



# Molecular grafting to improve adhesion of spray-deposited circuits on polymeric surface for flexible electronics



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## ABSTRACT

An efficient molecular grafting approach is presented to improve interfacial adhesion of logic circuits by virtue of the valuable molecules chemically linked to polymer surfaces. With spray-assisted layer-by-layer deposition, pure metallic Ag coatings with a thickness of 130 nm adhere well to the PET plastics and the homogeneity of the Ag coatings has been studied. In particular, the peel broken site is estimated inside polyester resin beneath the interface. The fabricated flexible circuits maintain high conductivity under various twisting conditions and bending tests, indicating the possibility of producing robust printed circuits onto flexible substrates.

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## Introduction

Flexible electronics have gained increasing attention recently because of its usefulness in diversified applications, such as robot sensors, structural health monitoring, personal health monitoring, sport performance monitoring and artificial skin [1–6]. To date, the crucial issues of the development of flexible electronics include logic circuits, mechanically durable materials, novel processing methods and system integration [7]. Especially for the logic circuits, as the circulation system of flexible devices [8], the demand is rapidly growing. Many innovative techniques including inkjet printing [9–11], pen writing [12,13], screen printing [14,15] and nanoimprinting [16,17], have been thus developed for design and fabrication of conductive circuits on flexible plastics. Generally, specific circuits of flexible electronics should sustain various kinds of repeated deformations, such as bending, stretching, compassing and folding [18,19]. It is, therefore, important to develop tough interfacial bonding to undertake the above extreme conditions. However, because plastic is hydrophobic and chemically unreactive, the conductive patterns cannot adhere well to the surface without pretreatments and thus it is unacceptable to prepare circuits directly on polymer materials [20].

To improve the adhesion of as-deposited metal to the substrate, two common interfacial bonding architectures have been designed, which are anchor absorption and covalent grafting [21]. Anchor absorption refers to change surface roughness and constructs robust interphase to grasp the coatings, including surface etching [22,23], plasma treatments [24,25] and chitosan attachment [26]. Covalent grafting proceeds via a “grafting to” mechanism with specific monomers, such as surface silanization [27–29], photocatalytic oxidation [30] and polymer grafting [31,32]. Now the commercially available process is still oxidant-containing etching, which will produce a rough interface to promote the uptake deposition of catalytic particles and increase the final adhesion between the flexible substrate and final circuits. However, the etching method will soon be replaced due to its unenvironmentally friendly processes. Some other innovative approaches have shown the great capability to tailor surfaces to improve adhesion, but most of them are still not feasible for the scalable cost-effective application. For instance, plasma treatments usually need expensive and inconvenient facilities; silane-modified surfaces are not chemical stability and thus are not suitable for long-time plating. Therefore, it is imperative to develop more low-cost and convenient method for surface modification of flexible plastics.

In our previous works, molecular bonding technology was integrated to metallize the rigid plastics (Acrylonitrile-Butadiene-Styrene) [33]. Herein, the molecular bonding technology was expanded for poly(ethylene terephthalate) (PET), which is the

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typical substrate materials for electronics, to grasp the conductive circuits for sustaining the repeated deformation. The modification processes and bonding mechanism were studied in detail and optimized by X-ray photoelectron spectroscopy (XPS). Meanwhile, the versatile spray-assisted layer-by-layer (LbL) method was applied to prepare conductive Ag patterns on the PET substrates. X-ray diffraction (XRD), Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize the phase, thickness and morphology. And the homogeneity of Ag films was investigated by analyzing surface features on different locations and spray distances. Certainly, the metallic coatings adhered well onto the plastic substrates. Integrating with a commercial laser printer, the above methods were used to prepare typical flexible circuits on PET and conductivity under various twisting conditions and bending tests were studied.

## Results and discussion

### Polymer modification

Fig. 1a shows the schematic flow of polymer modification and preparation of silver films. Ultraviolet light was employed for transforming the azides (in P-TES molecules) into highly reactive triazinyl nitrene, which would react with hydrocarbon on PET and thus introduce amino groups covalently linking onto the films (Fig. 1b). The species was then dipped into N-TES solution to perform self-assembly process. Ethoxysilyl groups of P-TES will then hydrolyze to silanol group, forming cross-linking networks (Si–O–Si) with N-TES drove by a standard condensation reaction (Fig. 1c). After solution spray of Ag films, Ag atoms will react with thiol groups of N-TES (Fig. 1d). As a result, the covalent bonding has formed at the interface between Ag films and PET substrates.

Fig. 2 presents XPS survey spectra of PET surfaces and Ag films on PET substrates. These spectra disclose some differences in peak position and intensity. Comparing with the spectrum of blank PET surfaces, significant peaks of N 1s and Si 2p were found in the spectrum of UV treated PET surfaces, which indicate the successful introduction of azides onto these polymer materials. After N-TES self-assembly, a weak S 2p peak has been found, which demonstrates that dehydration condensation reactions of P-TES and N-TES have smoothly taken place, and thiol groups were assembled on PET surfaces. Certainly, peaks of Ag elements would appear in the spectrum of the spray-plated Ag films. At the meantime, XPS was used to characterize the back side of PET surfaces against UV light and there is not any signal corresponding to Si element in the survey spectra (Fig. 2). PET is a kind of transparent material through which light can pass, but not the ultraviolet light (mainly at the wavenumber of 254 nm) that can

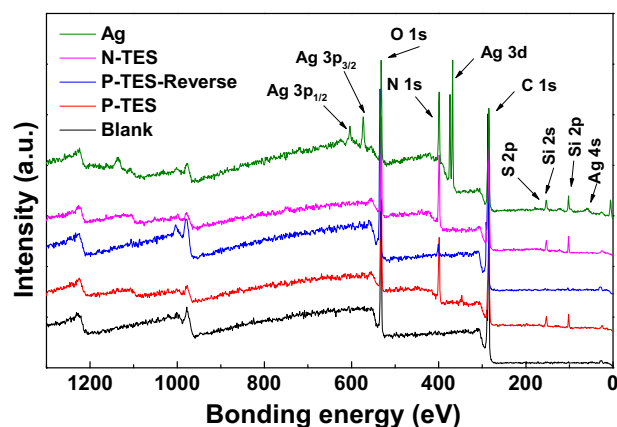


Fig. 2. XPS survey spectra of blank, UV treated, N-TES treated PET surface and Ag films.

activate azide groups to induce the molecular grafting onto polymer surfaces.

The high-resolution XPS spectra of these specific elements of N 1s, Si 2p, and S 2p core levels are shown in Fig. 3. In the N 1s spectrum of UV-treated PET surface (Fig. 3a), the broad peak was fitted by peaks at 400.1 and 398.7 eV, which correspond to C=N and C–N–H bonds in P-TES monomers respectively. The major peak of Si 2p at 102.1 eV (Fig. 3b) is assigned to Si–O–Si networks because these azido-silanes would be hydrolyzed and self-condensation even they dissolve in absolute alcohol. There is no S element, so not any significant peak arises in the spectrum of S 2p (Fig. 3c). After self-assembly of N-TES, the high-resolution N 1s and Si 2p spectrums are presented in Fig. 3c and d, and the fitting strategies employed as same as above. Noticeably, two peaks at 167.3 and 162.2 eV are found in the spectrum of S 2p (Fig. 3e) and represent C–S–Na and C–S–H signals severally, indicating the N-TES has been successfully coupled onto PET surface.

The fitting parameters of full width at half maximum (FWHM), peak area and atomic percentage were summarized in Table 1. The peak areas of N 1s and Si 2p increase for the reason that more triazine rings and siloxane have been attached on PET surface. For N 1s, the percent of C=N is larger than C–N–H, because there are three C=N bonds in P-TES but one C–N–H plus one or two after UV activation of  $-N_3$  group. Besides, S in N-TES would tend to couple with  $H^+$  in the aqueous solution to form thiol group rather than  $Na^+$ , the C–S–H accounted for more proportion than C–S–Na accordingly.

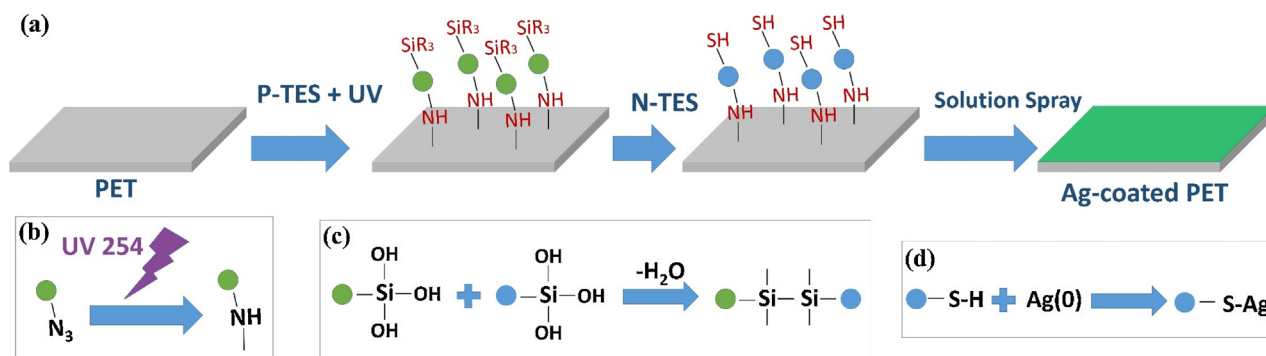


Fig. 1. Schematic flow of polymer modification and preparation of silver films.

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