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SYNTHESIS AND ECALUATION OF NOVEL INSECT-REPELLENT MCT REACTIVE DYE ON NYLON 6

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Abstract

Insect-repellency of fibre is a property which makes the fibre to be of interest in the field of military and health. The insect-repellent substrate could be prepared using either functional finishing or applying an insect-repellent dye. In this paper, Insect-repellent nylon 6 is obtained using a novel insect-repellent reactive dye containing N, N-diethyl-m-toluamide. To do this, N, N-diethyl-m-toluamide (DEET) was first nitrated at the para–position relative to amide functionality. The nitrated product was reduced in the presence of C_2H_5OH, $SnCl_2$ and HCl. The produced amine was then condensed with 2, 4, 6-trichloro-1, 3, 5-triazine (cyanuric chloride) as a reactive group in below 5 °C. The resultant adduct was finally reacted with an amino group present in 6-amino-1-hydroxy naphthalene-3-sulfonic acid to produce 7-(4-chloro-6-(4-(diethylcarbamoyl)-2-methylphenylamino)-1,3,5-triazin-2-ylamino)-4-hydroxynaphthalene-2-sulfonic acid. In order to synthesis azo dye, sulfanilic acid was diazotized using HCl and $NaNO_2$ and then coupled to the above prepared component to produce insect-repellent reactive dye. An analogue dye was prepared via the same route without insect-repellent group making stage. The novel dyes were characterized using FT-IR, ^{1}H NMR spectroscopy and UV-Vis Spectrophotometer. The novel dyes were then reacted with nylon 6 and bonded to it covalently to provide permanent insect-repellent substrate. The insect-repellent dye reacted nylon 6 showed insect-repellent activity using standard methods for Anophle mosquito repellent.

Keywords: Reactive dye; Insect-repellent; Nylon 6; DEET; ^{1}H NMR

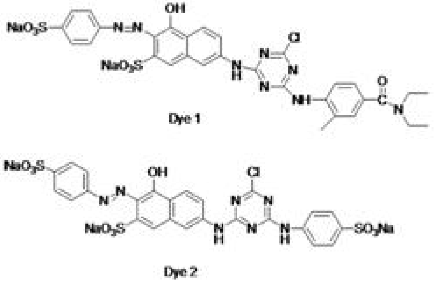
1. Introduction

N, N-diethyl-meta-toluamide (DEET) is an insect-repellent that was first marketed in 1957. DEET can be applied to clothing and skin to repel biting insects. Its use is recommended for prevention of several vector-borne diseases. There are over 225 insect-repellents brands containing DEET ranging in concentration from 4% to 100%. DEET is also used in combination with dermal sun screens [1-7]. It was developed and patented by the U. S. Army in 1946 for use by military personnel in insect-infested areas. It is now widely used, with approximately 30% of the U.S. population using DEET repellents each year. DEET products are currently available in a variety of forms: liquids, lotions, sprays, and even impregnated materials, such as wristbands [4, 6]. DEET products are available in numerous formulation types (e.g., aerosol sprays, non- aerosol sprays, creams, lotions, sticks, foams, and concentrations, products range from 4% to 100%) [4].

The use of effective insect-repellents provides certain public health benefits. The applicable technologies in insect-repellent finishing are padding and microencapsulation. To obtain long-duration protection from mosquitoes harm using insect-repellent N, N-diethyl-m-toluamide, and this compound was encapsulated in situ during the graft copolymerization of butyl acrylate onto chitosan in an aqueous solution [8, 9]. DEET is a widely used insect-repellent whose percutaneous absorption and evaporation in humans has been extensively studied in vitro and in vivo. DEET is generally considered to be safe for topical use if applied as recommended [10]. Spraying on substrate with an aqueous emulsion containing microencapsulated DEET led to a bio-cloth with long-lasting mosquito repellency compared to fabric treated with DEET in ethanol [8, 11]. DEET is the main or sole active ingredient of most commercial repellent formulation, and because of its efficacy and low toxicity proven over many decades of widespread consumer use is arguably the standard ingredient against which the performance of other compounds is generally evaluated [4,7]. The synergistic percutaneous enhancement between insect-repellent DEET and sunscreen oxy benzene has been proven using a series of in vitro diffusion studies [3].

Reactive dyes are bonded to fibres via covalent bond. They are known for their bright colors and very good to excellent light and wash fastnesses, though poor resistance to chlorine bleaches [12]. There are several broad classes of reactive dyes. Some of the reactive dyes are based on azo chromophore. The azo dyes are by far the most important class, accounting for around 60 -70% of all colorants [13].

However, less work has been done in the soluble dye field such as reactive dyes. In this paper, the main goal is to combine strengths of a reactive dye and an insect-repellent agent (DEET) to produce insect-repellent nylon 6. The reason for selecting nylon 6 as substrate is that nylon 6 fibres are used in blend with cotton to produce fabrics with military uniform application. In addition, nylon 6 has the -NH_2 group at the end of its polymeric chain that can covalently bond to reactive dyes. For this purpose, a novel reactive dye containing insect-repellent (DEET) is synthesized (figure 1). The dyes are characterized using FT-IR, ^{1}H NMR, melting point and UV/Vis spectrophotometer. In order to produce insect-repellent nylon 6, the synthesized dye is reacted with nylon 6 to make covalent bond. The insect-repellent activity of the reacted nylon 6 is evaluated using standard method for testing mosquito repellents effects by releasing 30 mosquitoes (Anophle mosquitoes) in a 45 ×37 × 35cm mosquito-rearing cage, 25 °C and a relative humidity of 65% [14-16].



Dye 1

Dye 2

Figure 1. Chemical structures of the dyes

2. Experimental

2.1. Materials

N, N-diethyl-m-toluamide, cyanuric chloride, HNO_3, H_2SO_4, J-acid (90%), sulfanilic acid, sodium nitrite, stannous chloride and hydrochloric acid (36%) were all obtained Aldrich Co. and used as received. FT-IR spectra were determined on a Nicolet magna-ir 560 infrared spectrometer (USA) using KBr pellets. ^{1}H NMR spectra were recorded on a Bruker AVANCE-500 MHZ (USA) spectrometer. Elemental analyses for carbon, hydrogen, and nitrogen were carried out at the Department of Chemistry, Guilan University, on a Carlo Erba 1108 elemental analyser.

Melting points of the products were determined via capillary method using a Barnstead electrothermal 9200 (UK). Visible absorption spectra were recorded using a Cintra 10 UV/visible spectrophotometer (GBC Co., Australia). Thin layer chromatography (TLC) was performed using aluminum plates coated with silica gel 60 F_{254} (Merck).

2.2. Synthesis

2.2.1. Synthesis of N, N-diethyl-3- methyl- 4- nitro benzamide

N, N-diethyl-3- methyl- 4- nitro benzamide (DEET-NO_2) was synthesized according to Kenneth's method [17]. DEET (80.6 mmol, 15.43 g) was dissolved in acetone (26 mL) in a two-neck flask. A mixture of nitric acid (162 mmol, 5 mL) and concentrated sulfuric acid (95%, 265 mmol, 13 mL) was added dropwise to the flask at room temperature. The whole mixture was allowed to react at 60-70 °C for 4 h. The pH was adjusted to 5-6 with sodium hydroxide aqueous solution (10%). The mixture was filtered off to remove impurities. The filtrate was then evaporated under vacuum to obtain the product. The synthesis route is shown in figure 2.

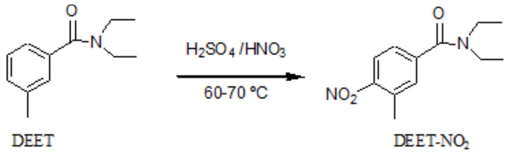


Figure 2. Synthesis route for N, N-diethyl-3- methyl- 4- nitro benzamide

2.2.2. Synthesis of 4-amino-N, N- diethyl – 3- methyl benzamide

4-amino-N, N- diethyl – 3- methyl benzamide (DEET-NH_2) was synthesized according to Liu's method [18]. DEET-NO_2 (12 mmol) was dissolved in ethanol (28 mL) in a two-neck flask. A mixture of $SnCl_2/2H_2O$ (32.4 mmol) and concentrated hydrochloric acid (36%, 140 mmol) was added dropwise to the flask at room temperature. The whole mixture was allowed to react at 60-70 °C for 6 h. reaction progress was determined with the aid of Ehrlich's reagent and TLC .The pH was adjusted to 6-7 with sodium hydroxide aqueous solution (10%). The mixture was filtered off to remove impurities. The filtrate was then evaporated under vacuum to obtain the product. The synthesis route is shown in figure 3.

Yield (73.6%); mp: oil; FT-IR (KBr, ν, cm^{-1}): 3352, 3446 (-NH_2); 1431, 1380 (-CH_2-CH_3 bending vibration); 2976, 2935 (-CH_2-CH_3 Stretching vibration); 1504 (C=C); 1155 (C-N); 1667 (C=O Stretching vibration); ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.21-1.08 (2 singlet broad peak, 6H, -CH_3); 3.50-3.23 (2 singlet broad peak, 4H, -CH_2), 2.50 (1 singlet, 3H, CH_3 on the benzene aromatic ring); 7.99-7.35 (complex, 3H, benzene).

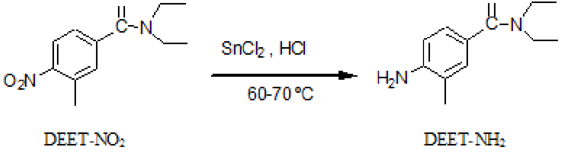
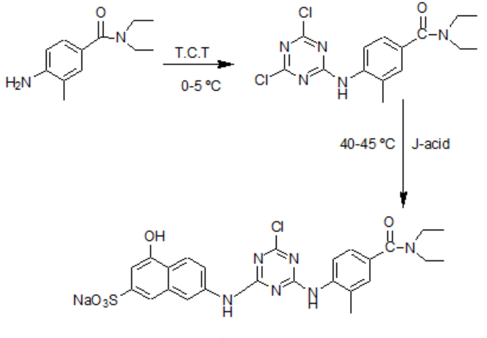


Figure 3. Synthesis route for 4-amino-N, N- diethyl – 3- methyl benzamide

2.2.3. Synthesis of sodium 7-(4-chloro-6-(4-(diethylcarbamoyl)-2-methylphenylamino)-1,3,5-triazin-2-ylamino)-4-hydroxynaphthalene-2-sulfonate

Sodium 7-(4-chloro-6-(4-(diethylcarbamoyl)-2-methylphenylamino)-1,3,5-triazin-2-ylamino)-4-hydroxynaphthalene-2-sulfonate, compound 1, was synthesized according to Mokhtari's method [19]. 2, 4, 6-trichloro-*s*-triazine, T.C.T., (2.43 g, 13 mmol) was dissolved in acetone (15 mL). The solution was then added dropwise to a mixture of crushed ice (40 g) and water (40 mL) to prepare a fresh suspension of 2, 4, 6-trichloro-s-triazine. To the resulting suspension, an aqueous solution of DEET-NH_2 (2 g, 9.5 mmol) in 40 ml water was added very slowly at below 5 ºC, pH 3-4. The reaction was continued for 1.5 h with stirring and completion of the reaction determined with the aid of Ehrlich's reagent and TLC. The resultant product was finally condensed with an amino group present in J-acid at 40-45 ºC and pH 3-4 for 2 h. The synthesis route is shown in figure 4.

Yield: (92%); mp: decompose at 260 °C; FT-IR (KBr, ν, cm^{-1}): 1440, 1366 (-CH_2-CH_3 bending vibration); 2973, 2779 (-CH_2-CH_3 stretching vibration); 1561 (C=C); 1155 (C-N); 1722 (C=O amide stretching vibration); 3423 (-OH); 1294, 1334 (aromatic secondary amine, C-N stretch); 1044 (C-Cl); 1221 (S=O stretching), 1H NMR (500 MHz, D_2O, δ, ppm): 1.19-1.02 (2 triplet, 6H, -CH3); 3.47-3.20 (2 quartet, 4H, -CH_2), 2.32 (1 singlet, 3H, CH_3 on the benzene aromatic ring); 2.80 (1 singlet, 1H, -$SO_3\underline{H}$), 2.97 (1 singlet, 1H, benzene C-N$\underline{H}$), 3.68 (1 singlet, 1H, naphthalene C-N<u>H</u>); 4.65 (complex, 1H, aromatic C-O<u>H</u>), 8-7.43 (complex, 3H, benzene), 7.36-7.11 (broad peak, 5H, 1-naphthalene). Elemental analysis results for $C_{25}H_{24}ClN_6NaO_5S$ (Calculated: C, 51.56%; H, 4.18%, N, 14.51%; S, 5.54%, Found: C, 51.31%; H, 4.64%, N, 14.13%; S, 5.92%).



Compound 1

Figure 4. Synthesis route for compound 1

2.2.4. Synthesis of sodium 7-(4-chloro-6-(4-(diethylcarbamoyl)-2-methylphenylamino)-1,3,5-triazin-2-ylamino)-4-hydroxy-3-((4-sulfonatophenyl)diazenyl)naphthalene-2-sulfonate (dye 1)

The sodium salt of sulfanilic acid (4.32 g, 0.025 mol) was dissolved in water (100 ml) at pH 7-8, and 20-25 °C. Sodium nitrite (1.16 g, 0.016 mol), dissolved in water (10ml), was added and the resultant mixture was added dropwise to cold water (25 ml), containing concentrated hydrochloric acid (2.29 g, 36%, 0.063 mol) during 45 min. The diazotization process was carried out at pH <2, and 0-5 °C over 75 min, after which excess nitrous acid was destroyed by the addition of sulphamic acid.

Compound 1 (coupling component) was dissolved in water (40 ml) with stirring at 5-10 °C and pH 7-8. The solution was then cooled to 5-10 °C by external cooling. To the aqueous solution of the coupling component, the above prepared diazonium salt solution was added over 30 min at 0-5 °C with vigorous stirring. The pH of the reaction mixture was adjusted to 7-8 by dropwise addition of aqueous sodium hydroxide solution (10%) and the reaction was continued at the same temperature for 3-5 h to completion, which is controlled by TLC and reacting the mixture with β-naphthol. The product was salted out with sodium chloride, filtrated off and dried. The residue was dissolved in acetone and indiscerptible salt was filtrated off. Finally, the filtrate was evaporated under vacuum to obtain the product (dye 1).

Yield: 69%; mp: decompose at 325 °C; FT-IR (KBr, ν, cm^{-1}): 1374 ($-CH_2-CH_3$ bending vibration);); 2925,2854 ($-CH_2-CH_3$ stretching vibration) ; 1496 (C=C); 1155 (C-N); 1675 (C=O amide stretching vibration); 3383, 3312 (-OH); 1248 (C-N); 1055(C-Cl); 1200 (S=O stretching vibration) ; 1575 (N=N) ; ^1H NMR (500 MHz, D_2O, δ, ppm): 1.20-1.05 (2 triplet, 6H, $-CH_3$); 3.79-3.39 (2 quartet, 4H, $-CH_2$), 2.35 (1 singlet, 3H, CH_3 on the benzene aromatic ring); 2.80 (1 singlet, 2H, naphthalene $-SO_3\underline{H}$ and sulphanilic acid $-SO_3\underline{H}$); 3.99(1 singlet, 2H, naphthalene C-N<u>H</u> and benzene C-N<u>H</u>); 4.99 (complex , 1H, aromatic C-O<u>H</u>); 6.92-8.1 (complex, 11H, aromatic ring). Elemental analysis results for $C_{31}H_{27}ClN_8Na_2O_8S_2$ (Calculated: C, 47.42%; H, 3.42%, N, 14.27%; S, 8.7%%, Found: C, 47.71%; H, 3.84%, N, 14.03%; S, 8.9%).

2.2.5. Synthesis of 4,6-dichloro- 1,3,5-triazin-2-ylamino)-4-hydroxynaphthalene-2-sulfonate

(4,6-dichloro-1,3,5-triazin-2-ylamino)-4-hydroxynaphthalene-2-sulfonate (compound 2) was synthesized according to Mokhtari's method [19]. 2, 4, 6-trichloro-*s*-triazine (2.5 g, 13 mmol) was dissolved in acetone (15 mL). The solution was then added dropwise to a mixture of crushed ice (40 g) and water (40 mL) to prepare a fresh suspension of 2, 4, 6-trichloro-*s*-triazine. To the resulting suspension, an aqueous solution of J-acid (4 g, 16 mmol) in water

(40 mL) was added very slowly at below 5 ºC, pH 3-4. The reaction was continued for 2 h with stirring and completion of the reaction determined with the aid of Ehrlich's reagent and TLC. The synthesis route is shown in figure 5.

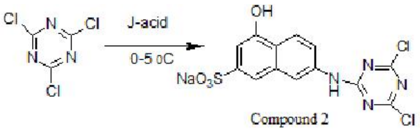


Figure 5. Synthesis route for compound 2

2.2.6. Synthesis of sodium 7-(4-chloro-6-(4-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)-4hydroxynaphthalene-2-sulfonate (compound 3)

Sulfanilic acid (2.3 g, 13 mmol) was dissolved in water (30 ml) at pH 7-8. The solution was then added very slowly to the reaction mixture prepared in previous section at 40-45 ºC and pH 4-5. The mixture was stirred for 2 h and completion of the reaction determined with the aid of Ehrlich's reagent and TLC. The synthesis route is shown in figure 6.

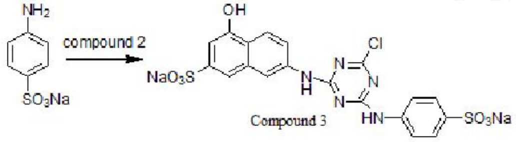


Figure 6. Synthesis route for compound 3

2.2.7. Synthesis of sodium (E)-7-(4-chloro-6-(4-sulfonatophenylamino)-1,3,5-triazin-2-ylamino)4-hydroxy-3-((4-sulfonatophenyl)diazenyl)naphthalene-2-sulfonate (dye 2)

The sodium salt of sulfanilic acid (1.3 g, 0.007 mol) was dissolved in water (50 ml) at pH 7-8, and 20-25 °C. sodium nitrite (0.75 g, 0.009 mol), dissolved in water (15 ml), was added and the resultant mixture was added dropwise to cold water (25 ml), containing concentrated hydrochloric acid (3.39 g, 36%, 0.109 mol) during 60 min. The diazotization process was carried out at pH <2, and 0-5 °C over 75 min, after which excess nitrous acid was destroyed by the addition of sulphamic acid.
Compound 3 (coupling component) was dissolved in water (50 ml) with stirring at 5-10 °C and pH 7-8. The solution was then cooled to 5-10 °C by external cooling. To the aqueous solution of the coupling component, the diazonium salt solution prepared above was added over 30 min, at 0-5 °C with vigorous stirring.
The pH of the reaction mixture was adjusted to 7-8 by dropwise addition of aqueous sodium hydroxide solution (10%) and the reaction was continued at the same temperature for 3-5 h to completion, which is controlled by TLC and reacting the mixture with β-naphthol. The product was salted out with sodium chloride, filtrated and dried. The residue was dissolved in acetone and indiscerptible salt was filtrated off. Finally, the filtrate was evaporated under vacuum to obtain the product (dye 2).
Yield: 85% mp: decompose at 279 °C; FT-IR (KBr, cm^{-1}): 3384 (-OH); 1628 (N=N); 1248 (C-N); 1057 (C-Cl); 1579 (C=C) ; ^{1}H NMR (500 MHz, D_2O, δ): 1.91 (1 singlet, 3H, $-SO_3\underline{H}$); 3.09 (1 singlet, 2H, aromatic $C\text{-}N\underline{H}$); 4.68 (complex , 1H, aromatic $C\text{-}O\underline{H}$); 5.58-8.11 (broad peak, 12H, aromatic ring). Elemental analysis results for $C_{25}H_{15}ClN_7Na_3O_{10}S_3$ (Calculated: C, 38.79%; H, 1.95%, N, 12.67%; S, 12.43%; Found: C, 39.15%; H, 2.01%, N, 12.80%; S, 12.76%).

2.3. Visible absorption spectra

Solutions of the two dyes, achieved in distilled water, were prepared in the concentration range 0.0081-0.011 g/l and the absorbance of each solution was measured at the λ_{max} of the dye, using 1 cm cells and a Cintra 10 spectrophotometer. The molar extinction coefficients (ε_{max}) of the dyes were determined using eq. 1.

$$A=\varepsilon\, l\, c \qquad \text{Eq. 1}$$

Where A is absorbance, l is the pass length (1 cm), c is concentration (mol/l) and ε is molar absorptivity coefficient ($lmol^{-1}cm^{-1}$).

2.4. Applying insect-repellent dye to nylon 6 fibres

In order to apply insect-repellent dye to nylon 6, a dyebath was set up with contents of dye (1% o.w.f., on weight of fibre), ammonium sulfate (1-2% o.w.f.), liquor to good ratio 20/1. The substrate was immersed in the dyebath at 40 °C for 5 min, and then the temperature of dyebath was raised to 80 °C with the rate of 1 °C/min. The reaction continued at 80 °C for 30 min and then alkali (1% o.w.f.) was added to dyebath. The reaction continued at the same temperature for further 30 min to completion. The mechanism of reaction is shown in figure 7.

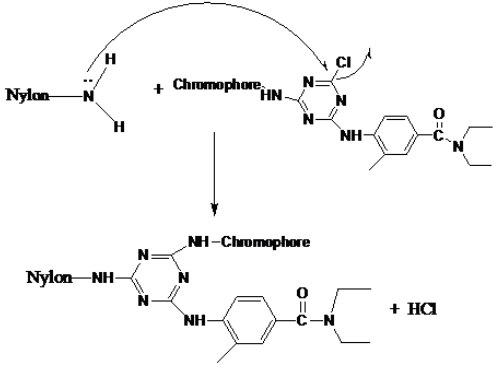


Figure 7. Mechanism of reacting nylon with insect-repellent dye

2.5. Insect-repellent efficacy of the reacted nylon 6

The insect-repellent properties of the functional dyes were evaluated according to standard method for testing mosquito repellent [15, 16].

Release 30 (local mosquitoes) in a 45 ×37.5 × 35 cm mosquito-rearing cage (25°C and a relative humidity of 65%). testing monitor keeps arm wrapped with rolled fabric in the cage for 2 min. During the time (2 min) that the textile was exposed to mosquitoes, the biting occurrence was reported by the test subjects. Fabric with no repellent and then progressively higher doses of repellent was sequentially exposed to mosquitoes immediately after spraying the fabric with repellent to obtain a dose profile for each emulsion in comparison with DEET in ethanol. The number of bites at the end of exposure was counted and recorded. The percentage of repellency was defined as the difference between the number of bites on control (untreated) textile and treated textile that almost equal 90% (figure 8).

Repelling rate (%) = the number of mosquitoes in control group minus that of tested group / the number of mosquitoes in control group×100

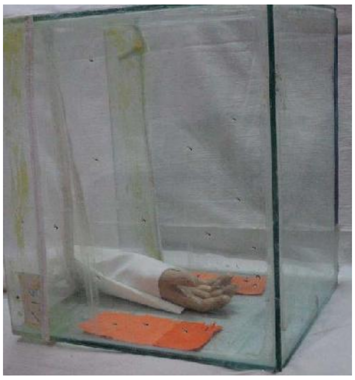


Figure 8. Insect-repellent testing cage

3. Result and discussions

3.1. Structure characterization

The structure characterization was studied using FT-IR and ^{1}H NMR spectroscopy. Considering the FT-IR spectra of DEET-NO_2, absorption bands which appeared at 1524 cm^{-1} and 1314-1348 cm^{-1} correspond to asymmetric and symmetric stretching vibration of a nitro (-NO_2) group, respectively. The stretching vibration of C-N bond appeared at 848-890 cm^{-1}.
In the case of DEET-NH_2, the amine (-NH_2) group showed stretching vibration absorption bands at 3352-3446 cm^{-1}. Commonly the C=O bond shows absorption bands at 1667-1775 cm^{-1}.
Considering FTIR spectra of dyes 1 and 2, there is only one peak in the region of 1575-1628 cm^{-1}, which can be attributed to stretching vibration of N=N group present in the dyes. Asymmetric and symmetric stretching vibrations for amide ethyl chain at the insect-repellent dye are shown at wavenumbers 2925 and 2854 cm^{-1}, respectively for dye 1. Also, the FT-IR spectra showed absorbance bands at wavenumbers, ν, of 1055, 1155, 1200, 1374, 1496, 1575, 1675, 2925 cm^{-1} and 3383 cm^{-1}, which can be attributed to the C-Cl, C-N, S=O, --CH_2-CH_3 bending vibration, C=C, N=N, C=O amide stretching vibration, -CH_2-CH_3 stretching vibration and OH stretching vibrations, respectively for dye 1. The results correspond with the literature data.
The chemical structures of the synthesized dyes were also confirmed by ^{1}H NMR analysis. By comparing the ^{1}H NMR spectra of the dyes, there are peaks at chemical shifts, δ, 1.05-1.20 and 3.19-3.89 ppm at the spectra of dyes 1, which confirms the presence of methylene and methyl group at DEET. The presence of ethyl group at DEET moiety on the dye structure led to insect-repellent dye. These peaks can be only observed in the ^{1}H NMR spectra of the dye 1.

3.2. Visible absorption spectra

The optical properties of the dyes were determined using eq. 1 and summarized in table 1.

Table 1. UV-Vis Spectral data of the dyes (in water)

Dye	1	2
λ_{max} (nm)	487	485
ε_{max} (l mol^{-1} cm^{-1})	22210	13745

According to the result, there is no difference in the λ_{max} of the dyes as the difference moiety for insect-repellent activity does not affect the resonance of the molecule.
Usually, ε_{max} is a widely accepted measurement of tinctorial strength. However, assessing the tinctorial strength of dyes is quite difficult and, in some cases, controversial results could be

obtained. As a general rule, steric hindrance always causes a reduction in tinctorial strength, which readily explains our experimental results, as shown in table 1.

3.3. Formation of covalent bond between the dye and nylon 6

There are two methods to make sure of covalent-bond fixation of the dye with the terminal amino groups of the nylon 6 as well as to remove unfixed dye from the fabrics; alkali soaping treatment [20] and extraction with solvents [21]. For this purpose, the dyed nylon 6 samples (after removing unreacted dyes with the surface of nylon 6) were treated in a flask containing 25% aqueous pyridine solution (liquor to good ratio 40:1) at 100 °C for 3 hrs. The colorless extracted liquor confirmed the formation of covalent bond between nylon 6 and the dye.

3.4. Insect-repellent efficacy of the reacted nylon 6

Nylon 6 reacted with dye 2 did not show insect-repellent activity due to not having insect-repellent group available on the dye structure. Whereas Nylon 6 reacted with dye 1 possessing insect-repellent group, particularly containing an ethyl chain group at DEET moiety, showed insect-repellent activity.

4. Conclusions

Insect-repellent nylon 6 was prepared successfully through synthesizing a novel dye together with its analogue and reacting it with nylon 6. The molecular structures of the dyes were fully characterized by FT-IR and ^{1}H NMR spectroscopy. The presence of ethyl group at DEET moiety on the dye structure led to insect-repellent dye. The novel dye was reacted with nylon 6 and produced insect-repellent nylon 6. Replacing the DEET moiety with sulphanilic acid did not affect the λ_{max} of the corresponding dye as it is not effective in the resonance of the molecule.

Acknowledgment

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