

Exhaustive and Affinitive properties of a thiophene substituted triazenyl based reactive dye on cellulose acetate phthalate-co-polyethylene glycol biopolymer film

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Abstract: The experimental exhaustion performance of a triply coupled triazenyl based reactive dye was used to establish the affinitive properties of the dye on 1:1, 1:2 and 2:1 formulations of cellulose acetate phthalate (CAP) and poly (ethylene glycol) (PEG) blends. The dye whose physicochemical properties include a melting point of 173 °C, theoretical yield of 73%, maximum wavelength of 535 nm and solubility in polar solvents was synthesized by doubly coupling it with 2-(aminomethyl)thiophene and singly coupled with 2-naphthol after diazotization. The maximum absorption peak at 535 nm ascertains the presence of conjugated double bond, functional groups such as hydroxyl and amino correspond to 3628 cm⁻¹ and 1334 cm⁻¹ respectively on the FTIR. The m/z = 415 confirms the breaking away of two ethyl thiophenyl cation while the fragmentation of the two residual amine groups is shown by the m/z value at 382 from the GC-MS. At 60°C, the first blend (CAP-PEG-1) has the highest degree of exhaustion of 89.92, partition coefficient of 180 (L⁻¹), dye affinity of 14300 kJ/mol, while the third blend (CAP-PEG-3) has the highest degree of levelness.

Keywords: Cellulose acetate phthalate, fibre blend, reactive dye, exhaustion, Partition coefficient, dye affinity

Introduction

Dyes are classes of compounds which possess one or more chromogenic groups for light absorption [1]. Reactive dyes possess reactive chromogens and have favourable structural features which include their anionic nature, water solubility and ability to form strong covalent bonds with fibres [2]. As a result of these properties, reactive dyes have therefore become popular for their quality of dyeing, fixation yield, and affinity to hydrophobic and hydrophilic fibre [3]. Various parameters that are used to estimate reactive dye performance include light fastness, chemical fastness, substantivity, affinity and levelness [4].

Heterocyclic amines have been widely exploited in the industrial synthesis of reactive and disperse dyes [5]. Reactive dyes which contains heterocyclic moieties like oxo and hydroxyl quinazoline, sulfonated aryl amine dichloro triazine, and disazo pyrazolopyrimidine give good affinity [6] and bright shades on various hydrophobic fibres like polyacryl amides and cellulose acetate [7]. From previous works, reactive dyes from heterocyclic amines like 2-aminothiazole have bright hues ranging from red [8], yellow to even green colour because the presence of groups like thiazole and pyrazole with different alkyl substituents have

bathochromic effect on the triazenyl rings of reactive dyes [5].

In previous literatures, reactive dyes have been applied on silk, wool, cotton, polyacrylonitriles and advance polyester fibres [8]. Generally, alkaline conditions are necessary for reactive dyeing process in the presence of electrolytes and the affinity of polyethylene glycol (PEG) for acid-levelling dyes is low [9]. The crosslinking of cellulose acetate phthalate and PEG will therefore reduce excess bond mobility in PEG and give room for the reactive dye to form strong covalent with the acetate and hydroxyl groups in the alkaline medium without hydrolytic effect [9].

Systems of monoazo reactive dyes which contain sulphur-heterocyclic groups like thiophene have been reported to have strong depth, levelness and affinity [10]. The only setback for these set of dyes is that they are hydrophobic and only have good performance report on hydrophobic polyester fibres [11]. The first objective of this research is to impart a thiophenyl substituted triazine based dye with an hydrophilic group to make the dye effective on both hydrophobic and moderately hydrophilic fibres while the second objective of the work is to study the effect of temperature on the interaction of this dye and cellulose acetate phthalate/PEG composite film so as to establish the optimum temperature for the best affinity performance.

Materials and Methods

Preliminary reactions and Diazotization

Cyanuric chloride (1.84 g, 0.01 moles) was stirred in 25 mL acetone at a regulated temperature below 5 °C and pH 7 for a period of an hour. A solution of amino sulphanilic acid (3.19 g, 0.01 moles) in aqueous sodium carbonate solution (10% w/v, 30 mL) was then

added dropwise for about an hour while the pH was kept neutral by simultaneous addition of sodium carbonate solution (1% w/v). Conc. HCl (10 mL) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C till a reddish brown solution was obtained; this solution was then cooled to 0-5 °C in an ice bath. Solution of NaNO₂ (1.38 g, 0.02 mole) in water (5 mL) was then added keeping the mixture cool in an ice bath at 0-5°C over a period of five minutes with continuous stirring, the stirring was continued for an hour maintaining the same temperature. The diazotized solution at 0-5 °C was obtained and used for subsequent coupling reaction [12].

Coupling

A 150 mL volume of water was heated to 60 °C, 7.5 g of 2-Naphtol was introduced to it while 55 g NaOH was added to the mixture to form a brown solution after which 7.5 g Na₂CO₃ was added to the solution to form a silver-brown precipitate. The diazotized solution was added to the coupling reagent at a regulated temperature between 4-5 °C to form a deep-red solution. The solution formed was then allowed to stand while precipitates begin to form gradually. The precipitate formed was heated to 60 °C and 45 g NaCl was added and stirring was continued for 1 hour. The solution was filtered to obtain a reddish-brown filtrate and a wine-red residue. The residue was then washed with brine to obtain an orange precipitate. This residue was dried at 100 °C to remove water. The residue was further coupled with 2-aminomethyl thiophene by a reflux process at 2°C in the presence of ammonium acetate and absolute ethanol. The final residue formed was appropriately dried [13].

Purification Process

Purification of the dye was done by dissolving the dried dye powder into boiling water and cooling to 75 °C. Then brine was added until precipitates begin to form. The precipitate is filtered to obtain the dye [12]

Fastness Tests

Fastness of the synthesized dye was investigated in accordance with BS: 1006-1978 and the wash fastness was investigated in accordance with IS: 765-1979.

Dyeing of Fibres

Three fibre films made from cellulose acetate phthalate and poly (ethylene glycol) in the respective ratios of 1:1, 1:2 and 2:1 (0.2 g: 0.2 g, 0.2 g:0.4 g, 0.4 g: 0.2 g) were dyed with the synthesized dye using the procedure of Shenai with little modification [14]

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Preparation of Fibre Blends

For the preparation of CAP-PEG-1 which contains 1:1 of CAP and PEG, 0.2 g of both polymers were cross-dissolved in 15 mL acetone. 0.4 g of CAP and 0.2 g was used to prepare CAP-PEG-2 which contains 2:1 of CAP and PEG while 0.2 g of CAP and 0.4 g of PEG were used to prepare CAP-PEG-3 which contains 1:2 of CAP and PEG. All the three fibre blends were conditioned at a temperature of 70°C for a period of four hours.

Results and Discussion

Physicochemical Properties

The synthesized dye has a semi-crystalline appearance and showed a yellowish brown colouration with an experimental yield of 79%. The sharp melting point of the synthesized reactive dye is 173°C and it shows that the dye obtained is pure and stable while its solubility in polar solvents and moderately polar solvents confirms its polarity. The dye has good fastness properties; the wash fastness is 2-3 while the light fastness is 3-4 [15].

UV-Visible

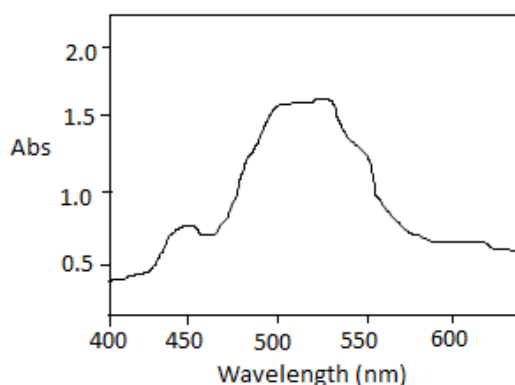


Figure 1. UV-Visible spectrum of the synthesized dye dissolved in methanol

The 535 nm maximum absorption peak of the dye in methanol can be attributed to the $\pi-\pi^*$ transition of the aromatic ring, while the maximum wavelength at 600 nm corresponds to $n-\pi^*$ [16]. The excitation at 420 nm corresponds to the transition from the non bonding electron on oxygen to the sigma bond in the -OH functional group, in the case of C=C the excitation is due to $\pi-\pi^*$ transition in this functional group [16]. The presence of the non-bonding electron on nitrogen and the pie bond linking the atoms together is responsible for the $n-\pi^*$ transition that is observed.

Maximum wavelengths of 535, 515, 498 and 316 nanometres were recorded for the solution of the synthesized dye in methanol, ethanol, acetone and n-hexane solvents. The experimental effect of solvent on the chromaticity of the dye thus evaluated shows that the dye has a positive solvent induced chromaticity as a result of the increase in the maximum wavelength with increase in polarity of the solvents [8].

Infra Red Interpretation

The peaks at 3628 and 3589 cm^{-1} correspond to the stretching vibrations of O-H group. The 3387 cm^{-1} peak indicate the presence of -NH group, while the peak at 3043 cm^{-1} corresponds to CH_3 asymmetric vibrations. The peaks at 1903 and 1620 cm^{-1} are as a result of C=C overtone for aromatic and the presence of a carbonyl group respectively. The transmittance peaks observed around 1585 and 1494 cm^{-1} correspond to C=C aromatic and C=N stretching vibrations [17].

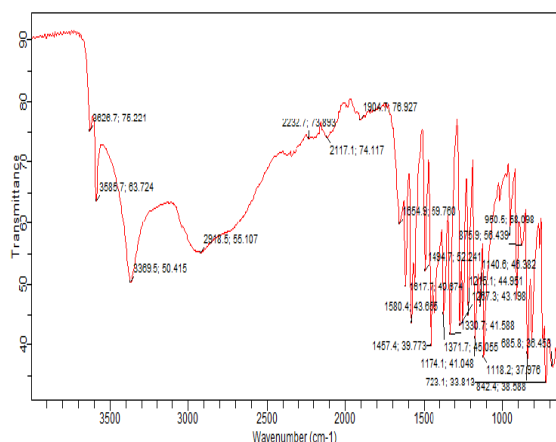


Figure 2. The FTIR of the synthesized dye.

The peaks at 1460 and 1381 cm^{-1} are as a result of CH_2 and CH_3 bending vibrations respectively. The $\text{N}=\text{N}$ functional group is identified by the peak at 1334 cm^{-1} while the $\text{C}-\text{S}$ bond is identified at 1174 cm^{-1} . The infrared spectrum also reveals the presence of $\text{C}-\text{O}$ and $\text{C}-\text{N}$ bending vibrations at 1118 and 950 cm^{-1} respectively while the peaks at 742 cm^{-1} correspond to CH_2 rocking vibrations and 623, 559 and 468 cm^{-1} correspond to CH_3 scissoring vibrations.

GC-MS analysis

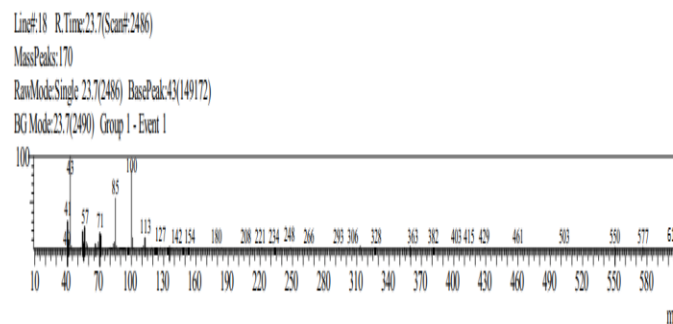
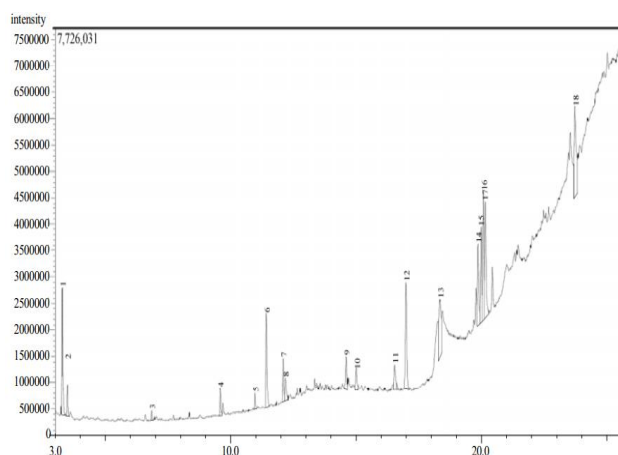


Figure 3: GC-MS of the synthesized dye.

From figure 3 above, the $m/z = 415$ confirms the breaking away of two ethyl thiophenyl cation while the fragmentation of the two residual amine groups is shown by the m/z value at 382. The GC-MS which further confirms the synthesis of the triazine based reactive dyes reveals the breaking away of the triazenyl cation at m/z value of 306. In a further sense, it was observed that a new heterocyclic ring which was formed from a rearrangement reaction between benzene and three nitrogen groups fragmented at m/z value of 180.

Dye Exhaustion

Dye exhaustion is a parameter that is used to estimate the amount of dye absorbed and adsorbed by the fibre [18]. It can also be used to determine the degree of levelness and dye-fibre bonding properties [12]. The third fibre formulation CAP-PEG-3 has PEG in excess and the hydroxyl groups on the glycolated polymer fibre tend to stabilize the formulation thereby improving its levelness.

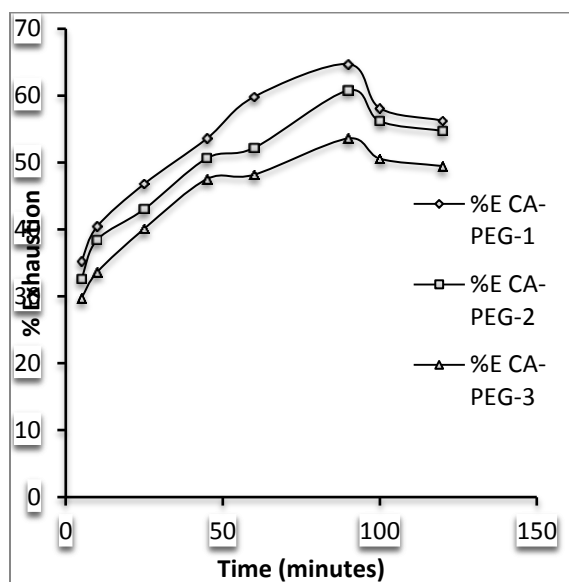


Figure 4. The exhaustion profile of the synthesized dye on CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 at 29°C

At 29°C, the percentage exhaustion of the CAP-PEG-1 fibre formulation range from 35.25 to 56.26 and reflects a high initial rate of exhaustion. The CAP-PEG-3 has the lowest percentage exhaustion range but also has the highest levelness which is shown from its low initial rate of dyeing. The influence of time is seen on figure 4, at ninety minutes, the equilibrium exhaustion is achieved for the three fibre formulations. The percentage equilibrium exhaustion occurs at 64.72, 60.78 and 53.60 for CAP-PEG-1, CAP-PEG-2, and CAP-PEG-3 respectively.

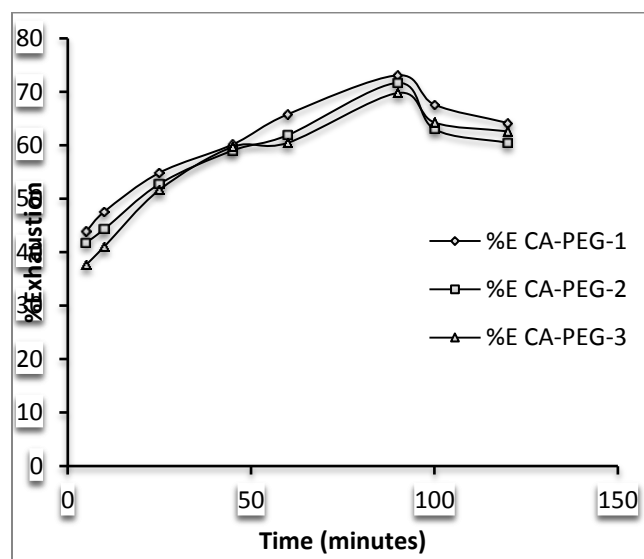


Figure 5. The exhaustion profile of the synthesized dye on CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 at 40°C

From the figure 5 above, at 40°C, the equilibrium exhaustion at 90 minutes increased to 73.11, 71.68 and 69.80 for CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 respectively. The percentage exhaustion of the fibres was relatively close at 45 minutes of dye-fibre adsorption. Since the third fibre formulation have the lowest initial gradient of dye exhaustion, it has the highest degree of levelness.

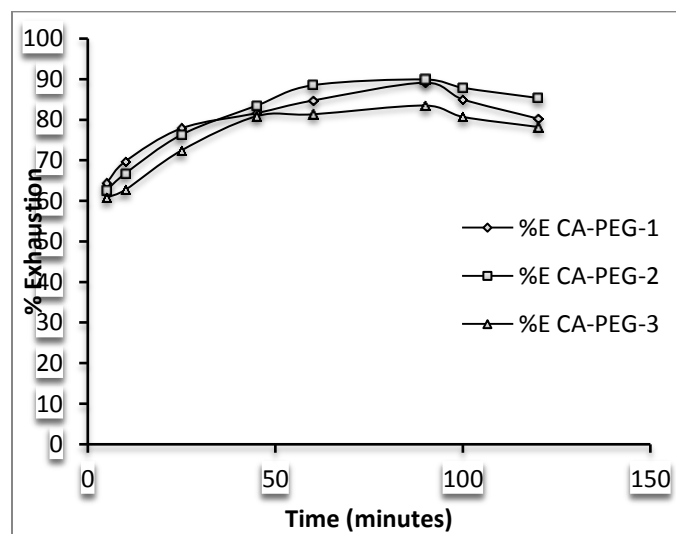


Figure 6. The exhaustion profile of the synthesized dye on CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 at 60°C

At 60°C, the highest level of exhaustion was achieved. The CAP-PEG-1 has the highest degree of exhaustion of 89.92% and the lowest degree of levelness. From figure 6, at 100 and 120 minutes, the rate of exhaustion reduces but it is still more than the optimal exhaustion rate of other temperature conditions. Therefore at 60°C, the dye ions gains optimal kinetic energy to penetrate the cellulose acetate and polyethylene glycol fibre formulation [5].

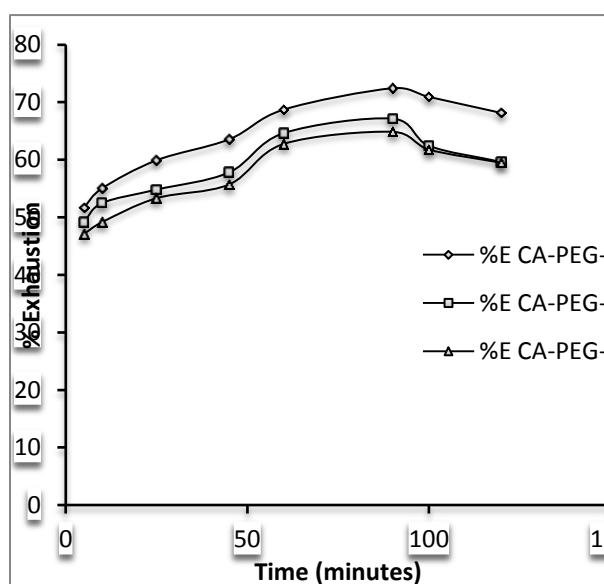


Figure 7. The exhaustion profile of the synthesized dye on CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 at 80°C

At 80°C, the general exhaustion values were less than those of 60°C. Although exhaustion increases with temperature, but at very high temperatures, rate of diffusion of dyes from surface of fibres into the fibre structure is more than the rate of adsorption of dyes by fibre from the dye bath due to the effect of dye bleeding at high temperature values [7].

Dye-Fibre Distribution

The distribution of a dye on the fibre (D_f) is evaluated by the amount of dye exhausted into 100 g of the polymer fibre blends while the distribution of dye in the dye bath (D_s) is evaluated by the amount of dye left in 1000 mL of the dye bath. For the three CAP and PEG blend, the amount of dye exhausted into the fibres increase with temperature; although, the D_f reduced at the highest temperature of 80°C. This reduced exhaustion at higher temperature is as a result of bleeding of the dye into hot water thereby reducing the fixing ability of the dye.

Table 1. The distribution values of the synthesized dye inside and outside the fibre

Temp	Weight of dye exhausted into 100 g polymer (D_f)			Dye left in 1000 mL (D_s)		
p	CA-PEG-1	CA-PEG-2	CA-PEG-3	CA-PEG-1	CA-PEG-2	CA-PEG-3
0°C						
29	64	60	54	1.8	2.0	2.3
40	74	72	70	1.3	1.4	1.5
60	90	90	84	0.5	0.5	0.8
80	72	68	64	1.4	1.6	1.8

The amount of dye left in the dye bath reduces as the temperature is increased. The CAP-PEG-1 fibre blend which have a balanced ratio of cellulose acetate phthalate and poly (ethylene glycol) has the lowest amount of dye left in 1000 mL of the dye bath after exhaustion and this shows that the interfacial tension of this fibre blend is low to allow the dye molecules to cross the dye solution and fibre boundary [14].

Partition Coefficient

One of the parameters that are used to establish the affinitive property of a dye is the partition coefficient which is also used to account for the dynamic equilibrium condition of the dyeing process [19]. The partition coefficient was seen to be highest at temperature of 60 °C and lowest at 29 and 80 °C. At high temperatures, the diffusion mechanism of dye migration into the fabric switches to convectional mechanism which disrupts the equilibrium of the dye molecules within the fibre internal structures [18].

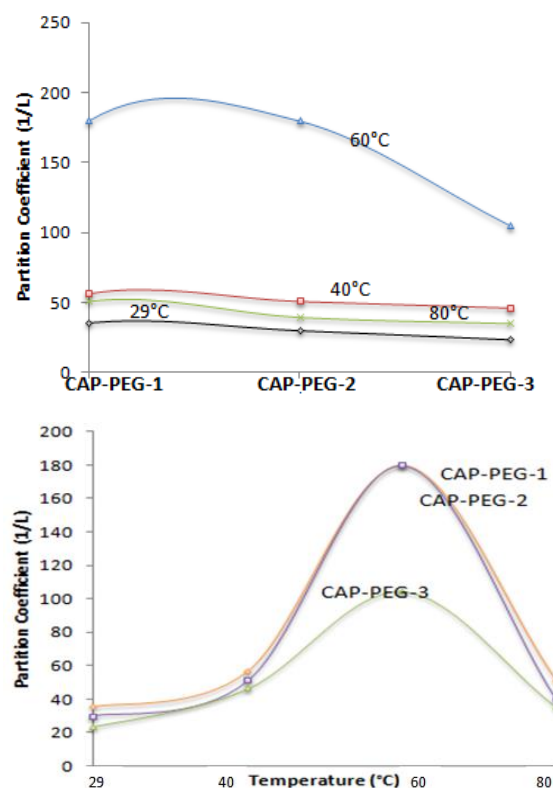


Figure 8: Partition Coefficient of CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 at 29, 40, 60 and 80 °C

From the general overview, CAP-PEG-3 had the lowest partition coefficient; this is as a result of the fact that the excess poly (ethylene glycol) has reduced the surface negative charges that

can enhance the migration of the dye cations into the cellulose acetate phthalate pores. Furthermore, the hydrophilic effect created by the excessive blending of PEG with CAP in third blend favours the migration of the dye molecules back into the dye bath by creating a high entropic effect in the fabric pores through its soft hydrophilic chain segments [9].

Dye Affinity

The affinity of a dye to a fibre is a measure of the energy needed to remove one mole of the dye from the internal pore of a fibre after a considerable extent of fixation [20]. Dye affinity is the preferential attraction of the dye for the fiber rather than for the solution of the dye bath, it also measures the tendency for the dye molecules to migrate from the solution to fiber [21].

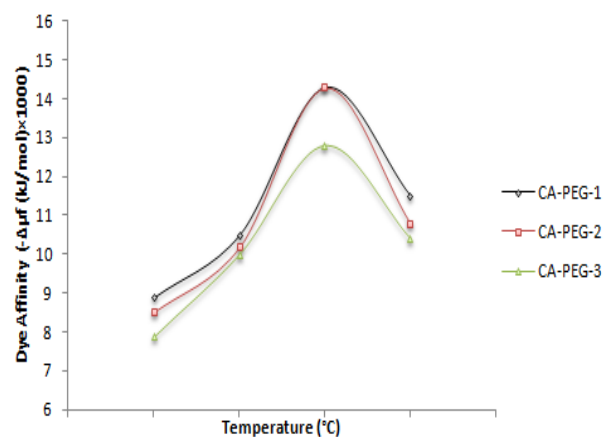


Figure 9: The calculated dye affinity values against Dyeing Temperatures for CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3

Figure 9 shows the plot of dye affinity against dyeing temperature for the dye and the numerical estimate of affinity calculated which was negative indicates that the dye was transferred from solution into the three fibre blends. The high negative values of the calculated affinity were recorded in thousands

and these also indicate the extent of the dye immobility within each fibre blends [17].

SEM of the Fibre formulations after Dyeing

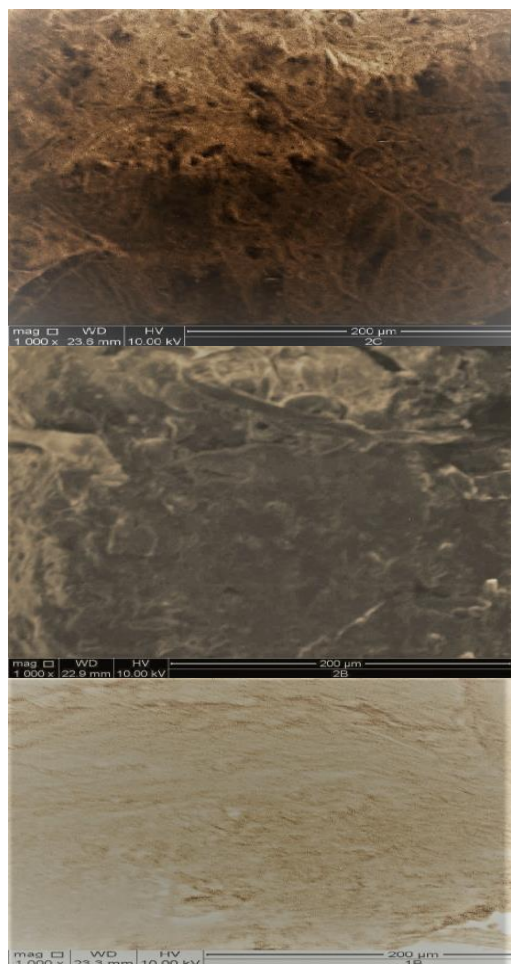


Figure 10: The SEM of CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3 after the dyeing process

Figure 10 (a) shows the condition of the cellulose acetate phthalate and polyethylene glycol fibre blend and its irregular terrain obviously shows the reason why it has the lowest degree of levelness among the three. The irregularity reduced on figure 10 b. Although, the third fibre blend (c) which has the polyethylene glycol in excess has the least degree of exhaustion; yet, it had the best form of levelness. This SEM images also reveals the

surface morphology of the first blend (a) to be rough and contains unstable surface pores which enhance better dye exhaustion while the third fibre blend(c) with a smooth surface terrain can aid surface deposition of dye thereby reducing overall dye exhaustion performance on this particular fibre blend.

Conclusion

This work contains the dyeing performance of a 2-(aminomethyl) thiophenyl substituted dye on three different fibre blends of CAP-PEG-1, CAP-PEG-2 and CAP-PEG-3. The research shows that CAP-PEG-1 which has a balanced proportion of both polymers have the highest exhaustion and affinitive properties while the third fibre blend with the smoothest surface which has PEG in excess has the lowest exhaustion and affinitive properties; although the smoother the surface of the fibres, the better the degree of levelness.

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