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Chapter

Evaluation of Camouflage Coloration of Polyamide-6,6 Fabric by Comparing Simultaneous Spectrum in Visible and Near-Infrared Region for Defense Applications

Md. Anowar Hossain

Abstract

Polyamide-6,6 (PA-6,6) knitted fabric was coated with a complex combination of liquid-phase oxidized carbon black pigment (CBP) as light absorber and monosulfonated telon violet 3R (TVR) as acid dyes. Nitric acid (NA) moiety was used as liquid-phase oxidation of CBP and hydrophilic transformation of CBP-TVR. Thermoplastic polyurethane (TPU) and N, N-dimethylformamide (DMF) were formulated as cross-linker between composite mixture (CM) and PA-6,6 fabric. Six different CMs were coded for coating of PA-6, 6 fabric such as TPU-DMF, CBP-TPU-DMF, TVR-TPU-DMF, CBP-TVR-TPU-DMF, NA-TVR-TPU-DMF, NA-CBP-TVR-TPU-DMF. Structural, chromatic, and spectral reflection of CM coated PA-6,6 fabric was investigated by scanning electron microscopy, color measurement spectrophotometer, and Fourier transform infrared spectroscopy. CBP formulated PA-6,6 fabric was significantly remarked as maximum light absorber in both visible and near-infrared spectrum without allowing other parameters of treated PA-6,6 fabric. Therefore, minimum light reflection principle of CBP was indicated as camouflage material for camouflage textile coloration/finishing/patterning of simultaneous spectrum probe in visible and near-infrared spectrum. PA-6,6 fabric is very common fabrication for defense clothing, weapon, and vehicle netting against every combat background. This approach of simultaneous spectrum probe may be extended for concealment of target signature against high-performance defense surveillance.

Keywords: camouflage coloration, carbon black pigment, polyurethane, reflection, visible–near infrared

1. Introduction

Camouflage textiles are incorporated with clothing of special workers and multidimensional equipment in the vein of army, air force, navy, marines, coastal

guards, paramilitary forces, uniforms for officers and soldiers in defense forces, tents, shelters and sheets, sandbags, flak jackets, helmets, camouflaged combat and flight uniforms, covering airplanes, guns and boats, creating deceptions, making armored vehicles, and so on [1]. Key parameters of camouflage coloration are spectral bandwidth of target signature, spectral characteristics of combat background, and reflectivity [2, 3]. Reflection of pigment formulation must match with combat background for design of high-performance camouflage textiles. Polyamide and polyester fabric coloration were experimented with carbon black pigment (CBP). The camouflage effect of CBP was recommended in near infrared (NIR), 1000–1200 nm [4]. Camouflage coloration was trialed with CBP for formulation of colorant on synthetic and regenerated textiles [5]. Visible-camouflage coloration was also investigated with pigment, reactive and vat dyes. Combination of CBP with other synthetic colorant depicted more prominent hue of black [6, 7]. CBP was used for camouflage coloration of polyethylene terephthalate textiles in comparison with natural brown hue against desert combat background. Hence, CBP property was also suggested for NIR camouflage [8]. In this experiment, reflection of CBP was compared with a synthetic dyes telon violet 3R (TVR).

1.1 Properties of CBP for suitability of technical coloration

CBP has versatile industrial applications as a pigment, which imparts a black hue [9, 10]. CBP is the most suitable for defense textiles due to having maximum properties of protection textiles. CBP has weatherability, chemical resistance [11, 12], abrasion resistance [13], electroconductivity [11], alkali resistance, light fastness [7], hydrophobicity [14], which are major considerations for coloration of defense textiles. CBP has ester bond, thioester bond, amide bond, amino bond, carbonyl bond, thiocarbonyl bond, sulfonyl bond [12], aldehyde bond, hydroxyl bond, hydrogen bond [9]. Crystalline CBP shows a high order of reactivity [15]. Quantitatively more application of CBP is found in the rubber industry to accelerate its mechanical properties, such as resistance to abrasion. CBP is generally termed as active carbon for improving the mechanical properties of rubber. CBP is widely used for black coloration in paints, varnishes, carbon paper, ribbons, printing inks [13, 16, 17]. Plastic articles, metal articles, wood, paper, inorganic materials [11], and polyamide fabric coloration with 70% nitric acid (NA) [18]. Oxidization process was used to improve the coloring property of printing inks, paint, and black coloration [13, 16, 17]. Due to hydrophobicity of CBP, it is difficult to apply textile substances. So CBP needs to be oxidized for improving jetness by chromic acid, ozone, hydrogen peroxide, sodium hypochloride, potassium permanganate, NA [14, 19] and sulfuric acid [7, 14]. CBP was grafted with hydrophilic polymeric monomer (alkali or ammonium carboxylate) for improving water compatibility and dispersibility [20]. CBP has dusting tendency [21], it is combined with the carrier to impart chromatic hue. CBP constituted generally as a pigment [22]. CBP with acid surface groupings is particularly suitable with binders [23]. Particle size, surface structure, surface size, pH, and dispersibility of CBP need to be considered for every polymeric binding system [24–26]. Diameter and nigrometer index of CBP critically modify the color of CBP. CBP shows high color for diameter 13 and 15 nm and nigrometer index 63 and 68, respectively. CBP depicts medium color for diameter 17, 20 nm and nigrometer index 71, 76. CBP shows regular color for diameter 25 nm and nigrometer index 80 [11]. Different categories of CBP are fisher lampblack (particle size 44 nm, p^H 7, carbon 96.7%, oxygen 0.9%, nitrogen 0.0%, sulfur 1.5%, hydrogen 0.6%), degussa special black (particle size 20 nm, pH 7, carbon 85.6%, oxygen 13.1%, nitrogen 0.3%, sulfur 0.4%, hydrogen 0.6%) and degussa color black FW 200 (particle size 13 nm, pH: 7, carbon 79.2%, oxygen 19.3%, nitrogen

0.4%, sulfur 0.4%, hydrogen 0.7%) [27]. Natural gas and hydrocarbon are the raw materials of CBP [28]. Coarser particle of CBP shows lower depth of color, and finer particle shows higher depth of color [23] due to its difference in scattering values with difference in size and surface area. Hence CBP can be applied for chromatic modification of textile substances such as PA-6,6, cotton, wool, and acrylic fabric.

1.2 Properties of TPU for suitability of textile coating

Thermoplastic polyurethane (TPU) elastomers are a cross-linking agent having low density and high resiliency [29], dispersibility, and polymeric film forming ability was considered the criterion for applying in acid medium coating. TPU is also applicable for printing paste formulation of synthetic fabric coloration [30]. TPU creates capsule shell of CBP [31]. TPU was formulated for the dispersion of pigment [18]. TPU has structural form of hydroxy-terminated polybutadiene and polyether-ester based prepolymers with diisocyanates such as hexamethylene diisocyanate [32]. Chemical reaction between polyols and polyisocyanates compounds existing hydroxyl groups reacts with isocyanates [18]. Therefore, structural features and properties of TPU are suitable for textile coating, textile finishing and printing.

2. Technical approach of camouflage textiles formulation with CBP

Reviewed patent and publications of CBP-based coloration exhibit that CBP has enumerated applications of coloring agent but limited applications on textile coloration. Simultaneous spectrum probe camouflage coloration is almost new concept in camouflage engineering. CBP has harmonized with the demanded textile properties for defense textiles such as low reflection, weatherability, chemical resistance, good rubbing fastness, and light-fastness properties, etc. Light scattering/absorbing principle of CBP materials have been predicted the possibility of deceiving reflection against combat background. CBP has multidimensional color forming functional groups such as carbonyl group, amide group, carboxyl group, which can deceive the surrounding color. The color tone of this functional group differs in spectral responses in Vis–NIR absorbance or reflectance-based spectrophotometric color evaluation and Vis–NIR spectral responses against wavelength. CBP has possibility to modify the hue of other color forming functional group. Light falling on CBP treated fabric diffuses or light is absorbed by the CBP influencing the chromatic hue/hiding the color hue. Hence the chromatic behavior of CBP on textile surface and its moiety with other colorant need to be identified for camouflage coloration. Color combination with CBP may conceal the chromatic hue of red, green, yellow, blue. CBP can be applied on textile substances for special worker's clothing like camouflage textiles as defense wear or protection tents for special requirements. There is very limited research on CBP formulated properties introduced for augmentation of camouflage textiles. Camouflage textiles can be identified by illumination properties of chromatic hue by spectral responses in both visible and NIR ranges as the chromatic hue in Vis and NIR range are not same. The reflectance can be identified by simultaneous spectrum in Vis and NIR region easily by using VIS–NIR/UV–Vis/UV–Vis–NIR reflectance spectroscopy.

3. Materials

130 GSM PA-6,6 knitted fabric collected from local supplier was used for experimentation. Water-insoluble and laboratory-grade CBP was used for PA-6,6 fabric

coloration. TPU-Texalon 598 A in tiny pellet, white color in appearance was selected as cross-linking agent. N, N-dimethylformamide (DMF) was used as solvent for making a viscous solution of TPU. Laboratory-grade NA (70%) moiety was used for liquid-phase oxidation of CBP surface, functioning as hydrophilic vehicle of CBP-TVR into PA-6,6 and overall enhancement of rheopectic property in composite mixture (CM). The components of CM were used without further purification as received from supplier. Mathis laboratory hot plate, Werser Mathis AG, Rutisbergstrasse 3, CH-8156, Oberhasli/Zurich, Switzerland, automatic temperature controllable dryer, and a hand-operated coating processor with 2 mm roller were used for camouflage coloration.

3.1 Structure of CBP-TVR-TPU chemical compounds formulated for experimentation

The chemical structure of CBP [9], TVR [33], TPU compounds [29], and PA-6,6 fabric [34] have been shown below in **Figures 1–4**.

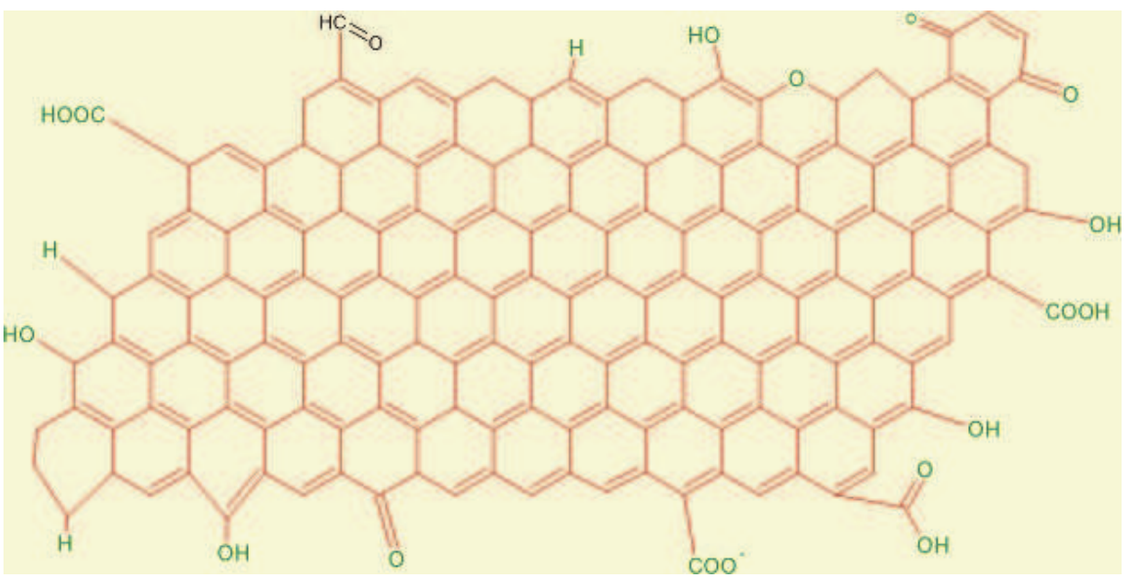


Figure 1.
Chemical structure of CBP used in this experimentation.

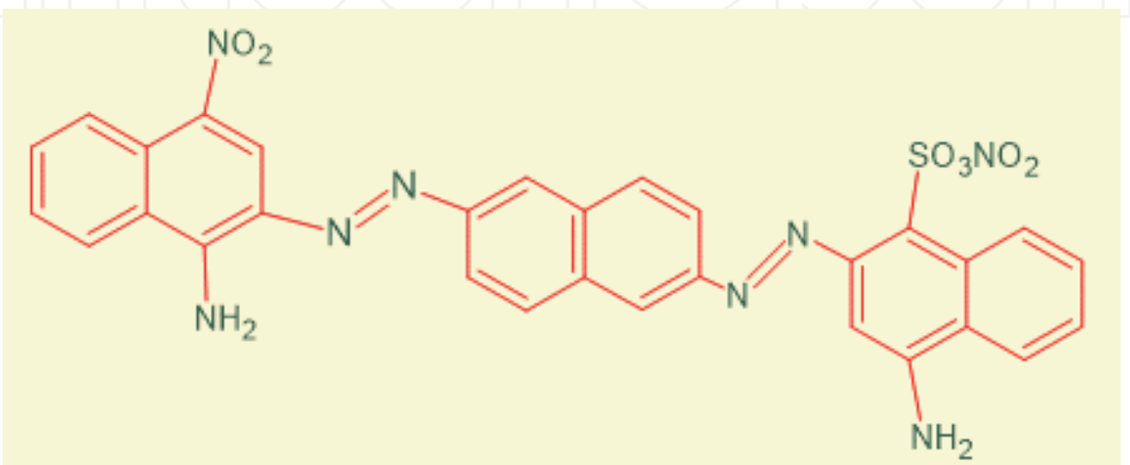


Figure 2.
Structure of TVR used in this experimentation.

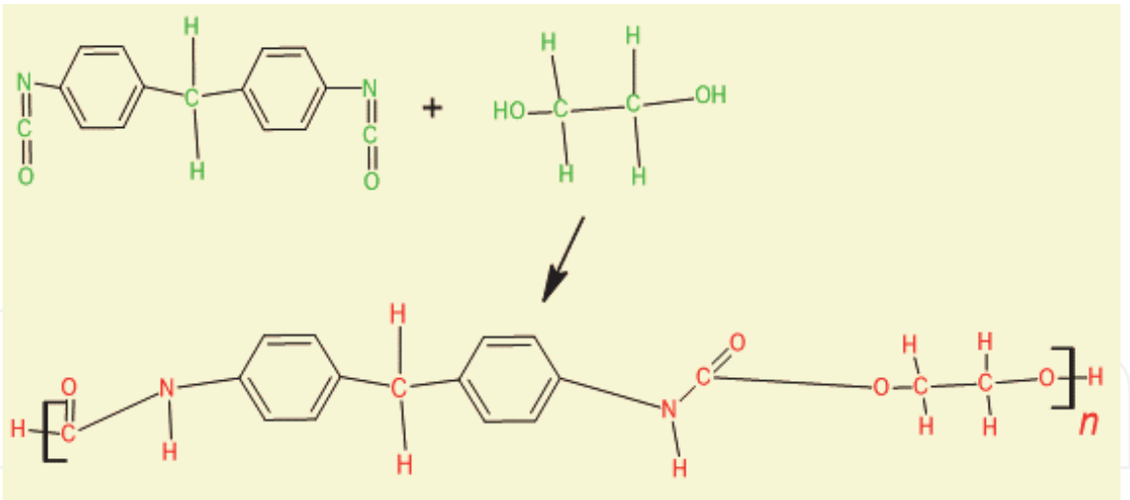


Figure 3.
Polymeric structure of TPU cross-linker used in this experimentation.

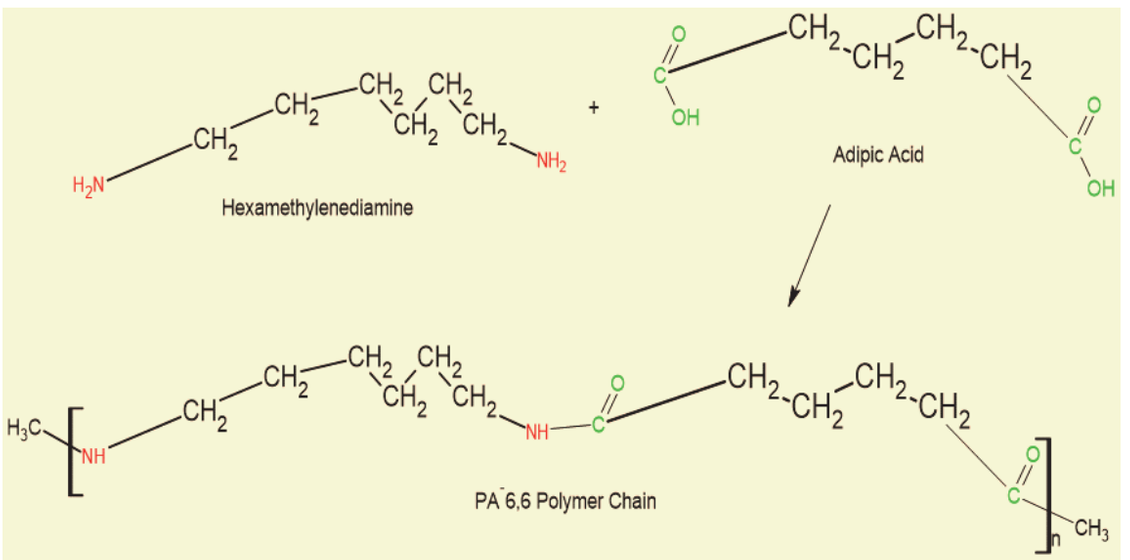


Figure 4.
Polymeric structure of PA-6,6 used in this experimentation.

4. Methods and preparation

Solution of TPU-DMF and its other variant of five more composite-mixed-complex formation of TPU-DMF were categorized and coded by CM-01 (TPU-DMF), CM-02 (CBP-TPU-DMF), CM-03 (TVR-TPU-DMF), CM-04 (CBP-TVR-TPU-DMF), CM-05 (NA-TVR-TPU-DMF), and CM-06 (CBP-NA-TVR-TPU-DMF).

4.1 Composite mixture-1

Tiny pellet of TPU (3%) was solubilized into DMF to form TPU-DMF solution, using a mini magnetic stirrer and an automatic shaker for 10 days in room temperature. The stirring and shaking periods were repeatedly checked and waited for maximum label of solubilization of TPU. The extended time was used for highest level of solubilization as no additional testing was implemented for this process of solubilization. TPU-DMF solution was added for each complex formation of CBP-TVR-NA.

4.2 Composite mixture-2

CBP 0.50 g and solution of 3% TPU-DMF were mixed in a beaker. It was kept on hot plate for 40 min at 80°C temperature for complex formation of CBP-TPU-DMF. TPU shell wall was kept just higher than the softening point. The droplet of TPU-DMF solution was poured into CBP until the viscous paste formation of CBP. It was continuously stirred in heating condition for making globule formation of CBP-TPU-DMF.

4.3 Composite mixture-3

The mixing process of TVR, 1.50 g and solution of 3% TPU-DMF were continued in a beaker. TVR-TPU-DMF was kept on hot plate for 40 min at 80°C temperature for complex formation. The droplet stirring process was followed for making bead formation of TVR-TPU-DMF. The droplet of TPU-DMF solution was poured into TVR until the viscous paste formation of TVR and continuously stirred for making bead formation of TVR-TPU-DMF.

4.4 Composite mixture-4

CBP 0.50 g, TVR 1.50 g, and solution of 3% TPU-DMF were mixed in a beaker and kept on hot plate for 40 min at 80°C temperature for complex formation of CBP-TVR-TPU-DMF. Firstly, the droplet of TPU-DMF solution was discharged into CBP until the viscous paste formation of CBP and continuously stirred for making bead formation of CBP-TPU-DMF. Consecutively and individually, the droplet of TPU-DMF solution was poured into TVR until the viscous paste formation of TVR and continuously stirred for making blob formation of TVR-TPU-DMF. Finally, a simultaneous complex formation was generated with the CBP-TPU-DMF and TVR-TPU-DMF (1:1) and formed a complex of CBP-TVR-TPU-DMF.

4.5 Composite mixture-5

TVR 1.50 g, NA (50%) and solution of 3% TPU-DMF were combined in beaker and heated for 40 min at 80°C temperature for complex formation of NA-TVR--TPU-DMF. The droplet of TPU-DMF and NA solution was poured into TVR until the viscous paste formation of TVR and continuously stirred for making bead formation of NA-TVR-TPU-DMF.

4.6 Composite mixture-6

CBP 0.50 g, TVR 1.50 g, NA (50%), and solution of 3% TPU-DMF were formed as paste in a beaker and kept on hot plate for 40 min at 80°C temperature for complex formation of CBP-NA-TVR-TPU-DMF. Firstly, the droplet of NA solution and the droplet of TPU-DMF (1:1) were poured into CBP for liquid phase oxidation of CBP and bead formation of CBP-TPU-DMF. The process was continued until the viscous paste formation, continuously stirred for making bead formation of CBP-TPU-DMF. Sequentially and separately, the droplet of TPU-DMF-NA was poured into TVR until the viscous paste formation of TVR and continuously stirred for making bead formation of NA-TVR-TPU-DMF. Finally, the paste of CBP-TPU-DMF and NA-TVR-TPU-DMF were combined for complex formation of CBP-NA-TVR-TPU-DMF.

4.7 Coating on PA-6,6 fabric

PA-6,6 fabric was cut into required sizes (width-3inch × length-6inch) was uncontaminated with dipping in deionized water, then dried 50 min at 80°C in a heating chamber, and then the fabric was relaxed and cooled for 30 min at room temperature. Back part of PA-6,6 fabric was wrapped with aluminum foil paper, having thickness less than 0.2 mm for creating the artificial plain surface on the backside of fabric. This method can be repeated and applied for different types of plain roller surface of industrial coating machine. The fabric ends were tightly attached and laid on coating plate by thin adhesive paper and then the coating roller was used for hand coating system. This method was followed repeatedly for three-stroke coating process for even dispersion of TPU-DMF and its other variant of five more composite-mixed-complex mixture on fabric surface. Decontaminated PA-6,6 was coated with TPU-DMF, a three-stroke coating process following first stroke coating-by second stroke coating and then third stroke coating for even dispersion of TPU-DMF. Similar coating process was thus carried out with CM-02 (CBP-TPU-DMF), CM-03 (TVR-TPU-DMF), CM-04 (CBP-TVR-TPU-DMF), CM-05 (NA-TVR-TPU-DMF) and CM-06 (CBP-NA-TVR-TPU-DMF). Also, for further research experimentation purpose, sequential overlapped coating of one formulation over other was also carried out by coating sequentially CM-2 (CBP-TPU-DMF) in first stroke coating process, and then CM-03 (TVR-TPU-DMF) coating was made on it by second stroke coating and finally then CM-04 (CBP-TVR-TPU-DMF) was coated on it by third stroke coating process. Similarly, CM-02 (CBP-TPU-DMF) was coated by first stroke coating process and then CM-03 (TVR-TPU-DMF was coated by second stroke coating and finally CM-06 (CBP-NA-TVR-TPU-DMF) was sequentially coated by third stroke coating process. All the coated PA 6,6 fabrics were dried at 60°C for 60 min to proceed for testing.

5. Testing methods

5.1 Color measurement spectrophotometer

CIE, color parameters (L*, a*, b*) were measured by Hunter lab reflectance spectrophotometer, Color Flex EZ; model, 45/0 LAV; under testing conditions with geometry, 45°/0°; viewing area, large; D65 illumimnant/10°standard observer; room temperature, 18°C. This hunter lab illuminant spectrophotometer uses a xenon flash lamp to illuminate the test specimen, PA-6,6. The tonal variation of PA 6,6 fabric was subjected to colorimetric evaluation for determining CIE color coordinates L*, a*, b* values. The Hunter Lab reflectance spectrophotometer was calibrated in terms of highest darker and highest lighter by using standard black and white standard, for checking and matching standard values kept in machine software. To ensure sample opaqueness by minimizing the transparency of incident light; test specimen, fabric size (width-3inch × length 6-inch) was single folded in lengthwise (width 3-inch × length 3-inch) for placing on reflectance port.

5.2 Fourier transform infrared spectrometry

NIR scanning of treated and untreated PA-6,6 fabric was performed by FTIRS. A NIR background was standardized under diffuse reflection standard. Every sample is covered by sample cup to create reflection environment under a specified black standard, which is termed as "spectralon reflection." The sample port has sapphire/crystal window to capture reflection of sample. Machine-specified glass vial was

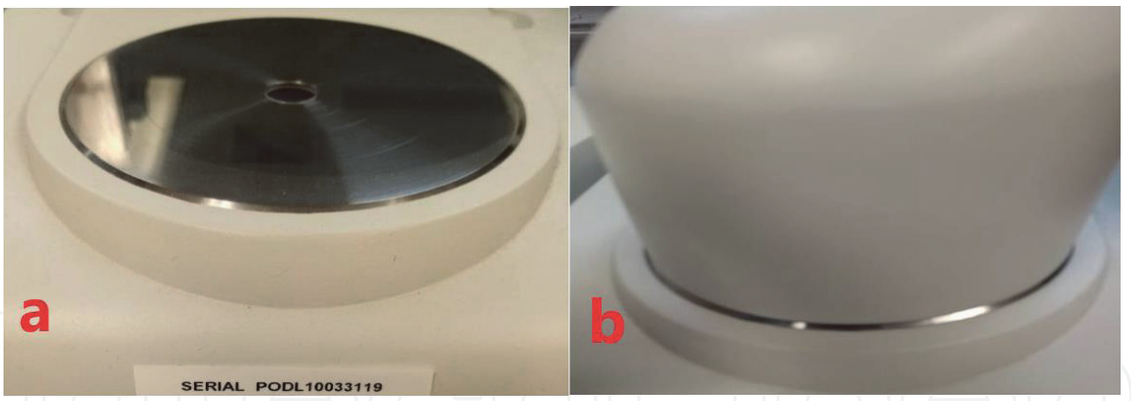


Figure 5.
Front view of FTIRS-NIR (a) uncovered diffuse sample port, (b) covered sample port with standardized black reference.

used for powder sample measurement of CBP-TVR. **Figure 5a** shows the sapphire window-sample port of FTIRS-NIR. **Figure 5b** shows the sample scanning condition under machine specified black standard.

5.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) image was captured by TM 4000Plus model, Tabletop SEM, HITACHI, Japan. 15 KV electron acceleration was selected for every scanning of SEM. 100 magnification was performed for all image except NA treated fabric. NA-TPU-DMF and NA-TVR-TPU-DMF were captured at 25 magnifications to connote TPU effect in NA-CM-PA-6,6. Carbon conductive black tape was used for each sample mounting.

6. Results and discussion

6.1 Characterization and structural analysis by SEM

Figure 6, uncoated PA 6,6 fabric (a); TPU-DMF coated PA 6,6 fabric (b); CBP-TPU-DMF coated PA-6,6 fabric (c); TVR-TPU-DMF coated PA-6,6 fabric (d); CBP-TVR-TPU-DMF coated PA-6,6 fabric (e); NA-TVR-TPU-DMF coated PA-6,6 fabric (f); NA-CBP-TVR-TPU-DMF coated PA-6,6 fabric (g); blended CBP in water (h); blended CBP after 24 hour precipitation (i); blended CBP after 48 hour precipitation (j); 3% TPU in DMF (k), 3% TPU in DMF after addition of five drop NA; 5% of 70% NA (l); solidification slice of TPU-DMF in the presence of NA (l); SEM magnification of CBP particle (m) and its color thresholding structure of CBP particle (n); particle size of CBP (o); SEM magnification of TVR particle (p) and its color thresholding image of particle size (q); SEM magnification of PA 6,6 uncoated fabric (r); TPU-DMF coated PA 6,6 fabric (s) and its color thresholding image to refine TPU-DMF on fabric surface (t); CBP-TPU-DMF coated PA-6,6 fabric (u) and its color thresholding image to signify TPU-DMF on fabric surface (v); TVR-TPU-DMF coated PA-6,6 fabric (w) and its color thresholding image to identify TPU-DMF on fabric surface (x); CBP-TVR-TPU-DMF coated PA-6,6 fabric (y) and its color thresholding image to signify TPU-DMF on fabric surface (z); NA-TPU-DMF coated PA-6,6 fabric (z_1); NA-TVR-TPU-DMF coated PA-6,6 fabric (z_2); NA-CBP-TVR-TPU-DMF coated PA-6,6 fabric (z_3).

Figure 6 (i, j), water medium diluted CBP has been shown to signify the dispersibility of raw CBP. 0.5gm CBP was blended (30 minutes) with 150 ml

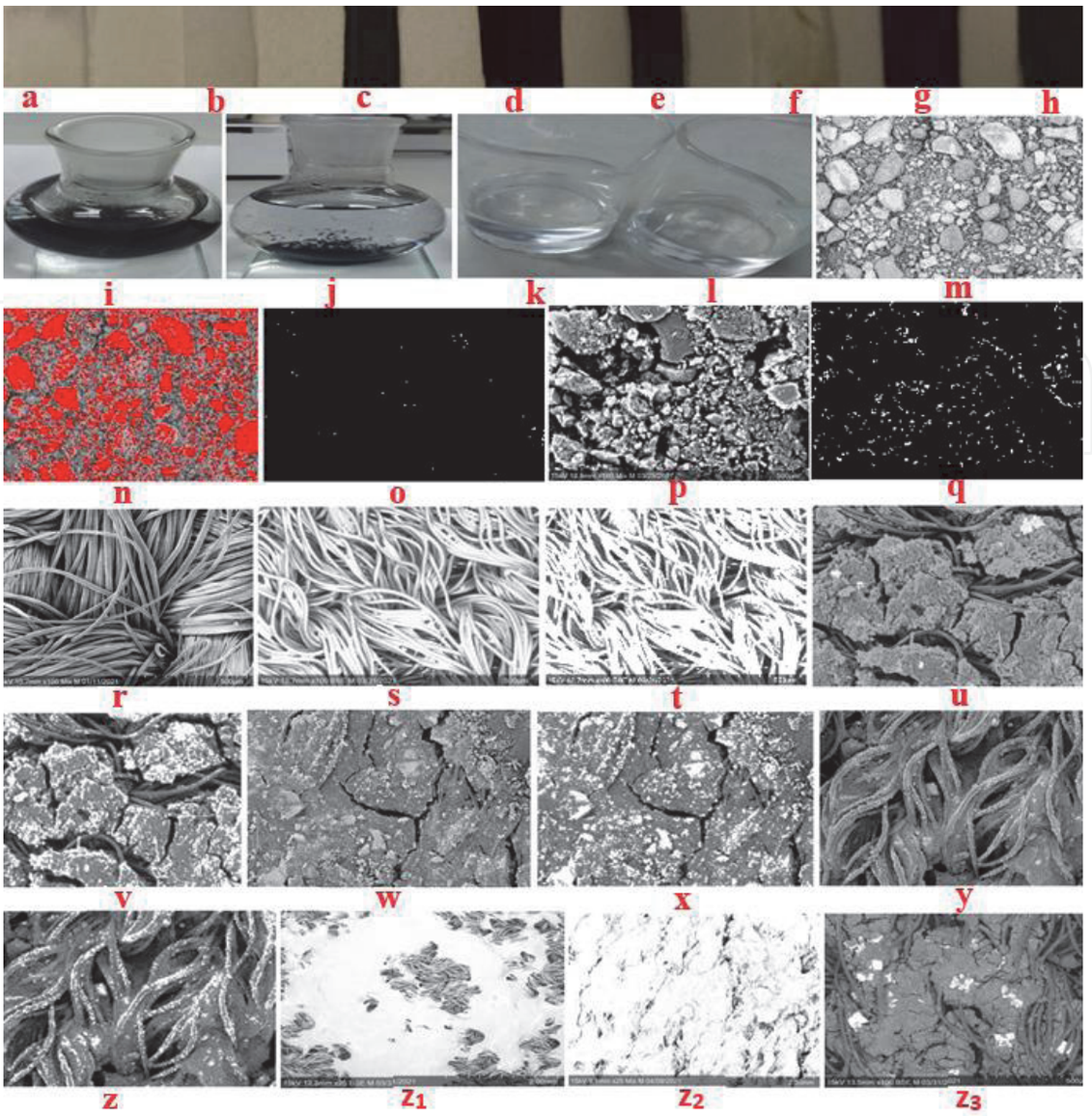


Figure 6.
Photograph of treated and untreated fabric (a-h), CBP and TPU-DMF derivative solution (i-l), SEM and color thresholding image of treated and untreated PA 6,6 fabric (m-z_3).

deionized water. The solution showed a precipitation/aggregation after keeping 24 and 48 hours in non-shaking condition. **Figure 6** (m) shows the structure of CBP. CBP particles are aggregated in different direction like a net structure which is demonstrated by red threshold, imageJ, **Figure 6** (n). The magnified cross section of CBP signifies the particle size, water insolubility, and randomly oriented micro-structure of surface for diffuse reflection due to surface roughness, **Figure 6** (m-q). Particle size of CBP denotes the higher degree of cracking on CBP coated PA-6,6 fabric rather than TVR coated surface, **Figure 6** (u-x). The existing of CBP-TPU-DMF has been clearly identified on PA 6,6 coated fabric, **Figure 6** (u, v, z_3). The cementing of CBP-TPU-DMF-PA-6,6 is higher in comparison with NA-CBP-TPU-PA-6,6. CBP-TPU formed a darker appearance due to higher prominence of black region on CBP-coated surface. CBP coating with TPU-DMF binder showed a cross-linking in CBP-TPU-DMF-PA-6,6. The functional group of CBP (-COOH) and the functional group of TPU (-NHCO) was formed a CBP-TPU matrix on the surface of PA-6,6 fabric. **Figure 6** (t, v, x, z, z_1, z_2, z_3), TPU was visualized in SEM image as whitish color surface. The prominence of TPU was recorded as minor when it was formed matrix with CBP. TPU binder was almost uniformly distributed on PA-6,6 fabric surface, **Figure 6** (t-z, z_3). TPU-CBP was implanted and well dispersed on

PA-6,6 surfaces. **Figure 6** (k, l), NA-TPU-DMF was also characterized in the presence of NA and TPU was showed freezing tendency. The application of TPU on PA-6,6 fabric was also confirmed by SEM, **Figure 6** (z_1, z_2).

6.1.1 Coupling of CM and SEM evidence of material suitability for visible-NIR camouflage

Figure 6 (o- z_3) shows the evidence of almost suitability of CBP material. The simultaneous applications of NA-TPU-CBP-TVR on PA-6,6 fabric surface have been confirmed by SEM image. The structural representation and coupling with similar functional groups have been revealed with individual coupling reactions with PA-6,6 **Figures 7–12**. Oxidized and aqueous CBP have amide group. PA-6,6 has also similar group, thus it may create a coupling of CBP-PA-6,6. CBP has amine group and TVR has also amine group. There is a possibility of bonding between CBP-TVR. Similarly, CBP has carbonyl group and TPU has also carbonyl group, thus CBP-TPU moiety may form in CBP modified PA-6,6 fabric. Carbonyl carbon of CBP may be bonded with two hydrogen atoms of TPU. Hence there is possibility of cross-linking. TPU may be adsorbed by CBP and dispersed the carbon black due to its structural formation of steric hindrance.

6.1.1.1 Coupling of TPU-DMF treated PA-6,6

Figure 6 (s, t) shows that polymeric coupling of PA-6,6-TPU, which are bonded with common functional group carbonyl (**Figure 7**). Structural resemblance of carbonyl and amine functional group in TPU-PA-6,6 may show the evidence of yellowish and greenish illumination on TPU treated PA-6,6 and without treated PA-6,6.

6.1.1.2 Coupling of CBP-TPU-DMF treated PA-6,6

Figure 6 (u, v) shows the coupling among PA-6,6-CBP-TPU. CBP shows multifunctional group including carboxyl, hydroxyl, aldehyde, carbonyl, ether, and it may have other functional group including color forming groups (**Figure 8**). CBP-TPU has amino group and carbonyl group. PA-6,6 has amino group and carbonyl

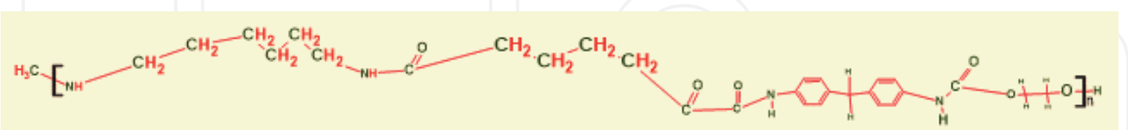


Figure 7.
Coupling of TPU-DMF treated PA-6,6.

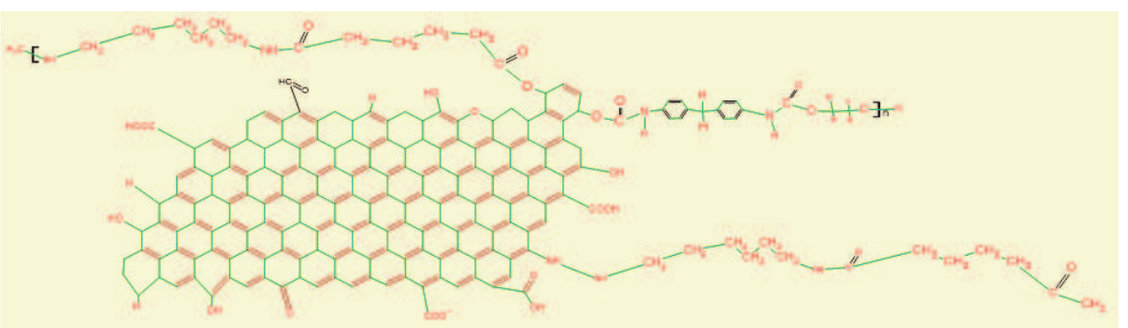


Figure 8.
Coupling of CBP-TPU-DMF treated PA-6,6.

group. Amino group and carbonyl group remaining PA-6,6 surface may generate reddish and yellowish hue but the reflectance of yellowish may be weakened and, it may be turned to bluish coordinates. So, the mechanism of tonal variation on textile surface/hiding of color hue may have occurred due to multidimensional color reflection of different hue as CBP has various numbers of functional groups for different color formation on same surface. Structure of CBP surface may also vibrate the camouflage concept of illumination due to spherical surface of CBP. COOH, carbonyl group, and OH group presence in CBP may reflect reddish hue. Amine group may be an indication of yellowish hue. Therefore, color combination of CBP may show darker hue by reflecting almost black hue. When any group with colorant of yellow, blue, and red are mixed with CBP, it may hide the chromatic intensity of added colorant and makes the dull shade to the observer due to remaining multifunctional and multicolored forming group. The multifunctional mechanism of hiding tendency of color hue of CBP may be functioning as key principle of camouflage coloration on textile substances.

6.1.1.3 Coupling of TVR-TPU-DMF treated PA-6,6

Figure 6 (w, x) shows the coupling of amide group among PA-6,6-TPU-TVR (**Figure 9**). TVR dyes has nitro group, amino group, and azo group. Nitro group may create blueish/yellowish hue, azo group may contain red/yellowish hue and amine group may prominent the yellowish reflection on the surface.

6.1.1.4 Coupling of CBP-TVR- TPU-DMF treated PA-6,6

Figure 6 (y, z) represents the NH coupling between CBP and PA-6,6 (**Figure 10**). Benzene coupling may occur between CBP and TVR. Correspondingly

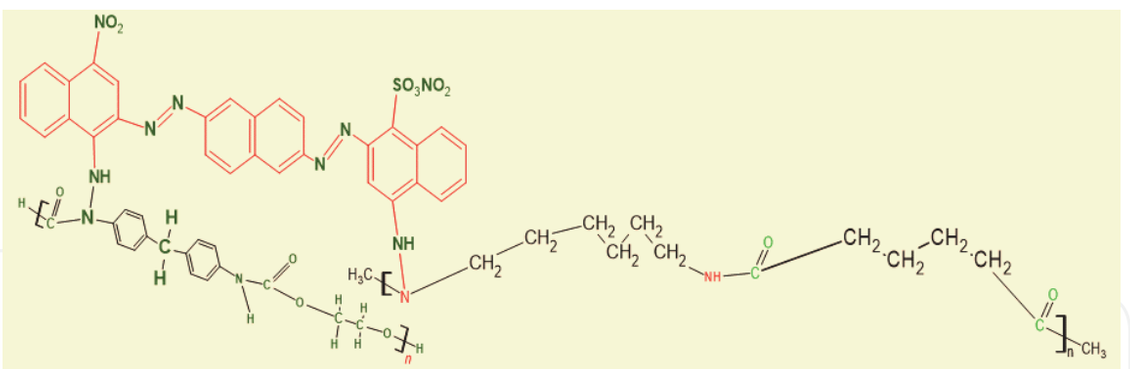


Figure 9.
Coupling of TVR-TPU-DMF treated PA-6,6.

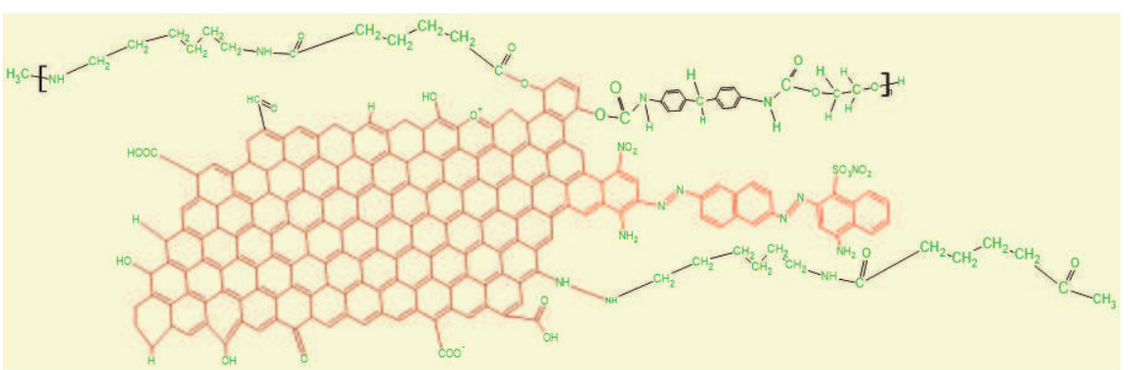


Figure 10.
Coupling of CBP-TVR- TPU-DMF treated PA-6,6.

carbonyl bonding is also evidenced between TPU and PA-6,6 due to structural view in SEM magnification. TVR dyes has nitro group, azo group and amino group. PA-6,6 and TPU has also amino group. Nitro group in TVR may create bluish and yellowish hue, azo group depicts red/yellowish hue and amine group may enhance the reflection of yellow hue. CBP and TVR has similarity in benzene group and amino group. TVR encompasses nitro group and azo group, which may reflect bluish and yellowish tone, azo group may illuminate red/yellowish hue and amine group may accelerate the yellow color reflection. Hydrophilic coupling between amine group of TVR and PA-6,6 may not be happened due to absence of hydrophilic vehicle NA. CBP has COOH, OH group, amino group, and carbonyl group, which may create chromatic change of color hue with another functional group.

6.1.1.5 Coupling of NA-TVR-TPU-DMF treated PA-6,6

Figure 6 (z_2) shows that amine group of TVR has related to both PA-6,6 and TPU, it seems the structural similarity (**Figure 11**). TVR has nitro group. Amino group of PA-6,6 and TPU may create a good color combination in NA-TVR-TPU-DMF when oxidized CBP has not been used in this process of coloration. For comparison, the reaction of oxidized carbon has been remarked with arrow sign connected with nitro group. In this coupling, there is no function of oxidized carbon due to missing of CBP in CM.

6.1.1.6 Coupling of NA-CBP-TVR-TPU-DMF treated PA-6,6

Figure 6 (z_3) shows amide linkage between CBP and PA-6,6 (**Figure 12**). Amine bonding may create between TVR and PA-6,6. Carbonyl bonding may form among CBP-TPU-PA-6,6. Oxidized carbon produces NO_2 and it has been showed with

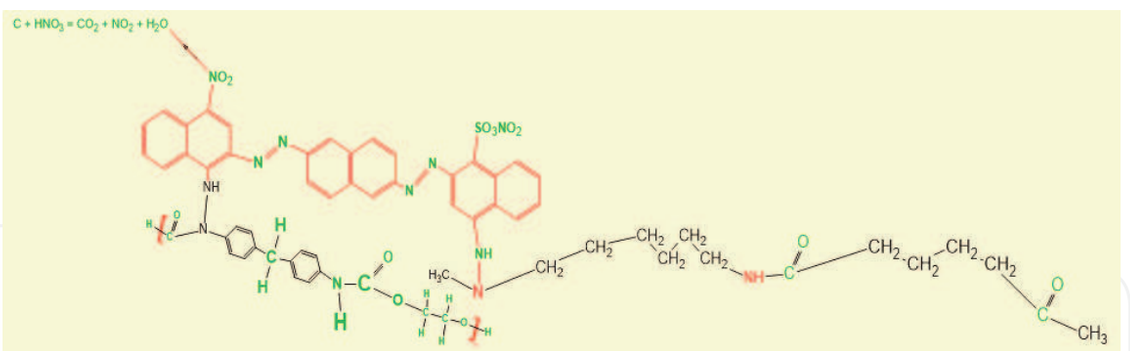


Figure 11.
Coupling of NA-TVR-TPU-DMF treated PA-6,6.

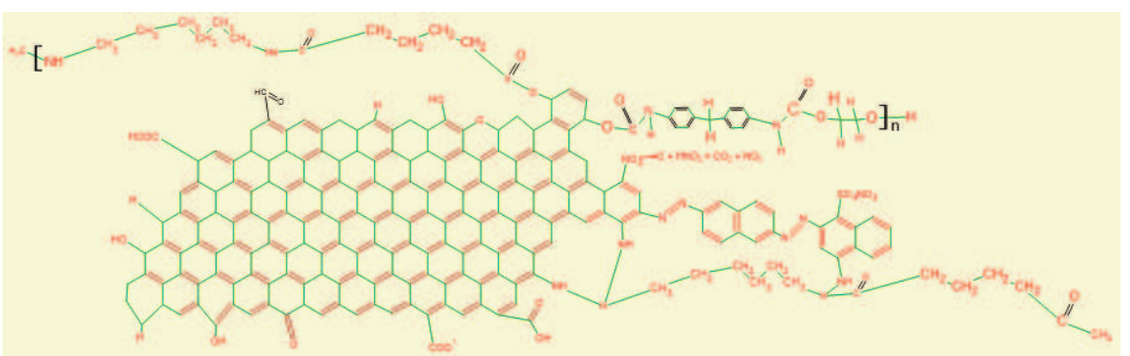


Figure 12.
Coupling of NA-CBP-TVR-TPU-DMF treated PA-6,6.

arrow marked to mention the similar group of TVR dyes (NO_2). The structure of oxidized carbon may be changed due to NA oxidation of CBP. The mechanism may influence the altering of reflection/wavelength in visible-NIR spectrum. The simultaneous combination of oxidized carbon and CBP modified PA-6,6 may replace the surface reflection significantly. The color forming functional group has been predicted the changing factors of chromatic hue. PA-6,6 has carbonyl group and amine group. TPU has also carbonyl group. Remaining unusual functional group of CBP like COOH, OH may reflect reddish hue, carbonyl group may reflect greenish/yellowish hue and amine group may illuminate greenish/reddish hue. Spherical shape of CBP may hide the real illumination of nitro and azo group in TVR when nitro group may reflect bluish and yellowish tone and azo group may illuminate red/yellowish hue. Hence the actual prominence of hue is being decisively changed/hided by the multifunctional tonal group of CBP.

6.2 Camouflage and chromatic analysis in visible spectrum

Established Beer–Lambert law [35] of optical absorption of material, $A = \varepsilon lc$, A = optical absorption of materials, ε = absorptivity of the materials, l = optical path length, c = concentration of the materials. The Beer–Lambert law can be implemented for the optical absorption on PA-6,6 fabric surface in different wavelength. The variation of optical absorption of CBP can be predicted for the feasibility of camouflage coloration. Optical absorption on PA-6,6 fabric surface versus replacement of CIE color hue is proportionally related for camouflage coloration. Higher degree of optical absorption depicts the reduced intensity of chromatic hue. In this experimentation, A = optical absorption of PA-6,6 fabric surface, ε = absorptivity of CBP-TVR-TPU, I = optical path length in 400–700 nm and c = concentration of CM which are TPU-DMF, CBP-TPU-DMF, TVR-TPU-DMF, CBP-TVR-TPU-DMF, NA-TVR-TPU-DMF, NA-CBP-TVR-TPU-DMF. CIE optical absorption and reflection of chromatic hue have been studied in optical path length, 400–700 nm. The concept demonstrates that "more optical absorption on textile surface = less reflection on textile surface = altering the chromatic hue = deceiving the target detection". Therefore, CBP can create chromatic variation on textile surface and confuse the target detection to the observer. But optical path length 400–700 nm and concentration of surface CBP materials can alter the chromatic behaviors of PA-6,6 fabric. Camouflage coloration was observed in complex formation of CBP for surface hue modification of PA 6,6 fabric. The color outcome was identified based on light absorption and reflection of CIE color hue, L^*, a^*, b^*. The reflection changing of CBP-NA-TVR-TPU-DMF treated PA-6,6 fabric was remarked in terms of CIE color coordinates. CBP-NA-TVR-TPU-DMF treated fabric showed comparatively less reflection of light and color hue hiding tendency.

6.2.1 Spectrophotometric color comparison of treated PA-6,6 and untreated PA-6,6

Figures 13–16 illustrate that CBP-TPU-DMF, CBP-TVR-TPU-DMF and NA-CBP-TVR-TPU-DMF treated PA-6,6 fabric modified the light absorption and intensity of chromatic hue in CIE L^*, a^*, b^* due to existence of CBP. The value of L^*, a^*, b^* represents higher light absorption and minor reflection of chromatic hue, which may be elucidated the reflection changing of CBP modified PA-6,6 surface. The moderation of chromatic hue intensity identifies camouflage categories of reflection in visible range due to having a minimum value of lightness (L^*), minimizing the value of red-green coordinates (a^*) and blue-yellow coordinates (b^*). **Figures 13–15** demonstrate that NA oxidized CBP shows maximum absorption of light than other CBP treated PA-6,6. NA oxidized NA-CBP-TVR-TPU-DMF reveals

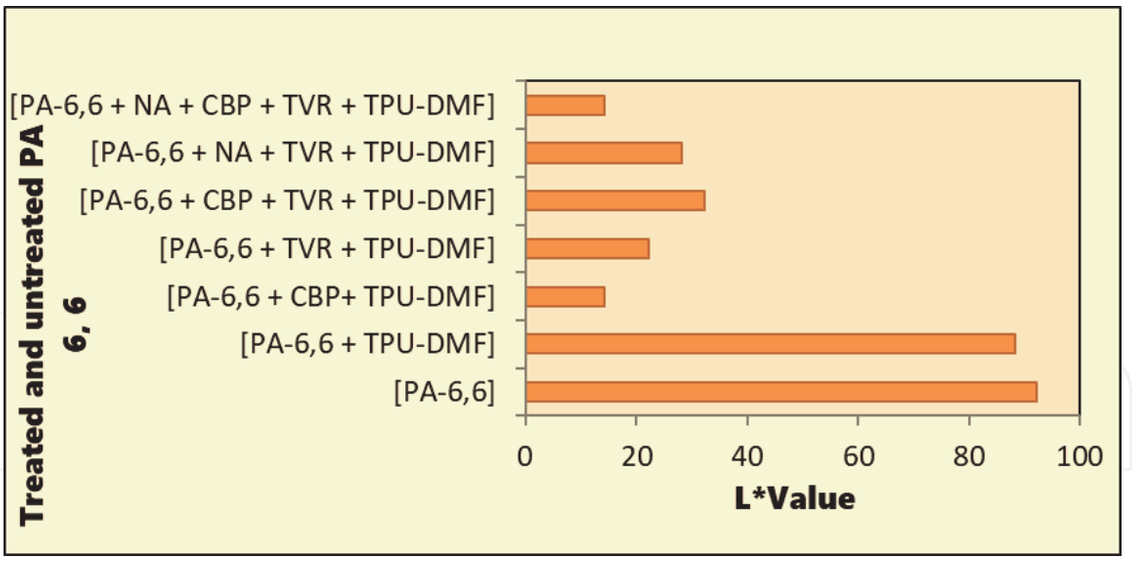


Figure 13.
CIE comparison of lightness hue (L) of treated and untreated PA-6,6 fabric.*

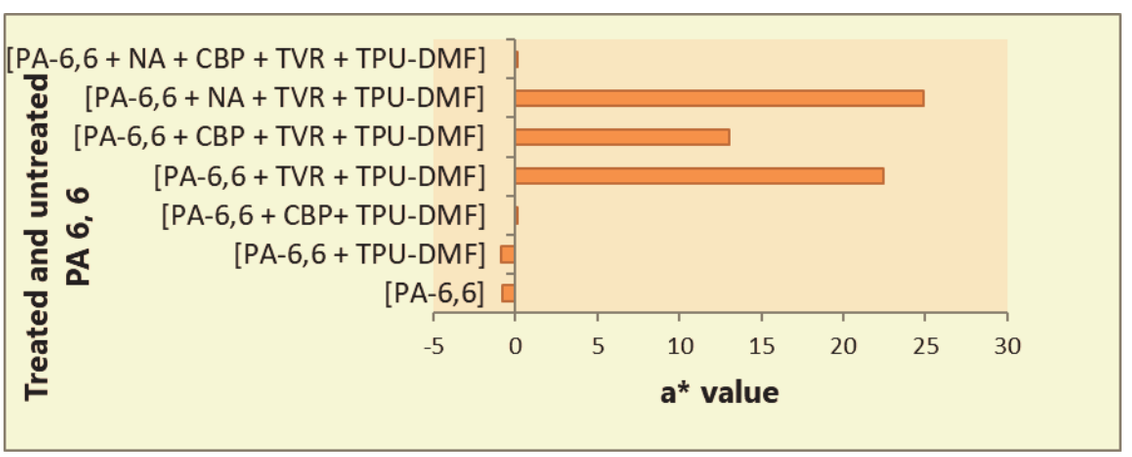


Figure 14.
CIE comparison of greenish/reddish hue (a) of treated and untreated PA-6,6 fabric.*

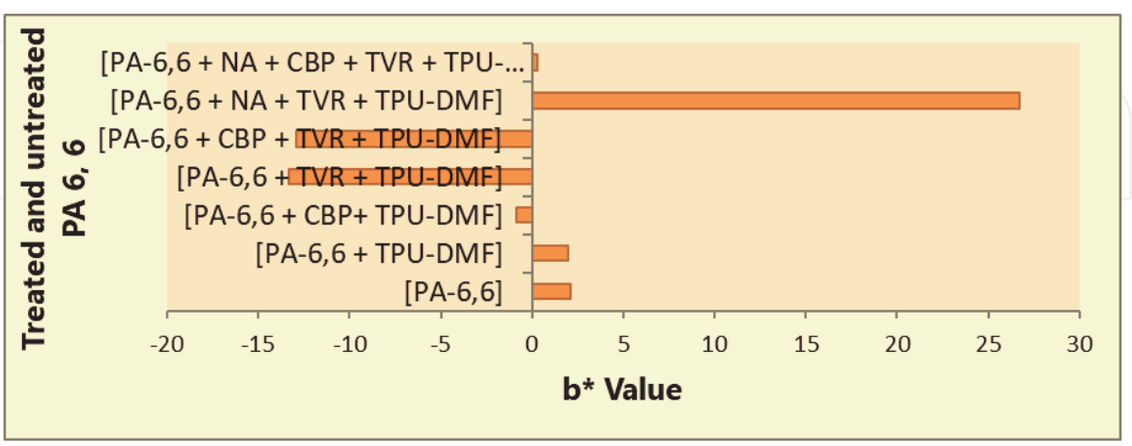


Figure 15.
CIE comparison of bluish/yellowish hue (b) of treated and untreated PA-6,6 fabric.*

CIE, L^* = 14.33, a^* = 0.15, b^* = 0.30 in wavelength, 400–700 nm. CBP is practically insoluble in water. In NA-CBP-TVR-DMF, NA is functioning to form hydrophilic transformation of CBP-TVR, as well as same time TPU-DMF is performing as artificial cross-linker between CM and PA-6,6 without influencing color reflection of any other component in CM. Thus, oxidized CBP molecules may be hided the

sulfonated group of TVR dyes in NA-CBP-TVR-TPU-DMF mixture whereas CBP-TVR-TPU-DMF does not exhibit hiding of red and blue color hue due to absence of NA and lacking hydrophilic reaction. CM of CBP-TPU-DMF and NA-CBP-TVR-TPU-DMF exhibit nearest of neutral value in three-dimensional CIE color coordinates. CBP-TVR-DMF mixture reveals the positive value of a^* remaining reflection of reddish hue although theoretically the CM cannot make a complex due to absence of NA. Here, NA is not acting as hydrophilic vehicle of CBP in this CM. A proper reaction of TVR-CBP colorant may be held in between polyamide-6,6 and NA-CBP-TVR-TPU-DMF. In general theory of chromaticity, the color channel, $a^* = 0$ and $b^* = 0$ displays the true natural/neutral black color. The color wheel of NA-CBP-TVR-TPU-DMF shows $a^* = 0.15$, $b^* = 0.30$, therefore CBP has a propensity to neutral black. Similarly, NA free mixture of CBP-TPU-DMF and NA-CBP-TVR-TPU-DMF may prove minimum L^* value due to having higher absorption of light and very minimum reflection of light. Therefore, CBP modified PA-6,6 may create a deceiving environment of color hue to the observers. Thus, a neutral or minimizing tendency of a^* and b^* value can create the effect of hiding reddish hue which have an outcome of declining reflection of color molecules and increasing the absorbency of light. CBP modified PA-6,6 fabric surface may conceal the reflection of remaining TVR coloring molecule of red, green, blue, yellow. CBP treated surface may be decisively reduced the formation of cone shaped receptor for visible range of color vision. Rough surface of CBP treated PA-6,6 may generate the properties of diffuse reflection. D65 light source measurement of the reflectance characteristics of CBP is the key phenomenon of camouflage have been demonstrated in visible range 400–700 nm.

6.2.1.1 Spectrophotometric color combination of untreated PA-6,6 and TPU-DMF-PA-6,6

Figures 13–16; TPU-DMF treated PA-6,6 fabric and untreated PA-6,6 fabric was compared for identification of three-dimensional chromatic hue (L*, a*, b*) and its effects on PA-6,6 fabric surface. Spectrophotometric color combination of PA-6,6 shows greenish (a* = −0.79) and yellowish (b* = 2.1) hue, which are the nearest of

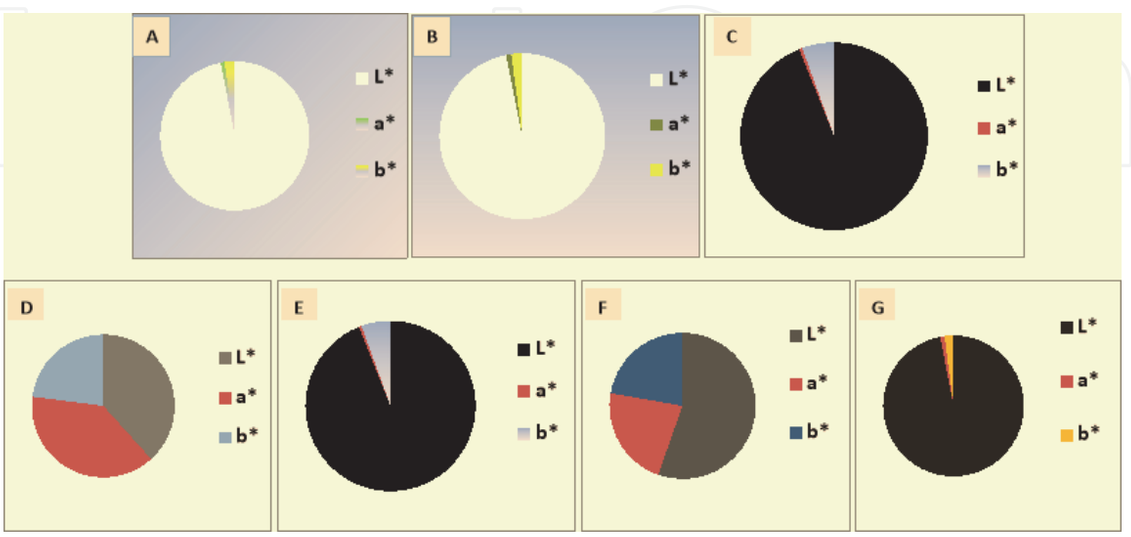


Figure 16.
Tristimulus intensity for variations and comparison of CIE L, a*, b* and representation of spectrophotometric color combination on a (PA-6,6), B (PA-6,6 + TPU-DMF), C (PA-6,6 + CBP+ TPU-DMF), D (PA-6,6 + TVR + TPU-DMF), E (PA-6,6 + CBP + TVR + TPU-DMF), F (PA-6,6 + NA + TVR + TPU-DMF), G (PA-6,6 + NA + CBP + TVR + TPU-DMF).*

neutral hue. A maximum value of L* = 92.29 indicates almost white color in gray hue on fabric surface. Hence color combination of PA-6,6 indicates the maximum reflection of hue. Oppositely TPU-DMF treated PA-6,6 depicts greenish (a^* = −0.90) and yellowish (b^* = 1.96) hue, which also identify the nearest of neutral hue. A maximum value of L^* = 92.29 indicates almost white color/gray hue on the surface of fabric. Therefore, the color combination of TPU-DMF treated PA-6,6 also remarks the maximum reflection in CIE color coordinates. So, it can be compared that the reflection properties of CIE color hue are almost nearest/similarity in untreated PA-6,6 and TPU-DMF treated PA-6,6 fabric. It can be strongly said that TPU-DMF has minor effect on color changing. This study can be simply recommended for application of TPU-DMF for cross-linking of camouflage materials on textile surface.

6.2.1.2 Spectrophotometric color combination of CBP-TPU-DMF-PA-6,6

Complex application of CM-2 shows red (a^* = 0.08) and bluish (b^* = −0.84) hue which are the nearest of neutral hue. A minimum value of L^* = 14.21 have been pointed to almost black color tone on the surface of PA-6,6 fabric. CBP-TPU-DMF treated fabric shows less reflection of color hue. It may clarify gray hue, which is tending to black and hiding the base color tone (yellow and green) of PA 6,6 fabric surface, which is replaced with opposite coordinates in color wheel.

6.2.1.3 Spectrophotometric color combination of TVR-TPU-DMF-PA-6,6

Complex application of CM-3 states reddish (a^* = 22.45) and bluish (b^* = −13.30) hue on PA-6,6 fabric. A maximum value of L^* = 22.22 signifies the actual violet color of TVR on the surface of fabric. TVR added CM-03 accelerates the reddish and bluish hue.

6.2.1.4 Spectrophotometric color combination CBP-TVR-TPU-DMF-PA-6,6

CBP added CM-04 indicates minor decreasing the R/color hue in reddish and bluish hue although it seems the combination of CBP-TVR was not properly dispersed on the surface due to absence of hydrophilic vehicle, NA. Spectrophotometric color combination shows reddish (a^* = 13.06) and bluish (b^* = −12.95) hue on fabric surface. A maximum value of L^* = 32.34 indicated the hiding tendency of reddish and bluish hue on the surface of fabric when CBP was mixed in CM. Even though proper reaction of complex formation was not found due to absence of NA vehicle.

6.2.1.5 Spectrophotometric color combination NA-TVR-TPU-DMF-PA-6,6

NA added CM-05 shows that reflection of color hue increases. Spectrophotometric color combination of NA-TVR-TPU-DMF depicts reddish (a^* = 24.90) and yellowish (b^* = 26.75) hue. A maximum value of L^* = 28.2 indicates the increasing of reddish and bluish hue when NA was mixed in the CM. This is clarified that dyes molecules showed higher affinity with PA-6,6 when NA was mixed with TVR dyes.

6.2.1.6 Spectrophotometric color combination of NA-CBP-TVR-TPU-DMF-PA-6,6

CBP added CM-06 may be concealed the red and yellow hue of PA-6,6 surface when gray color wheel tends to black color hue. It seems that NA is functioning as

hydrophilic transformation of CBP-TVR into PA-6,6. Combination of CBP mixture shows more absorbency of light as per less value of L^*. CBP modified PA-6,6 may be influenced the illumination of reflection of light/color hue. CBP modified PA-6,6 has an impact of camouflage creation and hiding factor of reddish and yellowish color under practical observation of CIE chromaticity-reflection mechanism. CBP may be acted as diminish behavior of reflection on PA-6,6 fabric surface which can create a camouflage effect of fabric under consideration CIE, L^*, a^*, b^*. It can be said that NA increased the thixotropic properties of CBP-TVR colorant for good level of CBP-TVR dispersion.

6.3 Camouflage and reflection comparison in NIR spectrum

Maximum reflection percentage of CM has been summarized in **Figure 17** for comparison among raw CBP, untreated and treated PA-6,6 fabric. The original FTIR spectra has been cited in supporting information, **Figures S1** and **S2**. FTIRS was used to reveal camouflage phenomenon of CBP in terms of low reflection principle in NIR, 1000–2500 nm. The range is covered by hyperspectral camera for target detection. CBP almost absorbs all spectrum in NIR, the intensity of color forming group is very minor for target identification. A narrow reflection profile is visualized for FTIRS scanning of raw CBP and CBP treated PA 6,6 fabric. CBP treated PA 6,6 fabric was detected as low reflection materials for camouflaging in NIR. CBP has maximum number of absorptions, and it has minimum intensity which may generate low reflection chromatic signal against combat background in NIR. Reflection of CBP spectra is always lower than any other combination of PA-6,6 fabric. Comparatively TVR combination cannot decline the reflectance of PA-6,6-TPU-DMF. CBP-TVR combination can highly decrease the reflection of PA-6,6-TPU-DMF. This concept of CBP-reflection can be implemented for synthetic dyes combination with CBP. It has been clearly signified that CBP treated fabric may act as target concealment under low reflection principle in NIR spectrum.

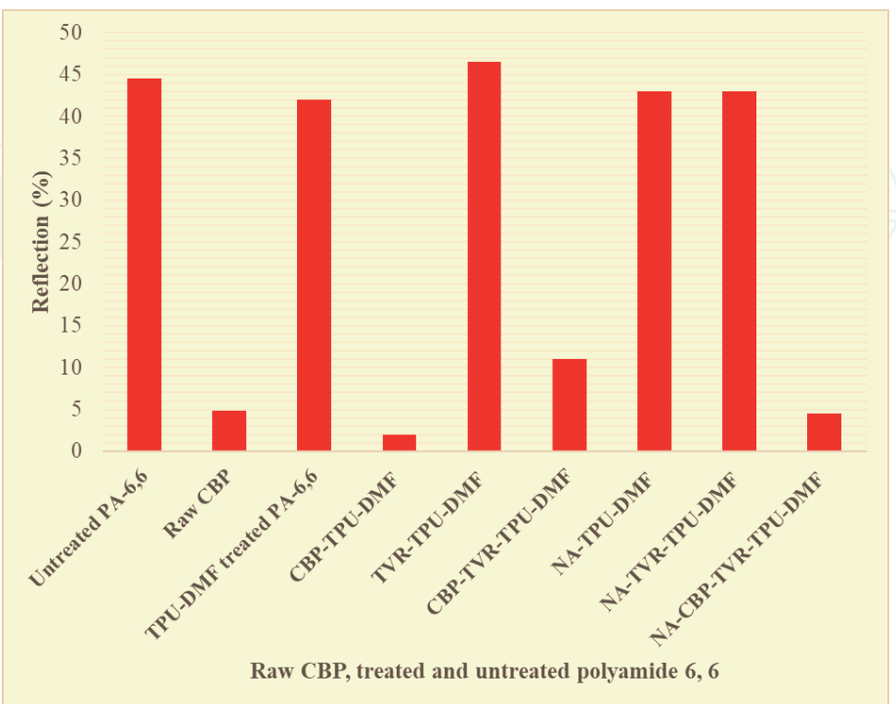


Figure 17.
Comparison of maximum reflection (%) in NIR spectrum.

7. Conclusion

L* coordinates reflect the lightness of color intensity to the observers ranges from 0 (completely black) to 100 (completely white). The luminous intensity and degree of lightness can be perceived by the target observers in remote sensing device. The amount of CBP adsorbed on PA-6,6 surface controls a* coordinates (red/green) and b* coordinates (yellow/blue), which identify the lightness of color perception for CBP modified PA-6,6 fabric to the observers. Hence, CBP influences a* coordinates for reflection of red or green hue to the target observers. Correspondingly CBP also effects on b* coordinates, which reflect yellow or blue color tone to the observers. The intensity of object reflection modifies the perception of red, green, blue, yellow color hue to the observers. Furthermore, CBP treated PA-6,6 fabric may generate diffuse reflection to hide the color hue of combat background. SEM, color measurement spectrophotometer and FTIRS have been confirmed the low reflection coloration of PA-6,6 fabric both in visible-NIR spectrum. The experimentation on CBP based camouflage textiles can confirm the feasibility of camouflage properties development on textile substances. So, it can be suggested that CBP can be implemented for camouflage coloration of textile materials in terms of low reflection principle. CBP can be combined with synthetic dyes of camouflage design for camouflage textiles in simultaneous spectrum probe in visible-NIR. CBP may be accepted for versatile applications of weapon/vehicle coloration in terms of low reflection principle of camouflage coloration. TPU can also be recommended as a suitable cross-linking agent due to transparent property of TPU without influencing the reflection properties of CBP on PA-6,6 fabric.

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Abbreviations

CBP	Carbon black pigment
CM	Composite mixture
NR	Near infrared
NA	Nitric acid

TVR	Telon violet 3R
TPU	Thermoplastic polyurethane
DMF	N, N-dimethylformamide
PA-6,6	Polyamide-6,6

Appendix

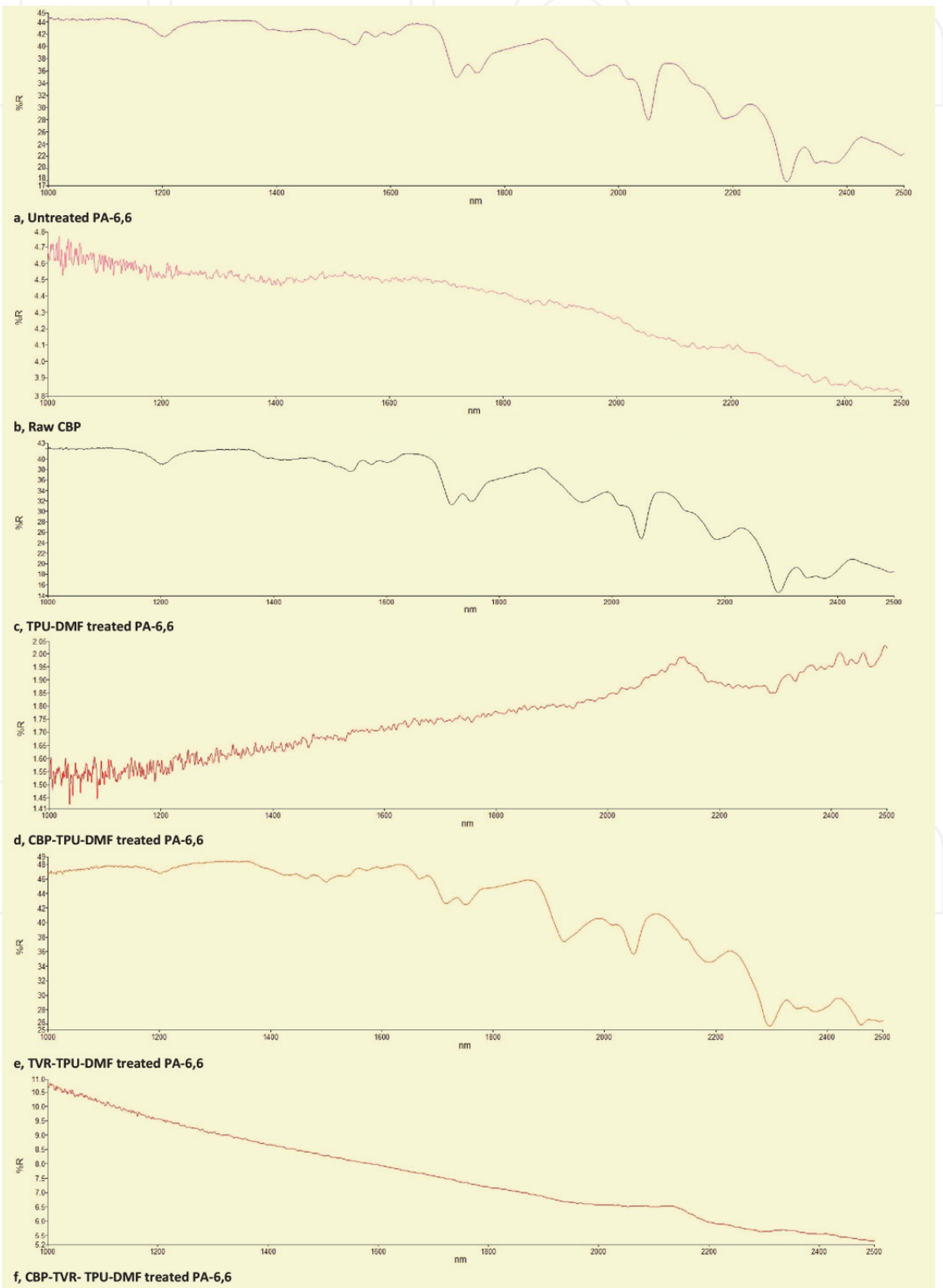


Figure S1.
Comparison of reflection (%) in NIR spectrum (part-a).

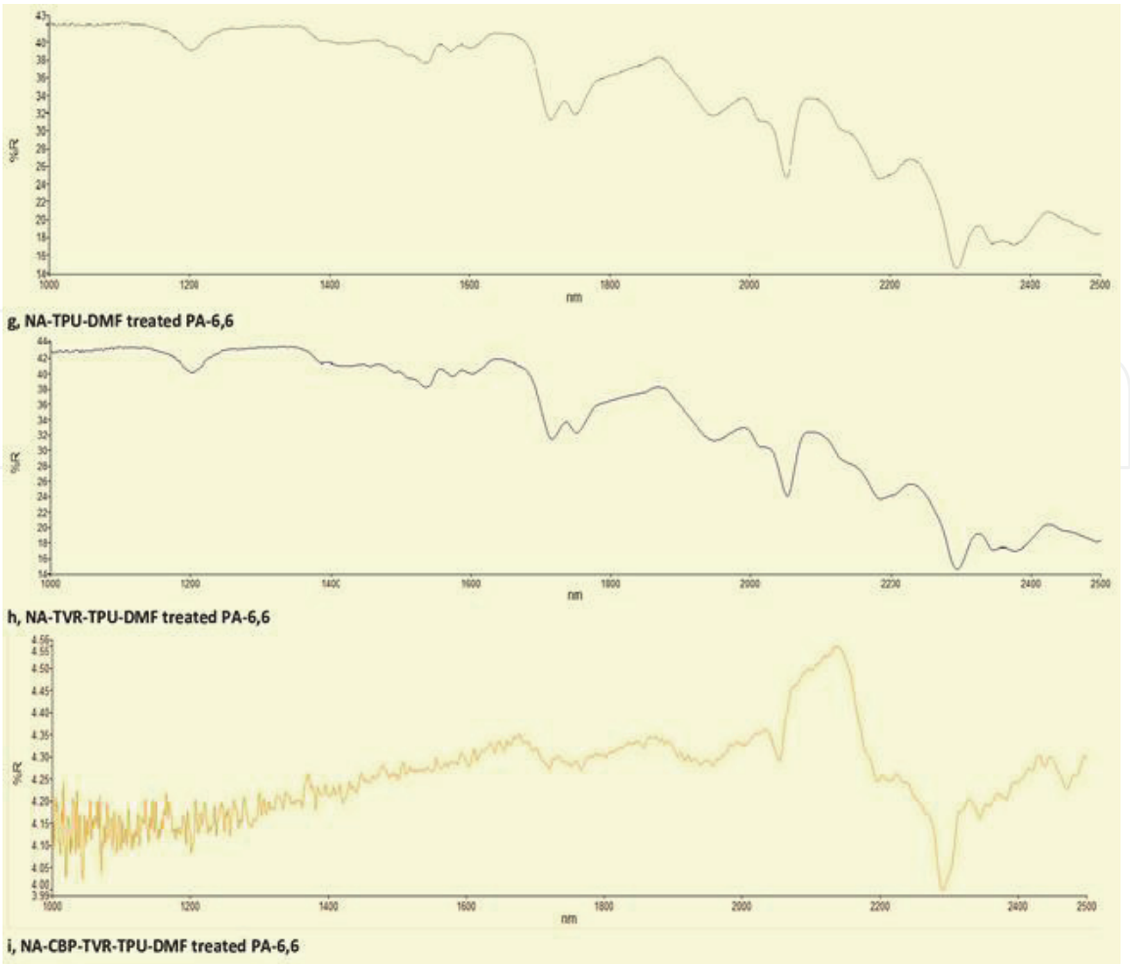


Figure S2.
Comparison of reflection (%) in NIR spectrum (part-B).

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