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“Drop-on-textile” patternable aqueous PEDOT composite ink providing highly stretchable and wash-resistant electrodes for electronic textiles

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ABSTRACT

We demonstrate a direct-write patternable water-based poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) composite ink which is capable of providing highly stretchable and washing-resistant electrodes on a fabric substrate for electronic textile applications. An aqueous composite ink consisting of PEDOT:PSS, graphene oxide nanosheets and anionic polyurethane does readily not permeated into hygroscopic fabric, which facilitate direct drawing of fine PEDOT electrode on the fabric without undesired blur effect. This limited permeation of aqueous PEDOT composite ink on the hygroscopic fabric is mainly originated from the intermolecular interactions of anionic polyurethane including hydrogen bonding with water molecules, and charge balancing interactions with PEDOT chains. Furthermore, addition of the graphene oxide nanosheets contributes to enhance the electrical conductivity of the composite by improving crystallization of PEDOT molecules. The PEDOT composite film shows unique structure of the PEDOT nanofibril network embedded by the polyurethane matrix, which resulted in an enough electrical pathway for charge carriers even though only 2.9 wt% of PEDOT:PSS existed in the composite film. The PEDOT composite film exhibited electrical conductivity of 4.6 S/cm, extremely high stretchability of 375% rupture strain, and high durability for repeated washing process with strong bleaching agent. Light emitting diode incorporated on the stretchable spandex with interconnects of the PEDOT composite pattern showed that LED light intensity was almost maintained even with stretching of PEDOT interconnects to 290%.

1. Introduction

Electronic textiles (e-textiles) have received considerable attention as the ideal platform for interactive and wearable electronic devices due to their comfortable, light weight, and flexible nature. However, compared to typical planar substrates (i.e. films or glass), textiles are a problematic substrate for electronic devices because it consists of knitted fibers with rough surfaces and porous structures. These structures severely limit deposition of smooth and continuous electronic materials, which can result in degradation of electronic function. Moreover, textiles are extremely deformable, foldable, and sometimes stretchable according to the weave pattern. Therefore, electronic materials for e-textile applications should be flexible and durable to mechanical deformation, as well as have a suitable function for the textile substrate.

Recent advances in flexible electronic materials and their operation allows thread or fabric to adopt electrical functions. A variety of conducting nanomaterials, including conducting polymers, silver nanomaterials, carbon black, reduced graphene oxide, and single-wall carbon nanotubes, have been integrated into textiles through coating of the fibers or fabric substrates [1–9]. One of the most promising classes of conducting materials for e-textiles is a poly (3,4-ethylenedioxythiophene) complex with a water-dispersible polyelectrolyte dopant of poly (styrene sulfonate) (PEDOT:PSS). The conductivity of PEDOT:PSS can reach metallic values of approximately 1000 S/cm, which is applicable for conductive interconnects or electrodes [10]. Due to its high

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conductivity, good compatibility with various electronic materials, biocompatibility, and easy processability using solution coating, a wide range of e-textile components have been demonstrated that utilize PEDOT:PSS, such as electrical interconnects [11], electrochromic pixels [12], electrodes for electrocardiography [13], electroluminescent devices [14] and organic solar cells [15], piezoelectric sensors [16], pressure sensors for stretchable keyboards [17], thermoelectric elements [2,11], and electrochemical transistors [18].

In order to fabricate such e-textile devices based on PEDOT:PSS, two approaches have been used. The first individually coats fibers with PEDOT:PSS and then embeds the fibers into the fabric by embroidery or knitting [11,18]. In the case of hygroscopic fibers such as cotton, linen, silk, etc., PEDOT:PSS can be easily absorbed into the fibers, forming a thin PEDOT:PSS layer on the surface of the fibers [11,18]. This is a simple process; however, a large amount of fibers is required to obtain a certain conductive area in the fabric, and contact between the PEDOT:PSS-coated yarns is critical to maintain electrical conductivity. The second approach is to directly pattern the PEDOT:PSS on the fabric substrate through PEDOT:PSS solution deposition. For example, established printing techniques, such as microcontact, inkjet, screen printing, and brush painting can be utilized [13–17,19]. This method does not require a sewing or knitting process, and the desired pattern can be obtained from a small amount of PEDOT:PSS solution. However, direct patterning of PEDOT:PSS on the fabric substrate is not easy because aqueous PEDOT:PSS solution penetrates into the micropores of the hygroscopic fabric, which blurs the desired PEDOT:PSS pattern. Furthermore, to guarantee electrical conductivity of the PEDOT:PSS pattern on the highly deformable fabric substrate, PEDOT:PSS should also be flexible and stretchable. Unfortunately, PEDOT:PSS film is not stretchable, and shows cracks even at film elongations as low as 5% [16]. Therefore, for direct patterning of PEDOT:PSS on textiles, the rheological properties of aqueous PEDOT:PSS solution as well as mechanical properties of PEDOT:PSS film should be modified.

To date, few studies of direct PEDOT:PSS pattering on textiles have been reported [13,14,16,19]. Inkjet printing of PEDOT:PSS on cotton fabric was first demonstrated by Calver et al. [16] To achieve low resistance of the PEDOT:PSS pattern, a repetitive coating process involving approximately 500 cycles was required. The printed PEDOT:PSS showed a drastic reduction in conductivity when the textile was elongated to 10%. Takamatsu et al. suggested a brush-painting method for the patterning of PEDOT:PSS on polyester fabric [13]. They used polydimethylsiloxane (PDMS) as the stencil guide to confine the aqueous PEDOT:PSS solution, and the PDMS guide was firstly transferred onto the textile before brush-painting the PEDOT:PSS solution. Although a well-defined PEDOT:PSS pattern was obtained using this method, the technique necessitates the preparation and transfer of a PDMS stencil guide. More recently, Guo et al. demonstrated a sponge stencil method to pattern PEDOT:PSS on a textile surface [19]. PEDOT:PSS ink concentrated by two orders of magnitude was transferred to non-woven PET fabric using a sponge applicator. A fine pattern with low resistivity was obtained by repeating the patterning and annealing at 110 °C for 1 h; however, the process was time-consuming. For practical e-textile applications of PEDOT:PSS, development of a highly efficient, direct patterning process is still required. Moreover, for daily use of textile devices, improvement in the long-term environmental stability and wash-resistance of PEDOT:PSS is also necessary.

Here, we propose a direct-write-patternable PEDOT:PSS composite ink which provides highly stretchable and washing-resistant electrodes in electronic textiles. Compared to typical PEDOT:PSS solution (T-PEDOT), which is rapidly absorbed and spread into the textile as soon as the solution is dropped on the fabric, the PEDOT:PSS composite ink does not permeate into high water permeability textiles, which allows direct drawing of the PEDOT:PSS electrode pattern on the fabric, without pre-patterning using a hydrophobic stencil guide. We refer to this non-permeation behavior of the PEDOT:PSS composite ink on the fabric as in terms of a “drop-on-textile” phenomena, and this composite ink with “drop-on-textile” behavior is referred as DOT-PEDOT throughout the remainder of the paper. DOT-PEDOT was obtained by mixing graphene oxide (GO) nanosheets and anionic polyurethane (APU) with aqueous PEDOT:PSS solution. The addition of GO increases the viscosity and surface tension of the aqueous PEDOT:PSS solution, and enhances the conductivity of PEDOT phase. Additional mixing of APU as a third component provided a stretchable matrix, as well as induced molecular interactions including hydrogen bonding with water molecules and charge balancing interactions with PEDOT chains, which contributed to limited permeation of aqueous PEDOT composite solution in a hygroscopic fabric substrate. Interestingly, DOT-PEDOT composite film incorporated the PEDOT nanofibrilar network structure in the polyurethane matrix, which might provide an electrical pathway for charge carriers even though only 2.9 wt% of PEDOT:PSS existed in the film. This unique structure resulted in high stretchability of over 375%, and excellent durability for mechanical bending. Even after repeated washing with strong oxygen bleaching agent, conductivity of the DOT-PEDOT composite was almost maintained. To highlight the potential application of this composite ink for e-textiles, we also demonstrate the direct-writing of stretchable PEDOT interconnects on the fabric for light-emitting diode operation.

2. Experimental section

2.1. Materials

All materials were used without additional purification. Poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) (CLEVIOS P Jet 700 N; solid content = 0.86 wt%; pH 6.9) was used in the experiments, as well as an anionic polyurethane aqueous dispersion (35 vol%, from Hepce Chem, South Korea). Graphene oxide (99.999% purity, −200 mesh) was purchased from Alfa Aesar, MAI (methylamine iodide) was purchased from Sigma-Aldrich, gold wire (0.1 mm diameter, 99.95%) was purchased from Alfa Aesar, silver paste (ELCOAT P-100) was purchased from CANS, and oxygen bleaching agent was purchased from JSholding. Sylgard 184 silicone elastomer as PDMS is supplied as a two-part liquid component kit, a pre-polymer base (part A) and a cross-linking curing agent (part B) by Dow Corning Co., USA. Polyimide film (SKCKOLON PI Co., 75 μm thickness) was also used.

2.2. Fabrication of DOT-PEDOT composite ink

Graphene oxide (GO) (20 mg) was added to the commercial aqueous PEDOT:PSS (T-PEDOT) solution (1.5 ml). The weight ratio of GO to PEDOT:PSS was 1.55: 1. After vortexing the mixture, named GO-PEDOT (T-PEDOT + GO), it was placed in an ultrasonic ice bath for 2 h (AS ONE, VS-100III ultrasonic cleaner, 45 kHz, 100 W). Then, 1.125 ml water dispersed anionic polyurethane (APU) with carboxylic acid functional group (35 vol%) was added to the GO-PEDOT in the same ratio as T-PEDOT to form the DOT-PEDOT (T-PEDOT + GO + APU) solution. DOT-PEDOT, with a solid content of 16.7 wt%, had a (PEDOT:PSS):GO:APU weight ratio of 1:1.55:32. This mixture was also vortexed and placed in the ultrasonic ice bath for 1 h. MAI treated DOT-PEDOT was added to the DOT-PEDOT composite ink by MAI (0.1 M) and vortexed for 3 min.

2.3. Sample preparation

To fabricate the patterning sample, a polyimide film mask (“KIST” mark) was placed on the linen, and the hot plate was heated to 130 °C. The patterning sample was then made by patterning T-PEDOT and DOT-PEDOT with an air brush (FALCON, FD-184, nozzle diameter: 0.5 mm). Stretching and bending test samples were prepared by applying 0.1 ml of MAI treated DOT-PEDOT (APU 15.5 wt%) solution to spandex and linen (30 × 5 mm), followed by overnight drying in the oven at 70 °C. We applied silver paste to electrodes at both ends of the sample and let it dry at room temperature.

To fabricate the free-standing film, PDMS (Polydimethylsiloxane) was mixed with a curing agent at a ratio of 10:1, and spin-coated on a petri-dish at 500 rpm for 30 s. Then, the PDMS substrate was cured at 70 °C for 2 h. A hydrophilic PDMS substrate was prepared by O2 plasma treatment (FEMTO SCIENCE, CUTE) at 100 W for 15 min. 0.05 ml of DOT-PEDOT composite ink was spread on the PDMS substrate (30 × 10 mm). After drying at 70 °C, the film was detached from the PDMS substrate. A wash-resistivity test sample was fabricated by sewing a gold wire on the linen at 10 mm intervals, instead of the silver paste, to prevent the electrodes from being oxidized by the oxygen bleaching agent. T-PEDOT, DOT-PEDOT, and MAI treated DOT-PEDOT were adsorbed on the linen and dried overnight at 70 °C.

2.4. Characterization

Scanning Electron Microscopy (FE-SEM, Inspect F) showed that a cross-sectional shape was absorbed on the linen. The surface energy was calculated by the pendant drop method at room temperature using the contact angle analyzer (GS 150, Surfacetech). Viscosity measurements of T-PEDOT, GO-PEDOT, DOT-PEDOT (APU 15.5 wt%), and T-PEDOT + APU were also conducted by using rotational rheometer (REOLOGICA INSTRUMENTS). Transmission Electron Microscopy (TEM, JEOL JEM-2010) images showed the PEDOT:PSS nanofibril network structure and dispersibility of the DOT-PEDOT solution. Differential scanning calorimetry (DSC) (NETZSCH, DSC214 Polyma) was measured under nitrogen purge with first heating from −100 to 250 °C at 10#x202f;°Cmin^{-1}, followed by cooling to −100 °C at 10#x202f;°Cmin^{-1}. Finally, the sample was heated again from −100 to 250 °C at 10#x202f;°Cmin^{-1}. The mechanical properties of the free-standing films were evaluated using a tensile universal testing machine equipped with a 200 N load cell. The strain rate was set to 50 mm min^{-1}, and films were stretched until failure. The electronic properties of the device were characterized at room temperature under ambient conditions using Agilent 1500 A and0 4284 A meters.

3. Results and discussion

3.1. “Drop-on-textile” patterning of DOT-PEDOT composite ink

Fig. 1a shows the molecular structure of the materials consisting of DOT-PEDOT composite ink. All components are well dispersed in water. Molecular interactions among all components and their influences on rheological properties and phase separation behavior are discussed later. Fig. 1b shows a comparison of the wetting behavior of typical PEDOT:PSS solution (T-PEDOT) and DOT-PEDOT droplets deposited on the linen fabric. A movie comparing the wetting behaviors of T-PEDOT and the DOT-PEDOT solutions on linen textile is provided in supporting information video S1. At this time, the DOT-PEDOT contains a solid content of 16.7 wt%, in which weight ratio of (PEDOT:PSS), GO and APU in a mixture was 1:1.55:32. After 0.01 ml of T-PEDOT solution was dropped on the linen, it was instantly absorbed and spread out within 6 s, leaving a blurred PEDOT stain larger than the droplet diameter. Notably, linen is a hygroscopic fabric, so aqueous T-PEDOT solution is easily absorbed into the linen. If direct patterning of aqueous DOT-PEDOT composite solution is achieved on a highly hygroscopic linen fabric, the PEDOT composite solution may also be applicable for various fabric substrates with relatively low hygroscopicity, on which wetting and absorption of the aqueous PEDOT solution is limited.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2018.03.024.

Interestingly, the DOT-PEDOT aqueous solution did not immediately wet the linen, and spreading of the PEDOT composite was not observed on the fabric as the droplet dried (approximately 10 min). Finally, a small circular pattern of DOT-PEDOT composite with a sharp edge and a similar diameter to that of the droplet was obtained. Cross-sectional structures of the films obtained from three solutions were observed using scanning electron microscopy (Fig. S1) For a T-PEDOT solution, no distinct film structure was observed due to complete permeation of the solution in the fabric. In contrast, the DOT-PEDOT droplet left a continuous 188–260 μm-thick film on the fabric. This confirmed that the DOT-PEDOT solution does not easily penetrate the microstructure of the fabric. This drop-on-textile patterning of DOT-PEDOT droplets was also observed for other fabric substrates including nylon, polyester, spandex, and mixed fabrics (Fig. S2), indicating the versatility of the DOT-PEDOT composite.

Direct patterning of PEDOT-based ink solutions on the linen fabric was tested, as shown in Fig. 1c and d. PEDOT solutions were deposited on the linen fabric through the mask using an air brush. A “KIST” pattern almost identical to the mask was obtained from the DOT-PEDOT, which exhibits sharp edges and no penetration of the solution to the other side of the fabric. In contrast, a spread pattern with severe penetration of the solution was observed for the T-PEDOT solution. Drop-on-textile patterning of the DOT-PEDOT solution allows direct drawing of the pattern on the fabric by continuously dispensing the solution without a pre-patterned mask, using, for example, a fountain pen, as shown in supporting information video S2. The DOT-PEDOT pattern strongly adhered to the fabric and did not detached from the fabric even after severe rubbing test, as shown in supporting information video S3.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2018.03.024.

Wetting and permeation properties of the PEDOT solution on the fabric substrate are related to the rheological properties of the solution; i.e. the instant wetting and permeation of the T-PEDOT solution on the fabric substrate can be explained by the low surface tension and viscosity of the solution. The surface tension of T-PEDOT solution, determined by the pendant drop method, was approximately 35.6 mN/m, which is much lower than pure water (72 mN/m). This is due to that PEDOT:PSS can interfere with the hydrogen bonding of water molecules and decrease the cohesive force of water molecules, thereby reducing the surface energy value. This results in the T-PEDOT droplet wetting the fabric substrate, enabling easy penetration of the solution into fabric micropores due to its low viscosity (0.055 Pa s, measured at a shear rate of 10 s^{-1}) and the hygroscopic nature of the linen fabric.

3.2. Influence of each additive on wetting properties of PEDOT:PSS composite ink

To show the influence of each additive on the wetting and permeation properties of PEDOT solutions in the fabric, droplets (0.01–0.02 mL) with various compositions on the fabric are displayed in Fig. 2a. Viscosities of the related PEDOT solutions are shown in Fig. 2b. As a surface tension enhancer and viscosity controller, GO was introduced first. It was reported that addition of GO to the T-PEDOT solution induced gelation of the composite [20,21]. In fact, we found that a 1.3 wt% addition of GO in the PEDOT:PSS increased the surface tension of the solution to 71.7 mN/m, which is close to that of pure water. Even though the surface tension and viscosity increased with GO addition, the droplet of GO-PEDOT solution on the linen remained a blurred PEDOT stain with small aggregation in the center. This aggregation is attributed to the gelated particle of PEDOT:PSS and GO [20,22]. This result indicates that incorporation of APU is critical to achieve drop-on-textile patterning of the solution.

To clarify the effect of APU on solution patterning, PEDOT solution droplets with various APU content were observed (Fig. S3). By increasing the APU content in the solution, permeation of PEDOT into the fabric was substantially reduced. The minimum content of APU in the PEDOT solution required for drop-on-textile patterning was approximately 15.2 wt%. In contrast to T-PEDOT solution, the surface tension of the APU dispersion was as high as that of pure water, which might be due to the strong hydrogen bonding of urethane moiety in APU with

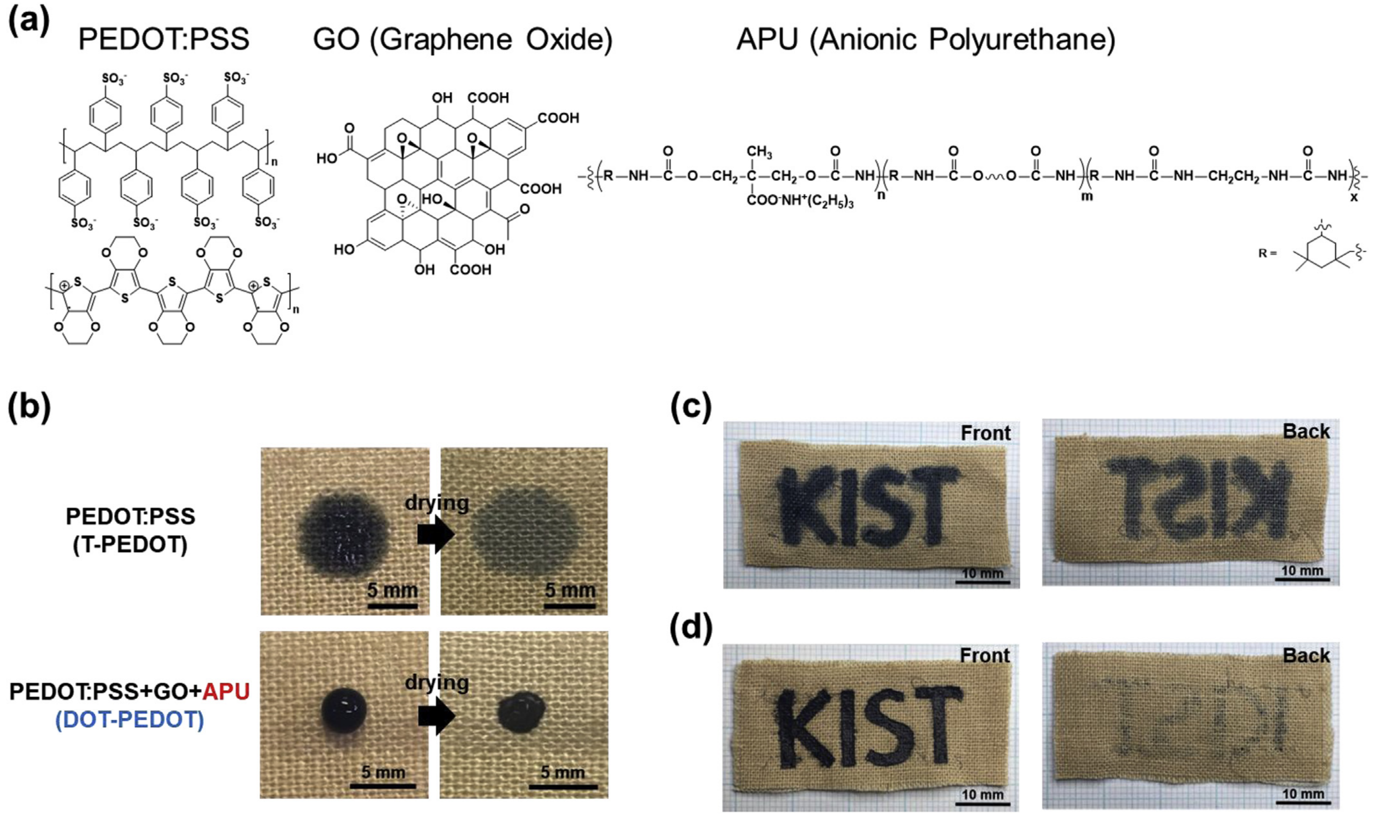

Fig. 1. (a) Chemical Structure of the materials in the DOT-PEDOT composite ink. (b) Photographs before and after drying when T-PEDOT and DOT-PEDOT were dropped on the linen. (c, d) Photographs of (c) T-PEDOT and (d) DOT-PEDOT patterned on the linen using an air brush.

water molecules (Fig. S4).

The limited permeation of DOT-PEDOT with APU, compared to the GO-PEDOT solution, was due to the molecular interaction of APU with PEDOT and GO, because there was almost no change in viscosity and surface tension of the GO-PEDOT after addition of the APU dispersion (Fig. 2(a and b)). To better understand the molecular interactions between PEDOT, GO, and APU components, differential scanning calorimetry (DSC) thermodiagrams of the composite films were analyzed (Fig. 2c). The endothermic peak shown in T-PEDOT in a temperature range of 155–180 °C was attributed to melting of the crystalline PEDOT phase. This endothermic peak was also observed in the GO-PEDOT mixture, indicating that the addition of GO did not disturb the crystalline structure of PEDOT chains. However, in the case of the PEDOT and APU mixture, this peak related to the crystalline PEDOT phase was not observed, and a weak, broad endothermic peak around 145 °C appeared. This indicates that APU interacted with the PEDOT chain, and hindered crystallization of the PEDOT chains. Carboxylate anions of APU might participate in charge-screening of positively charged PEDOT chains. This ionic interaction between APU and PEDOT might prevent the PEDOT chain migrating to the fabric structure with water flow. When GO was added to the mixture of PEDOT and APU, i.e. the DOT-PEDOT composite, the characteristic peak of the PEDOT crystalline phase clearly appeared at 175 °C, indicating that crystallinity of the PEDOT phase was effectively enhanced by incorporating GO in the composite. This result might correspond to the conductivity enhancement in PEDOT:PSS by GO addition [20]. The broad exothermic dissipation in the thermodiagram of DOT-PEDOT may be related to the removal of labile oxygen functional groups of GO [22]. Based on these results, it can be concluded that GO in the DOT-PEDOT composite contributed to increase the surface tension and viscosity of the PEDOT:PSS solution, as well as to improve the crystallinity of the PEDOT phase in the composite. Additionally, APU introduced for the stretchable matrix contributed to non-permeation of composite solution through intermolecular interactions with water and PEDOT chains. Fig. 3 is the schematic illustration showing molecular interactions among each component in the DOT-PEDOT composite ink.

3.3. Formulation optimization of DOT-PEDOT composite ink

To analyze the miscibility of the multicomponent solution, the phase diagram of the aqueous PEDOT mixture system is shown in Fig. 4. Without the APU component (red square), no phase separation was observed in the GO-PEDOT solution. When the solution was mixed with 4–12 wt% of APU (X mark), severe gelation was observed in the mixture. By increasing APU content to above 15 wt% in the mixture solution, all components became well dispersed in the solution. This DOT-PEDOT solution with APU content > 15 wt% showed drop-on-textile patterning on the linen fabric. Notably, the weight ratio of PEDOT:PSS to GO and APU in the mixture with the minimum APU content (15.5 wt %) was approximately 1:1.55:32. In particular, even though DOT-PEDOT contains a large amount of APU component, i.e., only 2.9 wt% of PEDOT:PSS existed in the film, the composite film was electrically conductive. The electrical properties of the composite film according to APU content are discussed later.

The yellow star in Fig. 4 corresponds to a solution with 15–22 wt% APU content. In this composition, the solution was separated into an upper bluish phase and a lower dark phase after 48 h. We anticipate that the upper bluish phase predominantly contains APU and PEDOT because of the low density of APU (less than 1 g/mL), while the PEDOT and GO mixture can be segregated to the bottom of the solution. This phase separation might be due to the poor miscibility of APU and GO (Fig. S5). When more than 22 wt% APU was added to the solution, corresponding to the blue circle in Fig. 4, this phase separation occurred after 24 h. However, the composite film prepared from the solution in this regime was not conductive. Thus, considering the miscibility of the solution and the conductivity of the composite, the optimized content

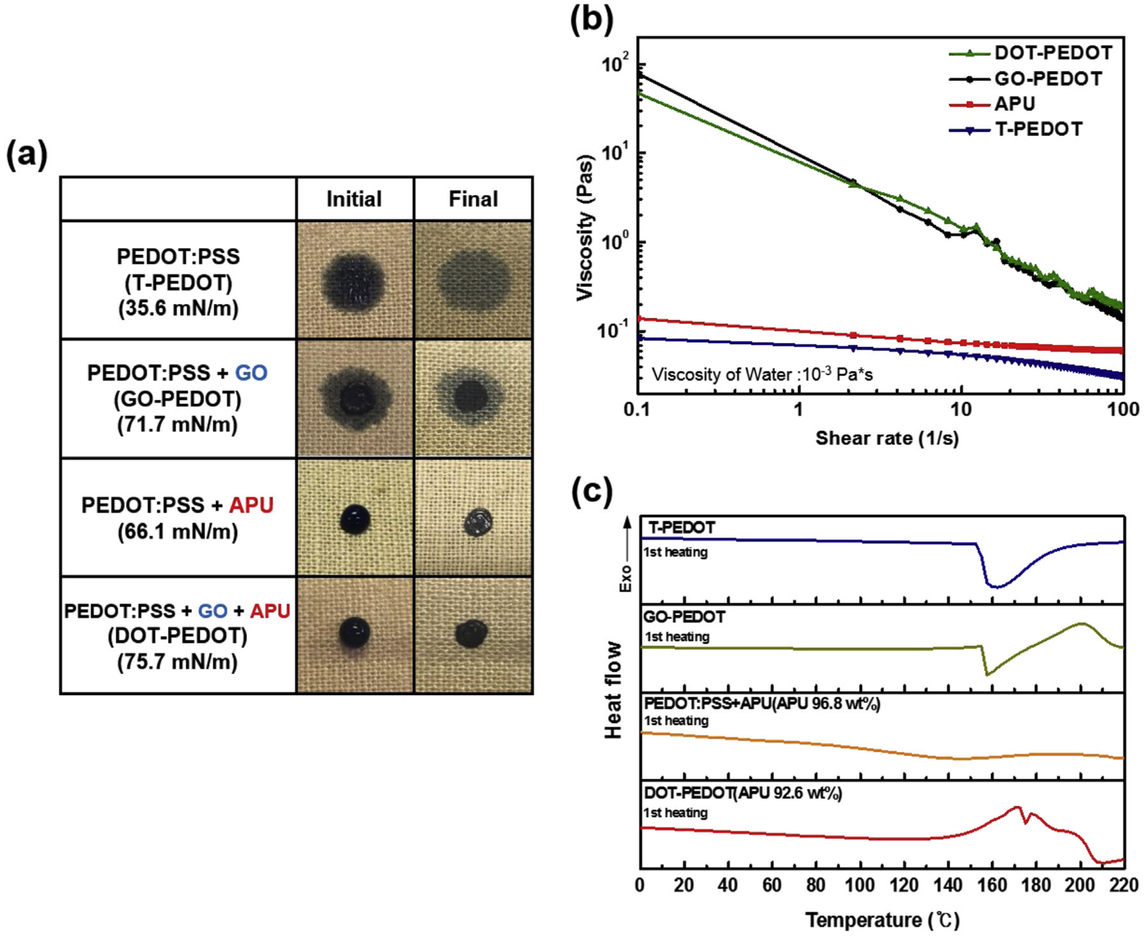

Fig. 2. (a) Initial and final state photographs of T-PEDOT, GO-PEDOT, PEDOT:PSS + APU solution, and DOT-PEDOT on the linen, and their respective surface tension values. (b) Viscosity measurements of T-PEDOT, APU, GO-PEDOT, and DOT-PEDOT. (c) Differential scanning calorimetry (DSC) thermograms of T-PEDOT, GO-PEDOT, PEDOT:PSS + APU, and DOT-PEDOT films.

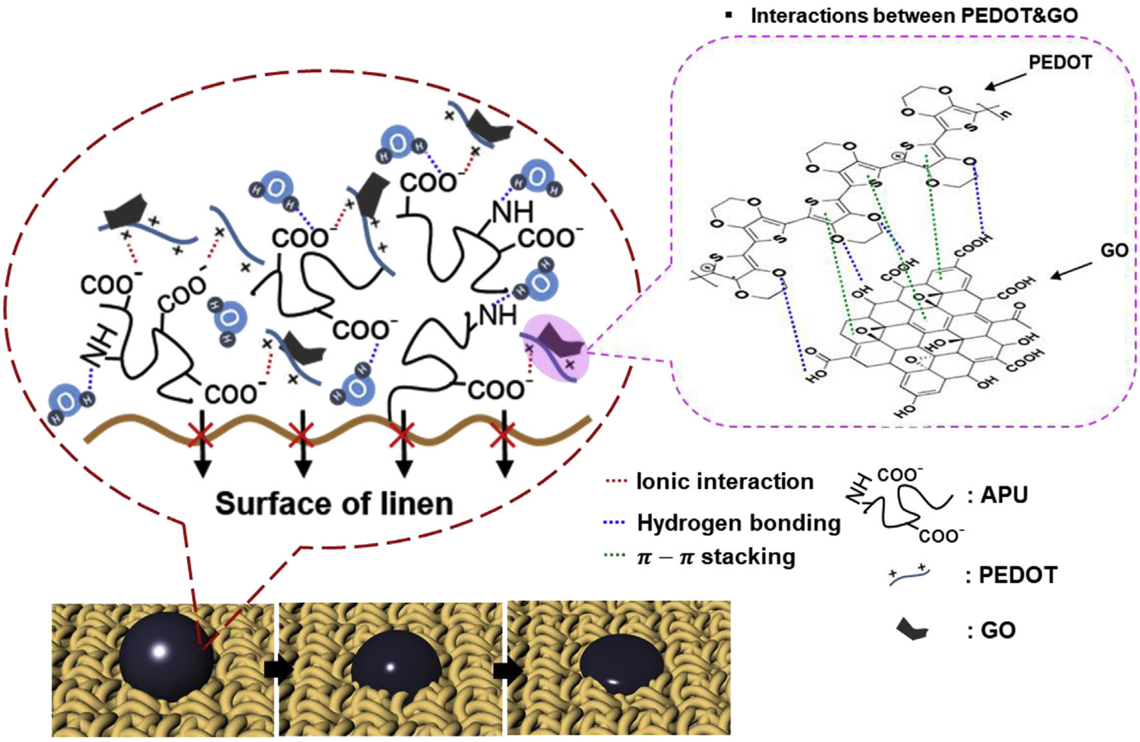

Fig. 3. Schematic illustration showing molecular interactions among PEDOT, GO, and APU molecules in the DOT-PEDOT composite ink.

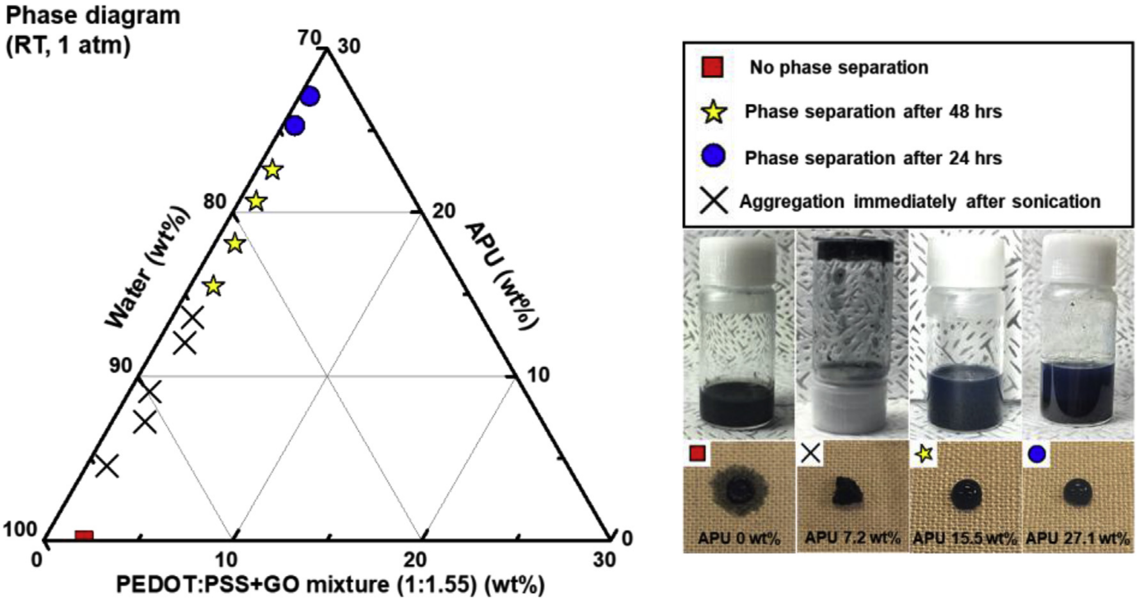

Fig. 4. Phase diagram of the DOT-PEDOT composite solution, divided into four sections depending on the phase separation time (left). Photographs of DOT-PEDOT solutions in vials and DOT-PEDOT droplets on the linen (right).

of APU in the PEDOT composite ink for drop-on-textile patterning is approximately 15.5 wt%.

To further elucidate the structure of the DOT-PEDOT composite, transmission electron microscopy (TEM) analysis was performed. The pristine PEDOT:PSS film showed the PEDOT nanofibril (dark contrast) structure (Fig. 5a). As shown in Fig. 5b, the PEDOT nanofibrillar network structure was distinctively observed in the DOT-PEDOT composite film, which was homogeneously distributed throughout the entire film. Wrinkles of GO nanosheets definitely distinguished from the PEDOT nanofibrills was exhibited, indicating that GO nanosheets with few layers were well mixed with PEDOT nanofibrils without severe aggregation. Considering that the composite film consisted of 92.6 wt% APU, it can be reasonably inferred that the DOT-PEDOT composite has the unique structure of the PEDOT nanofibril network embedded in the APU matrix. As a result, this embedded PEDOT network guaranteed an electrical pathway in the composite, even though only 2.9 wt% PEDOT:PSS existed in the film. Additionally, APU acted as a stretchable matrix, as well as passivation support for chemically and environmentally unstable PEDOT.

3.4. Electrical properties of DOT-PEDOT composites

The electrical properties of the PEDOT composite are shown in Fig. 6. Conductivity of the PEDOT composite film is mainly governed by the content of the non-conductive APU component. The DOT-PEDOT composite with 90 wt% APU, showing good drop-on-textile patterning, has a conductivity of 0.6 S/cm, which is much lower than that of the pristine GO-PEDOT film (20 S/cm). The conductivity of the PEDOT:PSS film can be enhanced by segregation of the excess insulating PSS chain from the PEDOT:PSS, which has been achieved by treatment of strong acids such as sulfuric acid [23,24]. However, this approach is not appropriate for the DOT-PEDOT composite because strong acid can induce breakage of the polyurethane chain, and aggregation of polyurethane with the carboxylic acid functional group. Recently, Yu et al. discussed methods to increase PEDOT:PSS conductivity without the use of strong acids, instead using a salt such as methylamonium iodide (MAI) [25]. Methylamonium cations strongly bind to PSS, and iodide anions can compensate for the positive charges on PEDOT chains. Motivated by this work, we attempted to induce phase segregation of anionic PU and PSS from PEDOT. In fact, we found that the conductivity of DOT-

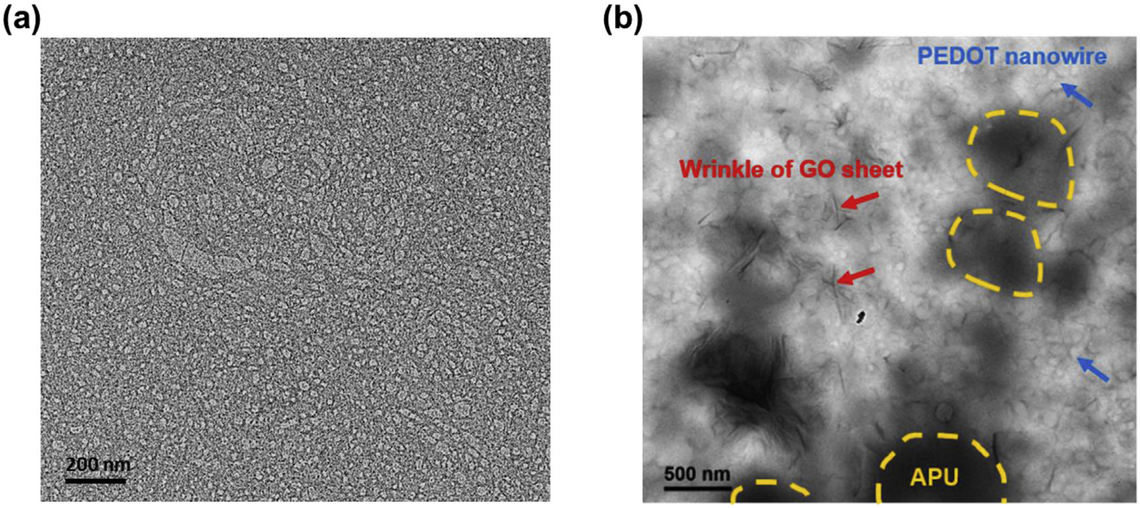

Fig. 5. TEM images of (a) the T-PEDOT solution and (b) the DOT-PEDOT composite ink.

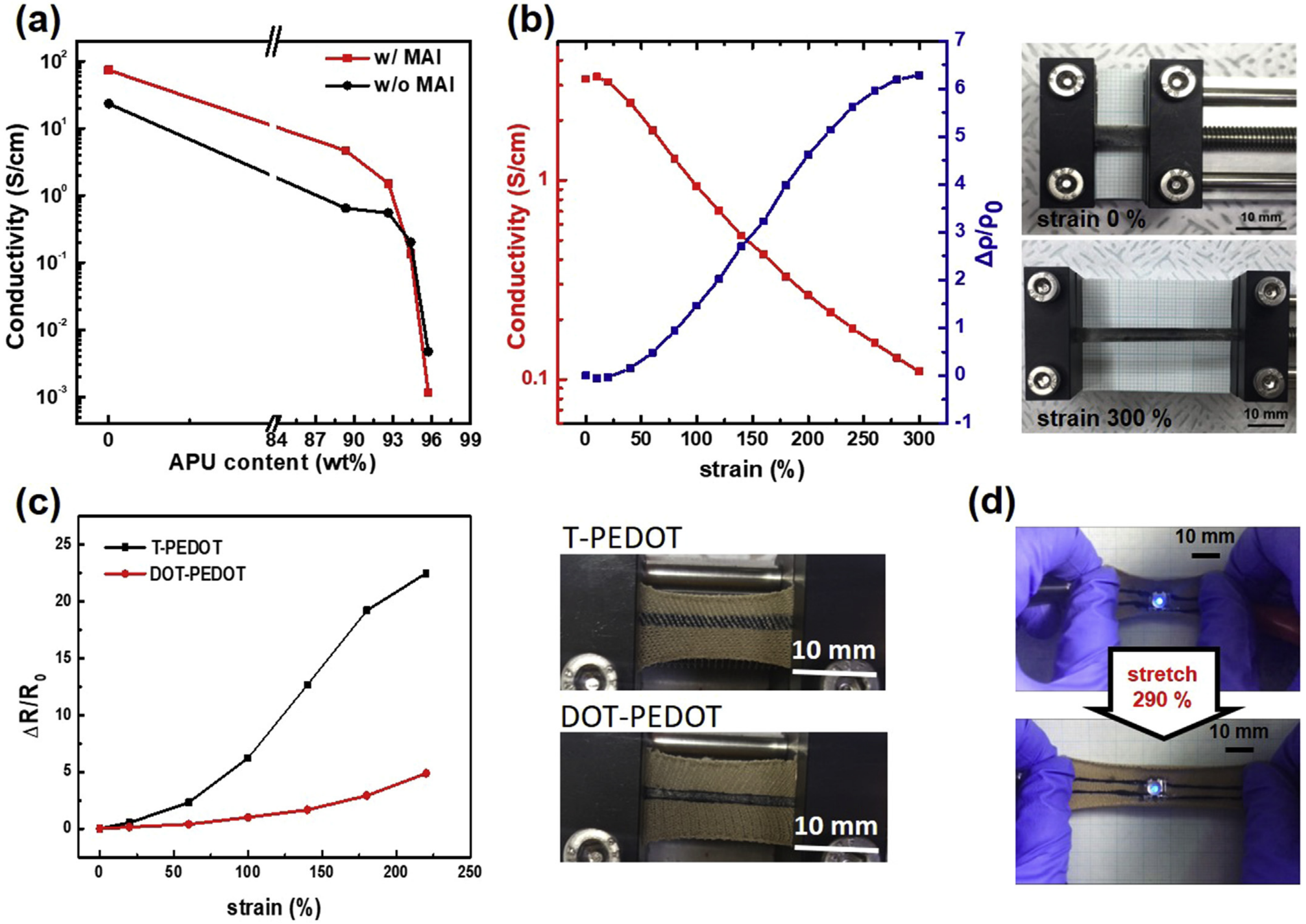

Fig. 6. Electrical properties of the DOT-PEDOT composite. (a) Conductivity change in the film according to APU content and presence of MAI. (b) Changes in conductivity and relative conductivity of the stretched film with MAI treated DOT-PEDOT (left). Photographs of films under stretching strain of 0% and 300% (right). (c) Relative resistance changes in T-PEDOT and DOT-PEDOT patterns on the spandex fabric according to the elongation of the fabric (left). Photographs of the 220% stretched T-PEDOT (top) and DOT-PEDOT patterns on the fabric (right). (d) Photographs of LED connected with the DOT-PEDOT pattern at 0% and 290% elongation.

PEDOT with 90 wt% APU content increased to 4.6 S/cm by a factor of 7.6 by adding 0.1 M MAI salt to the composite solution. Although the conductivity of the DOT-PEDOT is lower than that of recently reported PEDOT:PSS films [10], it is comparable to the PEDOT:PSS impinged in textiles or yarns, which can be applicable to textile electronic devices including thermoelectric fabrics [2], electrochromic textiles [12], interconnect [11], sensor [16]. To improve the conductivity of the DOT-PEDOT, further investigations including optimization of GO content and its distribution, the amount of the added salt, and increase of PEDOT component have been performed.

Fig. 6b shows the conductivity change in the DOT-PEDOT composite film according to film elongation. It was well-known that pristine PEDOT:PSS is susceptible to breaking at film elongation as low as 6% [26]. However, the DOT-PEDOT composite film was highly stretchable up to an average of 375% without breaking (Fig. S6). The tensile modulus of the film was approximately 11 MPa. Notably, the DOT-PEDOT composite shows electrical conductivity of above 0.1 S/cm even after 300% film elongation. In previous literature, stretchable PEDOT:PSS composite with hydrogel matrix exhibiting 400% stretchability was reported by Lee et al., however, the composite has low conductivity of approximately 0.01 S/cm [27]. To the best of our knowledge, this is the first demonstration that PEDOT:PSS composite shows good electrical conductivity above 0.1 S/cm under extreme elongation above 300%.

Fig. 6b shows that the conductivity of DOT-PEDOT elongated at 25% remained almost 100% of the initial value before stretching. Then, a substantial decrease in conductivity of the DOT-PEDOT composite film was observed with elongation in a range of 25–300%. The change in conductivity of the stretchable conductor with strain may also be affected by geometrical changes in the films, i.e. a reduction in the cross-sectional area of the film as the film is lengthened [28]. In order to determine the intrinsic resistivity change of the DOT-PEDOT composite film, the geometric contribution was estimated and subtracted from the measured resistance. The contraction in thickness and width was calculated, assuming that the film undergoes Poisson's compression using the Poisson ratio of the film ($\upsilon_t = 0.22$ and $\upsilon_w = 0.0838$ for thickness and width, respectively). A detailed explanation of the estimated variation in resistance induced by the geometric change is described in supporting information S8. As shown in Fig. 6b (right axis), we found that the resistivity of the DOT-PEDOT composite film did not change in the low strain regime (under 20%), and showed a linear increase in the high strain regime (from 80 to 200%). Although further investigation of conductivity changes under tensile stretching is required, we speculate that entangled PEDOT fibril structures may retain their connection in low strain regions, but with increasing film elongation, disconnection among PEDOT nanofibrils network may occur, which can lead to a gradual increase in resistance. This gradual increase in resistance of the composite film indicates its potential use as a strain indicator. We found that, after an initial cycle of 100% stretching, stable and reversible resistance changes were observed in the DOT-PEDOT composite film over repetitive stretching and releasing cycles (Fig. S7).

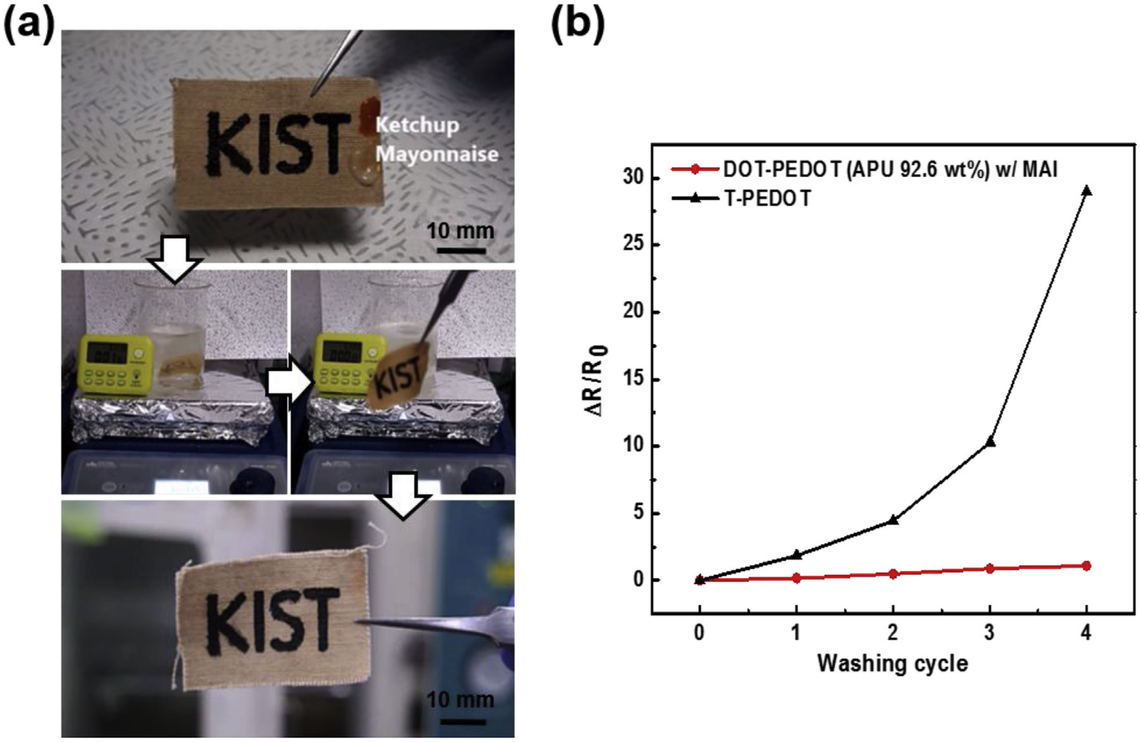

Fig. 7. (a) Photographs of one washing cycle, involving stirring the linen patterned with the composite in an oxygen bleach followed by drying. (b) Relative resistance of T-PEDOT, DOT-PEDOT (APU 92.6 wt%), and MAI treated DOT-PEDOT (APU 92.6 wt%) composite patterned on the linen over four washing cycles.

Resistance change of T-PEDOT and DOT-PEDOT pattern deposited on the spandex fabric according to the elongation of the fabric was investigated. As shown in Fig. 6c, resistance of T-PEDOT pattern dramatically increased by more than a factor of 23 after the fabric is stretched up to 220%. This is due to the disconnection of the T-PEDOT pattern after the film elongation. By contrast, DOT-PEDOT pattern showed much smaller increase in resistance, which is attributed to highly stretchable nature of the DOT-PEDOT composite without the breaking of the film. Notably, there was no delamination of the DOT-PEDOT pattern from the spandex fabric even after severe stretching of the fabric up to 300%, indicating good adhesion of the DOT-PEDOT composite on the fabric substrate.

To demonstrate the feasibility of the DOT-PEDOT composite for e-textile applications, we fabricated a simple light emitting diode (LED) circuit with interconnects of the DOT-PEDOT composite pattern, as shown in Fig. 6d. DOT-PEDOT was drawn on the spandex fabric using a fountain pen, and the LED was connected to the composite connect line. The electrical conducting properties of the DOT-PEDOT interconnect were appropriate to light the blue LED lamp. Even with stretching the textile to 290% after turning on the LED, the DOT-PEDOT composite maintained the interconnect well, and the intensity of the LED was nearly identical. Video S4 (supporting information) shows the durability of the LED interconnect even after several stretching episodes.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2018.03.024

3.5. Wash-resistance of DOT-PEDOT composite

A conductive polymer composite designed for e-textile applications should be able to withstand sweat and washing environments. Previous research on the washing effect of PEDOT:PSS coated textiles showed that the conductance of PEDOT:PSS decreased to almost 10% of its initial value after three washing cycles (washing in soap and water, and drying at 60 °C for 12 h) [19]. More recently, Ryan et al. demonstrated that the conductivity of silk fibers dyed with PEDOT:PSS did not significantly decrease after repeated machine-washing cycles with a common color detergent [11]. In this study, we investigated the washing durability of the DOT-PEDOT pattern on textiles in harsher washing conditions, using a strong oxygen bleach agent.

Fig. 7a shows one cycle of the washing cycle. The DOT-PEDOT pattern was deposited on the linen with ketchup and mayonnaise stains and dipped in an oxygen bleaching agent (strong base with pH 14), with a 10 times higher concentration than the recommended concentration, and stirred at 950 rpm for 15 min. After rinsing of the fabric with running water for 1 min, placed the sample in a vacuum oven at 70 °C for 15 min. This process represents one cycle. After this washing step, the ketchup and mayonnaise stains were completely removed. For typical PEDOT:PSS, the resistance of the pattern increased by a factor of 29 compared to its initial resistance after four cycles of washing. This rapid increase in resistance might be due to oxidation of the PEDOT chain by strong reagents including hydrogen peroxide [29]. In contrast, the resistance of DOT-PEDOT increased by a factor of less than 2, indicating high durability against the ordinary washing process. This improvement can be explained by the fact that PEDOT fibrils embedded in the polyurethane matrix structure of DOT-PEDOT preferentially prevent penetration of the bleaching reagents in the composite film; thus, PEDOT chains are protected from the oxidant molecules.

4. Conclusions

In this study, a direct-write patternable, stretchable, and wash-resistant PEDOT:PSS composite ink (DOT-PEDOT) was demonstrated by incorporating anionic polyurethane and graphene oxide nanosheets in aqueous PEDOT:PSS solution. The anionic polyurethane provided a stretchable matrix, as well as induced molecular interactions including hydrogen bonding with water molecules and charge balancing interactions with PEDOT chains, which resulted in limited permeation of aqueous PEDOT composite solution in a hygroscopic linen substrate. Additionally, the graphene oxide nanosheets contributed to improved surface tension and viscosity of the PEDOT aqueous solution, as well as enhanced electrical conductivity of the composite through an increase in the crystallinity of the PEDOT chain. Considering the patterning ability and resistance of the DOT-PEDOT composite, we found that the optimized weight ratio of PEDOT:PSS to GO and APU was 1:1.55:32, in which 92.6 wt% of the film was occupied by polyurethane component. TEM analysis proved that the proposed DOT-PEDOT composite film was composed of the PEDOT nanofibril network embedded by the polyurethane matrix, which resulted in an electrical pathway for charge carriers even though only 2.9 wt% of PEDOT:PSS existed in the film. Finally, the DOT-PEDOT film with salt-controlled PEDOT phase segregation showed an electrical conductivity of 4.6 S/cm and extremely high stretchability of 375% rupture strain. It was confirmed that DOT-PEDOT composite has substantial resistance to mechanical stretching deformation. Interestingly, we found that DOT-PEDOT deposited on the fabric showed almost no resistance change, even after the sample was exposed to a repeated washing process with a strong bleaching agent. This might be due to the encapsulation of PEDOT chains by the polyurethane matrix, which hinders penetration of bleaching reagents into the composite film. Based on the DOT-PEDOT drawn on the stretchable spandex, the stretchable interconnect for simple LED circuit was successfully demonstrated, where the brightness of the LED lighting was maintained even with stretching of DOT-PEDOT interconnects to 290%. This work may offer a promising strategy for preparation of highly deformable and durable functional materials for e-textiles applications.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Cross-sectional SEM images of PEDOT:PSS and composite films deposited on the linen substrate. Comparison of wetting behavior when dropping DOT-PEDOT composite ink on various fabric substrates. Comparison of wetting behaviors when various concentration of PEDOT:PSS and APU mixed solutions were dropped on the linen. Initial and final state photographs of water, GO dispersion, and APU solution on the linen, and their respective surface tension values. Comparison of phase separation in (i) PEDOT:PSS and APU mixed solution and (ii) GO and APU mixed solution after sonication. Strain-stress curves of the DOT-PEDOT and salt-treated DOT-PEDOT free-standing films. Relative resistance of salt-treated DOT-PEDOT film during 10 repetitive stretching cycles at 100% strain. A detailed explanation of the estimated variation in resistance induced by the geometric change.

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2018.03.024.

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