

IMIDAZOLIUM SALT AND DIELECTRIC BARRIER DISCHARGE PLASMA TREATMENT TO ENHANCE THE CONDUCTIVITY OF FABRICS IMPREGNATED WITH PEDOT:PSS

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ABSTRACT

Conductive textiles are a class of materials with a growing interest due to their potential applications in medical, healthcare, comfort, protective clothing, and sportswear sectors. They can be used for the development of smart textiles able to answer to different external stimuli such as thermal, mechanical, chemical, electrical, magnetic, and optical. The complex poly (3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS) is the most explored polymer to prepare conductive textiles. Dopants can be introduced to add or remove electrons from the backbone of PEDOT:PSS, resulting in increased conductivity. Salts such as 1-butyl-3-methylimidazolium octyl sulphate (IZ) may promote ionic interactions with PEDOT:PSS, stimulating a microstructure reorganization. Moreover, the dielectric barrier discharge (DBD) plasma treatment has been shown to improve the adhesion of coatings by modifying the surface roughness, surface chemistry, and hydrophilicity of the fabrics. In this work, untreated and DBD plasma-treated polyester (PES) fabrics were impregnated with PEDOT:PSS with and without the addition of imidazolium salt (0.2M) as a dopant. Using the IZ, it was possible to adapt the textile materials into resistors, where the applied current converted electrical energy into heat. The developed textiles can be used to produce heating garments.

Key words: Imidazolium salt, conductive textiles, DBD plasma treatment, dopant, smart textiles

1. INTRODUCTION

Smart textiles are opening a promising window, full of new challenges and prospects, for the textile industry. This generation of textiles has been characterized by the ability to interact with the surrounding environment and can be labelled by three different categories, according to their level of intelligence as passive, active or very active smart materials. The ability to sense and react to external stimulation by releasing heat, changing its colour, conducting electricity, performing computational operations, storing energy, among other intelligent reactions defines their categories^{1,2}. An important feature of smart textiles is their conductive properties, so the development of electroconductive textiles is a crucial step to achieve better performance³. One common approach to impart conductivity to textiles is the use of intrinsically conductive polymers, which ensures excellent mechanical properties of the textiles, whilst retaining the desirable conducting properties of the polymers⁴. Poly (3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS) is the most widely used conductive polymer, owing to its conductivity, environmental stability, flexibility, processability and thermoelectric properties⁵⁻⁸. A considerable enhancement in the conductivity of PEDOT:PSS is possible by using secondary dopants such as organic solvents, surfactants, metal salts or ionic liquids⁹. Salts such as 1-butyl-3-methylimidazolium octyl sulphate (IZ) may promote ionic interactions with PEDOT:PSS, promoting a microstructure reorganization by phase segregation of protonated PSS chains

from PEDOT:PSS and further conformational change of PEDOT¹⁰. DBD plasma activation treatment of fabrics can also be applied to improve the hydrophilicity, increase the PEDOT:PSS affinity and, consequently, allow the fixation of the conductive polymer^{11,12}. Herein, electrically conductive textiles for heat generation were prepared and characterized. Polyester (PES, DBD plasma-treated and not treated) fabrics were impregnated with five layers of a PEDOT:PSS dispersion interspersed with five layers of the IZ solution (0.2M), to increase the conductivities. The samples were characterized for their electrical conductivity, electrochemical and Joule heating behaviour, and surface chemical composition.

2. MATERIALS AND METHODS

2.1. Materials

Poly (3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS, 1.3 wt % dispersion in H₂O), was purchased from Sigma Aldrich. 1-butyl-3-methylimidazolium octyl sulphate (IZ) was obtained from Alfa Aesar. Commercial polyester (PES) fabric (weight per unit area of 103.2 g.m⁻² and warp/weft density of 28/30) was supplied by T-GRAMA (Braga, Portugal). To minimize the contaminations, the fabric was pre-washed with a non-ionic detergent solution (1.0 g.L⁻¹) at 40°C for 30 min with a liquor ratio of 1:100, rinsed with distilled water and dried at 40°C.

2.2. DBD plasma treatment

A semi-industrial prototype machine (Softal GmbH/University of Minho) was used to conduct the DBD plasma treatment at room temperature and atmospheric pressure in the air. It used a system of metal electrodes coated with ceramic and counter electrodes coated with silicon with 50 cm effective width, gap distance fixed at 3 mm, and producing the discharge at a high voltage of 10 kV and low frequency of 40 kHz. The discharge power supplied by the electrodes and the speed may change, with a maximum discharge of 1.5 kW and a speed of 60 m min⁻¹. The machine operated at optimized parameters, 1.0 kW of power and velocity of 4.0 m.min⁻¹ for 5 passages on both sides of PES samples, corresponding to a dosage of 2.5 kW.min.m⁻²¹³.

2.3 Samples preparation

Fabric samples with 9.0 x 1.5 cm² were prepared through an impregnation process which comprises the following steps. First, the samples (PES and PES DBD) were immersed in a pristine PEDOT:PSS solution for 10 min. After that, samples were passed through a squeezed rollers system at a pressure of 2.0 Pa. The treated fabrics were then dried in an oven for 60 min at 60 °C and, subsequently, cured for 2 min at 150 °C. Finally, the same samples were immersed in an IZ solution (0.2 M) for 5 min, passed through squeezed rollers and dried for 10 min at 60 °C. The whole process was repeated five times to complete 5 layers of conductive polymer deposition.

2.4 4-Point Probe resistivity

Conductivity measurements were carried out using a 4-point-probe system composed of a DC power supply (Mercury® 650.682) and a digital multimeter (TENMA® 72-2590). The measurements were performed under an applied voltage of 12.5V with a distance between the probes of 2 cm. All the electrical resistance values were measured under ambient conditions and the assays were repeated three times to guarantee the reproducibility of the results.

2.5 Electrochemical tests

Electrochemical impedance spectroscopy (EIS) was made in a three-electrode configuration, where impregnated textile samples ($3 \times 1.5 \text{ cm}^2$) were used as working electrode (WE), Ag/AgCl served as reference electrode (RE) and the platinum electrode was considered as a counter electrode (CE). The assay occurred in a 9 gL^{-1} NaCl electrolyte, and all the potentials were measured according to the RE electrode. EIS measurements were conducted at a frequency range of 0.1 Hz – 100 kHz and an amplitude of the sinusoidal signal at 10mV. The experiment was performed using a Gamry Potentiostat/Galvanostat (model Reference - 600) and all the measurements were performed in triplicate under ambient conditions.

2.6 Joule heating effect

The Joule heating effect was investigated under a constant voltage of 12V, generated by a DC power supply (Agilent technologies, model N5772A), for 45 min. The thermal response of the fabrics was recorded using an infrared camera (Testo 890). Two copper stripes were attached to the extreme of the samples to ensure the connection between the power circuit and fabric heaters. All the measurements were carried out under ambient conditions.

2.7 FTIR

Fourier transform infrared measurements were recorded using a Nicolet Avatar 360 spectrophotometer (Madison, USA), with an attached ATR accessory. The transmittance spectra were obtained over the range $4000 - 400 \text{ cm}^{-1}$, applying 60 scans and a resolution of 8 cm^{-1} .

2.9 XPS

XPS spectra were recorded using a K-Alpha Thermo Scientific (ESCALAB™ XI+, East Grinstead, UK) spectrometer equipped with a 180° double focusing hemispherical analyzer. Survey spectra were recorded at a pass energy of 50 eV to determine the elemental composition treated textiles surface. High-resolution spectra for C1s, O1s, N1s and S2p binding energy regions were measured at a pass energy of 20 eV in order to evaluate the elemental bonding states of the as-resulted materials. Peak position was calibrated according to the standard C1s peak associated to adventitious carbon, positioned at 285.0 eV. The spectra acquisition and data processing were performed by using the advanced Avantage data software, using combined Gaussian-Lorentzian profiles and Shirley-type background subtraction.

3. RESULTS AND DISCUSSION

3.1 4-Point Probe

The conductivity of all samples (PES and PES DBD) was investigated using a 4-point-probe (Figure 1). The data have shown a significant increase in the conductivity of the fabrics in two orders of magnitude. The conductivity of untreated PES fabric with only PEDOT:PSS increased from $4.17 \times 10^{-4} \text{ S.m}^{-1}$ to $3.86 \times 10^{-2} \text{ S.m}^{-1}$ with the addition of the imidazolium salt. For the DBD plasma-treated PES sample, the conductivity increased from $6.53 \times 10^{-4} \text{ S/m}$ to $4.65 \times 10^{-2} \text{ S.m}^{-1}$ after the dopant application. It was clear that PES DBD plasma-treated fabrics attained a slightly better performance compared to untreated sample. The introduction of the IZ as a dopant may promote a structural rearrangement in PEDOT:PSS chains induced by a phase segregation process. This provided the formation of highly

ordered crystalline PEDOT:PSS, leading to a better charge transport pathway and stimulating a boost in conductivities ¹⁴.

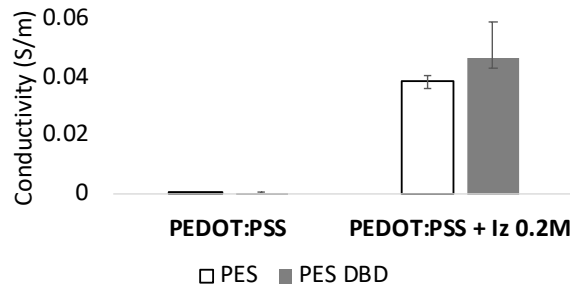


Figure 1: Conductivity of the samples only with PEDOT:PSS and the samples with PEDOT:PSS + IZ (0.2M).

3.2 Electrochemical analysis

EIS was carried out to access the electrochemical properties of the samples. It was reported that in the low-frequency region, the phase angle close to -90° indicates the behaviour of an ideal capacitor ¹⁵. The Bode plot analysis revealed that PES fabrics treated with PEDOT:PSS + IZ (0.2M) were the samples with better results (Figure 2). The impedance ($|Z|$) values registered in the low and middle ranges of frequencies correspond to the electrochemical resistance of the textile samples ¹⁶. Thereby, it was shown that the lower $|Z|$ values were recorded to PES fabrics treated with PEDOT:PSS + IZ (0.2M). In both cases (phase angle and $|Z|$), DBD plasma treatment showed to improve even more the performance of PES.

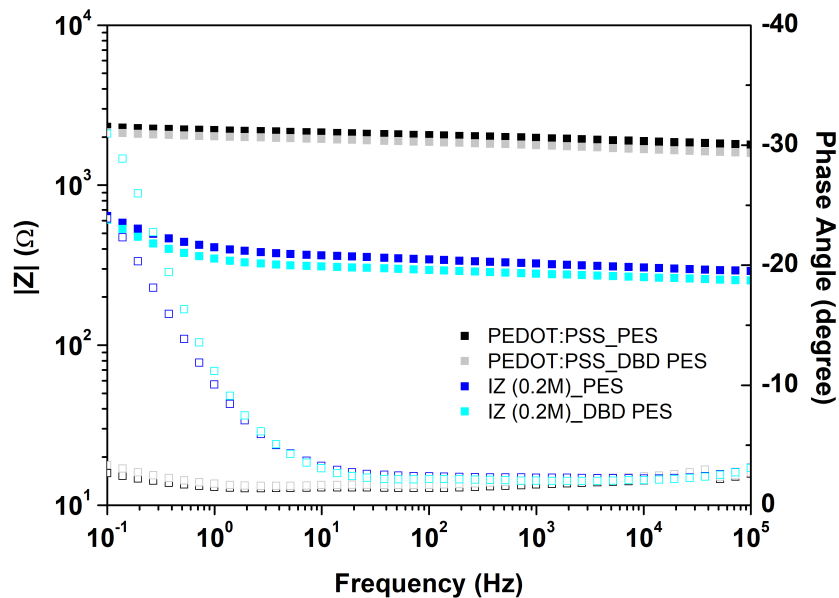


Figure 2: EIS spectra of the sample in form of a Bode diagram.

3.3 Joule effect

The heating behaviour of the samples (PES and PES DBD) were registered by an infrared camera. The Joule heating effect has been monitored over 45 min, under an applied voltage

of 12 V and the images were collected in a time range of 15 min (Figure 3). As observed from infrared images, PES and PES DBD fabrics presented a uniform heat generation. This means that both the PES samples set an excellent bonding between conductive polymer and fabric. Thus, the current can flow through the samples uniformly when voltage is applied¹⁷. All the measurements take place under ambient conditions and the surface temperatures were recorded. In the PES fabric only with PEDOT:PSS the temperature increased from 18.1 °C to 26.1 °C. In the PES sample with PEDOT:PSS and DBD plasma, the temperature raised from 18.6 °C to 26.6 °C.

It was noticed that during the assays the sample heaters get a quick temperature increment in the first seconds and a steady temperature profile was reached afterwards. It was an important parameter in evaluating the performance of the textile heaters as the rapid thermal response was another positive feature of the smart textiles applications¹⁸.

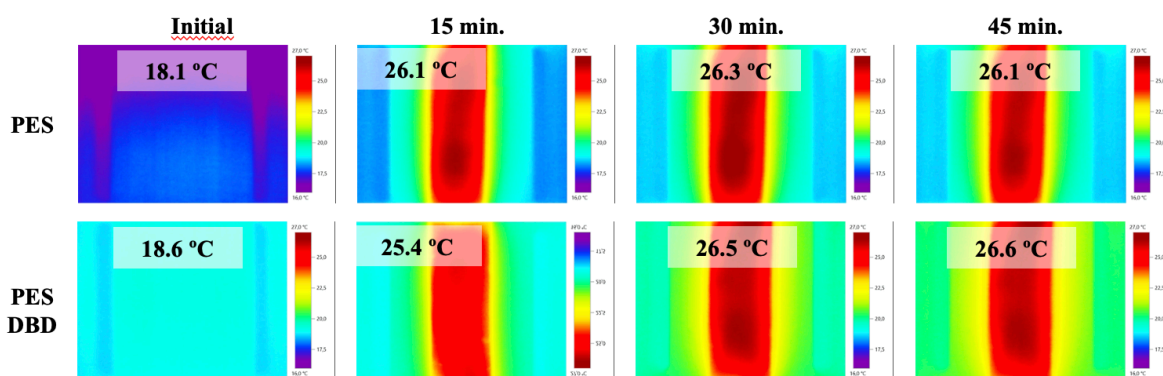


Figure 3: Joule heating effect on PES (not treated and DBD plasma-treated) fabrics impregnated with PEDOT:PSS + IZ.

3.4 FTIR

The FTIR spectra of the original and modified samples were analysed (Figure 4). In the FTIR spectra of the PES samples, all the prominent peaks are attributed to the PES structure. The characteristic peaks of PES were noticed at 1713 cm^{-1} attributed to the C=O stretching vibration band of the ester carbonyl group in conjugation with an aromatic ring. Peaks at 1241 and 1095 cm^{-1} are due to asymmetric and symmetric vibrations of C-O and aromatic C-H wagging at 721 cm^{-1} ^{11,19}.

The characteristic peaks of the PES DBD plasma-treated sample showed to be the same as untreated PES samples, which motivated the absence of that spectra. Using the FTIR analysis it was possible to observe that the impregnation with PEDOT:PSS and IZ, and DBD plasma treatment did not change the bulk chemical properties of the fabrics. Thus, the FTIR spectra did not allow us to understand the obtained chemical changes, which might be ascribed to the fact that these elements and treatments were only achieved on the surface of the fabric. Whereby, XPS analysis was performed to clarify the elementary composition of the samples and chemical changes obtained with the functionalization.

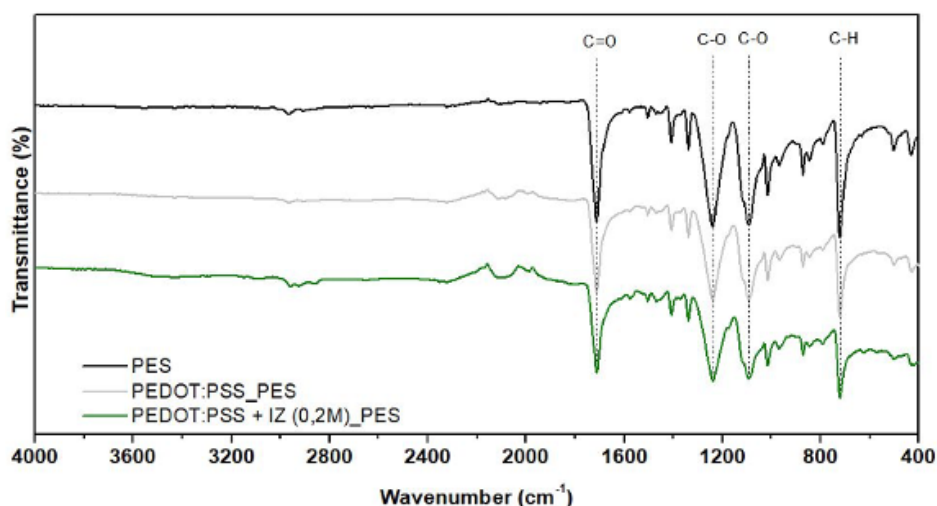


Figure 4: FTIR spectra of PES samples.

3.5 XPS

XPS analysis was performed in the samples with better conductivity to gain further insight into the chemical changes occurring on the surface of the fabrics during the functionalization (Figures 5 and 6). The survey XPS spectra were used to identify the general elements in the samples' surface (Figure 5-a). In the spectra from the control PES and control PES DBD, only the peaks in the regions attributed to carbon (C 1s) and oxygen (O 1s) were identified. In the samples with PEDOT:PSS a peak in the region of the sulphur (S 2p) emerged. Lastly, when the PES sample was functionalized with PEDOT:PSS and IZ, the peak from nitrogen (N 1s) appeared, confirming the adherence of both on the fabrics' surface (Figure 5-a). The C 1s high-resolution spectra of the samples showed three common peaks at 285.0, 286.4 and 288.8 eV attributed to the C-C/C-H, C-O/C-S and O-C=O, respectively from PES and PEDOT:PSS (Figure 5-b). An extra peak emerged with the addition of the IZ as dopant at 287.0 eV attributed to the $-C=N^+$ group in the imidazolium salt structure¹⁹⁻²⁴.

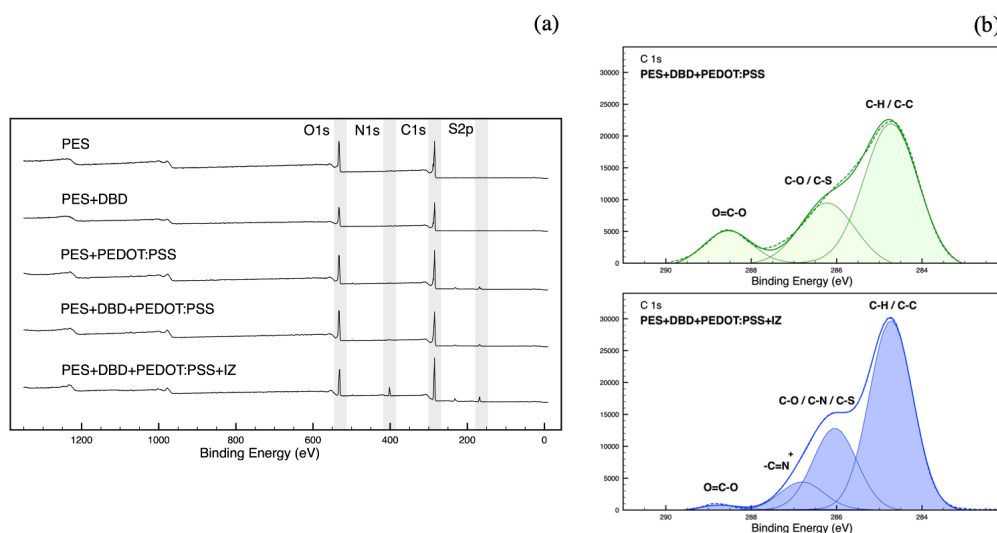


Figure 5: XPS spectra of the PES samples: survey spectra (a), and C 1s high-resolution spectra (b).

In the S 2p high resolutions spectra of samples, it was possible to detect the characteristic peaks from PEDOT:PSS from 162 to 172 eV. Two distinct types of sulphur atoms emerged due to the thiophene group in PEDOT and the sulfonate group in PSS structure. The broad peak at higher binding energy (167.7-169.2 eV) can be attributed to the overlap of the S 2p_{3/2} and S 2p_{1/2} peaks in PSS, while the doublet S 2p_{3/2} and S 2p_{1/2} at lower binding energy (163.1 eV and 164.5 eV) appeared from the sulphur atoms in PEDOT²⁵. In the sample pre-treated with DBD plasma and impregnated only with PEDOT:PSS an extra peak emerged at 165.6 eV attributed to the development of oxidized species from PEDOT²⁶. These species showed to disappear from the fabrics' surface when the IZ was added as dopant (Figure 6).

The O 1s spectra presented three major peaks from PEDOT:PSS and PES at 531.6 eV, 533.1 eV and 534.4 eV assigned to S=O and C-O and C=O bonds, respectively (Figure 6)^{22,27}.

The N 1s high resolution spectra of the sample with DBD plasma treatment, PEDOT:PSS and IZ showed a broad peak at 401.4 eV, which corresponds to the absorption of the imidazolium cation on the surface of the fabric (Figure 6)²⁸.

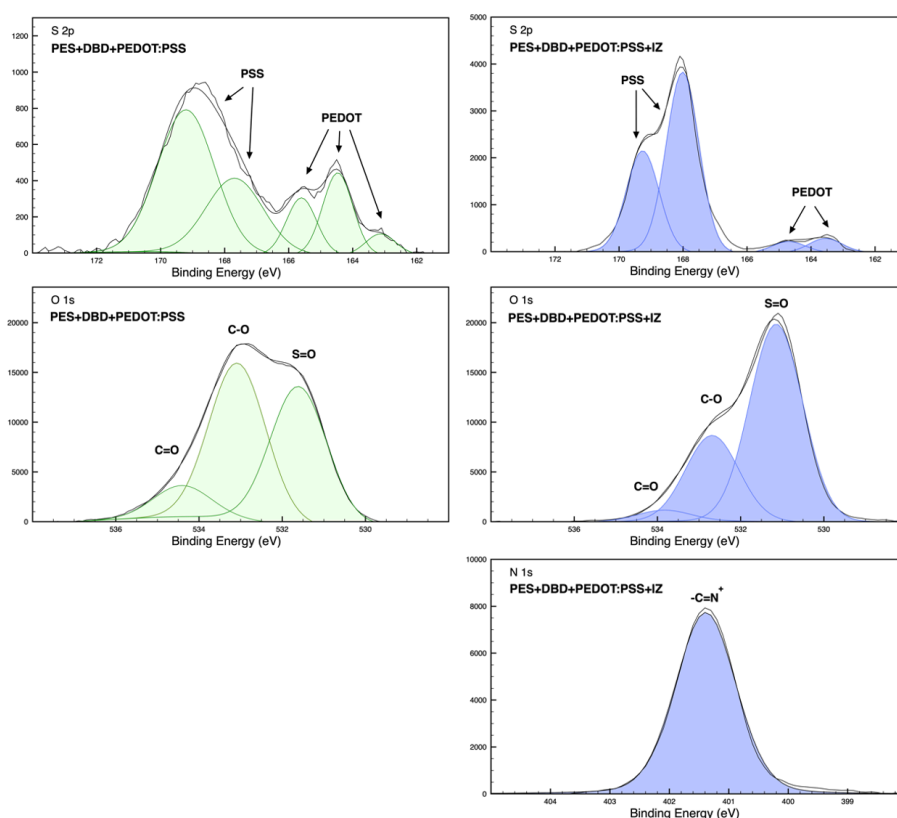


Figure 6: High resolution spectra of the XPS analysis in the PES samples (S 2p, O 1s and N 1s).

4. CONCLUSIONS

The present research work described a simple impregnation method that considerably strengthens the conductive pathways of PEDOT:PSS treated textile samples by the usage of a secondary dopant method such as IZ (0.2M) solution. It was seen that PES fabrics with DBD plasma treatment activation accomplished better electrical conductivities and consequent better heating behaviour. The development of a flexible material based on the Joule effect has a huge potential for applications in wearable textiles due to the lower operative power and short thermal response. The Joule heating experiment depicts good

heating stability. The flexible textiles possess remarkable thermal stability and could have promising prospects in thermotherapies like wearable healthcare, joint pain relief and sports rehabilitation.

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