Journal of Polymer Research (2022) 29:128
https://doi.org/10.1007/s10965-022-02973-z

ORIGINAL PAPER

The use of mussel-inspired polydopamine interlayer for high-efficiency surface functionalization of PET fabrics

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Received: 6 October 2021 / Accepted: 3 March 2022
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Abstract

The surface modifications of polymer materials are carried out to improve surface properties, add new functionalities and thus enlarge their application areas. Polyethylene terephthalate (PET) is a commonly used textile fabric to achieve functional properties via surface modification techniques. However, its inert and non-reactive nature necessitates an activation process before the surface modification to create functional surfaces. Plasma treatment and chemical methods are commonly used for this aim. However, these techniques can easily damage the surface of the PET fabric and result in decreased mechanical properties. In this study, we proposed a new method to activate the surface of PET using polydopamine (PDA) interlayer, known as substrate-independent coating material, to form a better and more homogenous polyaniline (PAni) coating via an in-situ polymerization technique. The surface appearance of the samples was investigated using scanning electron microscopy, and the distribution of elements was analyzed using an energy-dispersive (EDS) detector. Thermal properties of the samples were explored using thermogravimetric analyses and Fourier-transform infrared spectroscopy was used to compare the chemical structures of the coated and uncoated samples. It was found that the PDA interlayer between PAni and PET significantly reduced the sheet resistance by providing more homogenous and chemically stable PAni coatings. Moreover, the effect of the PDA and PAni coating on the optical properties was investigated, and it was found that the PDA + PAni coated fabric exhibited a maximum of 10% reflectance in the range of 400 and 700 nm while uncoated fabric showed over 90%.

Keywords Surface activation · Polydopamine · PET fabric · Conductive textiles · Polyaniline · In-situ polymerization

Introduction

Surface modifications play a vital role in enlarging textile fabrics' applications and fabricating technical textiles [1]. Modifying the surfaces allows control of surface properties and imparts new functionalities such as electrical conductivity [2], UV-protective properties [3], and antibacterial activity [4]. Electrically conductive surface-modified textiles can find applications in many critical areas such as actuators[5], sensors [6], supercapacitors [7], energy harvesting systems [8], wearable electronics [9], and more. Although there are different approaches to impart electrical conductivity to textile fabrics, conductive polymeric coatings distinguish due to their easy processability and scalability and polyaniline is one of the most commonly used conductive polymers and [10–13].

Polyethylene terephthalate (PET) is one of the most used textile substrates to achieve functional properties via surface modification techniques. The high melting temperature (260 °C), good resistance against chemicals, high tensile strength, and flexibility are the major parameters that make PET promising for substrate use. However, there is one and significant challenge in surface modification of PET fabrics: its non-reactive and inert nature [14]. It is essential to apply a surface activation process to functionalize a PET material. Only after a surface activation step it could be possible to achieve high durability and homogenous surface modifications.

In the literature, many different approaches were investigated to activate the surface of PET materials. Plasma treatments [14] and chemical methods [15] seem to be the most promising techniques to provide functional groups on the surface of PET fabrics. However, both techniques may be

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Published online: 14 March 2022

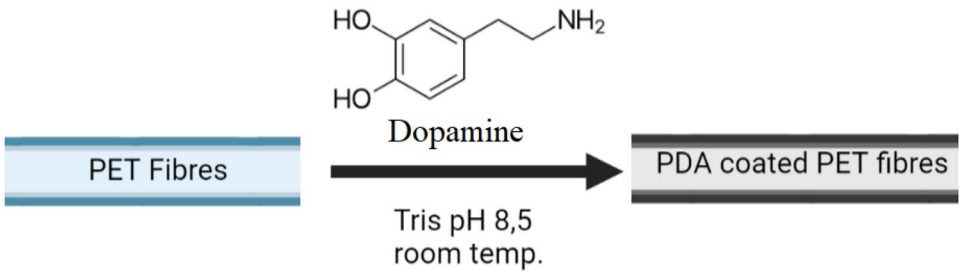


Fig. 1 The schematic representation of in-situ polydopamine coating

damaging for the surface and can cause a reduction in the mechanical properties of the PET fabrics.

On the other hand, using an interlayer with functional groups between the coating and the PET itself can be a promising approach. Mussel-inspired polydopamine (PDA), synthesized by the oxidation polymerization of dopamine, is a biopolymer that is known with unique properties such as its ability to be deposited easily on nearly all types of inorganic and organic substrates [16], strong reactivity thanks to functional groups in chemical structure (catechol, amine, and imine [17]) and easy applicability. It can be a promising candidate to provide functional surfaces in the form of a thin layer. Therefore, we proposed a new method to activate the PET surface using polydopamine interlayer for high-efficiency polyaniline coatings in this study. The difference in electrical conductivity of two samples, having PDA interlayer and coated directly with PAni, were investigated to understand the benefit of PDA interlayer. Moreover, the surface appearance of the samples was investigated using scanning electron microscopy, and the distribution of elements was analyzed using an energy-dispersive (EDS) detector, and around 30% of N content was detected on the surface in PDA and PAni coated fabric. The change in thermal properties of PET fabric after each fabrication step has been investigated using the TGA technique between 150 and 600 °C. Moreover, the effect of both PDA and PAni coating time in changing PET fabrics` optical properties was also investigated in the visible region (between 400 and 700 nm).

Materials and methods

Materials

PET fabric (100%) was purchased from a local supplier and repetitively washed at 40 °C to ensure any contamination was left. For the polydopamine coating onto the PET fabric, dopamine hydrochloride (99 wt.%) and Tris (hydroxymethyl)-methylamine (99 wt.%) were both purchased from Sigma Aldrich (Germany) and used without further purification. Aniline (98 wt.%), hydrochloric acid (37 wt.%), and ammonium persulphate (99%) were all used for the in-situ polyaniline synthesis and purchased from Sigma Aldrich.

Methods

Characterization techniques

A scanning electron microscope (SEM) having energy dispersive spectroscopy detector, FEI Quanta 650 Field Emission SEM, was used to investigate surface morphology of the samples and explore their elemental composition. 8 nm of gold coating was applied to enhance the electrical conductivities of the samples before the analyses. Jasco FTIR spectra of the samples at 500–4000 cm^{-1} were taken FT/IR-6700. To investigate the effect of applied coatings on thermal behaviour of PET fabric between 150 and 600 °C, Mettler Toledo TGA 3 + was used. Optical properties of the samples were analyzed using Minolta CM 3600 D spectrophotometer, in

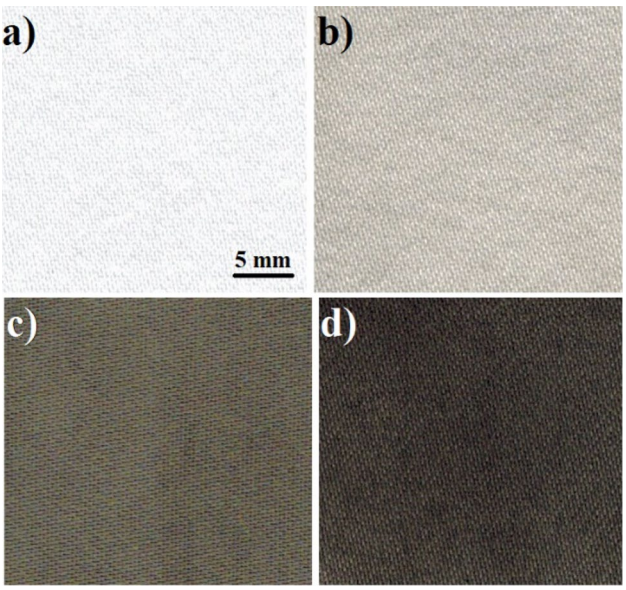


Fig. 2 The surface appearance of uncoated fabric **a**) 3 h, **b**) 12 h, **c**) and 24 h **d**) PDA coated fabrics

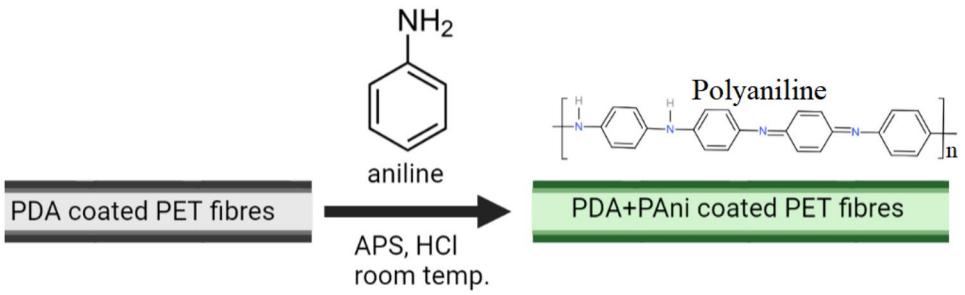


Fig. 3 The schematic representation of in-situ PAni coating on PDA coated PET fabric

the visible region. Lastly, sheet resistance values of the samples were measured using Elme professional surface meter.

Preparation of PDA interlayer on PET fabric

The schematic representation of in-situ polydopamine coating is given in Fig. 1. Firstly, 1.2 g of Tris (hydroxymethyl)-methylamine was dissolved in 1000 ml of distilled water. Then, 2 mg/ml of dopamine hydrochloride were added to the solution and mixed using a magnetic stirrer until completely dissolved at room temperature.

The solution was then poured into an uncovered tray, and pre-washed PET fabric was placed inside it. According to current theory, by dissolved oxygen at alkaline pH of the solution, dopamine hydrochloride firstly auto-oxidized to dopamine quinone and 5,6-dihydroxyindole, then followed by a nucleophilic intramolecular cyclization reaction which result with the formation of 5,6-dihydroxyindole on the surface [18]. Moreover, the reaction time has a direct influence on both the degree of polymerization and the thickness of the coating.

Samples are cut from the fabric from time to time to analyze their optical properties, which can provide information about the polymerization process and the thickness of the PDA coating as well. The coated fabrics were rinsed using deionized water and dried at room temperature for 24 h before further analysis. After 24 h of coating time, the colour of the fabric changed to dark brown-black. This was proof of irreversibly bonded polydopamine layers on PET surfaces, as shown in Fig. 2.

In-situ polyaniline coating

The schematic representation of in-situ PAni coating on PDA coated PET fabric is given in Fig. 3. Firstly, two 1000 ml of HCl solution (0.2 M) were prepared. 40 ml of aniline (300 mM) was added to the first solution, while around 80 g of ammonium persulfate dissolved in the other to obtain around 1:1 molar rate of aniline and ammonium persulfate. Then, two solutions were mixed together and poured into a tray in which the samples were located inside. The polymerization started immediately, as understood from the color change observed.

Two different samples (PET + PAni and PET + PDA (24 h) + PAni) were fabricated to investigate the benefit of PDA interlayer. Samples were cut from the fabrics to analyze the effect of polymerization time on electrical properties. The surface appearances of the PDA coated, PDA + PAni coated, and PAni coated fabric is given in Fig. 4.

Results and discussion

SEM and EDS results of the samples

The SEM images of samples are given in Fig. 5. As seen, uncoated PET fibres had a smooth surface structure because of the production technique, melt spinning. Although a thin PDA layer achieved after PDA coating, some accumulations of PDA nanoparticles has been observed. This was attributed to the long polymerization time and the high concentration used for the in situ polymerization technique.

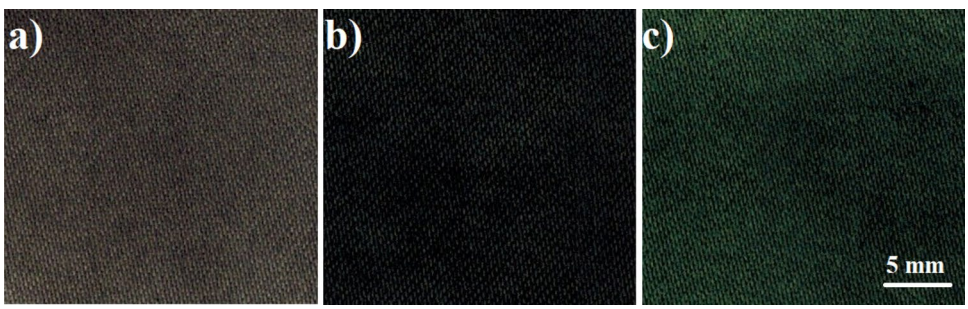


Fig. 4 The surface apperance of PDA coated fabric **a**) PDA + PAni coated fabric, **b**) and PAni coated fabric **c**)

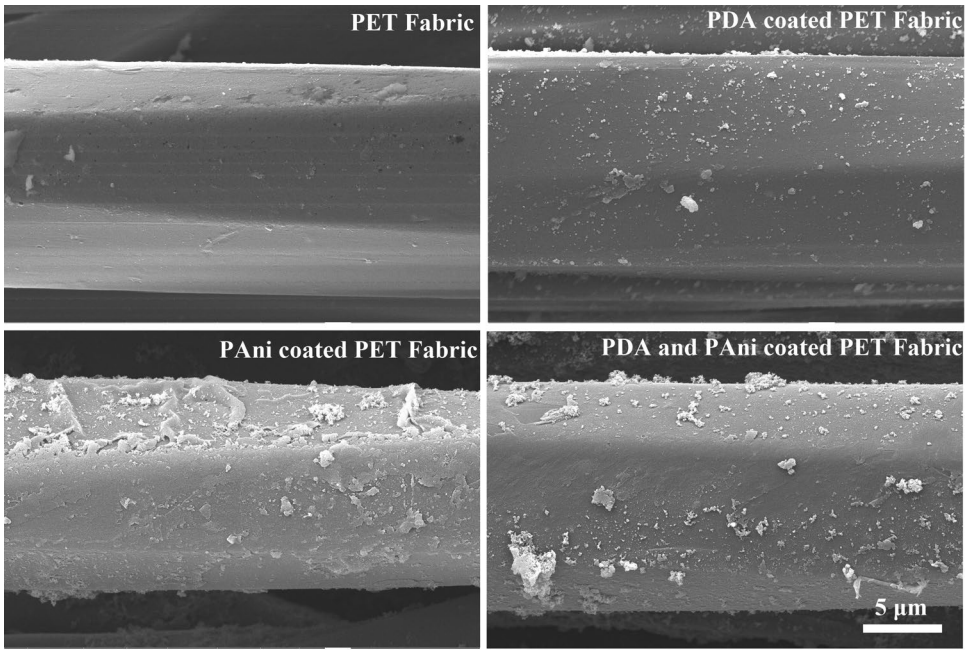


Fig. 5 SEM images of PET fabric, PET + PDA, PET + PAni and PET + PDA + PAni samples

On the other hand, direct polyaniline coating on the PET surface caused a much rough surface structure. It can be seen that when the PDA coating was used as the interlayer, polyaniline coating provided a relatively smooth surface morphology. The reason for this effect is the chemical attraction between the layers. It has been reported that to functionalize the surface of PET, it is nearly mandatory to activate the surface first to create functional groups. Without an activation step, it is not easy to apply homogenous coatings to impart functional properties.

The chemical compositions of the samples are given in Table 1. As expected, no N content was detected from the uncoated PET sample as the chemical structure of PET does not contain N. However, after both PDA and PAni coating were carried out, more than 30% of N content was determined. When the chemical structure of PET is compared to the chemical structures of PAni and PDA, it can be easily seen that all of them contain C, O, and H but only the PAni and PDA has N on their structure. Results also confirmed that no solvent or auxiliary chemicals were left after samples were rinsed with water.

Moreover, EDS mapping images of the samples are given in Fig. 6. Blue color represented N while red and green represented C and O respectively. Results confirmed that coatings of both PDA and PAni successfully achieved by using the in-situ polymerization technique.

FTIR and TGA spectra of the samples

The FTIR spectra of the PET fabric and PET + PDA + PET fabric are given in Fig. 7. Characteristic peaks of the PET fabric were found at 1712 cm^{-1}, which indicates the CO (ester groups), 1410 and 1240 cm^{-1} are ascribed to $–CH_2–$, and asymmetric and symmetric aliphatic C–H stretching vibrations were detected in 2907 and 2968 cm^{-1} for PET [19]. However, although the coating of both PDA and PAni has clearly been observed on the surface thanks to a clear change in substrate colour, only one of the characteristic peaks of polyaniline could be detected in the FTIR spectrum at around 1540 cm^{-1}. The reason was the effect of nanoscale coating, which can provide low intensity of the peaks and the dominant character of PET peaks.

TGA spectra of the samples between 150 and 600 °C are given in Fig. 8. No significant changes in thermal behaviour after PDA and/or PAni coatings have been detected. However, the PET fabric sample had the lowest residual weight

Table 1 EDS data of atomic percentages of the samples prepared

	PET Fabric	PET + PDA	PET + PAni	PET + PDA + PAni
C (Atomic %)	65.18	55.34	56.76	56.95
O (Atomic %)	34.82	10.93	12.85	12.2
N (Atomic %)	N/A	33.73	30.39	30.85

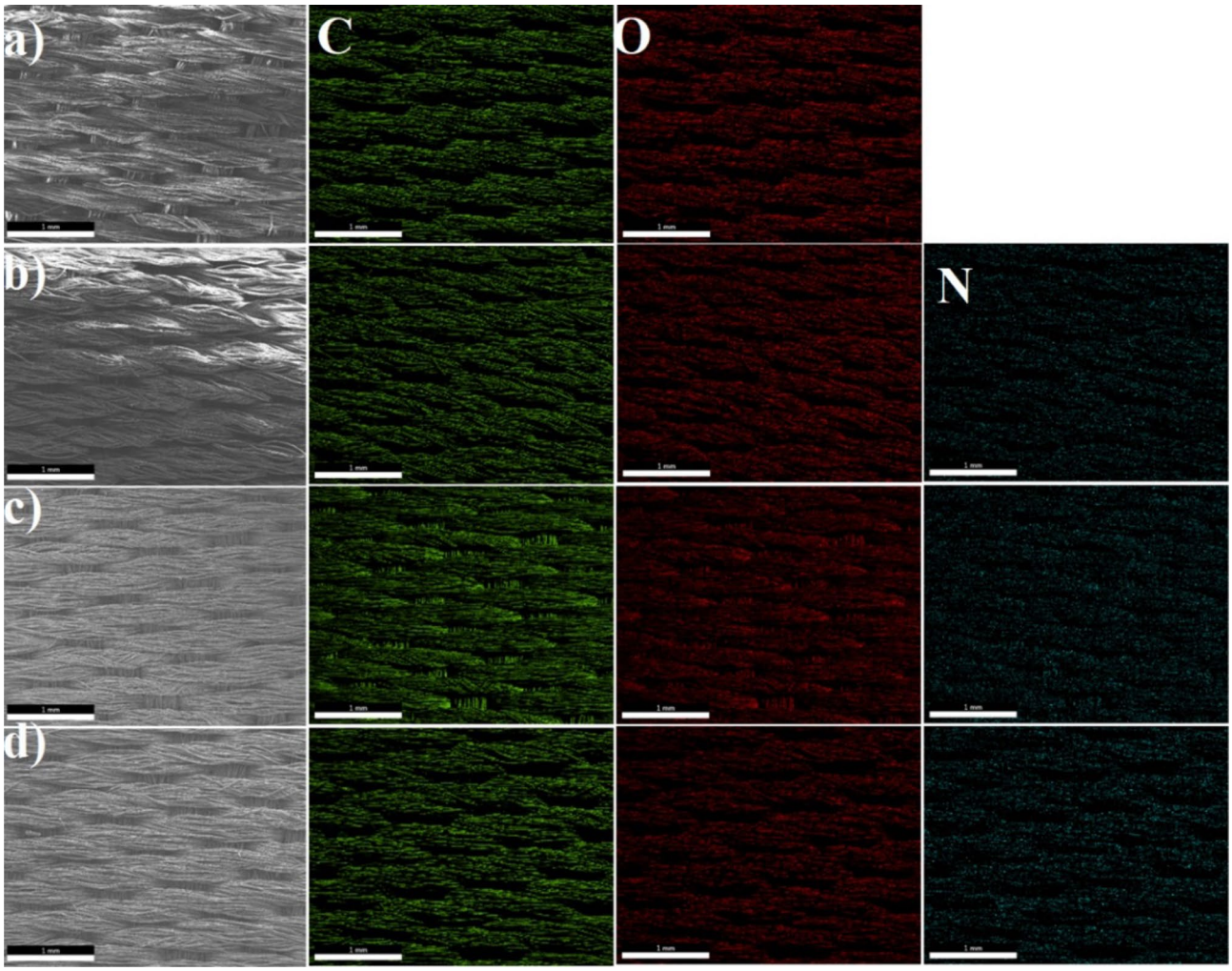


Fig. 6 EDS mapping data of **a**) PET fabric, **b**) PET + PDA, **c**) PET + PAni and **d**) PET + PDA + PAni samples (green = carbon, red = oxygen and blue = nitrogen)

at 600 °C with 14%, while the PET + PDA + Pani had the highest one with 20%. As known, thermal analysis of most organic material results in the formation of residual carbonaceous or nitrogenous compounds if the heating is carried out under an inert atmosphere. Thus, it can be said that PDA and PAni increased the residual content by forming different carbonaceous and nitrogenous structures.

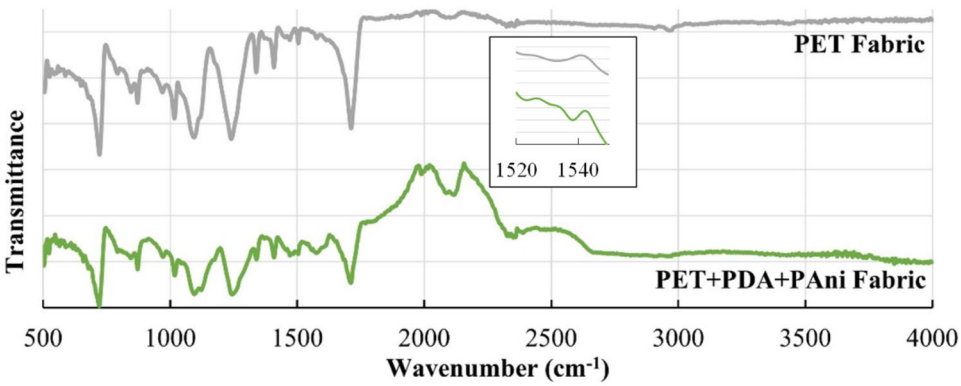


Fig. 7 FT-IR spectra of PET and PDA + PAni coated PET fabric inset: FT-IR spectra of the samples between 1520 and 1550

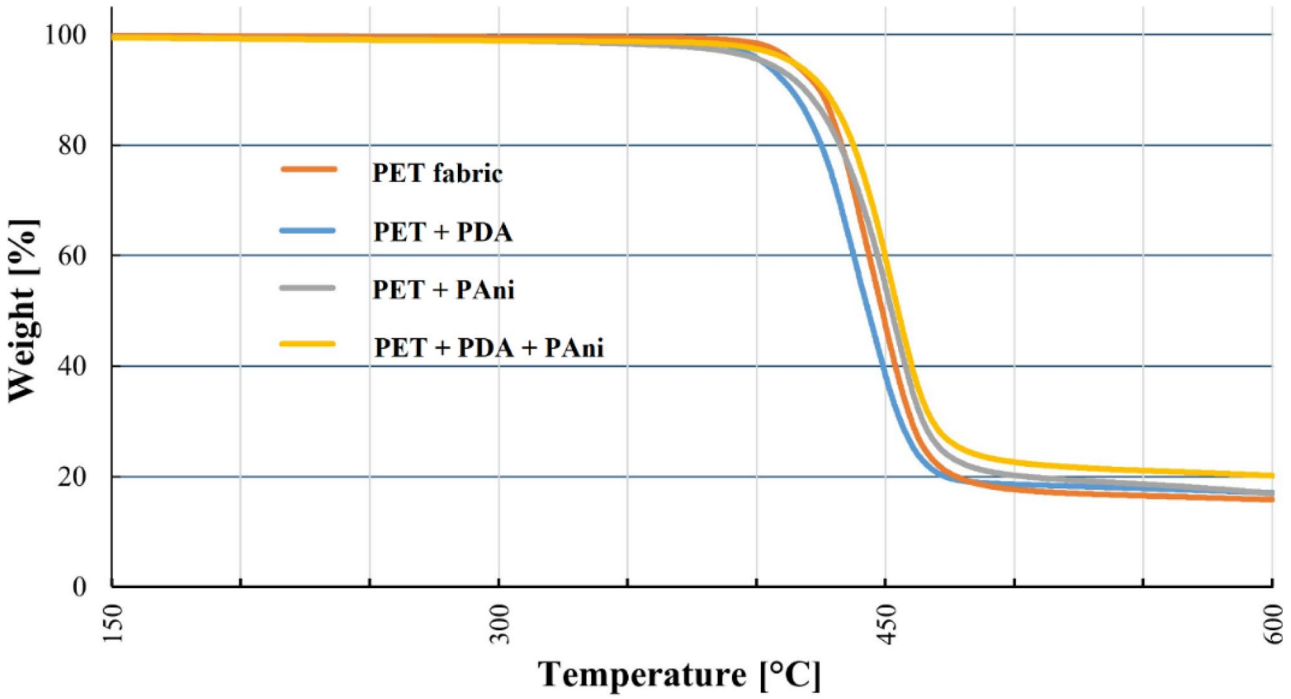


Fig. 8 TGA spectra of the sampes

The effect of the PDA and PAni coating time on the optical properties of the fabric

PDA is considered as the artificial melanin, which can absorb a wide range of visible light [20]. Therefore, it can significantly increase the absorbance of the visible light through itself or the substrate coated with it. Figure 9 shows the reflectance spectra of the samples, having different coating times, in the visible region (400–700 nm). As seen, there is a strong inverse correlation between the coating time and the reflectance of the samples. When the coating time increased, the reflectance of the samples decreased with it. The relationship between reflectance, absorbance and transmittance properties of a material is given in Eq. 1.

$$R = 1 - (T + A) \tag{1}$$

However, because of high thickness of the fabric and the semicrystalline nature of cellulose, the transmittance of the cotton fabric was close to zero as shown in Fig. S1 (supporting information). Thus, Eq. 2 was applied to understand the relationship between reflectance and absorbance properties.

$$R = 1 - A \tag{2}$$

The reason for the increased absorbance of the samples was the increased accumulation of the PDA, which has an excellent ability to absorb visible light, on the surface of PET fabric with longer coating times. While the reflectance value of the uncoated sample was around 98% at 450 nm of wavelength thanks to the whitening agent, it decreased to 10% after 24 h of PDA coating.

Moreover, the change in CIELab L* (lightness index) is given in Fig. 9. As known, a white object has a lightness value of 100 while a black object has 0 [21] at CIELab L* color space. Uncoated PET fabric had around 82 lightness values, and during the polymerization of PDA, the color of the PET fabric was blackened as low as a lightness value of 47. These results are also confirmed that the polymerization reaction continued during the coating time.

Reflectance spectra of PDA coated, PAni coated, and PDA + PAni coated fabrics are in the visible region, also given in Fig. 10. The addition of PAni coating contributed to the lower reflectance values of the PET fabric which indicates higher rates of absorbance. It was also clear that the existence of both PDA and Pani coatings provided better efficiency in terms of visible light absorbance.

Sheet resistance results

The sheet resistance results of PAni coated, and PDA + PAni coated PET fabrics are given in Fig. 11. The sheet resistance values of both samples were taken at 45, 90, 180, and 720 min of polyaniline coating. It can be seen that when

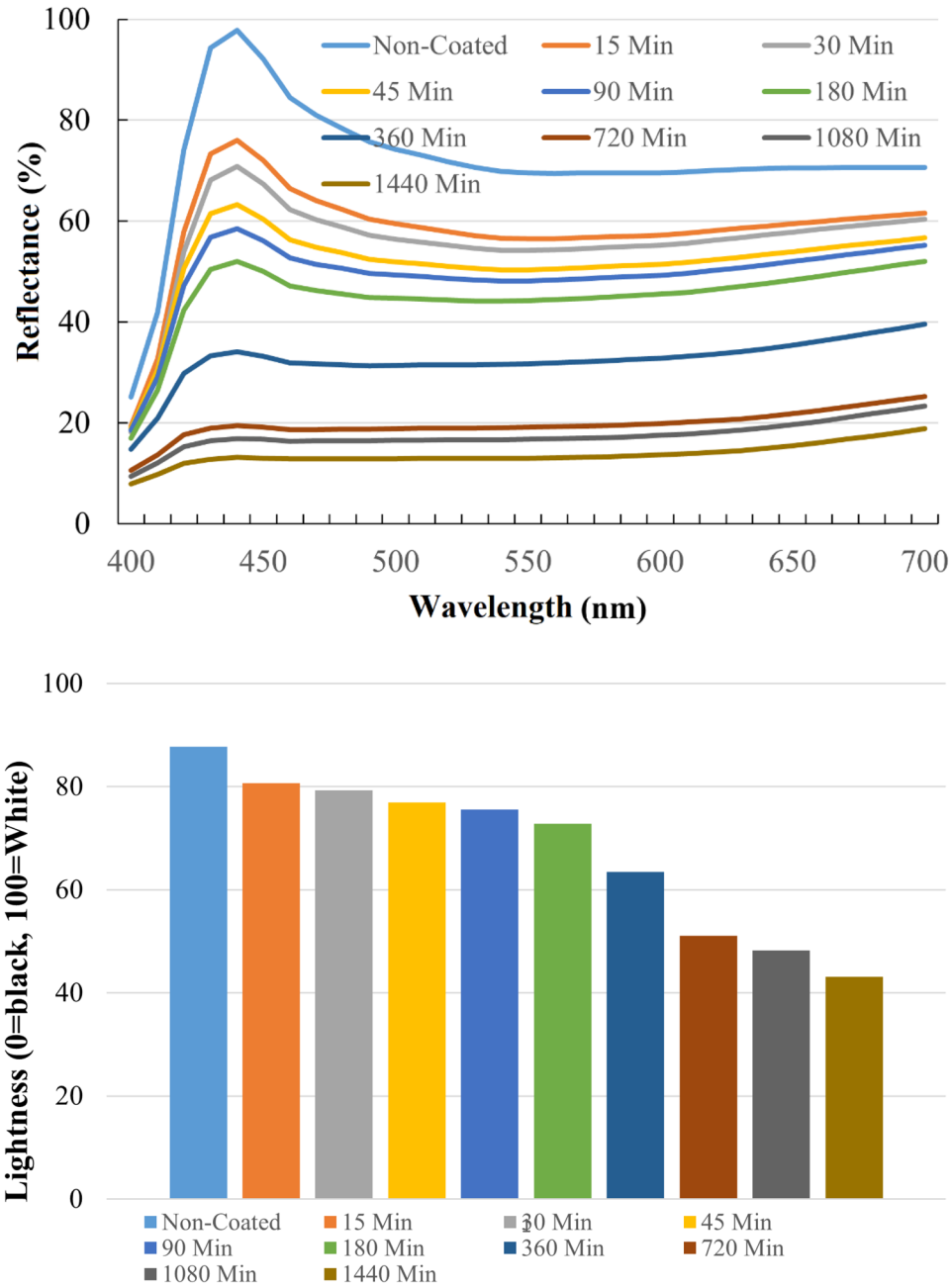


Fig. 9 Reflectance spectra and lightness values of PDA coated PET fabric with different coating times

the PDA interlayer is used, the sheet resistance decreases significantly regardless of coating time. The lowest sheet resistance of the PDA + PAni coated achieved was around 4 kOhm/sq with 90 min of coating time, and for the same coating time, the average sheet resistance of only PAni coated PET was around 129 kOhm/sq. It is also worth noting that the PDA interlayer provided a much lower standard deviation of the sheet resistance. Although the sheet resistance of PAni coated PET fabric decreased with the increasing coating time, it was dramatically lower than PDA + PAni coated PET fabric after 24 h with 5.2 and 129 kOhm/sq, respectively. To explain this, the chemical structures of both PET and PDA need to be well understood. Polydopamine is composed of dihydroxyindole, indoledione, and dopamine units [22], providing a higher amount of functional groups than PET itself.

On the other hand, PET is known for its chemical inertness and low surface energy, making it harder to apply coating, lamination, or dying. The chemical attractions between the layers, especially hydrogen bonding, which

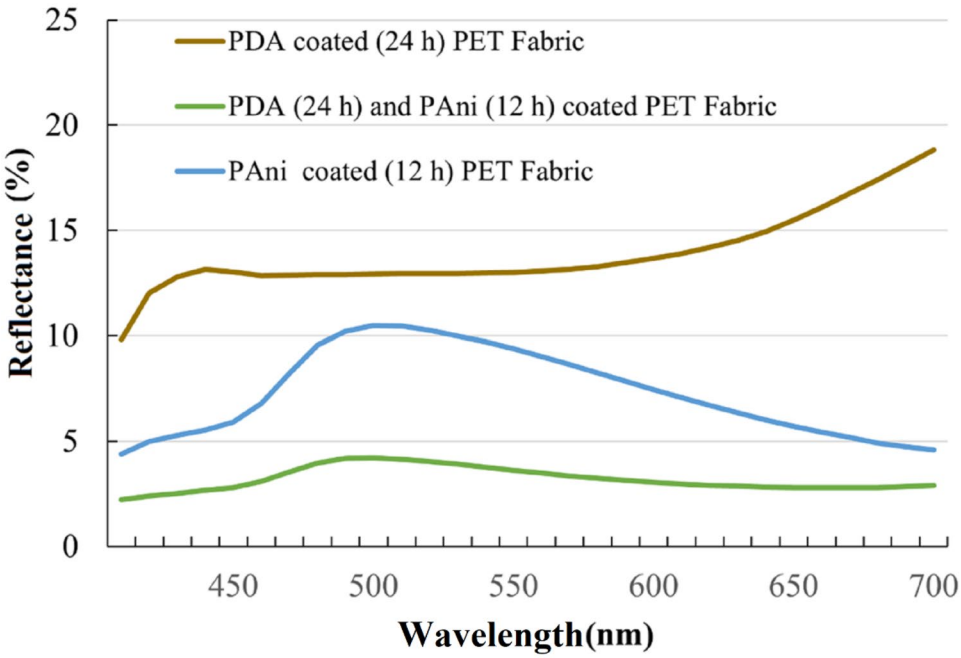


Fig. 10 Reflectance spectra of PDA coated, PAni coated and PDA + PAni coated PET fabrics

was the main chemical attraction for both PET/PAni and PDA/PAni interlayer, played a vital role in coating efficiency and homogeneity. There is only one type of hydrogen bonding in the PET/PAni interface, in which ester groups in PET acts as the hydrogen bond acceptor and form hydrogen bonds with -NH groups of PAni. However, there should be a higher number of hydrogen bonding in PDA/PAni compared to PET/PAni interlayer due to a higher amount of functional groups as the possibility of hydrogen bonding was increased. The effect of the PDA in the homogenous nucleus of PAni was also observed during the coating, and relatively homogenous coatings were achieved using a PDA interlayer, compared to one without a PDA interlayer.

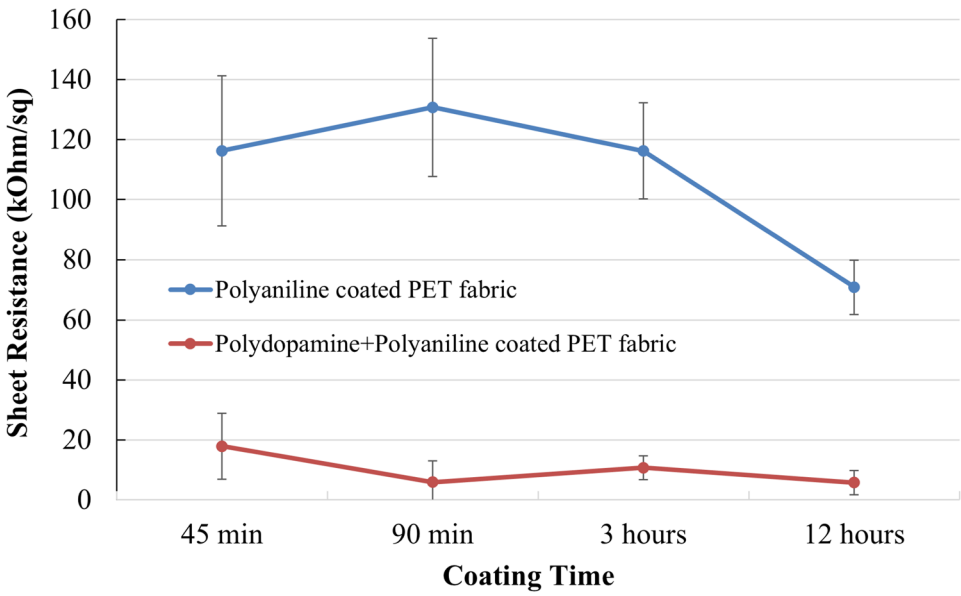


Fig. 11 Sheet resistance values of PAni coated and PDA + PAni coated PET fabrics

Conclusion

In this study, we proposed a new method to activate the surface of PET using polydopamine, which can be deposited on almost all types of organic or inorganic surfaces regardless of functional groups on the surface with high durability and stability to form a better and more homogenous coating of polyaniline. It was found that when PDA has been used as an interlayer, a significant improvement in sheet resistance of PAni coated PET fabrics was achieved. The best sheet resistance result was taken from 90 min of PAni coated PET fabric as 5 kOhm/sq from the PDA interlayer involved design, while 129 kOhm/sq sheet resistance was obtained from the sample without PDA interlayer. Moreover, the effect of both PAni and PDA coating on the optical properties of the samples was investigated. As high as 95% of visible light absorbance efficiencies were obtained using both coatings which can enlarge its application areas.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s10965-022-02973-z.

Acknowledgements This work was supported by Cukurova University Scientific Research Projects Unit (Project Code: FBA-2021-13420).

Declarations

Conflict of interest The authors declare no conflict of interest.

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