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FACILE SYNTHESIS AND DYEING PERFORMANCE OF SOME DISPERSE MONOMERIC AND POLYMERIC DYES ON NYLON AND POLYESTER FABRICS

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ABSTRACT. Monoazo disperse polymeric dyes consisting of polyarylazocarboxybenzene-formaldehyde (PACB-F) and polyarylazohydroxynaphthalene-formaldehyde (PAHN-F) were synthesized through diazotisation, coupling and polycondensation reactions in the presence of formaldehyde and aqueous oxalic acid. The structure of the as synthesised dyes was acquired using UV-visible absorption maxima and FT-IR spectroscopy and their color, yield, melting point, solubility, and viscosity determined via standard methods. UV-visible and FTIR results showed successful formation of the polymeric dyes due to shift of wavelength of maximum absorption (λ_{max}) (420-470 nm, 460-510 nm) and new absorption peak at around (2800-2995 cm⁻¹) for methylene bridge, respectively. The yield of the monomeric dyes was 67.1-85.7% and polymeric 45.1-59.3%, melting point was 104.1-131.2 °C, and 136.0-143.5 °C, respectively. They are soluble in acetone, ethanol, and methanol and insoluble in n-hexane and water. The dyeing process was achieved via high temperature and carrier dyeing techniques on nylon and polyester fibers. The dyeing characteristics of the synthesised dyes were analyzed in comparison with commercial disperse dyes (terasil brillint violet and terasil scarlet brown). The dyeing produced a very attractive hue brown shades with good to excellent washing, light, hot pressing, and rubbing fastness.

KEY WORDS: Carbocyclic, Dyeing activity, Monoazo, Monomeric, Polymeric

INTRODUCTION

The antiquity of synthetic colorants is strongly related to the current progress of theoretical organic chemistry and measured by social and economic influences in the emerging industrial states of the late 19th century [1]. Over the last century, the investigation for more readily accesssible sources of colouration contributed to the creation of synthetic dyesand pigments, whi ch in effect contributed to modern industrial chemistry [2, 3]. Fiber coloration technology is the term used to explain the methods for the application of dyes molecules unto to fibre, yarn, or textile in aqueous medium. Synthetic dyes play an important role in textile coloration because of their availability, inexpensive, providing very attractive shades, and their good color fastness properties [4]. However, they have some shortcomings when used for dyeing of natural and synthetic fibers such as the requirement of a high amount of dye to obtain uniform dyeing, and poor substantivity and fixation which results in fading during usage. To address these limitations of synthetic dyes, high molecular weight dyes with excellent fiber fixation, substantivity,

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migration, and outstanding fastness rating need to be developed. Over the years, a variety of dyes and pigments have been synthesized to meet the unique requirements of several applications such as liquid crystal displays, organic photoconductors, photosensitizers and in many non-textile applications [4, 5]. Presently, polymeric dyes have been identified and introduced as a substitute to the conventional system of coloration. This class of dyes address the limitations encountered using conventional dyes in textile industries due to their unique properties such as high fiber substantivity, fixation ability, high thermal stability, and outstanding fastness properties [7].

Reports on the synthesis and application of polymeric dyes have drawn the attention of many researchers in recent years because of their distinctive features which have many advantages in comparison with monomeric counterparts [6]. A small amount of the polymeric dye can give adequate colour that can only be achieved when comparatively large amounts of the monomeric dye are used. When applied onto the fiber, they were found to have higher substantivity, outstanding fastness properties, less fading, a higher degree of fixation. Polymeric dyes are high molecular weight coloured substances that contain many repeat units in a molecule [9]. They colorant consists of chromophoric groups connected to or in polymers which provided the advantage of having a broad variety of physical properties, such as solubility, absorption, migration, and viscosity [9, 10]. They cannot sublime, are non-abrasive, and usually have low toxicity [10-12].

Azo dyes are considered as the largest class of synthetic dyes studied so far synthesized on the polymer backbone due to the fact that azo polymeric dyes containing benzene rings has ability to exist in cis and trans isomer producing photoresponsive material which has application in a variety of areas in sciences such as photographic application, electronic devices, storage devices, and textile colouration [11, 13]. Researchers established that a very vast variety of products were generated by a combination of colour and polymer chemistry and is virtually inexhaustible [14-15]. Polymeric colorants can include: a polymer chain that is chemically altered so that it has chromophores as added groups[16], a non-coloured polymer that has a chromophore as an end group, a polymer where chromophores are present in the backbone of a copolymer which includes a functionalized dye and other monomers, or where the repeat unit of the polymer itself is a dye [17]. They have been extensively added to fibers due to their fast leveling, excellent fastness toward the light effect and wet treatments, low rate of sublimation, and very good chemical/heat resistance [18]. Polymeric dyes have outstanding brightness and are extremely fadeless [14, 17]. Therefore, in the last few decades, they have been well documented by many research scientists [18]. Several polymeric dyes were reported in the literature for many applications such as for textile colouration. They have been used in food colouration, surface coating of plastic objects, solid-phase laser dyes, hair dyes, jet printing [10, 12, 14].

In this research, modern azo disperse polymeric dyes were synthesis from their corresponding monomeric dyes which are derived from diazotisation and coupling reactions. The resulting azo disperse monomeric dyes were subjected to polycondensation reaction in the presence of formaldehyde and aqueous oxalic acid to produce azo disperse polymeric dyes. All the synthesised dyes were analyzed using FT-IR, UV-Visible, viscosity, solubility, percentage yield, and melting point, and the as-synthesised and two commercial disperse dyes(terasil brilliant violet and terasil scarlet, brown) were applied on nylon and polyester fabrics via carrier and high-temperature dyeing techniques and their substantivity on these fibers were assessed using standard methods.

EXPERIMENTAL

Chemical reagents

2-Chloroaniline (Sigma-Aldrich), 4-aminophenol (Sigma-Aldrich), 2-chlorobenzoic acid (Sigma-Aldrich), 1-naphthol (Sigma-Aldrich), sodium nitrite (Sigma-Aldrich) and HCl (Sigma-Aldrich) were used in the synthesis of the monomeric disperse dyes. Aqueous oxalic acid and formaldehyde solution (37% w/v) were used as crosslinking agents to produce the polymeric disperse dyes.

Synthesis of diazonium salt by diazotization

The diazo components were synthesised using the standard procedure as reported by Habibu *et al.* [14]. The 2-chloroaniline (7.65 g, 0.06 mol) was dispersed in distilled water (20 mL) contained in a beaker that stands in an ice bath. As much as 10 mL of concentrated HCl was added to this solution over a period of two minutes while the dispersion was stirred with a magnetic stirrer. The temperature of the ice bath was maintained at 0-5 °C by the addition of common salt (NaCl). Sodium nitrite (4.3 g, 0.06 mol.) was dispersed in distilled water (20 mL) and added dropwise to the stirred suspension over a period of one hour to attain complete diazotization.

Coupling reaction

Coupling component (0.06 mol) was suspended in distilled water (20 mL) contained in a 250 mL beaker at 0-5 °C in an ice bath. The diazonium salt solution was added dropwise to the coupling component over a period of 10 min while continuously stirring. The stirring was continued for further 45 min as the dye crystals precipitated. The dye was filtered, washed with water, and recrystallized in acetone [19]. The dyes were weighed, and their percentage yields were calculated using the formula [20].

% yield =
$$\frac{\text{Weight of the dye}}{\text{Theoritical yield}} \times 100 \%$$
 (1)

Polycondensation of monomeric dyes by crosslinking reaction

Monomeric dye (0.05 mol) was suspended in distilled water (50 mL) and then 37% w/v formaldehyde solution (0.5mL) and oxalic acid (0.5 g), were added. The reaction mixture was gradually heated to 90-95 °C and maintained at that temperature for 1 hour. The reaction mixture was cooled, filtered, and washed with water till the filtrate was neutral. Finally, it was washed with 20 mL methanol and air-dried[14, 20].

Characterisation

The solubility of the dyes was carried out according to the method adopted from [14]. The solubility of each sample was carried out in a variety of solvents which include water, ethanol, methanol, chloroform, CCl₄, dichloromethane, petroleumether, and acetone. As much as 5 mL of each solvent was added to about 0.1 g of the sample in a test tube and shaken vigorously. The solubility was carefully observed and recorded. The melting point of each dye sample was determined using a microprocessor melting point apparatus (WRS-IB) model (England). The samples were grounded into a fine powder and the one-end-closed melting point capillary tube was filled to half with the powdered dye sample and placed in the machine. The samples were heated, and the melting range was carefully observed and recorded. The viscosity of synthesized dyes was acquired using Ostwald capillary viscometer. The solution containing 1.0, 0.75, 0.50, and 0.25 g of each dye sample in 100 mL of acetone was prepared and used in the measurement [23]. UV-visible spectroscopy was used to obtain the wavelength of maximum absorption of the as-synthesized dye samples using New Line medical instrument England (Spectrum Lab752S) UV-visible spectrophotometer in the region between 400-600 nm. The Agilent Technology (Cary 630FTIR) Fourier Transform Infra-red (FTIR) Spectrophotometer was used. The spectra of all the synthesised monomeric and polymeric dyes were acquired within the frequency range of 4000- 600 cm^{-1} .

High-temperature dyeing technique of nylon and polyester fabrics

High-temperature dyeing was carried out using a domestic pressure cooker. As much as 0.25 g of each dye together with the same quantity of detergent was taken in 50 mL of distilled water. Then 2 g of each fiber was placed in the pressure cooker and the temperature was raised to120 °C and maintained for about 1 hour with slow and continuous agitation. The fiber was then removed, rinsed with detergent, water, and dried [21].

Dyeing of polyester and nylon using carrier dyeing technique

As much as 0.1 g of finely divided dye sample was dissolved in 10 mL ethanol. About 30 mL of distilled water was added and the dye solution boiled to remove the ethanol. The solution was filtered, and 2 mL of dispersing agent (Dispergator SM-SN) solution was added followed by the addition of 6 mL of a carrier, 1-methylnaphthalene, and the solution made up to 100 mL by addition of distilled water. Then, 2 g of the fiber (nylon or polyester) was placed in the dye bath at 60 °C. The temperature was raised within 90 min and the dyeing process continued at mentioned temperature for further 30 min. The dye bath was cooled, and the dyed fiber was thoroughly washed with hot and then cold water. Finally, the unfixed dye molecules and the dye assistants was removed by treating the fiber for 30 min at 70 °C in a solution containing sodium hydroxide (2 g/L), sodium dithionite (2 g/L), and 0.1% dispergator [20, 22].

Light fastness

The light fastness properties of the dyed samples were assessed using the standard procedures ISO 105-BO2:1988 method. It was done on a non-natural light fastness tester MK1 tailored with mercury-tungsten (MBTF) 500-watt lamp. The samples were exposed simultaneously with blue wool values for 96 hours and assessed [21].

Rubbing fastness

The dyed fabric piece was scrubbed on a smooth dry white cloth and later observed. The staining of the adjacent white cloth was observed and assessed which agrees with the test method provided by ISO 105-X12: 2001 method [24] (dry and wet) standard.

Hot pressing fastness

Dry, damp, and wet pressing fastness tests were carried out according to the standard method ISO 105-POI 1993 method [24]. The dyed fabric (5 x 4 cm) was sandwiched between two pieces of dried white cloth to form a composite specimen. Hot pressing iron was then placed on top and allowed to stay for 15 s. The degree of staining of adjacent white cloth was then assessed using greyscale.

Wash fastness

The test for colour fastness to washing was determined using the ISO 105-CO6:2010 test method [25]. The fastness of the dyed washed samples was assessed using standard methods. The samples were cut to 5×4 cm and placed in between two pieces of undyed materials of the same size. These samples were sewed together to produce a composite sample. The composite samples were distinctly absorbed into washing liquor comprising 100 mL of 4 g dm⁻³ detergent solution and disturbed for 30 min at 50 °C. The samples were systematically cleaned, unlocked, and air-dried. The colour variation in dyed material and staining degree of the undyed fabric were evaluated using greyscale.

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RESULTS AND DISCUSSION

The proposed synthetic steps for the synthesis of polymeric dyes through diazotization, coupling and polycondensation reactions is illustrated in Scheme 1.



Scheme 1. Steps for the synthesis of monomeric, polymeric dyes through diazotization, coupling and polycondensation reactions.

The proposed structure of monomeric and polymeric dyes are shown in Figure 1.





Figure1. Dye (A) 2-chlorophenylazo-3-chloro-4-carboxybenzene, (A₁) poly(2-chlorophenylazo-3-chloro-4-carboxybenzene), (B) 4-hydroxyphenylazo-4-hydroxynaphthalene and (B₁) poly (4-hydroxyphenylazo-4-hydroxynaphthalene).

Colour, yield and melting points results of synthesised monomeric and polymeric dyes

The colour, yield, and melting point of the synthesised monomeric/polymeric dyes are given in Table 1. The colour of the dyes was brown with the polymeric dyes having deeper shades and both the monomeric/polymeric dyes were of good yield and relatively low melting points but an increase in melting points were observed when comparing the monomeric dyes with corresponding polymeric dyes which might be as a result of an increase in molecular weight [26].

Table 1. Colour, percentage yield, and melting point of monomeric and polymeric dyes.

Dyes sample	s	Colour	(%) Yield	Melting point (°C)
Monomeric	Α	Light brown	67.1	130.8 - 131.2
	В	Reddish brown	85.7	104.1 - 106.1
Polymeric	A ₁	Dark brown	45.1	138.3 - 143.5
	B ₁ Dark brown		59.3	136.0 - 154.7

Solubility results of synthesised monomeric and polymeric dyes in various solvents

The monomeric/polymeric dyes solubility in various solvents are presented in Table 2. The monomeric/polymeric dyes are soluble in acetone, ethanol, and methanol this might be attributed to the polar nature of some of the dyes and solvents but insoluble in n-hexane, benzene, and water. Their insolubility in an aqueous medium confirmed the dispersed nature of these dyes [14, 26].

Solvents/Dyes	Monor	neric	Polymeric		
	Α	В	A ₁	B_1	
Water	SS	SS	SS	SS	
Methanol	S	S	S	S	
Ethanol	S	S	S	SS	
Acetone	S	S	S	S	
Ethyl acetate	SS	SS	SS	SS	
Benzene	SS	SS	SS	Ι	
Toluene	Ι	SS	Ι	Ι	
n-Hexane	Ι	Ι	Ι	Ι	
Chloroform	SS	S	SS	S	

Table 2. Solubility of monomeric and polymeric dyes in various solvents.

S = soluble; SS= sparingly soluble I = insoluble.

Viscosity results of synthesised monomeric and polymeric dyes in acetone

The dilute solution viscosity of these dyes are presented in Table 3. Polymeric dyes were found to have higher viscosity compared to their corresponding monomeric counterparts even at infinite dilution this implies the increase of conjugation in the polymer molecule this clearly shows that the polymeric dyes will be absorbed and remain fixed into the fiber matrix, and it is one of the reasons for higher substantivity and fixation of polymeric dyes on fiber in comparison to monomeric dyes [7, 13]. As described by the Mark-Hou wink-Sakurada equation: in which viscosity of substances is proportional to its molecular weight. The polymer is expected to have higher molecular weight in comparison to monomer due to the increase in the repeat unit in the polymer chain leading to increase in molecular weight.

 $[\eta] = K M_v^{\alpha}$

(1)

where $\eta = \text{viscosity}$, Mv = viscosity average molecular mass of the solution, K, α , = are constant for polymer/solvent at a given temperature [22, 27].

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Dves samples	Conc.	Average flow	Relative	Specific	Intrinsic						
5 1	(gdL ⁻¹)	time	viscosity	viscosity (η_{sp})	viscosity nsp/C						
	ιų γ	(s)	(η_{rel})	5 (11)	2 11						
Monomeric											
Α	0.25	13.08	1.008	0.008	0.032						
	0.50	13.13	1.012	0.012	0.024						
	0.75	13.19	1.016	0.016	0.021						
	1.00	13.61	1.049	0.049	0.049						
В	0.25	14.12	1.088	0.088	0.352						
	0.50	14.23	1.096	0.096	0.192						
	0.75	14.26	1.099	0.099	0.132						
	1.00	14.31	1.102	0.102	0.102						
		Po	olymeric	·	•						
	0.25	14.76	1.137	0.137	0.548						
	0.50	14.85	1.144	0.144	0.288						
A ₁	0.75	15.16	1.168	0.168	0.224						
	1.00	15.33	1.181	0.181	0.181						
	0.25	16.17	1.246	0.246	0.984						
B_1	0.50	16.62	1.280	0.280	0.56						
	0.75	16.91	1.303	0.303	0.404						
	1.00	16.89	1.301	0.301	0.301						

Table 3. Viscosity of synthesised disperse monomeric and polymeric dyes in acetone using Ostwald viscometer.

UV-visible analysis

The wavelength of maximum absorption of the synthesised dyes is given in Table 4. The UVvisible analysis was carried out on both monomeric and polymeric dyes to determine the wavelength of maximum absorption (λ_{max}). The dyes UV-Vis spectra revealed conventional electronic spectra, with many absorptions in the UV region between 274 and 400 nm, known as the B-band, and others in the visible range between 450 and 800 nm (Q-band). The Q-band is caused by the n- π transition of the dye molecules conjugated chain from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [24]. Generally, all the synthesized dyes absorbed Q-band, i.e. near the visible region of the spectrum, particularly the polymeric dyes which clearly indicates the formation of conjugation. The intensity of the polymeric dyes colour increases compared to their corresponding monomeric counterparts (monomeric dye A light brown (λ_{max}) 420 nm while polymeric A₁ dark brown colour (λ_{max}) 470 nm) and (monomeric dye **B** reddish-brown (λ_{max}) 460 nm while polymeric **B**₁ dark brown colour (λ_{max}) 510 nm. Therefore, the shift of λ_{max} and deepened in colour of the polymeric dyes compared to monomeric dyes as shown in Table 4 indicates a bathochromic shift of the wavelength of maximum absorption. This indicates an increase in conjugation and confirmed polycondensation has been achieved as reported previously [14, 26].

Table 4. UV-Visible results of various monomeric and polymeric dyes.

Dyes sampl	e	$\lambda_{max}(nm)$	Absorbance (cm ⁻¹)
Monomeric	А	420	2.242
	В	460	2.684
Polymeric	A ₁	470	2.782
	B_1	510	3.221

FT-IR analysis

FT-IR analysis was used for the identification of various types of functional groups present in the monomeric and polymeric dyes Figure 2. The FT-IR scales show the shift in the absorption band of hydroxyl stretching vibration for the dye samples at 3362, 3056 cm⁻¹ for monomeric dyes A and B, respectively, while 3375 and 3058 cm⁻¹ were assigned to their corresponding polymeric dyes A₁ and B₁, respectively. Spectral bands in the region 1574–1592 cm⁻¹ were due to the presence of -N=N- group, and the spectral bands observed in the region 1253–1320 cm⁻¹ were assigned to (C–N) Table 5. All the absorption peaks present in the polymeric dyes were found to be similar to those of the monomeric counterparts except some shifts were observed for the prominent absorption peaks. The only difference between the monomeric spectra and their corresponding high molecular weight counterparts is the presence of (-CH₂-) methylene bridge at 2815 and 2993 cm⁻¹ for A₁ and B₁, respectively. These results agree with the findings of [13, 20].



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Figure 2. FTIR spectra of carbocyclic monomeric dyes A, B with corresponding polymeric A₁, B₁ dyes.

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Dyes samples		$-N=N-(cm^{-1})$	-OH (cm ⁻¹)	$C-N(cm^{-1})$	CH2
Monomeric	A 1592		3362	1266	-
	В	1592	3056	1253	-
Polymeric	A ₁	1592	3375	1315	2815
	B_1	1574	3058	1320	2993

Fastness rating of the synthesized dyes on nylon and polyester

Comparatives colour fastness properties of the monomeric, polymeric dyes and commercial disperse dyes (terasil brilliant violet and terasil scarlet, brown) on nylon and polyester fibers were assessed and compared according to ASTM standard. Tables 6 and 7 show results of fastness properties of nylon and polyester fabrics dyed with monomeric, polymeric, and commercially available disperse dyes (terasil brilliant violet and terasil scarlet brown).

Fastness to hot pressing (sublimation)

Colour staining on undyed white fabric was used to measure the resistance of the dye to sublimation treatment. The findings are presented in Tables 6 and 7, which indicated that the synthesized and commercial dyes showed good to excellent ratings (grade 3-4 to 5). Moreover, the polyester and nylon fabrics treated with polymeric dyes showed excellent hot pressing (sublimation). This might be attributed to the formation of long conjugation and the presence of polar groups (OH, NH₂) which results in the formation of intermolecular hydrogen bonding [24].

Fastness to rubbing

The purpose of the test was to measure the degree of colour transfer from the dyed fabrics surface to an adjacent undyed cloth surface by rubbing. Tables 6 and 7, which show that all the dyes had good to excellent rubbing fastness values of grades 4 and 5, implying very good results using the greyscale method, but polymeric dyes were found to have excellent fastness to rubbing in comparison to monomeric and commercial disperse dyes. This performance may be due to adequate dye absorption and fixation on the fibers using both high temperature and carrier dyeing methods [28].

Fastness to washing

The wash fastness of the dyed nylon and polyester fabric treated with monomeric, polymeric, and commercial disperse dyes are presented in Tables 6 and 7 and varied from good to excellent. However, the fibers treated with polymeric dyes were found to have excellent fastness to washing. This might be attributed to their fixing ability on the fabrics hence the dye molecules are absorbed onto the matrix of the fiber and remain fixed due to covalent and hydrogen bonding that exists between the dye molecules and the fiber [28].

Fastness to light

The as synthesised and commercial disperse dyes demonstrated good to excellent fastness to light, ranging from grade 6 to 8 according to the standard blue wool for colour changes as presented in Tables 6 and 7. However, the polymeric dyes were found to have excellent fastness to light. The presence of electron-withdrawing groups in the proximity of the azo group and the formation of high molecular weight leading to the intermolecular hydrogen bonding may be responsible for the light fastness.

Generally, the result reveals that polymeric dyes have higher fastness or resistance external agencies compared to monomeric dyes and commercial disperse dyes, this improvement of fastness properties is a result of the formation of long polymer conjugation which makes the polymeric dyes be fixed on the fiber-matrix [28]. Moreover, the carrier dyeing technique was found to be the best method for dyeing nylon and polyester with polymeric dyes [22, 29].

Table 6. Fastness ratings of monomeric, polymeric, and commercial disperse dyes on nylon and polyester fabric were using the carrier dyeing method.

Dyes samples		Nylon				Polyester			
		Hot	Rubbing	Washing	Light	Hot	Rubbing	Washing	Light
		pressing				pressing			
Monomeric	Α	4	4-5	4	4	4	4	4	4
	В	4	4-5	4	5	4	4-5	4	5
Commercial	\mathbf{C}^{a}	4-5	4	4-5	6	4	4-5	4	6
disperse	F ^b	4	4	4	6	4-5	4-5	4	6
Polymeric	A_1	5	5	7	6-7	5-6	5-6	7	7
	B_1	5	5	7	6-7	5-6	5-6	8	8

^aC; terasil brilliant violet, ^bF; terasil scarlet brown.

Table 7. The fastness rating of monomeric, polymeric, and commercial disperse dyes on nylon and polyester fabrics was using high-temperature dyeing method.

Dyes sample			Nylon		Polyester				
		Hot	Rubbing	Washing	Light	Hot	Rubbing	Washing	Light
		pressing				pressing			
Monomeric	Α	3-4	4-5	4	4	3-4	4-5	4	5
	В	3-4	4-5	4	5	3-4	4-5	4	5
Commercial	C^a	4-5	4-5	4-5	5	3-4	4-5	4	6
disperse	F ^b	3-4	4	4-5	4	2-3	4-5	4	4
Polymeric	A_1	5	5	6-7	6	4-5	5	6	6
	B1	5	5	6-7	6	5	5	7	7

^aC; terasil brilliant violet, ^bF; terasil scarlet brown.

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Comparative discussion of present work with previous literature

The preparation of high-quality, cost-effective polymeric dyes for textile and various application is a critical topic of interest by many scientist in recent years. The application of polymeric dyes is influenced by several factors such as yield, melting point, viscosity and fastness properties on fibers. In the present discussion, the as-synthesised polymeric dyes important parameters were discussed with other relevant literature based on physical properties and fastness rating on fibers [32].One of the important parameter that confirm the successful formation of polymeric dye is viscosity, as can be seen, present study finding confirm the production of high viscous dye substance which shows and increase in conjugation (molecular weight). This is supported by the FTIR result due to the formation of absorption peak 2815, 2993 cm⁻¹ for methelyne (A₁ and B₁) which act as brigde between dye monomer molecules. They have relatively moderate melting point and high yield in comparison to the reported data in the literature. Polymeric dyes applied on nylon and polyester were found to have excellent fastness to light and wash in comparison to the reported once in the literature and commercial disperse dyes used in this research as control, this might be due to the good methods of their synthesis, application unto fiber (carrier dyeing technique) improve the dye migration from the dye bath to the fiber matrix, fixation and affinity as presented in Table 8.

Dyes type	Application	Fastness		Viscosity	Yield	M.p.	Ref
		Light	Washing		%	(°C)	
Polymeric dyes	Polyester	8	7	High	59.3	136.0 -	Present
	and nylon	7	6-7			154.7	study
1,4-Diamino	polyester	6 - 7	5	Low	54.5	265 -	[11]
Anthraquinone						267	
Polyamides							
Polymeric	polyester	4-5	5	Low	38.9	138-	[14]
Monoazo						142	
Disperse Dyes							
Polymeric (1,2-	Polyester	4	4	-	40	89	[33]
diol azo dyes)	and nylon						

Table 8. Comparison of basic properties of synthesised dyes and once reported in the literature.

CONCLUSION

Polymerization of various carbocyclic monoazo disperse dyes synthesized via diazotisation, coupling, and polycondensation reactions have been achieved. The resulting monoazo disperse monomeric and polymeric dyes were characterised as described, the monomeric, polymeric, and commercially available disperse dyes (terasil brilliant violet, terasil scarlet, brown) were applied on nylon and polyester fabrics using carrier and high-temperature dyeing techniques and fastness properties were assessed using blue wool and greyscale standards. The polymeric dyes were found to have better washing and light fastness (grade 8) compared to the monomeric (grade 4, and 6) and commercially (grade 4, and 6) available disperse dyes, this is due to the increase in conjugation which leads to the formation of high molecular weight compounds. When they are absorbed into the fiber matrix become fixed and highly sustentative to the fiber through covalent and hydrogen bonding that exists between nylon and polyester fabrics with the dyes. The result of fastness properties reveals that carrier dyeing is better than the high-temperature dyeing technique because the resistance of the dye on the fiber to washing and light reveals how the dyes are held in the fibers matrix. In the future study, it is recommended to synthesise polymeric dyes in situ (in the fiber matrix) and is expected to have very outstanding substantivity, fixation,

migration, and fastness properties due to the possibility of the formation of hydrogen and covalent bonding between the fiber and dyes molecules.

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REFERENCES

- Yihan, S.; Mingming, L.; Guo, Z. Ag nanoparticles loading of polypyrrole-coated superwetting mesh for on-demand separation of oil-water mixtures and catalytic reduction of aromatic dyes. J. Colloid Interface Sci. 2018, 527, 187–194.
- Yussuf, A.; Al-Saleh, M.; Al-Enezi, S.; Abraham, G. Synthesis and characterization of conductive polypyrrole: The influence of the oxidants and monomer on the electrical, thermal, and morphological properties. *Int. J. Polym. Sci.* 2018, 2018, Article ID 4191747.
- Baloo, L.; HasnainIsa, M.; Bin Sapari. N.; Jagaba, A. H.; Wei, L. J.; Yavari, S. Razali, R.; Vasu, R. Adsorptive removal of methylene blue and acid orange 10 dyes from aqueous solutions using oil palm wastes-derived activated carbons. *Alexandria Eng. J.* 2021, 60, 5611– 5629.
- Bhuiyan, M.A.R.; Shaid, A.; Bashar, M.M.; Haque, P.; Hannan, M.A. A novel approach of dyeing jute fiber with reactive dye after treating with chitosan. *Open J. Org. Polym. Mater.* 2013, 3, 87–91.
- Song, Y.; Fang, K.; Bukhari, M.N.; Zhang, K.; Tang, Z.; Wang, R. Disperse dye/poly (styrenemethacrylic acid) nanospheres with high coloration performance for textiles. *J. Clean. Prod.* 2020, 263, 121538.
- Otutu, J.O. Synthesis and fastness properties of disazo disperse dyes derived from 4-amino-3-nitrotoluene. Orient. J. Chem. 2011, 27, 937.
- Ali, Y.A.; Parveen, T.; Umar, K.; Ibrahim, M.N.M. Role of nanomaterials in the treatment of wastewater: A review. *Water* 2020, 12, 495.
- 8. Raj, M.; Raj, L. Studies on application of chemical modified epoxy resin as a coupling agent in polymeric azo dyes. *Orient. J. Chem.* **2013**, 29, 457–464.
- Wang, S.; Boyjoo, Y.; Choueib, A.; Zhu, Z.H. Removal of dyes from aqueous solution using fly ash and red mud. *Water. Res.* 2005, 39, 129–138.
- Tang, B.; Zhang, S.; Yang, J.; Liu, F. Synthesis of a novel water-soluble crosslinking polymeric dye with good dyeing properties. *Dye. Pigment.* 2006, 68, 69–73.
- Gumel, M.S.; Yakubu, M.K.; Ibrahim, M.B.; R. Kumar. Synthesis and characterisation of colorants derived from 1,4-diamino anthraquinone polyamides. *Advan. Chem. Eng. Sci.* 2012, 2, 300–308.
- Almahbashi, N.M.Y.; Kutty, S.R.M.; Muhammad, A.; Noor, A.; Salihi, I.U.; Ahmed, A.; Jagaba, A.H.; Aldawi, B.N.S.; Ghaleb, A.A.S. Optimization of preparation conditions of sewage sludge based activated carbon. *Ain. Shams. Eng. J.* **2020**, 12, 1175–1182.
- Kapupara, P.P.; Dholakia, S.P.; Patel, V.P.; Suhagia, B.N. Design, synthesis and pharmacological screening of 4-amino-5-pyrimidinecarbonitriles as potential antiinflammatory agents. J. Chem. Pharm. Res. 2011, 3, 287–294.
- Habibu, S.; Gumel, S.M.; Ibrahim, M.B.; Ladan, M.; Fagge, I.I. Synthesis, characterization and application of some polymeric dyes derived from monoazo disperse dyes. *J. Appl. Chem.* 2013, 5, 42–47.
- Ali, Y.A.; Parveen, T.; Umar, K.; and Ibrahim. M.N.M. Silver nanoparticles: Various methods of synthesis, size affecting factors and their potential applications-a review. *Appl. Nanosci.* 2020, 10, 1369–1378.

- Patel, M.G.; Desai, K.R.; Patel, H.S. Synthesis and characterization of colored poly(urethaneurea). Int. J. Polym. Mater. Polym. Biomater. 2005, 54, 775–782.
- Rowley, J.V.; Exley, J.; Yu, H.; Mircale, G.S.; Hayward, A.S.; Thornton, P.D. Covalent polyester colouration byin situchromophore creation. *Chem. Commun.* 2020. 56, 6360–6363.
- Jagaba, A.H.; Kutty, S.R.M.; Noor, A.; Birniwa, A.H.; Affam, A.C.; Lawal, I.M.; Kankia, M.U.; Kilaco, A.U. A systematic literature review of biocarriers: Central elements for biofilm formation, organic and nutrients removal in sequencing batch biofilm reactor. *J. Water. Process.* Eng. **2021**, 42, 102–178.
- Schell, D.J.; Cynthia, J.R.; Nancy, D.; Jody, F.; Kelly, N.I.; Mark, F.R.; Susan, T.T.; Robert E.L. A bioethanol process development unit: initial operating experiences and results with a corn fiber feedstock. *Bioresour. Technol.* 2004, 91,179–188.
- Lams, Y.Y.; Nkeonye, P.O.; Bello, K.A.; Yakubu, M.K.; Lawal, A.O. Synthesis of malononitrile-condensed disperse dyes and application on polyester and nylon fabrics. *J. Text.* 2021, 2014, Article ID 460794.
- 21. Patel, H.S.; Prajapati, M.D. Polymerizable dyes-Part I. Eur. Polym. J. 1990, 26, 1005-1007.
- Maradiya, H.R.; Patel, V.S. Studies of novel monomeric and polymeric azo disperse dyes. J. Appl. Polym. Sci. 2002, 84, 1380–1389.
- Gumel, S.M.; Abdulmalik, A.; Habibu, S.; Ladan, M. Influence of auxiliaries in dyeing of wool with acid dyes. *Int. J. Text. Sci.* 2015. 4, 78–83.
- Otutu, J.O.; Ossai1, E.K.; Ameuru, S.U.; Itoya1, P.O.; Morka1, W.E. The application of disperse dyes derived from 4-bromoaniline and 3-chloroaniline on to polyester fabric. *Bull. Chem. Soc. Ethiop.* 2019, 33, 127–134.
- Otutu, J.O.; Asiagwu, A.K.; Onyesom, I.E.; Ebigwai J.K.; Itoya, P.O. Improving the efficiency of nesogordonia papaeverifera (danta) as a natural dye in textile making industry. *Bull. Chem. Soc. Ethiop.* 2019, 33, 415–424.
- Salisu, Z.M.; Yakubu, M.K.; Nkeonye, P.O.; Abba, H. The synthesis of diaminoanthraquinone coloured cross linked epoxy resins and their application in paint and selected polymers. *Open. J. Appl. Sci.* 2014, 4, 13–21.
- Maradiya, H.R.; Patel, V.S. Monomeric and polymeric disperse dyes based on heterocyclic compound for hydrophobic fabric. *Polym. Plast. Technol. Eng.* 2002, 41, 735–749.
- Musa, H.; Abdulmumini, A.; Folashade, M.O.; Bishir, U.; Hamza, A. Studies on the dyeing of wool and nylon fabrics with some acid dyes. *IOSR J. Appl. Chem.* 2013, 5, 11–17.
- Maradiya, H.R.; Patel, V.S. Polymeric dyes based on thiadiazole derivatives. *Fibers Polym.* 2001, 2, 212–220.
- Qian, H.F.; Feng, G.; Bai, G.; Liu, Y.C.; Hu, L.L. A contrastive study of adsorption behaviors on polyurethane fiber with diester/diurethane tethered and non-tethered azo disperse dyes. *Dyes. Pigm.* 2017, 145, 301–306.
- Irfan, M.; Zhang, H.; Syed, U.; Hou, A. Low liquor dyeing of cotton fabric with reactive dye by an eco-friendly technique. J. Clean. Prod. 2018, 197, 1480–1487.
- Ng, J.Y.; Wong, D.L.; Kutty, S.R.M.; Jagaba, A.H. Organic and nutrient removal for domestic wastewater treatment using bench-scale sequencing batch reactor. *AIP Conf. Proc.* 2021, 2339, 020139.
- Sheikh, H.K.; Kazmi, M.H. Synthesis of novel 1,2-diol containing azo dyes for polymeric substrates. J. Chil. Chem. Soc. 2017, 62, 3496–3500.