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ORIGINAL ARTICLE

Enhanced adhesion of PEDOT:PSS to substrates using polydopamine as a primer

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Abstract
Utilization of the conducting polymer PEDOT:PSS in flexible optoelectronic devices is hindered by poor adhesion to flexible, polymer-based substrates. In this communication, the ability of poly(dopamine) (PDA) to act as a primer and improve adhesion is probed. The presence of hydrophilic PDA on the surface of the substrate increased the wettability of polypropylene (PP); however, it was reduced for poly(ethylene terephthalate) (PET). Despite this, PDA was established as an effective primer to improve the quality and adhesion of pristine PEDOT:PSS and PEDOT:PSS/Tween 80 films on glass, PP and PET substrates. In addition, PDA did not negatively impact the sheet resistance of the PEDOT:PSS/Tween 80 films, indicating its suitability as a primer in flexible optoelectronic devices.

Introduction

The use of the conductive polymer poly(3,4–ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) in flexible optoelectronic devices has been reported in the literature [1–3]. These applications require flexible substrate materials, and polymers such as poly(propylene) (PP) and poly(ethylene terephthalate) (PET) are typically used. However, a noteworthy challenge arises from the fact that PEDOT:PSS exhibits weak affinities toward such substrates, primarily due to poor adhesion and hydrophobicity [4]. As a potential solution, surface modification techniques (e.g., corona treatment) have been shown to enhance PEDOT:PSS adhesion; however, these methods are both time-consuming and expensive [5]. Research into the adhesion of PEDOT:PSS on polymer substrates remains relatively limited at present.

The literature discusses several variables that contribute to adhesion [6, 7]. PEDOT:PSS adhesion is more complicated since it involves two distinct states of the polymer, an aqueous liquid, and a solid film. Among the various factors influencing PEDOT:PSS adhesion, molecular bonding and wettability are likely the most significant contributors.

Molecular bonding occurs when materials are brought into close contact, and it relies on the presence of suitable functional groups. Wettability is the crucial parameter to consider since it determines the amount of aqueous PEDOT:PSS solution in contact with the substrate surface. On hydrophobic surfaces, aqueous PEDOT:PSS shows suboptimal wetting characteristics owing to significant disparities between the substrate surface energy and solution surface tension. Additionally, the wettability influences the electrostatic interactions since diminished surface contact reduces the potential for the formation of molecular bonds.

Polydopamine (PDA) belongs to the melanin family of biopolymers and is produced through the oxidative polymerization of dopamine (Fig. 1a) [8]. It is based on 2,4-dihydroxyphenylalanine (DOPA) (Fig. 1b), a compound synthesized by mussels to allow them to adhere to rocks and boats in harsh conditions [9]. PDA has a number of functional groups that facilitate strong interactions with other molecules. These interactions encompass coordination bonding, π-π stacking, hydrogen bonding, covalent bonding, hydrophobic interactions and cation-π interactions [10]. Despite its usefulness, there is uncertainty surrounding its chemical structure. Hong et al. (2012) [11] described the PDA structure as a covalently linked polymer formed via self-assembly of dopamine and dihydroxyindole, while

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Dreyer et al. (2013) [12] discussed monomers of 5,6-dihydroxyindole involved in π-π stacking and hydrogen bonding. More recent studies proposed combinations of covalent bonding and π-π stacking [13].

PDA has attracted attention as a surface modifier or primer layer due to its ability to adhere to various substrates, including noble metals, metal oxides, ceramics, and polymers [8], and alter their hydrophilicities [14]. Considering the reported enhancements in wettability and adhesion achieved with a PDA primer [8, 14], its presence is likely to enable adhesion of PEDOT:PSS to polymer substrates.

This communication explores the use of PDA as a primer on glass and polymer substrates to produce PEDOT:PSS/Tween 80 films. The surfactant Tween 80 has previously been shown to increase the conductivity of PEDOT:PSS [15], highlighting the importance of assessing both pristine and surfactant-containing PEDOT:PSS. The wettability, film quality, adhesion, and sheet resistance of PEDOT:PSS/Tween 80 formulations on glass and polymer substrates with and without PDA are evaluated to determine the effects this primer has on the solution and film properties.

Materials and methods

Materials

A high conductivity, surfactant-free, aqueous dispersion of PEDOT:PSS (1.2 wt%), Tween 80 (Polysorbate 80), tablets of tris(hydroxymethyl)aminomethane (Tris)-buffered saline, dopamine hydrochloride (98%) and NaOH (0.1 molL^{-1}) were used as received and supplied by Sigma–Aldrich (Gillingham, UK). The polymer substrates were fabricated from PP (Sabic, Redditch, UK) and Melinar laser plus PET (DuPont, Stevenage, UK).

Methods

PP and PET sheet processing

A Moore E1127 hydraulic hot press (Birmingham, UK) was used to make PP and PET sheets (1 mm) by heating at 190 °C and 280 °C, respectively. A Memmert Universal Digital oven (Schwabach, Germany) was initially used to dry the polymer pellets at 70 °C for 2 h. Samples (30 g PP, 40 g PET) were then placed in 155 × 175 × 1 mm PTFE molds and heated for 3 min in the press. Following this, a pressure of 10 tonnes was applied for 5 min before the samples were removed and allowed to cool in ambient air.

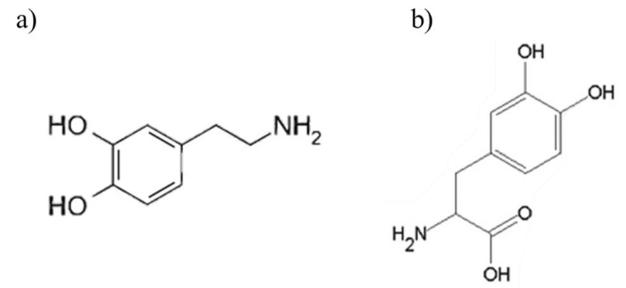

Fig. 1 Chemical structures of **a** dopamine and **b** 2,4-dihydroxyphenylalanine (DOPA)

Wettability

A single droplet of each solution was pipetted onto the substrates. An image was taken, and the contact angle between the droplet and substrate was analyzed using ImageJ software (LOCI, University of Wisconsin).

Polydopamine synthesis and casting

Glass, PP and PET substrates were coated with PDA to evaluate their impacts on the adhesion and sheet resistance of the PEDOT:PSS/Tween 80 films. Substrate cleaning was employed prior to casting. The glass substrates were washed with hot water and detergent followed by acetone cleaning before being rinsed with distilled water and dried. The PP and PET were simply rinsed with distilled water and dried.

The PDA synthesis followed the method used by Lee et al. [8]. A Tris-buffered saline solution (0.05 mol L^{-1}) was produced by placing a tris(hydroxymethyl)aminomethane (Tris)-buffered saline tablet in distilled water. A Hanna Instruments HI2211 pH meter (Leighton Buzzard, UK) was used to monitor the solution pH, which was adjusted to pH 8.5 with NaOH (0.1 molL^{-1}). Dopamine hydrochloride (2 mg mL^{-1}) was added to the buffer, and this was immediately followed by fully submerging the substrates into the solution. Magnetically stirring the buffer solution for 24 h ensured full polymerization of the PDA onto the substrates. After polymerization, the substrates were removed, washed with distilled water, and dried in an oven for 8 h at 40 °C before film casting.

Dip casting of films

PEDOT:PSS solutions containing Tween 80 were created with a range of concentrations (0.00–2.50 wt%). All solutions were magnetically stirred and sonicated for 10 min to ensure sufficient mixing and breakdown of agglomerates. Dip casting of these solutions on various substrate materials (10 × 20 mm) was performed with the procedure described by Carter et al. (2022) [15]. Substrate cleaning was

Table 1 Contact angles (°) for PEDOT:PSS/Tween 80 formulations on glass and polymer substrates with and without a PDA primer

Substrate	Tween concentration (wt%)			
	0.00	0.37	1.32	2.50
Glass	21.8 (6.0)	28.5 (2.0)	27.6 (3.0)	23.8 (0.5)
Glass + PDA	25.8 (1.1)	37.6 (1.1)	34.0 (2.3)	37.8 (1.5)
PP	72.5 (2.3)	56.1 (1.5)	48.8 (1.1)	40.1 (3.1)
PP + PDA	60.2 (2.8)	49.7 (2.3)	52.0 (2.5)	49.7 (2.8)
PET	52.0 (2.4)	44.8 (3.0)	36.7 (2.8)	39.0 (0.8)
PET + PDA	70.5 (0.4)	58.8 (3.7)	42.1 (3.9)	42.2 (0.6)

The standard deviations for two measurements are included in brackets

employed prior to casting. The glass substrates were washed with hot water and detergent followed by acetone cleaning before being rinsed with distilled water and dried. PP and PET were simply rinsed with distilled water and dried. Each substrate was dipped into the PEDOT:PSS/Tween 80 solutions for 30 s, ensuring that approximately half the slide was submerged. The resultant films were left to dry and equilibrate in ambient air for 12 h prior to testing. The same process was followed for the substrates coated with PDA.

Adhesion testing

Adhesion testing was conducted with the PEDOT:PSS/Tween 80 films, with and without a PDA primer, using glass, PP and PET substrates. Adhesion was assessed via a scratch tape test according to ASTM Standard D3359-17 (2019) [16], which was adapted to suit the samples in this study. Cross-hatched patterns were cut into the samples with 1 mm spacings between the cuts. Elcometer 99 adhesive tape (Manchester, UK) was then applied to the film and removed after 90 s. Adhesion was evaluated visually with the standard classification system, ranging from 5B (0% film removal) to 0B (>65% film removal) [16].

Sheet resistance

The sheet resistance was measured with an Ossila 4-point probe (Sheffield, UK) at a maximum voltage of 1 V and a current of 100 µA. Ten readings were taken at 6 locations across each film to avoid orientation bias.

Results & discussion

Wettability

Contact angle measurements were used to assess the wettability of the PEDOT:PSS/Tween 80 solution on each substrate, with and without PDA (Table 1). Glass was found to have the best wettability, and the polymers exhibited poorer wetting due to their hydrophobic natures. The use of a PDA primer with pristine PEDOT:PSS appeared to alter the contact angle differently for each substrate. No significant changes were observed on glass, whereas PDA improved the wetting of PP but reduced it for PET. The contact angles for PEDOT:PSS/Tween 80 on the polymeric substrates decreased with increasing concentrations of the surfactant, likely due to its amphiphilic nature. No overall trend was observed for the contact angles when PDA was applied to the polymer substrates with formulations containing Tween 80.

PDA has previously been reported to improve the wettabilities of substrates because of its hydrophilicity [14]. As the contact angle of PDA is comparable to that of glass (16.8 [17] versus 21.8°), little variability was expected. However, since PP and PET are both hydrophobic, incorporating PDA should significantly improve the hydrophilicity of the surface and generate lower contact angles. This was seen here with PP and has been previously reported for other polymers [18].

However, the contact angle on PET was found to increase with PDA, which indicated poorer wetting. The presence of both a catechol and primary amine in the PDA structure provides a wide range of bonding mechanisms [10]. PDA has been reported to bond through hydrogen or coordination bonds with hydrophilic surfaces and π-π stacking or CH-π interconnection with hydrophobic surfaces [19]. The bonding mechanism for the polymerization of PDA onto a substrate could vary the orientation of the 5,6-dihydroxyindole structure [10, 14, 20]. It is possible that for PET, polar groups attached to the carbonyl of the PDA, keeping the primary amine at the surface and therefore reducing the contact angle.

Regardless of these factors, the PDA coating was expected to be less than 50 nm thick [8], possibly allowing some interaction with the substrate material. If the coating was thicker, then each substrate would show similar contact angles and vary only with the PDA bonding orientation.

Film quality

The quality of the film on each substrate was assessed visually. High-quality films were produced on glass regardless of the presence of PDA. PEDOT:PSS containing 0.00 (Fig. 2a–d) and 0.37 wt% of surfactant (Fig. 2e–h) produced poor films on the two pure polymer substrates; however, these films were significantly improved by the addition of PDA. Higher concentrations of Tween 80 formed coherent films on the polymer substrates regardless of the PDA primer.

The capacity of these substrates for PEDOT:PSS/Tween 80 deposition via dip casting primarily relied on the wettability and the presence of surface polar groups. The glass

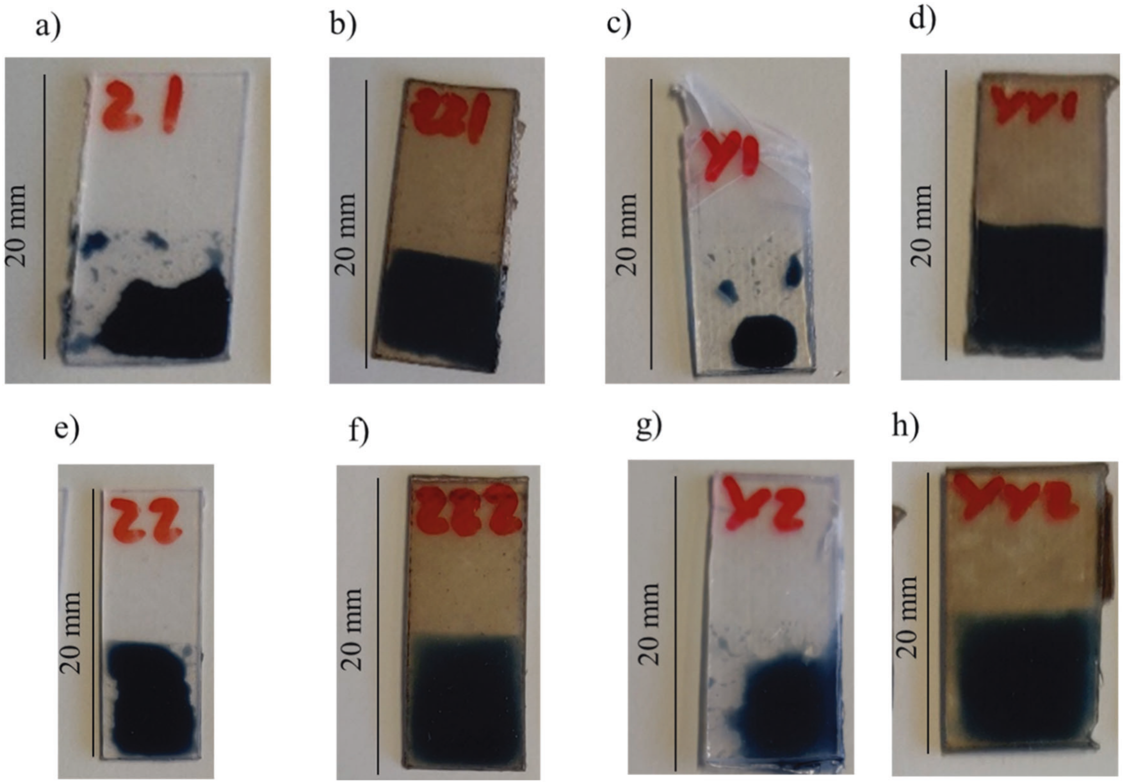

Fig. 2 Photographs of pristine PEDOT:PSS films on substrates of **a** PP, **b** PP/PDA, **c** PET, and **d** PET/PDA, and PEDOT:PSS/Tween 80 films (0.37 wt% surfactant) on substrates of **e** PP, **f** PP/PDA, **g** PET & **h** PET/PDA. The film quality improved when PDA was used as a primer

substrate employed was untreated soda lime glass containing Si-O bonds, which are polar and readily interact with both water and PEDOT:PSS. However, the carbonyls in PET are less polar, and PP contains no polar groups. This lack of polarity, coupled with poor wettability, meant that the low surfactant concentrations of the PEDOT:PSS/Tween 80 solutions were less likely to accumulate on the substrate, resulting in poor film formation.

Improvements in the wettabilities of hydrophobic polymers have been observed in the presence of PDA [18], which partially explains the improvements observed in film formation on the PP/PDA substrates. However, the introduction of PDA decreased the wettability of PET, suggesting that an additional mechanism controlled the deposition of PEDOT:PSS. It is postulated that the functional groups present in PDA readily interacted with PEDOT:PSS and extracted the polymer from the solution. This mechanism likely occurred with the PP/PDA substrate as well, with the added advantage of increased wettability.

Film adhesion

The adhesion of the PEDOT:PSS/Tween 80 film to various substrates was assessed with scratch tape testing (Table 2). Cracked or incoherent films suggested poor adhesive properties and were not tested. PDA improved the adhesion of each formulation to the substrates, as indicated by improved classifications. Although both polymer substrates still showed poor adhesion, improvements with PDA were indicated by the formation of coherent films.

Table 2 Classification of the scratch tape test results for PEDOT:PSS/Tween 80 films on various substrates (5B, 0%; 4B, <5%; 3B, 5–15%; 2B, 15–35%; 1B, 35–65%, 0B, >65%)

Tween 80 concentration (wt%)	Substrate					
	Glass		PP		PET	
	No PDA	PDA	No PDA	PDA	No PDA	PDA
0.00	0B	4B	N/A	0B	N/A	0B
0.37	0B	0B	N/A	0B	N/A	0B
1.32	2B	4B	0B	0B	0B	0B
2.50	5B	5B	0B	2B	0B	3B

Not applicable (N/A) outcomes were reported for incoherent films (see Supporting Information 1)

These improvements are consistent with previous findings [21] and are thought to be a result of strong PDA binding to the substrates, increased hydrophilicity and the many functional groups present in PDA. Visual inspection of the slides revealed residual PDA after adhesion testing.

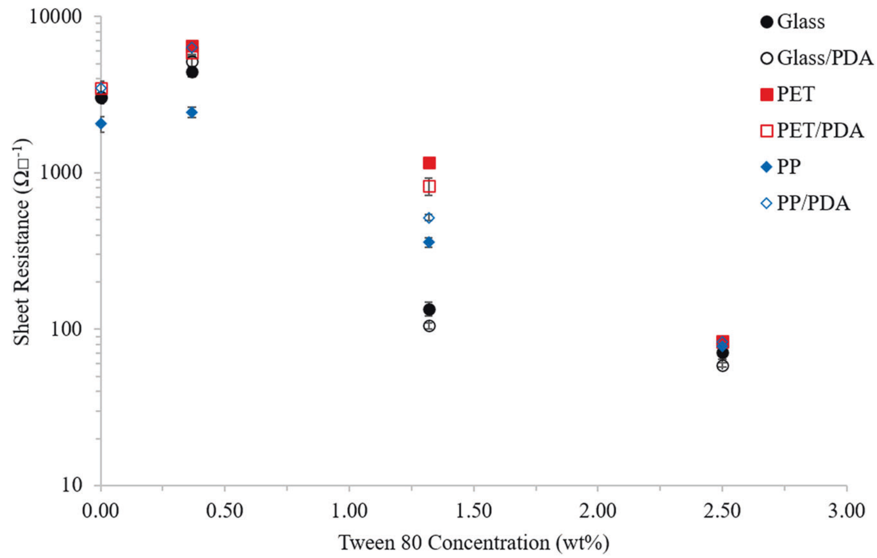

Fig. 3 Sheet resistance ($\Omega\square^{-1}$) of PEDOT:PSS films with varying Tween 80 concentrations (wt%) on glass (black circle), PET (red square) and PP (blue diamond) substrates without (solid) and with (hollow) a PDA primer layer. Error bars represent ±1 standard deviation of 6 repeat measurements across each film (see Supplementary Information "Sheet Resistivity Data"). The presence of PDA has little effect on the sheet resistances of the PEDOT:PSS/Tween 80 films

However, some untested areas were darker in color (Supporting Information 1), indicating partial removal of the PDA during testing. This suggested that the PDA-PEDOT:PSS and PDA-substrate interfaces were strong, but the PDA was brittle and broke during testing.

Generally, the presence of Tween 80 alone was found to improve adhesion to all substrates. The amphiphilic nature of Tween 80 may enable adhesion between the hydrophobic polymers and hydrophilic PEDOT:PSS while providing suitable functional groups for bonding to glass. It was noted that at the highest concentration, the surfactant separated from the film and resided on the surface. This interfered with adhesion of the tape to the sample, causing possible errors in these results.

Sheet resistance of PEDOT:PSS/Tween 80 films on varying substrates

Sheet resistance analyses of PEDOT:PSS/Tween 80 films on varying substrates were conducted to assess whether PDA adversely impacted electrical properties. Typically, annealing is performed to reduce the sheet resistance of PEDOT:PSS/Tween 80 films [15, 22]. However, this was found to cause delamination or cracking of the films and was, therefore, omitted. Instead, the films were allowed to dry and equilibrate at room temperature for 24 h.

The addition of Tween 80 to PEDOT:PSS has previously been shown to reduce the sheet resistance of the resultant film through increased chain alignment and separation of the conductive/nonconductive regions [15]. Generally, the presence of PDA did not change the sheet resistance of the PEDOT:PSS/Tween 80 films on any of the substrates used, but in some cases, the sheet resistance was reduced (Fig. 3). This showed that utilizing a PDA primer to improve adhesion did not compromise the electrical properties of the PEDOT:PSS/Tween 80 films.

Conclusions

This study assessed the wettabilities, adhesion stabilities, and sheet resistivities of PEDOT:PSS/Tween 80 films on glass, PET, and PP substrates, with and without a PDA primer. Pristine PEDOT:PSS exhibited a low contact angle on glass, and higher values were observed on PET and PP, indicating inferior wetting. The use of a PDA primer resulted in improved wettability on PP but led to higher contact angles on PET. This variability is believed to occur because the PDA molecules adopted different orientations depending on the substrate. The low wettabilities of the polymer substrates resulted in poor film quality; however, this was greatly improved by the presence of PDA. Furthermore, the PDA primer significantly increased the adhesion of PEDOT:PSS to glass.

In cases without PDA, higher concentrations of Tween 80 were found to enhance the wettabilities of PET and PP, with good quality films produced at 1.32 wt% and above. Incorporating a PDA primer further improved the film quality and adhesion of each PEDOT:PSS/Tween 80 formulation with the glass and the polymer substrates.

In summary, the use of PDA proved effective in enhancing the quality and adhesion of pristine PEDOT:PSS and PEDOT:PSS/Tween 80 films on glass, PET, and PP substrates. Although Tween 80 improved wettability and film quality, its effect alone was not as substantial as that of PDA. Finally, PDA did not diminish the sheet resistances of the PEDOT:PSS/Tween 80 films, establishing it as a suitable primer.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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