Coloured and low conductive fabrics by *in situ* laccase-catalysed polymerization

Jing Su<sup>a,b</sup>, Jennifer Noro<sup>b</sup>, Jiajia Fu<sup>a</sup>, Qiang Wang<sup>a</sup>, Carla Silva<sup>b</sup>, Artur Cavaco-Paulo<sup>a,b,⁎</sup>

<sup>a</sup> International Joint Research Laboratory for Textile and Fiber Bioprocesses, Jiangnan University, Wuxi, 214122, China
<sup>b</sup> Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal

**ABSTRACT**

Coloured and conductive fabrics were obtained through *in situ* laccase polymerization of catechol and p-phenylenediamine under high-pressure homogenization. Both monomers, catechol and p-phenylenediamine, were polymerized by different laccase forms, namely native, PEGylated and Epoxy-PEGylated. All the catalysts were placed inside a textile fabric bag which served simultaneously as enzyme support and as substrate for coating with the newly produced polymers. The PEGylated laccase forms gave rise to a higher amount of oligomers/polymers and higher colouration level of polyethylene terephthalate (PET), cotton and wool fabrics compared to native laccase. Both functional polymers were able to confer conductivity to the substrates however in a different extent. Fabrics coated with poly(p-phenylenediamine) present higher conductivity, rather due to its polymerized structure than to the amount of polymer produced by enzyme catalysis. Herein a green approach was presented to produce polyphenols with increased fixation onto different textile substrates. These substrates reach high levels of colouration and good fastness behaviour after washing.

**1. Introduction**

Phenolic and aromatic amine compounds like catechol and p-phenylenediamine have been widely used as industrial reagents to produce pharmaceutical products, cosmetics, dyes, rubber and plastics [1,2]. These industrial activities produce polluted wastewater containing these compounds which may accumulate in the soil, ground and surface water, when released into the environment [3]. Therefore, their removal from wastewater is of extreme importance in the referred areas. Oxidoreductive enzymes have been explored to catalyse the transformation of the toxic phenols and arylamines in valuable products for diverse applications [4–6]. Among the different existing oxidant enzymes, laccases (benzenediol: oxygen oxidoreductases; EC 1.10.3.2) are considered as one of the most important ones since they can catalyse the oxidation of phenol/amine compounds and their derivatives. Laccase-assisted reactions take place under mild conditions in the absence of toxic reagents and rarely cause the formation of by-products. This oxidation ability has been presented as a promising route to obtain ecological functional oligomers and polymers with varied functions such as dyeability, antioxidant activity, conductivity and other properties, for application in several fields [7–10]. Polymeric dyes are coloured polymers synthesized through controlled reactions, such as monomer polymerization and macromolecule modification, to bring chromophore to the main or side polymers [11]. Their higher colouration ability and colour fastness make them good alternatives for the dyeing of textile fibres since traditional dyes involve high energy consumption and wastewater drawbacks. Recently, laccases have been investigated for the biosynthesis of bio-colourants and decolouration of synthetic dyestuffs in the dyeing industry with some researches focusing on the enzymatic colouration of natural fibres. Shin et al. proved that laccase had the ability to dye wool fabric after padding with hydroquinone [12]. Tzanov et al. also confirmed that laccases could be applied to wool dyeing [13]. Later, Kim et al. explored the ability of laccase for the colouration of cotton and flax, aiming fibre surface modification [14–16]. Despite the promising results obtained the washing and rubbing fastness results were not adequate, due to the low substantivity of the new polymers onto the fibres surface. Deeper studies including the use of different devices for the *in situ* polymerization of the phenolics would help to overcome the substantivity problems associated to this green colouration method.

Besides colouration, the new polymers supply generally additional properties to the substrates on which they are applied, namely electrical conductivity, antimicrobial and antioxidant behaviour, among others [17–19]. Electrical conductivity conferred by these polymers is the...
result of the delocalization of π -electrons in a conjugated system. The presence of electric charges in their molecular structure is capable of translocating along the polymer chains without involving other conducting materials such as metals or graphite [19]. In literature one can find already a considerable number of works related to the enzymatic approaches for the production of conductive products. Recently Zhang et al. successfully developed an enzymatic approach for dyeing wool fabrics with special pH-responsive, colour-changing and conductive properties, via in-situ polymerization of 2,5-diaminobenzenesulfonic acid (DABSA) by laccase from Trametes versicolor [20]. High-redox-potential laccase, isolated from Aspergillus, was used by the same researchers as a biocatalyst in the synthesis of conducting polyaniline/lignosulfonate (PANI-ES-LGS) complex using atmospheric oxygen as the oxidizing agent [21]. Salas et al. found the optimal enzymatic conditions for the polymerization of aniline using a commercial Trametes villosa laccase [22]. All these studies involve mostly the use of water bath reactors to conduct the polymerization and colouration. In previous studies, we explored the role of high energy environments on the enzymatic polymerization of catechol. Our findings suggested that the use of devices like high-pressure homogenizers (HPH) for the enzymatic polymerization of phenolics greatly improve the conversion rates and polymerization degrees [23]. High-pressure homogenization is a technology generally applied to reduce the particles size using continuous or semi-continuous pressures between 60–400 M P [24]. High-pressure homogenizer pump a fluid through a narrow gap valve (the heart of homogenizing equipment) using high pressure intensifiers, which increases its velocity to a great extent, resulting in depressurization with consequent cavitation and high shear stress [25].

The main objective of this study is to colourize and confer electrical conductivity to textile fabrics through a green in situ polymerization of catechol and p-phenylenediamine under high pressure homogenization. Within this methodology we foresee to overcome the substantivity problems associated with the biocolouration of fibres with poly(phenolics), where low fastness levels are normally obtained. Laccase was used as the biocatalyst for the biosynthesis and in situ coating of textile fabrics (polyethylene terephthalate, cotton and wool) with the newly polymers formed. The polymerizations were conducted with different laccase forms, namely native laccase, PEGylated laccase and PEGylated laccase immobilized onto an epoxy-resin. The latter catalyst form was deposited inside of textile fibre bags (polyester, cotton and wool) during processing, as well as the other forms for control purpose. The ability of the produced polymers as dyestuff and conductive additives was evaluated. The conversion rates of the polymerization reactions were assessed by 1H NMR spectroscopy and gravimetrically.

2. Material and methods

2.1. Materials and equipment

Laccase from Myceliophthora thermophila was supplied by Novozymes, Denmark. Catechol, p-phenylenediamine, poly(ethylene glycol) methyl ether and sodium carbonate were purchased from Sigma Aldrich, Spain. Deuterated dimethyl sulfoxide was obtained from Cortecnet, France.

The fabrics used for the study were supplied by a textile company with the following characteristics: polyethylene terephthalate (PET): 96 g/m²; 24°40 /cm², cotton: 65 g/m²; 35°40 /cm² and wool: 420 g/m²; 15°15 /cm².

The high-pressure homogenizer used for the experiments was the EmulsifiFlex-C3 (ATA Scientific, Taren Point NSW, Australia) with a constant flow-through capacity of 3L/hr with the ability to process 10 ml samples; the homogenizing pressure is adjustable between 500 and 30,000 psi or 35 and 2000 bar; the flow rate is independent of pressure.

2.2. Methods

2.2.1. PEGylation of laccase

Laccase from Myceliophthora thermophila was PEGylated as previously reported [26] using the procedure of Daly et al. [27]. Briefly, 14.0 mL of 12 mg/mL laccase were reacted with 20 kDa, poly(ethylene glycol) methyl ether at pH = 5, 10 mM sodium phosphate buffer with 20 mM sodium cyanoborohydride. A control reaction without mPEG was also conducted in every experiment. The reactions were stirred rapidly for 17 h at 4 °C. After 10 min of mixing, the reactants were completely dissolved, and an aliquot (namely time 0 h) was taken, as well as at each time point of reaction. These samples were ultrafiltrated using a 30 kDa cellulose membrane mounted in an ultrafiltration apparatus. Then, the activity of laccase was measured against ABTS according to the methodology described by Childs and Bardsley [28].

2.2.2. Immobilization of PEGylated laccase onto epoxy resin supports

The immobilization of PEGylated laccase onto epoxy methacrylate resins (Purelite Lifetech ECR enzyme immobilization resins: 300–600 Å) was conducted as follows: 2 mg/mL PEGylated laccase in 0.5 M acetate buffer (pH 5.0) were mixed with epoxy methacrylate (50 mg/mL) and then stirred for 48 h at 4 °C. The powder was then washed several times with water by centrifugation and dried under vacuum.

2.2.3. Enzymatic-assisted polymerization of catechol and p-phenylenediamine

The biotransformation of catechol and p-phenylenediamine into their functional polymers was conducted in acetate buffer (pH 5) through high-pressure homogenization. Catechol and p-phenylenediamine polymerization were processed by incubating 50 mM of monomer in different solutions: a) 100 U/mL native laccase and b) 100 U/mL PEGylated laccase, c) 100 U/mL epoxy-PEGylated laccase, in acetate buffer (pH = 5). The immobilized enzyme was confined in a polyethylene bag and placed in the sample receptor of the high-pressure homogenizer. This receptor is fed with the fluid that undergoes homogenization inside the device and crosses the fabric sample, at this stage, with reduced pressure. The other enzyme forms were also placed inside the bag for control purposes. Afterwards the monomer solution was added, and the homogenization proceed for 2 h (corresponding to 360 homogenization cycles). The starting temperature was set to 40 °C and the temperature was monitored during processing to follow the inherent increase due to high-energy device processing. Further the polymer powder was collected from the HPH device by dissolution with dimethyl sulfoxide to solubilize the insoluble polymers and posteriorly dried under vacuum for characterization.

Controls comprising fabric samples incubated only with laccase were also conducted in order to evaluate the influence of the catalyst colour on the fabrics after homogenization.

2.2.4. Polymers characterization by 1H NMR spectroscopy and gravimetrically

The polymers produced were collected from solution and characterized by 1H NMR. For this the precipitates obtained after washing and centrifugation were dissolved in deuterated solvent, DMSO-d₆, for 1H NMR evaluation. The spectra were acquired in a Bruker Avance III 400 (400 MHz) using the peak solvent as internal reference.

The weighing of the final polymer powder took place by weighting the powder collected from the final solution and the weight of polymer on the coated fabric samples (the weight of samples after coating is subtracted to the initial weight in dry conditions).

2.2.5. Wettability evaluation: water contact angle and water drop test

Dataphysics equipment using OCA software with video system (Dataphysics, Filderstadt, Germany) for the capturing of images in static and dynamic modes was used for the measurement of contact angle of the water drop in the non coated and in the coated fabrics, at
Contact angles were measured after 15 s and the data were obtained from the averages of measurements taken from ten different points on the surface of each sample. The volume of the water droplet was set as 5 μL using a Hamilton 500 μL syringe type and the model select to measure the water contact angle was the Ellipse-fitting model (evaluation of the outline by fitting an ellipse).

The degree of wettability of the coated samples was evaluated by means of the water drop test according to AATCC standard method [29]. The wetting time was determined by placing a drop of distilled water on the stretched fabric sample (2 cm × 2 cm) from a burette held 1 cm from the fabric. The time of disappearance of the water-mirror on the surface (the time for the water drop to lose its reflective power) was measured as the wetting time. This procedure was applied to both uncoated and coated fabrics.

### 2.2.6. Scanning electron microscopy

All the fabric samples were added to aluminium pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™), with the excess removed using compressed air. Samples were coated with 2 nm of Au for improved conductivity. The aluminium pin stub was then placed inside a Phenom Standard Sample Holder, and different points for each sample were analysed for elemental composition. The samples were characterized using a desktop scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS).
analysis (Phenom ProX with EDS detector (Phenom-World BV, Netherlands)). All results were acquired using the ProSuite software integrated with Phenom Element Identification software, allowed for the quantification of the concentration of the elements present in the samples, expressed in either weight or atomic concentration.

2.3. K/S evaluation of coloured fabrics

The colour strength (k′s values) was evaluated by using a Datacolour apparatus at standard illuminant D65 with the Kubelka-Munk equation (Eq. 1), in which K is the absorbance coefficient, S is the scattering coefficient and R is the reflectance ratio.

Since not all the samples presented the same maximum wavelength, the data were presented as the sum of all K/S values obtained in the wavelength range 400–700 nm (checksum K/S) at the measuring intervals of 10 nm. The measurements were done in triplicate and the data presented are the mean values of these measurements.

\[ K = \frac{(1-R)^2}{2R} \quad (1) \]

Colour difference was qualitatively evaluated using the software Spectraflash 600 from Datacolour using the K/S values for difference evaluation and attributing values from 1–5.

2.4. Conductivity measurement of coated fabrics

Electrical conductivities were measured with a Fluke 123 Scopmeter (20Mhz) using two -point probe technique placing them under a pre-2.4. Conductivity measurement of coated fabricsherent to polymer formation, the peak intensity increases. At the same colourless to dark brown. The spectra of the soluble oligomers present a spectral behaviour during polymerization for catechol and through high-pressure homogenization and followed by UV spectroscopy (Fig. 1). Observing both spectra sets one can infer a difference in the conversion yield of catechol into poly(catechol) was improved up to 73% with PEGylated laccase, while the conversion of p-phenylenediamine into poly(p-phenylenediamine) was improved up to 85%. These findings have been reported previously by us (data not shown) where we found that the chemically modified laccases are able to improve the polymerization of catechol. Moreover, the role of high-energy environments was also previously described as potentiating the enzymatic polymerization to produce higher polymers and convert higher amount of monomer [23,26]. A higher amount of produced oligomers and polymers not always corresponds to a higher deposition onto the fibre substrates used as containers. This may depend on the type of fibre and variations may occur as discussed further (Table 1).

3. Results and discussion

3.1. Catechol and p-phenylenediamine polymerization

The bioransformation of catechol and p-phenylenediamine into their functional polymers was conducted in acetic acid buffer (pH 5) through high-pressure homogenization and followed by UV–vis spectroscopy (Fig. 1). Observing both spectra sets one can infer a different spectral behaviour during polymerization for catechol and p-phenylenediamine. During laccase-assisted polymerization of catechol under high-pressure homogenization, all the reaction mixtures changed from colourless to dark brown. The spectra of the soluble oligomers present a typical peak around 300 nm and, due to molecular arrangements inherent to polymer formation, the peak intensity increases. At the same time, a new peak at around 430 nm appears confirming polymerization. The spectra of p-phenylenediamine presents a different feature. The colourless monomer presents a typical spectrum with a peak at around 300 nm. As the oxidation starts (≈15 min.) the solution gets blue-violet and a new absorption band is developed at around 520–530 nm as well as a new shoulder at around 350 nm. After 2 h of oxidation, the soluble oligomers maintain the described spectra (Fig. 1) and some precipitates can be observed at the bottom of the solution container, corresponding to the insoluble oligomers. Despite the different spectra observed, both events are governed by an increase in the UV–vis absorption intensity indicating a greater degree of π-conjugation correlated with the occurrence of polymerization [30].

These preliminary findings seem to point out that PEGylated and Epoxy-PEGylated laccase forms are more prone to polymerize both catechol and p-phenylenediamine. However, the tendency is not the same for all the samples since depending on the fibre used as enzyme container, the amount of soluble oligomers available for detection is different. These is discussed further on the spectra estimation discus-

The 1H NMR of poly(catechol) (Figure S1-A) shows that after polymerization, the OH peak (proton c) from the catechol starting material disappeared or decreased in intensity, indicating the polymerization of catechol by the hydroxyl groups. Based on the pattern of the aromatic peaks, two doublets of doublets, we propose the polymer structure as indicated in Figure S1-A. The 1H NMR spectra of p-phenylenediamine is represented by only one aromatic peak at δ=6.3 ppm (proton c). When the polymerization occurs, this peak decreases in intensity, and two new peaks are observed: one at δ=5.9 ppm (broad singlet) and the other at δ=6.6 ppm (doublet). These peaks lead us to propose the polymer structure of Figure S1-B. The amount of oligomers and polymers produced by the different forms of laccase under high-pressure homogenization was evaluated by the weighting of the final powder obtained after the reaction. For both poly(catechol) and poly(p-phenylenediamine), the catalysis with PEGylated laccase and Epoxy-PEGylated laccase is enhanced independently on the enzyme container used. Comparing with the native form of laccase the conversion yield of catechol into poly(catechol) was improved up to 73% with PEGylated laccase, while the conversion of p-phenylenediamine into poly(p-phenylenediamine) was improved up to 85%. These findings have been reported previously by us (data not shown) where we found that the chemically modified laccases are able to improve the polymerization of catechol. Moreover, the role of high-energy environments was also previously described as potentiating the enzymatic polymerization to produce higher polymers and convert higher amount of monomer [23,26]. A higher amount of produced oligomers and polymers not always corresponds to a higher deposition onto the fibre substrates used as containers. This may depend on the type of fibre and variations may occur as discussed further (Table 1).

3.2. Surface characterization of coated fabrics

We investigated the wettability surface properties of the fabrics by water contact angle analysis and by time of water drop absorption evaluation (Table 2). Cotton is a well-known hydrophilic natural polymeric material and when a droplet of water was placed on its surface, it was rapidly soaked into the fabric. After coating with both polymers, the water contact angle of cotton fabrics increased up to maximum 144.4° and the time of water drop absorption increased from 0.1 min. to over 5 min., indicating an increase of the hydrophobicity. The hydrophobic character of PET was also incremented by coating with both poly(catechol) and poly(p-phenylenediamine) as it could be shown by the increase of the water absorption time and by the water contact angle. The wool fabric demonstrated however a distinct behaviour depending on the polymer. When coated with poly(catechol), an increase of hydrophobicity was observed whereas when coated poly(p-phenylenediamine) the hydrophobicity character decrease

<table>
<thead>
<tr>
<th>Fabric container</th>
<th>Poly(catechol)*</th>
<th>Poly(p-phenylenediamine)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Native laccase</td>
<td>PEGylated laccase</td>
</tr>
<tr>
<td>PET</td>
<td>60.8 %</td>
<td>72.8 %</td>
</tr>
<tr>
<td>Cotton</td>
<td>61.2 %</td>
<td>69.8 %</td>
</tr>
<tr>
<td>Wool</td>
<td>64.6 %</td>
<td>71.8 %</td>
</tr>
</tbody>
</table>

* The conversion rates were calculated through samples weighing.
significantly. While that for PET and cotton it was observed that the coating remained mostly at the surface of the fabrics, for wool a deeper penetration of both polymers inside fibrils was perceptible. For this reason, the textile substrate did not acquire a hydrophobic behaviour. It is well-established that the water or humidity in the air exerts a significant influence on the charge decay and conductivity stability of conductive materials [31]. The good hydrophobicity of the fabrics would enhance their humidity resistance properties and suppress conductivity decay. This phenomenon was observed for both PET and cotton coated fabrics which revealed higher conductivity, while on wool was only possible to observe a small increment.

From the scanning electron microscopy (SEM) (Fig. 2), the changes of the micromorphology of coated fabrics are evident. The smooth surfaces of PET and cotton surfaces were found to be covered with both poly(catechol) and poly(p-phenylenediamine) layer. On wool, the covering was also confirmed by visualisation of the covering of the typical fibre scales. The overall coverage of the fabrics with the conductivity decay. The amount of polymers formed and fibres coverage might be established.

However, despite the lower affinity observed for PET, the methodology applied revealed to be efficient not only for cotton and wool fibre colouration but also for synthetic substrates. The effect of “hot spots” and mass transport phenomena governed by high-pressure homogenization allowed to obtained high coverage of cotton and wool fibres also to colourize a fibre which naturally would not be prone to colourization. It is noteworthy that no additives were applied as in the traditional fabrics colouration. This promising technology showed potentialities for the green colouration of natural and synthetic fibres under mild reaction conditions, opening up an all new field of colouration where a panoply of polymers may be used as colourants. We foresee the possibility of the technology industrialization due to the great performance at industrial scale of the high-pressure homogenizers.

### 3.3. "In situ" colouration of fabrics

As we have previously highlighted, laccases have been applied for the "in situ" synthesis of colourant compounds, especially for protein and cotton fibres, however less explored for synthetic fibres [16,32,33]. Herein, we explore the “in situ” polymerization and colouration of textile fibres by placing the enzymes used inside a textile fabric bag with different fibre composition (PET, cotton and wool). The photographs of the colored fabrics are shown in Table S1. Besides colouration, the newly polymers are expected to confer differentialed properties to the coated fabrics, namely electrical conductivity [15].

The spectral estimation of the textile fibres after “in situ” colouration is presented in Table 3 as checksum K/S quantification after a washing step with a non-ionic detergent. From the data obtained one might observe a deep colouration, especially of cotton and wool fabrics. The controls consisting on fabric samples incubated only with laccase were also conducted in order to evaluate the influence of the catalyst colour on the fabrics after homogenization. Insignificant colouration could be observed for these fabric controls.

Despite the lower coating, PET fibres are also coloured independently on the catalyst used. This corroborates our previous findings [23] where we studied for the first time the in situ enzymatic colouration of PET using native laccase. Herein, we confirm these results and deepen the study by using chemically modified laccases which incremented the polymerization. As expected, protein fibres like wool have great affinity to the newly polymers produced, as confirmed by the deep colouration obtained. From what concern poly(p-phenylenediamine), the role of the different laccase forms is not perceptible since high colouration is obtained for all. In the case of poly(catechol) the role of the different enzyme forms is more evident. As previously observed for the conversion rates, PEGylated enzyme promoted also the higher levels of colouration on cotton and wool. In the case of PET, this enzyme form contributes to a higher colouration with poly(p-phenylene-diamine) but not with poly(catechol). Due to its hydrophobicity, lower affinity and lack of bonding with the formed polymers, the colouration of PET is still not uniform and no direct relation between the amount of polymers formed and fibres colouration might be established.

### 3.3.1. Colour fastness after washing

The colour fastness of coated samples with the colouring polymers produced was studied by washing the samples with a non-ionic detergent. The standard washing fastness procedure was not feasible due to the limited size of the samples. The colour difference between coated samples before and after washing is presented in Table 3 after grey scale evaluation by the software Datacolour spectra. The data obtained reveal acceptable colour fastness with exception of the coloured PET samples. This result was expectable given the low affinity of the polymers to this substrate. The other substrates, cotton and wool, being natural fibres with higher affinity to these compounds, present, as expected low colour loss after washing. No tendency is observed relating the colour loss with the type of enzyme used for the in situ polymerization. Apparently, the colour loss is more related to the substrate used rather than the ratio (oligomers: polymers) produced, which, considering our previous findings [23], are expected to be different depending on the enzyme formed used. One would expect a higher colour fastness of the samples coloured polymers produced by PEGylated laccase forms,
which gave rise to higher amount of polymer. This tendency was not however observed.

In comparison with other related works, the coated fabrics reveal reasonable colour fastness to washing [16,34]. The mass transport effect promoted by the high-pressure homogenization is directly related with a higher substantivity of the new polymers onto the fabrics surface, which was confirmed in our previous study about the polymerization of catechol with native laccase using water bath reactor and high-pressure homogenizer reactor [23]. A higher polymer adhesion corresponds, in most cases studied, to a higher substantivity and low colour loss during washing process.

The colour fastness is a prime importance parameter especially for

Table 3
Checksum (K/S) estimation of the colourized fabrics after in situ polymerization with native laccase, PEGylated laccase and Epoxy-PEGylated laccase under high-pressure homogenization (before and after washing with non ionic detergent); the control samples were not coated with polymers.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Poly(catechol)</th>
<th>Poly(p-phenylenediamine)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Native lac</td>
<td>PEGylated lac</td>
</tr>
<tr>
<td>PET</td>
<td>Checksum K/S (after colouration)</td>
<td>1.73</td>
<td>96.41</td>
</tr>
<tr>
<td></td>
<td>Colour difference (after washing)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Cotton</td>
<td>Checksum K/S (after colouration)</td>
<td>1.36</td>
<td>114.69</td>
</tr>
<tr>
<td></td>
<td>Colour difference (after washing)</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Wool</td>
<td>Checksum K/S (after colouration)</td>
<td>9.70</td>
<td>594.89</td>
</tr>
<tr>
<td></td>
<td>Colour difference (after washing)</td>
<td>5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

* S: GOOD; I: FAIR.
daily-use garments, however if one consider the coated conductive fabrics as technical textiles, this parameter loses importance. Moreover, even after washing the samples maintained the conductivity character at similar levels (data not shown).

3.4. Conductivity of poly(catechol) and poly(p-phenylenediamine) coated fabrics

As mentioned previously, the coating of the fabrics within the newly formed oligomers/polymers is expected to confer additional properties to the substrates besides the colouration itself. Since the polymerization of both natural and artificial monomers with undivided electron pair goes through a radical mechanism, oxidoreductases like laccase, were used herein as biocatalysts for these reactions. The conductivity of the textile fibres after coating with poly(catechol) and poly(p-phenylenediamine) were evaluated (Fig. 3). When in monomer state these compounds present poor conductivity, acquiring higher conductivity when polymerized [35]. As can be depicted in Fig. 3A and B, the coated PET and cotton fabric samples with poly (catechol) and poly(p-phenylenediamine) varied from antistatic (control samples) to low conductive fabrics. The conductivity behaviour of coated wool is still negligible. The differences of conductivity between fabrics might be due to several reasons. Despite the similar conversions rates observed, the different level of polymer penetration into the fibres may influence greatly the surface conductivity. In the case of wool, one could observe a higher colouration, as seen by checksum K/S, but deeper colour penetration (data not shown), which might influence the amount of polymer at the surface of the fabric able to act as electricity conductor.

The conductivity of fabrics coated with poly(p-phenylenediamine) is higher than the fabrics coated with poly(catechol) (Fig. 3B). The electric conductivity of both materials is related with the delocalization of the π-electron systems with alternating single and double bonds, which can be easily oxidized and reduced. The final structure of poly(p-phenylenediamine) containing fused aromatic rings [36], in comparison with the poly(catechol), allows a higher electron delocalization which might be responsible for the conductivity differences obtained.

4. Conclusions

We successfully coated textile fabrics (PET, cotton and wool) with poly(catechol) and poly(p-phenylenediamine) to obtain coloured fabrics with additional conductive properties. The in situ oxidation of catechol and p-phenylenediamine with native and chemically modified laccases, properly contained inside fabric bags which had served simultaneously as enzyme containers and substrates for coating, resulted in a green colouration of these fabrics. The fixation of the polyphenols to the textile substrates was incremented, relatively to other works reported, due to the inherent mass transport phenomena involved within the high-energy environment applied. Besides colouration, the polymers deposited conferred electric conductive properties to the coated fabric substrates. One can also highlight that this additional property is not directly related to the form of enzyme used for oxidation.
the product of associated with the type of starting monomer. It is clear that a higher algalities for the green colouration of natural and synthetic fibres under mild reaction conditions, opening up new routes for colouration where a panoply of polymers may be used as colourants.

Declarations of interest statement

The authors declare no competing financial and non-financial interests.

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