric, the nylon fiber component had the lowest wash fastness staining results in this wash fastness examination. Therefore, the wash fastness staining values for only the nylon fiber component of the multifiber adjacent standard test fabric is given in Table 4. It is very clear that PLA and PET fiber fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 disperse disazo dyestuffs displayed commercially acceptable wash fastness staining performance with very good to excellent levels (Table 4). In the case of PA 6.6 fiber fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 disperse disazo dyes, slightly lower washing fastness staining levels were monitored. In here, the measured wash fastness staining levels for nylon fiber component were in the range of 3/4 - 4/5 gray scale ratings depending on the synthesized disperse dyes (Table 4). Nevertheless, it is important to point out that PA 6.6 fiber fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 disperse disazo dyestuffs exhibited good to very good wash fastness staining performance. Overall, it is clearly visible from Table 4 that dyed PET fibers exhibited slightly higher wash fastness values when compared to dyed PLA and PA 6.6 fiber fabrics. This is actually in parallel with the previous studies.

***Color fastness to perspiration*:** Similar to washing fastness evaluation, in this perspiration fastness evaluation, nylon fiber component displayed the lowest perspiration fastness staining values amongst the other fibers (wool, acrylic, polyester, cotton and acetate) in the multifiber adjacent standard test fabric. Therefore, the perspiration fastness staining values for only the nylon fiber component of the multifiber adjacent standard test fabric is given in Table 4. All acidic and alkaline perspiration fastness values of dyed PLA, PET and PA 6.6 fiber fabrics were in the commercially adequate level (Table 4). All dyes investigated had flawless alkaline and acidic perspiration fastness values of dyed PLA and PET fiber fabrics, with 5 gray scale ratings. The alkaline and acidic perspiration fastness levels of dyed PA 6.6 fibers were likewise fairly high, with scores ranging from 4 to 5 on the gray scale.

Color fastness to sublimation: Shade changes and staining degrees of dyed PLA, PET and PA 6.6 fiber fabrics after respective sublimation fastness tests are shown in Table 4. Shade changes after sublimation fastness test were excellent for all dyed fibers; either 4/5-5 or 5 gray scale ratings leading to commercially acceptable fastness levels. In the case of sublimation fastness staining evaluation, polyester fiber component exhibited the lowest sublimation fastness staining values amongst the other fibers (wool, acrylic, nylon, cotton and acetate) in the multifiber adjacent standard test fabric. Therefore, the sublimation fastness staining values for only the polyester fiber component of the multifiber adjacent standard test fabric is given in here (Table 4). Fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 dyes generally displayed moderate (3) to excellent (5) sublimation staining levels with few exceptions which displayed lower degrees of sublimation staining for example 2 and 2-3 gray scale ratings. It is clear from Table 4 that dyed PLA fibers exhibited better sublimation fastness performance than other two dyed fibers. Indeed, PLA fiber fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 dyes showed quite high and commercially acceptable sublimation fastness staining levels (Table 4). This is not surprising and this outcome could be expected, since the significantly lower sublimation fastness heating temperature was applied for PLA fiber because of the heat sensitivity of PLA fiber (130^{o}C for PLA fiber versus 180^{o}C for PET and PA 6.6 fibers). Since 130^{o}C heat-setting temperature is advised for PLA fiber due to the low melting-point of PLA fiber in order to protect the fiber integrity. Applied lower heat condition, at 130^{o}C, can be the cause for higher sublimation fastness grades even though PLA fiber generally displayed higher color strength because of higher dye molecule content inside the fiber [31,35]. Dyed PET fabric generally exhibited slightly less sublimation fastness levels than its PA 6.6 fabric counterpart (Table 4). It is clear that dyed PLA, PET and PA 6.6 fabrics possessing higher color strength values generally displayed lower sublimation fastness performance with more staining because of their higher dye molecule content in the fiber when compared with dyed fabrics exhibiting lower color strength (Table 4). In general, this determination is clearly visible in the case of B1, A3, B3 disperse dyes for each fiber case.

Table 4 Fastness values of PLA, PET and PA 6.6 fiber fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 dyes

Fiber Type	Dye Type	*K/S*	*Washing*		*Perspiration (Staining)**		Rubbing *(Cotton Staining)*		Sublimation		Water *(Staining)**	Sea Water *(Staining)**	Light
			Shade Change	*Staining**	Alkaline	Acidic	Dry	Wet	*Shade Change*	*Staining***			
PLA	A1	2,62	4/5 - 5	4/5 - 5	5	5	4/5	4/5-5	5	5	5	5	3
	B1	31,2	4/5 - 5	4 - 4/5	5	5	3-3/4	4	5	4	5	5	4
	C1	1,42	4/5 - 5	4/5 - 5	5	5	4/5-5	4/5-5	5	5	5	5	5
	A2	12,4	4/5 - 5	4/5 - 5	5	5	3/4-4	4/5	4/5-5	5	5	5	5
	C2	7,06	4/5 - 5	4/5 - 5	5	5	3/4-4	4/5	5	5	5	5	6
	A3	20,4	4/5 - 5	4 - 4/5	5	5	3/4	4/5	5	4/5	5	5	5
	B3	21,7	4/5 - 5	4 - 4/5	5	5	4	4	5	4	5	5	4
	C3	4,01	4/5 - 5	4 - 4/5	5	5	3-3/4	4-4/5	5	5	5	5	5
PET	A1	2,42	5	5	5	5	5	5	5	5	5	5	5
	B1	25,7	5	4/5 - 5	5	5	5	4/5-5	5	2	5	5	6
	C1	1,81	4/5 - 5	5	5	5	5	5	4/5-5	4/5	5	5	6
	A2	15,9	5	4/5 - 5	5	5	4/5-5	5	5	3/4	5	5	5
	C2	10,7	5	5	5	5	5	5	5	3/4	5	5	6
	A3	21,7	5	5	5	5	5	5	4/5-5	2/3	5	5	5
	B3	19,8	5	5	5	5	4/5	4/5-5	5	2/3	5	5	6
	C3	8,44	5	5	5	5	5	5	5	4/5	5	5	6
PA 6.6	A1	2,79	5	4	4/5	4/5 -5	4/5-5	4/5-5	5	4/5	5	5	4
	B1	12,6	4 - 4/5	3/4	4	5	5	5	5	2	5	4/5	3
	C1	1,81	4/5	4/5	4/5 -5	4/5 -5	5	5	4/5-5	4/5	5	5	4
	A2	8,09	4/5	3/4 - 4	4/5	4/5	5	5	5	4	4/5	5	4
	C2	4,14	4/5	4- 4/5	4/5 -5	4/5 -5	5	5	5	4	5	5	4
	A3	3,99	4 - 4/5	3/4 - 4	4/5	4/5	5	5	5	4/5	5	5	3
	B3	12,9	4/5 - 5	4	4/5	4/5	5	5	5	3/4	4/5	4/5	3
	C3	3,42	4/5	4/5	4/5 -5	4/5 -5	5	5	5	4	5	5	3

** Color fastness values for staining of the nylon fiber component of the multifiber adjacent standard test fabric (In here, nylon fiber component displayed the lowest color fastness values amongst the other fibers in the multifiber adjacent standard test fabric) ** Color fastness values for staining of the polyester fiber component of the multifiber adjacent standard test fabric (In here, polyester fiber component exhibited the lowest sublimation fastness values amongst the other fibers in the multifiber adjacent standard test fabric)*

Color fastness to rubbing: All wet rub fastness values of dyed PLA, PET and PA 6.6 fiber fabrics were at the commercially satisfactory level, which was equal to 4 or above, according to gray scale evaluation (Table 4). Also dyed PET and PA 6.6 fiber fabrics showed excellent and commercially acceptable dry rub fastness values. So, dyed PA 6.6 and PET fabrics exhibited outstanding wet and dry rub fastness performance leading to commercially acceptable rub fastness levels. In the case of dry rub fastness staining levels of dyed PLA fabrics, the measured dry rub fastness staining levels for cotton fabric were in between 3-3/4 and 4/5 gray scale ratings depending on the synthesized disperse dye type (Table 4). Only few dyed PLA fabrics led to dry rub fastness degrees less than 4 points. Therefore, overall, rub fastness levels of dyed PET and PA 6.6 fiber fabrics showed excellent gray scale ratings and are better than their dyed PLA fiber fabric counterparts.

Color fastness to water and sea-water: Similar to washing and perspiration fastness evaluations, nylon fiber component displayed the lowest water and sea-water fastness staining values amongst the other fibers (wool, acrylic, polyester, cotton and acetate) in the multifiber adjacent standard test fabric. Hence, the perspiration fastness staining values for only the nylon fiber component of the multifiber adjacent standard test fabric is displayed in Table 4. The water and sea-water color fastness results of all studied fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 disperse disazo dyes were very good to excellent leading to commercially acceptable levels (Table 4). Especially the water fastness and sea-water fastness values of all dyed PLA and PET fabrics were 5 degree according to gray scale ratings. Only two dyes (A2 and B3) for PA 6.6 fabric resulted in 4/5 gray scale rating in the case of water fastness performance. On the other hand, only B1 and B3 dyes led to 4/5 gray scale rating for sea-water fastness performance in the case of PA 6.6 fabric. Nevertheless, although PA 6.6 fabrics dyed with these dyes exhibited slight staining, the measured water and sea-water color fastness results were still quite high and in the commercially adequate levels.

Color fastness to light: Synthesized novel disperse dyestuffs led to moderate to high light fastness levels particularly in the case of PLA and PET fabrics according to blue wool scale ratings (Table 4). It is very clear that light fastness performances of dyed PET fabrics were better than their PLA and PA 6.6 counterparts which is in parallel with the previous studies [31, 47]. Higher UV-radiation transmittance characteristic of PLA fiber versus PET fiber in the 370-240 nm wavelength range results in lower light fastness levels for PLA fiber because of more potential dye destruction inside the fiber [31, 47]. Furthermore, PA 6.6 fabrics dyed with A1, B1, C1, A2, C2, A3, B3 and C3 disperse disazo dyes generally exhibited less light fastness levels than their PLA and PET counterparts. The less color strength levels of polyamide 6.6 fabrics versus other dyed fabrics may be the cause for less light fastness performance because of less dyestuff ingredient inside the PA 6.6 fiber.

4. Conclusion

In this study, 8 different novel disperse dyestuffs were applied to 3 different types of synthetic fiber fabrics. The colorimetric properties of the fabrics investigated and as seen from a*, b*, and hue angle (h^o) values of PLA, PET, and PA 6.6 fiber fabrics that yellow, orange, and red color tones are obtained.

On PLA, PET, and PA 6.6 fiber fabrics rather high color strength values (K/S) were obtained, particularly for pyrazole dispersion dyes including p-OCH3 (B1) and o-OCH3 (B3) dyes.

In here, synthesized and studied pyrazole disazo disperse dyes displaying the lowest solubility parameter levels as well as the closest solubility parameter to the solubility parameters of PLA and PET fibers generally resulted in quite high color strength and chroma levels for poly(ethylene terephthalate), poly(lactic acid), and polyamide 6.6 fabrics.

According to fastness evaluations, washing, perspiration, rubbing, sublimation, water and sea water color measurement tests are in the commercially acceptable range for all fabrics. On the other hand, synthesized novel disperse dyestuffs led to moderate to high light fastness levels particularly in the case of PLA and PET fabrics. Light fastness performances of dyed PET fabrics were better than their PLA and PA 6.6 counterparts.
In future work these dyestuffs can be applied to other synthetic fiber fabrics and their colorimetric and fastness properties can be studied.

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References

1. Ghanavatkar C. W., Mishra V. R., Sekar N. 2020. Benzothiazole-pyridone and benzothiazole-pyrazole clubbed emissive azo dyes and dyeing application on polyester fabric: UPF, biological, photophysical and fastness properties with correlative computational assessments. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 118064.
2. Sreenath M. C., Joe I. H., Rastogi V. K. 2018. Experimental and theoretical investigation of third-order nonlinear optical properties of azo dye 1-(2, 5-Dimethoxy-phenylazo)-naphthalen-2-ol by Z-scan technique and quantum chemical computations. *Dyes and Pigments*, *157*, 163-178.
3. Fang S., Feng G., Guo Y., Chen W., Qian H. 2020. Synthesis and application of urethane-containing azo disperse dyes on polyamide fabrics. *Dyes and Pigments*, 108225.
4. Al-Etaibi A. M., El-Apasery M. A. 2019. Dyeing performance of disperse dyes on polyester fabrics using eco-friendly carrier and their antioxidant and anticancer activities. *International Journal of Environmental Research and Public Health*, *16*(23), 4603.
5. Ansari A., Ali A., Asif M. 2017. Biologically active pyrazole derivatives. *New Journal of Chemistry*, *41*(1), 16-41.
6. Karrouchi K., Radi S., Ramli Y., Taoufik J., Mabkhot Y. N., Al-aizari F. A. 2018. Synthesis and pharmacological activities of pyrazole derivatives: a review. *Molecules*, *23*(1), 134.
7. Şener N, Erişkin S, Yavuz S, Şener I. 2017. Synthesis, characterization, solvatochromic properties and antimicrobial-radical scavenging activities of new diazo dyes derived from pyrazolo [1, 5-a] pyrimidine. *Journal of Heterocyclic Chemistry.* 54(6), 3538-3548.
8. Ciçen G, Atay ÇK, Tilki T. 2017. Disazo dyes containing pyrazole and benzothiazole moieties: synthesis, characterization, absorption characteristics and tautomeric structures. *Research on Chemical Intermediates.* 43(12), 6803-6816.
9. El- Borai MA, Rizk HF, El- Hefnawy GB, Ibrahim SA, Aser SS, El-Sayed HF. 2016. Synthesis and spectral characterization of novel azomethine disperse dyes derived from pyrazolone moiety and their dyeing performance on polyester fabrics. *Fibers and Polymers.* 17(5), 729-737.
10. Rizk HF, İbrahim SA, El-Borai MA. 2015. Synthesis, fastness properties, color assessment and antimicrobial activity of some azo reactive dyes having pyrazole moiety. *Dyes and Pigments.* 112, 86-92.

11. Karabacak Ç, Tilki T, Tuncer BÖ, Cengiz M. 2015. Antimicrobial pyrazole dyes: synthesis, characterization, and absorption characteristics. *Research on Chemical Intermediates.* 41(4), 1985-1999.
12. Sayed GH, Azab ME, Anwer KE, Raouf MA, Negm NA. 2018. Pyrazole, pyrazolone and enaminonitrile pyrazole derivatives: Synthesis, characterization and potential in corrosion inhibition and antimicrobial applications. *Journal of Molecular Liquids*, *252*, 329-338.
13. Malladi S, Isloor AM, Isloor S, Akhila DS, Fun HK. 2013. Synthesis, characterization and antibacterial activity of some new pyrazole based Schiff bases. *Arabian Journal of Chemistry*, *6*(3), 335-340.
14. Xu Z, Gao C, Ren QC, Song XF, Feng LS., Lv ZS. 2017. Recent advances of pyrazole-containing derivatives as anti-tubercular agents. *European journal of medicinal chemistry*, *139*, 429-440.
15. Das A, Ishitani H, Kobayashi S. 2019. Toward Continuous-Flow Synthesis of Biologically Interesting Pyrazole Derivatives. *Advanced Synthesis & Catalysis*, *361*(22), 5127-5132.
16. Turkan F, Cetin A, Taslimi P, Karaman M, Gulçin İ. 2019. Synthesis, biological evaluation and molecular docking of novel pyrazole derivatives as potent carbonic anhydrase and acetylcholinesterase inhibitors. *Bioorganic chemistry*, *86*, 420-427.
17. Erten G, Karcı F, Demirçalı A, Söyleyici S. 2020. 1H-Pyrazole-Azomethine Based Novel Diazo Derivative Chemosensor For The Detection Of Ni2+. *Journal of Molecular Structure*, 127713.
18. Şener N, Bayrakdar A, Kart HH, Şener İ. 2017. A combined experimental and DFT investigation of disazo dye having pyrazole skeleton. *Journal of Molecular Structure*, *1129*, 222-230.
19. Yıldız B, Güzel E, Akyüz D, Arslan BS, Koca A, Şener MK. 2019. Unsymmetrically pyrazole-3-carboxylic acid substituted phthalocyanine-based photoanodes for use in water splitting photoelectrochemical and dye-sensitized solar cells. *Solar Energy*, *191*, 654-662.
20. Gudmundsson KS, Johns BA, Wang Z, Turner EM, Allen SH, Freeman GA, Boyd FL, Sexton CJ, Selleseth DW, Moniri KR, Creech KL. 2005. Synthesis of novel substituted 2-phenylpyrazolopyridines with potent activity against herpesviruses. *Bioorganic & Medicinal Chemistry.* 1*3*(18), 5346-5361.
21. Belal A, Abdelgawad MA. 2017. New benzothiazole/benzoxazole-pyrazole hybrids with potential as COX inhibitors: design, synthesis and anticancer activity evaluation. *Research on Chemical Intermediates.* 43(7), 3859-3872.
22. Shaki H, Gharanjig K, Khosravi A. 2015. Synthesis and investigation of antimicrobial activity and spectrophotometric and dyeing properties of some novel azo disperse dyes based on naphthalimides. *Biotechnology Progress.* 31(4), 1086-1095.
23. Deeb AA, El-Hossami MB, AbdelGawad AA. 2014. Pyridazine derivatives and its related compounds. Part 31. Synthesis of some disperse dyes derived from 3-amino-1H-pyrzolo [3, 4-c] pyridazine and their color assessment on polyester fabrics. *European Journal of Chemistry.* 5(4), 639-643.
24. Mohamed F, Youssef YA. 2012. Synthesis and application of bifunctional reactive dyes pyrazolo[1,2-a] pyrazole 3- carboxylic acid. *Pigment & Resin Technology.* 41(1),49-54.
25. Bagdatli E, Ocal N. 2012. Synthesis, spectroscopic and dyeing properties of new azo and bisazo dyes derived from 5-pyrozolones. *Journal of Heterocyclic Chemistry.* 49(5), 1179-1186.

26. Al-Etaibi AM, Al-Awadi NA, El-Apasery MA, Ibrahim MR. 2011. Synthesis of some novel pyrazolo [1, 5-a] pyrimidine derivatives and their application as disperse dyes. *Molecules.* 16(6), 5182-5193.
27. Rizk HF, El-Badawi MA, Ibrahim SA, El-Borai MA. 2010. Synthesis, fastness and spectral properties of some new azo pyrazole and pyrazolotriazole derivatives. *Journal of Korean Chemical Society.* 54(6), 737-743.
28. Shams HZ, Youssef YA, Mohamed FA, El-Zawahry MM, Helal MH, El-Kharadly EA. 2009. Synthesis and application of novel disazo pyrazolo[1,2-a]pyrazole reactive dyes. *Pigment & Resin Technology.* 38(6), 372-379.
29. Helal MH, Elgemeie GH, Masoud DM. 2008. Synthesis of a new series of polyfunctionally substituted thiazole azo dye systems for dyeing of synthetic fibers. *Pigment & Resin Technology.* 37(6), 402-409.
30. Kamel MM, Youssef YA, Ali NF, Abd El Megiede SA. 2014. Synthesis and application of novel bifunctional pyrazole[1,5-a]pyrimidine reactive dyes. *International Journal of Current Microbiology and Applied Sciences.* 3(10), 519-530.
31. Bakan E, Karcı F, Avinc O. 2018. Synthetic fiber dyeing with new pyrazole disperse dyes and their colorimetric and fastness properties. *Fibers and Polymers.* 19(3), 670-681.
32. Karcı F, Bakan E. 2015. New disazo pyrazole disperse dyes:Synthesis, spectroscopic studies and tautomeric structures. *Journal of Molecular Liquids.*206, 309-315.
33. Karst D, Yang Y. 2005. Using the solubility parameter to explain disperse dye sorption on polylactide. *Journal of Applied Polymer Science.* 96(2), 416-422.
34. *DyStar Textilfarben GmbH & Co. Deutschland KG. IngeoTM Fiber Coloration Pack.* DyStar plc. (2004).
35. Avinc O, Owens H, Bone J, Wilding M, Phillips D, Farrington D. 2011. A colorimetric quantification of softened polylactic acid and polyester filament knitted fabrics to 'Water-spotting'. *Fibers and Polymers.* 12(7), 893-903.
36. Avinc O, Wilding M, Bone J, Phillips D, Farrington D. 2010. Color fastness properties of dyed, reduction cleared and softened poly(lactic acid) fabrics. *AATCC Review.* 10(5)I, 2-58.
37. Avinc O, Wilding M, Bone J, Phillips D, Farrington D. 2010. Evaluation of color fastness and thermal migration in softened polylactic acid fabrics dyed with disperse dyes of differing hydrophobicity. *Coloration Technology.* 126(6), 353-364.
38. Tungtriratanakul S, Setthayanond J, Avinc O, Suwanruji P, Sae-Bae P. 2016. Investigation of UV Protection, Self-Cleaning and Dyeing Properties of Nano TiO^ sub 2^-Treated Poly (lactic acid) Fabric. *Asian Journal of Chemistry.* 28(11), 2398.
39. Avinc O, Bone J, Owens H, Phillips D, Wilding M. 2006. Preferred alkaline reduction-clearing conditions for use with dyed Ingeo poly (lactic acid) fibers. *Coloration Technology. 1*22(3), 157-161.
40. Avinc O. 2011. Clearing of dyed poly (lactic acid) fabrics under acidic and alkaline conditions. *Textile Research Journal*, *81*(10), 1049-1074.
41. Avinc O. 2011. Maximizing the wash fastness of dyed poly (lactic acid) fabrics by adjusting the amount of air during conventional reduction clearing. *Textile research journal*, *81*(11), 1158-1170.
42. Khoddami A, Avinc O, Mallakpour S. 2010. A novel durable hydrophobic surface coating of poly (lactic acid) fabric by pulsed plasma polymerization. *Progress in Organic Coatings*, *67*(3), 311-316.
43. Deopura BL, Alagirusamy R, Joshi M, Gupta B. 2008. *Polyesters and Polyamides,* Woodhead Publishing Series in Textiles. Elsevier.

44. Avinc O, Phillips D, Wilding M. 2009. Influence of different finishing conditions on the wet fastness of selected disperse dyes on polylactic acid fabrics. *Coloration Technology.* 125(5), 288-295.
45. Avinc O, Day R, Carr C, Wilding M. 2012. Effect of combined flame retardant, liquid repellent and softener finishes on poly (lactic acid)(PLA) fabric performance. *Textile Research Journal.* 82(10), 975-984.
46. Avinc O, Khoddami A. 2010. Overview of poly (lactic acid) (PLA) fiber. *Fiber Chemistry.* 42(1), 68-78.
47. Nakamura T, Ishii K, Kubokawa H, Mogi K, Bommu RR. 2001. *AATCC International Conference and Exhibition*.