Electronic Supplementary Information (ESI)

Transient Behavior of Self-Healable Ultra-Stretchable Carboxylic Acid-Doped Polyaniline Films for Sustainable and Re-processable Polymer Electronics

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1 Methods

1.1 Materials

A 10 wt.% poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (average molecular weight: 800,000 g/mol) aqueous solution was purchased from Thermo Scientific Chemicals (Waltham, MA). Aniline (ACS grade) and ammonium persulfate (ACS grade) were purchased from Sigma-Aldrich (St. Louis, MO). The small molecule dopants used (1,2,4-benzenetricarboxylic acid ($\geq$ 99%), citric acid ($\geq$ 99.5%, FCC, FG), diphenic acid (97%) were purchased from Millipore Sigma. All chemicals were used as received without further purification/modification.

1.2 Preparation

The synthesis procedure began by mixing a 10 wt.% aqueous solution of PAAMPSA (50 g), 0.5 g of aniline monomer, 1.25 g of deionized (DI) water and the respective carboxylic acid based dopant. The dopant amounts were: 1,2,4-benzenetricarboxylic acid – 0.39 g, citric acid – 0.36 g, and diphenic acid – 0.45 g. These values were calculated using a molar ratio approach adapted from Lu et al.[1]. For oxidative polymerization, ammonium persulfate (APS) (0.685 g) dissolved in 1.10 g of DI water was prepared and added to the reaction mixture as an initiator. The mixture was stirred at 500 rpm in an ice–water bath at 0 °C for the first 3 hours, followed by stirring at room temperature for an additional 21 hours. After stirring, the resulting homogeneous solution was cast into a poly(tetrafluoroethylene) (PTFE) Petri dish and left in a fume hood for two days to allow excess water to evaporate (Figure S1). Since the samples are highly sensitive to humidity, they were stored in a humidity controlled chamber at a relative humidity of 50-55%. A control film was prepared using the same procedure without the addition of any dopants.

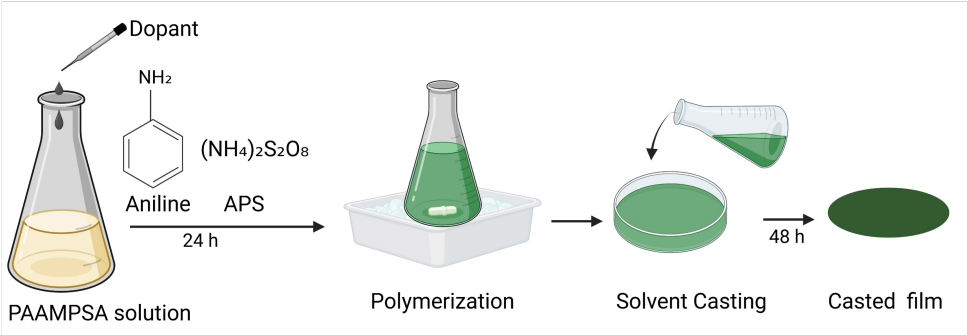

Figure S1: Schematic illustration of the synthesis procedure of PANI/PAAMPSA/CABDs

1.3 Characterization

1.3.1 FTIR Spectroscopic Measurements

The Attenuated Total Reflection Fourier transform infrared (ATR FTIR) mode was used to record the spectra in the wavelength range of 400 to 4000 cm^{-1} using a Nicolet iS20 (Thermo Fischer Scientific Inc.), with 28 scans and a 0.25 cm^{-1} resolution.

1.3.2 Conductivity Measurements

The electrical properties of the conducting film were measured using a Keithley 2450 source meter by the four-probe method[1]. The sample for this study was fabricated using commercial transparent double-sided adhesive tape (3M VHB-4910 tape) with wires attached at both ends on a 40 mm X 10 mm sample.

1.3.3 Mechanical Testing

The elongation and mechanical self-healing studies were performed using a INSTRON 68TM-5 universal testing machine. The gauge length was set at 20 mm, while the strain rate was set at 10 mm/min. The sample was cut into a rectangular strip measuring 40 mm X 10 mm for testing.

1.3.4 Thermogravimetric Analysis (TGA) analysis

TGA was performed using a TGA Q500 model (TA Instruments) by heating the sample from 30 to 780 °C in an N_2 atmosphere. The heating rate was set to 10 $°C$/min.

1.3.5 Differential Scanning Calorimetry (DSC)

DSC was performed using a DSC 2500 (TA Instruments, New Castle, DE) to analyze all film samples. A small piece of each sample was sealed in hermetic aluminum pans prior to the testing and heated from 30°C to 400 °C at a rate of 10 °C per minute.

1.3.6 Dynamic Light Scattering (DLS)

Zeta (ζ)-potential values and particle size measurements of the polymer dispersions were collected using a Malvern Nanoseries Zetasizer. The solid films were dissolved in deionized water at concentrations of 1.5 w/v% (0.3 g/20ml), 0.3 w/v% (0.06g/20ml), and 0.05 w/v% (0.01 g/20 ml) for the measurements of ζ-potential. Particle size measurements were

performed using a 0.3 w/v % dispersion. The solutions were sonicated using Misonix Inc. Microson ultrasonic cell disruptor at 0.07 watts for 10 minutes prior to each measurement, to ensure uniform dispersion.

1.3.7 UV-Vis Spectrometry

UV-Vis spectrometry measurements were performed using a GENESYS 10S spectrophotometer (Thermo Scientific). A 0.8 mg mL^{-1} dispersion was prepared by dissolving the sample in 5.0 mL of deionized water for UV–Vis measurements.

1.3.8 Scanning Electron Microscope (SEM)

Surface morphology of the materials was observed using a HITACHI TM3000 scanning electron microscope.

1.4 Soil, Water, & UV degradability

Soil degradation test: The soil degradation experiment was carried out in petri dishes containing plant potting soil purchased from Miracle-Gro, model number 75686300. The soil consists of sphagnum peat moss, coir, perlite, fertilizer, and a wetting agent and exhibits a mildly acidic to near-neutral pH in the range of 6.3-6.8. Some analyzed fertilizer ingredients include 0.25% nitrate, 0.13% phosphate and 0.19% soluble potash. The samples (1 cm * 1 cm) were buried in soil at 1 cm depth and the petri dish was maintained in a humidity chamber at 55% relative humidity and room temperature. As the soil was obtained in a dry state, a small amount of distilled water was added dropwise until a uniformly damp texture was achieved. The samples were monitored until they degraded into small fragments, making it impossible to collect all parts of a specimen. The degree of degradation was determined by the physical appearance and FTIR spectroscopy after 24 hours.
Water Solubility test: To assess the water solubility and degradation behavior, the samples were immersed in 20 mL of DI water, tap water, and river water. The degradation behavior with continuous stirring at 400 rpm at room temperature and static immersion was evaluated. The dissolution process was visually monitored, and the time required for complete dissolution was recorded.
UV degradation test: To evaluate the photodegradation behavior of the polymer samples, a QUV accelerated weathering tester was used. The samples were exposed to UV-A light (340 nm) at a set chamber temperature of 50 °C, with an ambient temperature of 24.57 °C and relative humidity maintained at approximately 38%. The UV light intensity was set to 0.89 W/m^2. Samples were placed horizontally inside the chamber and irradiated continuously under controlled conditions. The degradation process was carried out for 24 hours.

1.5 Self-healing Studies

Conductivity self-healing studies were conducted on a 40 mm x 10 mm sample. The sample were fabricated using commercial transparent double-sided adhesive tape with electrical wires attached at both ends, then connected to a Keithley 2450 source meter for resistance measurement before and after the cut-heal process. The mechanical self-healing tests were performed with a tensile testing apparatus on a 40mm x 10mm sample. The maximum

elongation before and after the cut-heal process is noted to calculate the mechanical self-healing efficiency. For both electrical and mechanical self-healing experiments, the samples were completely cut at the midpoint using a sharp blade and the cut surfaces were immediately realigned and brought into contact. The samples were allowed to heal for 3 h in a humidity-controlled environment maintained at 55% relative humidity and room temperature.

1.6 Re-processibility

To evaluate the re-processability of the sensor material, previously used samples were re-dissolved in distilled water under manual stirring. Upon complete dissolution, the solution was recast into a Petri dish and allowed to dry under a fume hood to form a new film. The re-processed samples were then reevaluated for conductivity, stretchability, and self-healing performance. Additionally, FTIR analysis was performed to compare the changes in chemical structure of the re-processed film with the original sample.

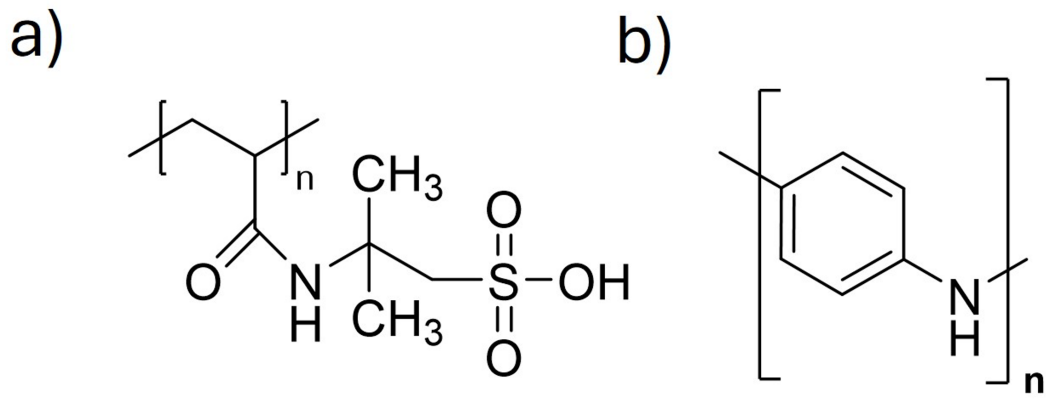

Figure S2: Chemical structures of (a) poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA) and (b) polyaniline (PANI)

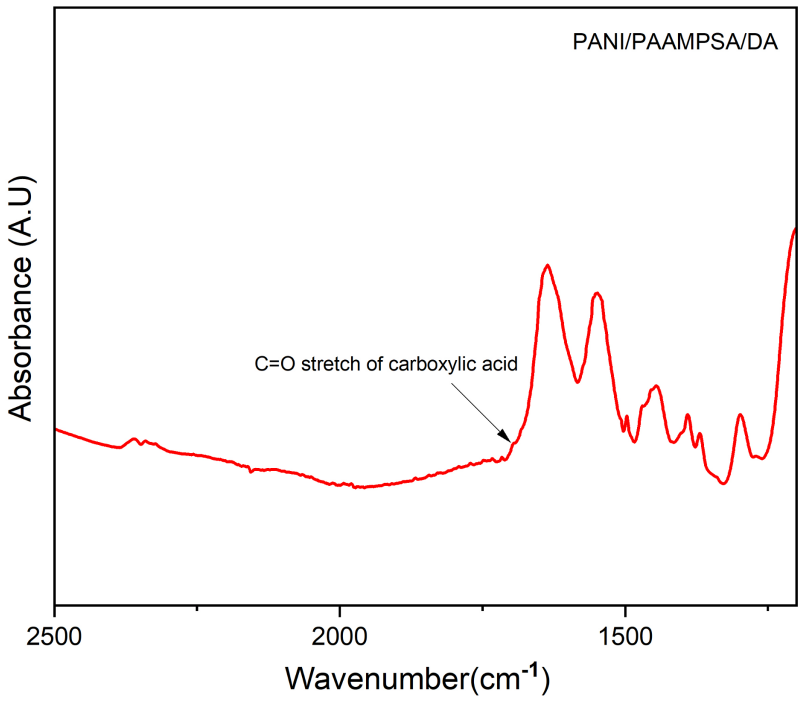

Figure S3: Focused FTIR spectra of PANI/PAAMPSA/DA

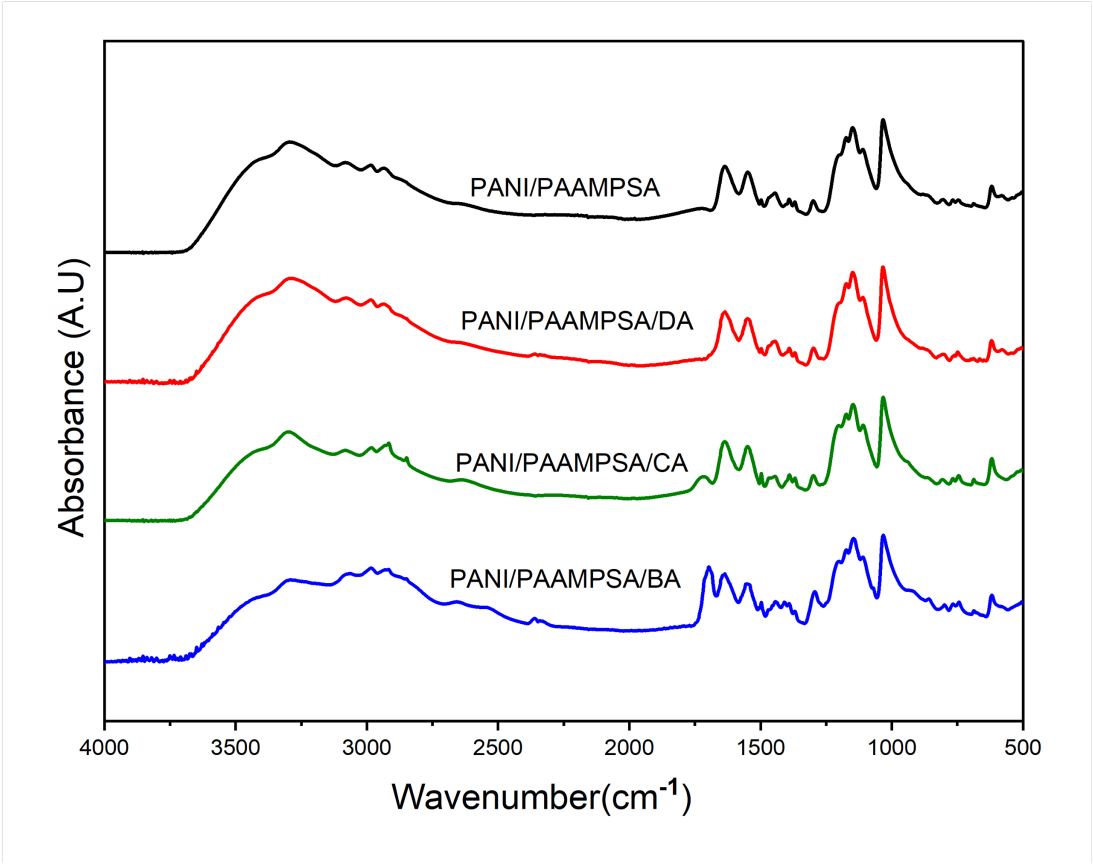

Figure S4: FTIR spectra containing PANI/PAAMPSA - control sample

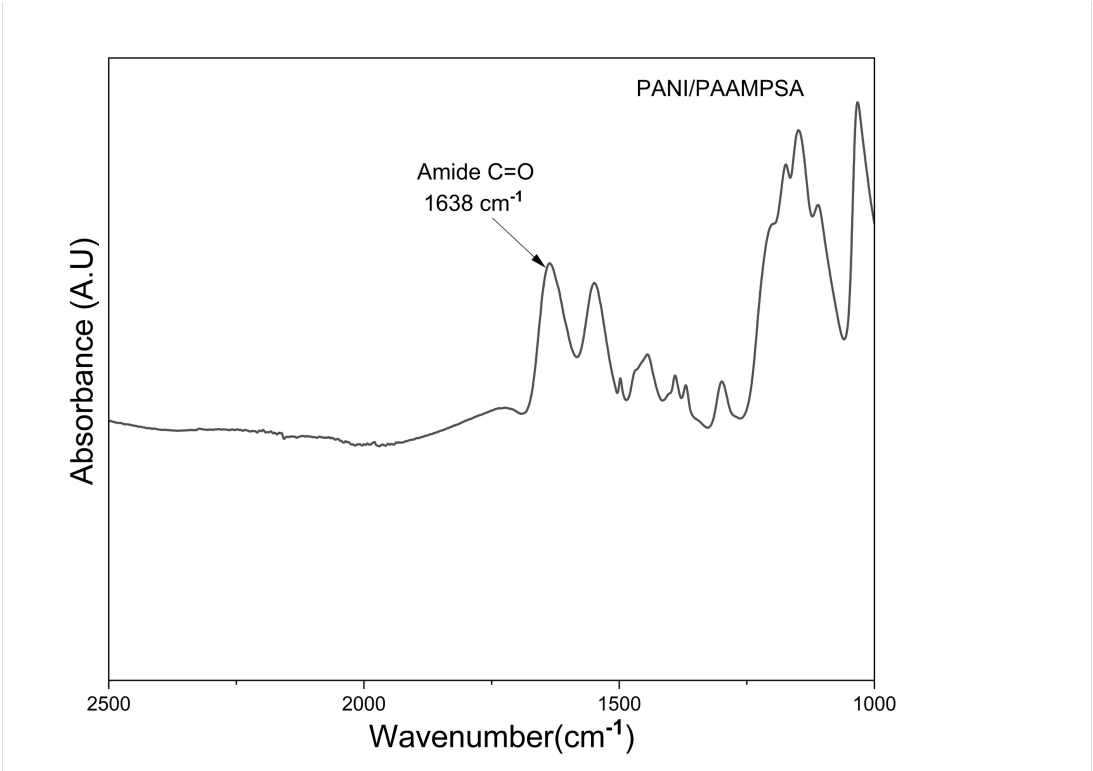

Figure S5: Enlarged FTIR spectra containing PANI/PAAMPSA - control sample

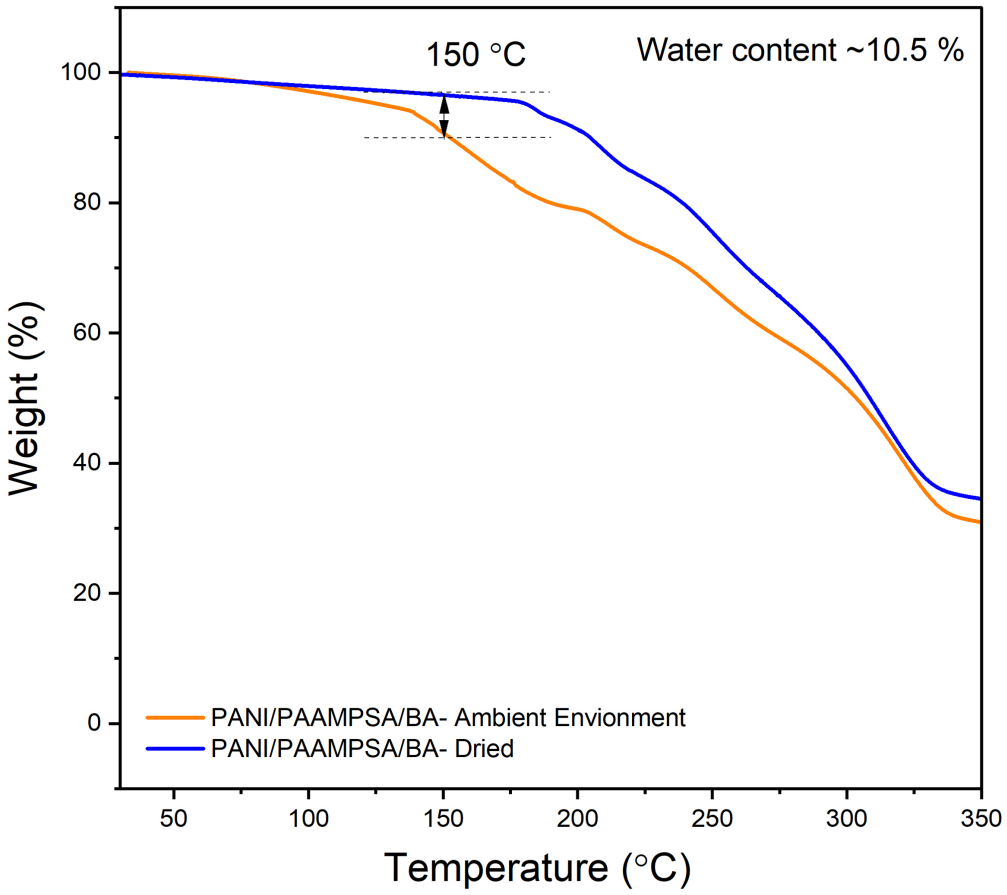

Figure S6: Retained water of PANI/PAAMPSA/BA

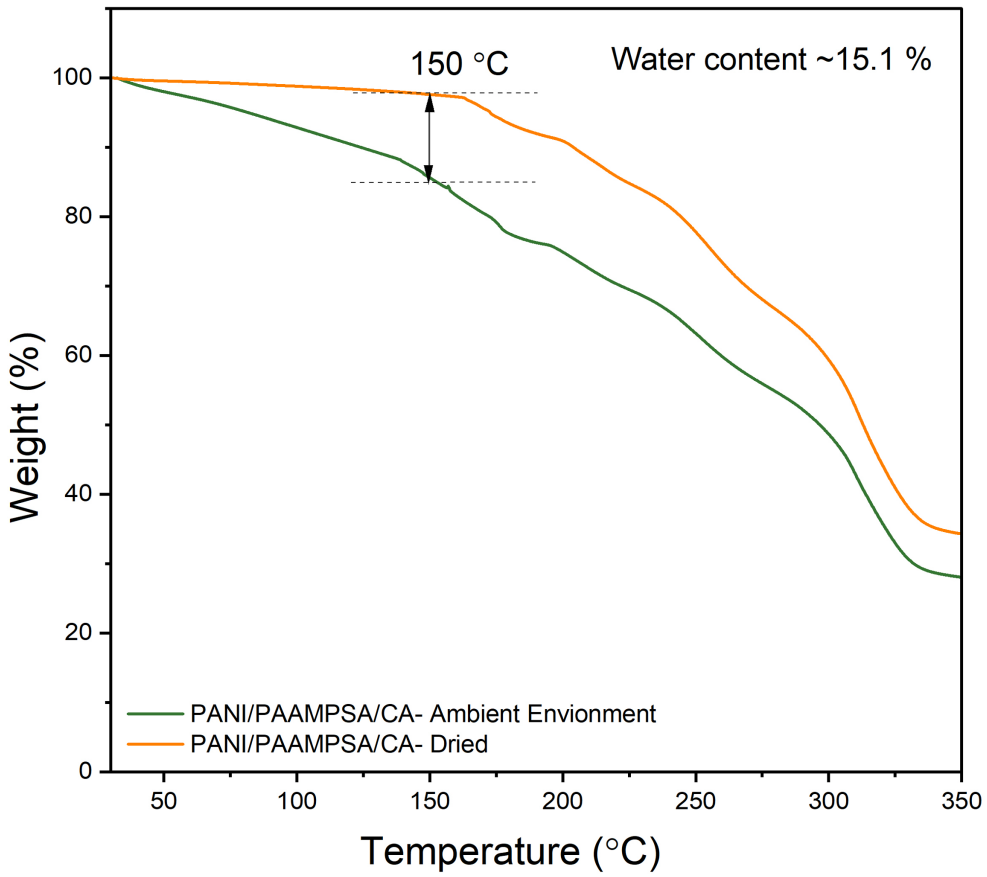

Figure S7: Retained water of PANI/PAAMPSA/CA

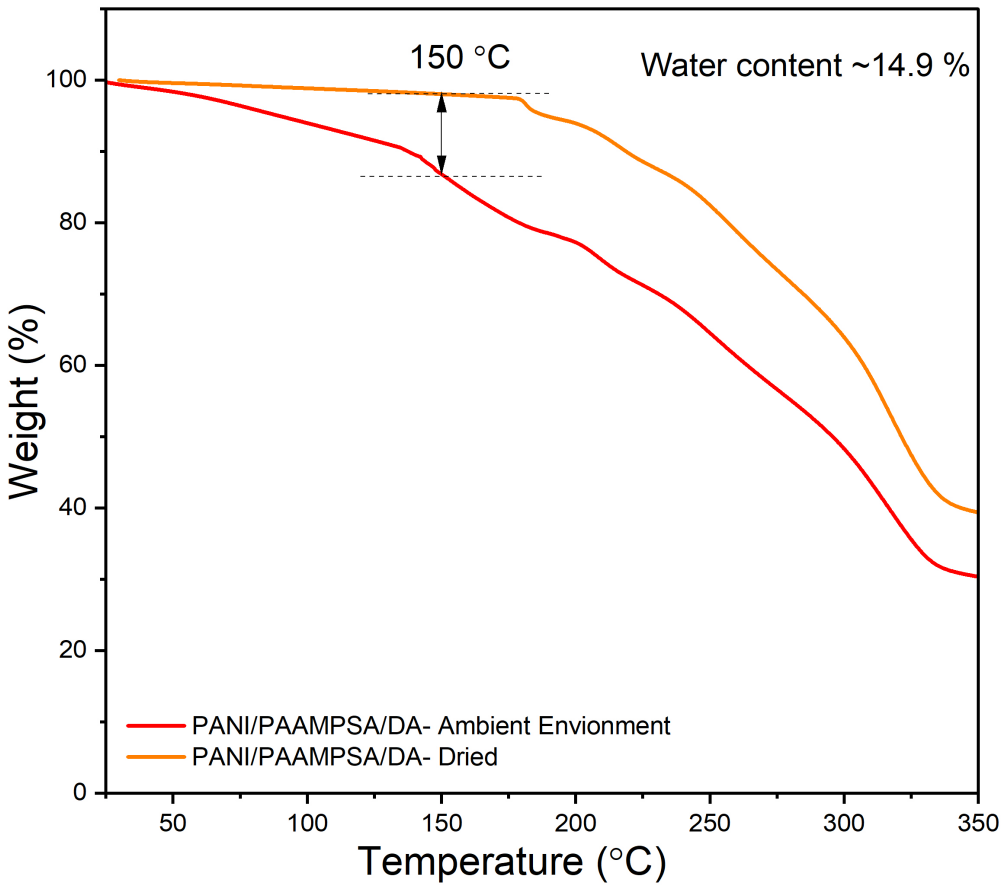

Figure S8: Retained water of PANI/PAAMPSA/DA

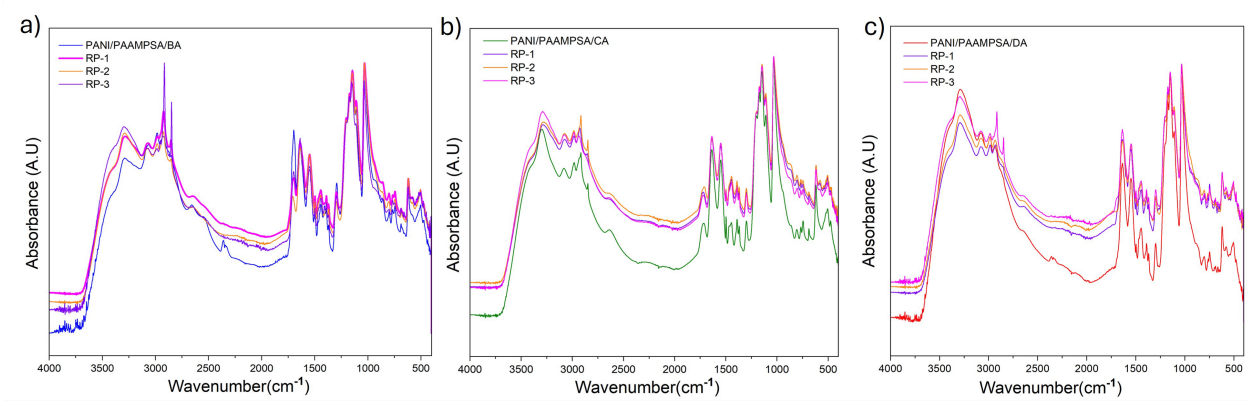

Figure S9: FTIR spectra of reprocessed PANI/PAAMPSA composite films doped with (a) benzenetricarboxylic acid (BA), (b) citric acid (CA), and (c) diphenic acid (DA) over three reprocessing cycles (RP1–RP3)

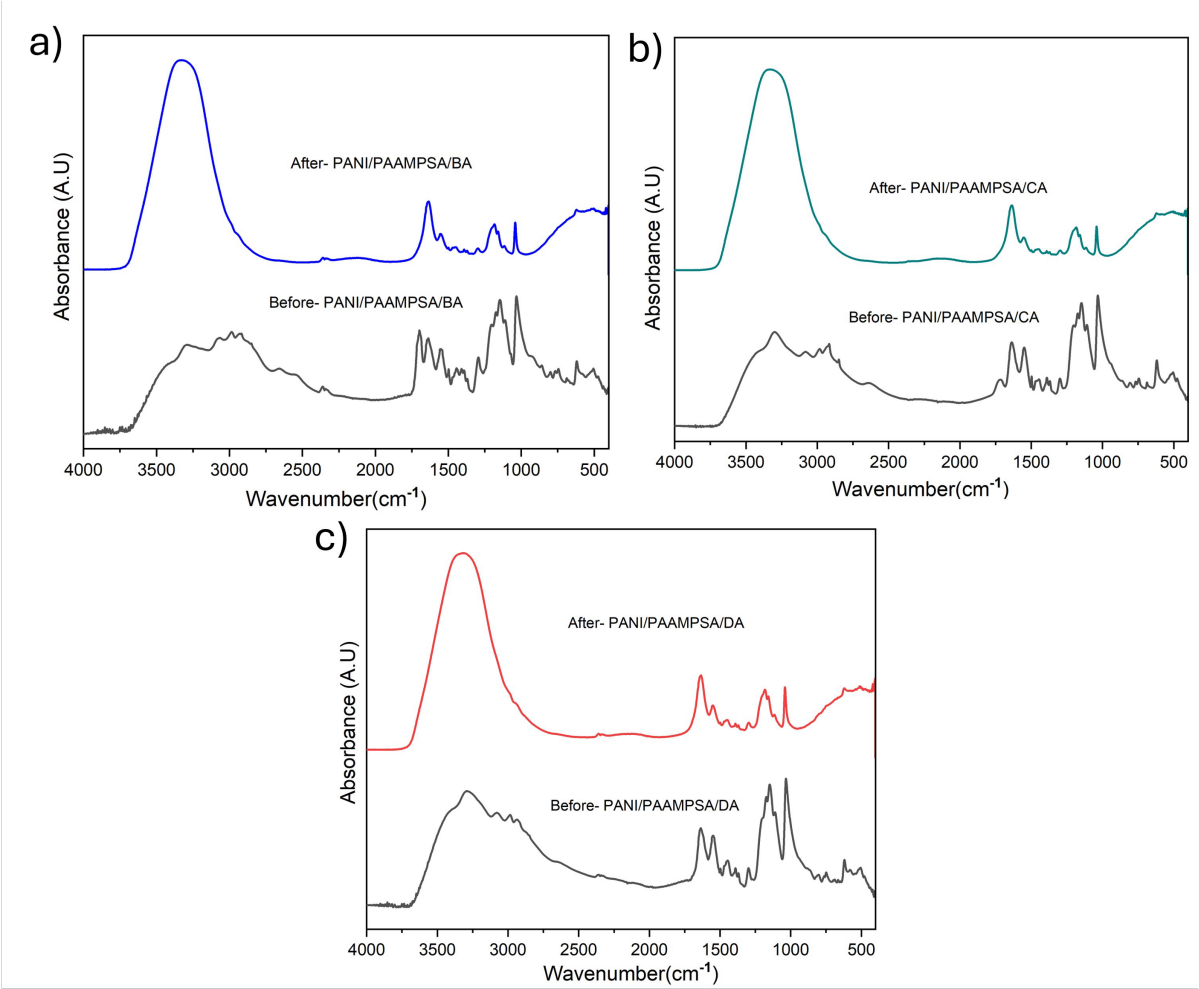

Figure S10: FTIR spectra before and after soil degradation a) PANI/PAAMPSA/BA , b) PANI/PAAMPSA/CA, c) PANI/PAAMPSA/DA

UV degradability- Figure S11 a-c shows the scanning electron microscopy (SEM) images of pristine PANI/PAAMPSA/BA, PANI/PAAMPSA/CA and PANI/PAAMPSA/DA films. A 24 hour UV exposure test was conducted to assess the potential photo-degradation of the samples. SEM was also performed after exposure to UV for 24 hours, and is shown in Figure S11 b, e, h. Notably, the FTIR spectra (Figure S11 c, f, i) showed no significant changes in the characteristic vibrational bands before and after exposure. This suggests that the cracks observed in the SEM images are likely associated with the drying stress and local heating during prolonged UV irradiation rather than extensive photochemical degradation of the polymer backbone under the present UV conditions.

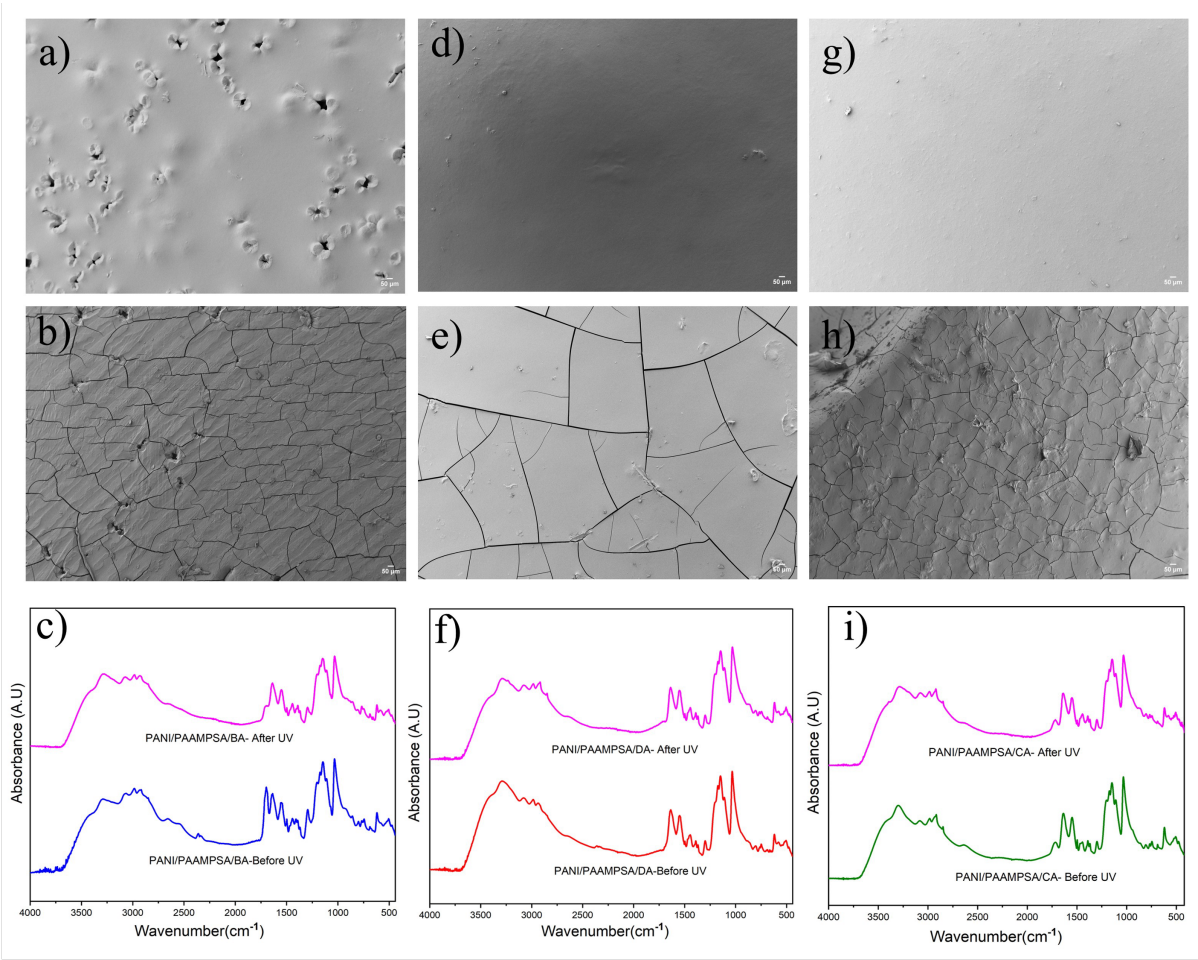

Figure S11: UV degradation study of PANI/PAAMPSA composite films doped with carboxylic acid-based dopants. (a–c) PANI/PAAMPSA/BA: SEM images before and after 24 h of UV exposure, and FTIR spectra comparing before/after degradation. (d–f) PANI/PAAMPSA/CA: SEM images before and after 24 h of UV exposure, and corresponding FTIR spectra. (g–i) PANI/PAAMPSA/DA: SEM images before and after 24 h of UV exposure, and corresponding FTIR spectra

References

1. Y. Lu, Z. Liu, H. Yan, Q. Peng, R. Wang, M. E. Barkey, J.-W. Jeon and E. K. Wujcik, *ACS Applied Materials & Interfaces*, 2019, **11**, 20453–20464.