

Conducting Polymer Based Adhesives for Electrochemical Applications

Hojin Choi^{*} and Hyeonseok Yoon^{*,**}

^{*}Department of Polymer Engineering, Graduate School, Chonnam National University, Gwangju 500-757, South Korea.

^{**}Alan G. MacDiarmid Energy Research Institute & School of Polymer Science and Engineering, Chonnam National University, Gwangju 500-757, South Korea, hyoon@chonnam.ac.kr.

ABSTRACT

There has been huge demand for developing advanced materials and devices for enhanced energy storage. However, relatively little attention has been devoted so far to the development of efficient binders for electrode materials. In this work, we report the preparation of an intrinsically conductive quaternary polymer glue through the combination of polyaniline (PANI) with three additives as a ternary dopant for both conducting and gluing properties. With an optimized composition and no heat treatment process or conductive fillers, the conductive adhesive (Q-PANI) had a conductivity of 0.9 S cm^{-1} and excellent performance as binders for electrochemical capacitor electrodes. The maximum peel strength was 20–25% better adhesive ability than polyvinylidene fluoride insulating binder. Q-PANI with an optimized composition showed good redox properties in an acidic electrolyte. Importantly, Q-PANI itself had a high specific capacitance of 108.7 F g^{-1} . As a result, Q-PANI as a binder was found to significantly enhance the electrode performance of pseudocapacitive nanomaterials (polypyrrole nanospheres and PANI nanofibrils) and electric double-layer capacitive nanomaterials (carbon black), while insulating binders degrade the capacitance. Synergistic effects between the three compounds introduced into the conducting polymer led to an inherently conductive quaternary polymer adhesive, which was demonstrated as an excellent binder for electrochemical capacitor electrodes. Therefore, it is further expected that the combination of conductive and adhesive characteristics will make Q-PANI a very promising conductive paste and coating agent for various applications other than as an electrode binder. It is anticipated that our PANI binder will be suitable as an adhesive for emerging all-organic flexible or wearable devices.

Keywords: polyaniline, adhesives, electrochemical capacitors, conductivity

1 SYNTHESIS OF PANI BINDERS

For the chemical oxidative polymerization of aniline monomers, APS (0.05 mol) was dissolved in 50 mL of 1 M HCl solution, and aniline (0.22 mol) was dissolved in 75

mL of 1 M HCl. Both solutions were cooled to $3 \text{ }^\circ\text{C}$, and then APS solution was slowly added to the aniline solution with constant stirring. The oxidative polymerization proceeded for 1.5 h. The resulting dark green precipitate was filtered using a Buchner funnel and flask with a polypropylene membrane (0.45 mm pore size) and thoroughly washed with distilled water and 1M HCl until the filtrate became colorless. The filter cake was dried for an additional 10 min on the Buchner funnel and then suspended in 125 mL of 0.1 M NH_4OH . After 15 h, the suspension was filtered and the resulting product was further washed by distilled water and ethanol. Finally, deep blue PANI powder was obtained and dried in a vacuum at room temperature. The obtained PANI powder (3.3×10^{-2} – 2 g mL^{-1}) was mixed with CSA (1.3×10^{-2} to $2.1 \times 10^{-1} \text{ g mL}^{-1}$) and/or DBSA (1.2×10^{-2} to $3.6 \times 10^{-2} \text{ g mL}^{-1}$) in NMP with constant stirring for 15 min. The mixed solution was sonicated for 2.5 h and then centrifugation (1640g, 30 min) was used to remove residues, yielding a PANI solution. GCT powder was dissolved in NMP (w/w 1/1) at $90 \text{ }^\circ\text{C}$ and then the GCT solution (0.3–5.0 wt% in total solution) was homogeneously mixed with the PANI solution at room temperature.

2 RESULTS AND DISCUSSION

Conducting polymers feature a reversible doping/dedoping process. Doping of the conducting polymers with counter ions is usually done for controlling the electrical conductivity. However, the judicious introduction of functional components into conducting polymers can further create unexpected useful functions, which might expand the application range of conducting polymers. In this work, PANI was homogenized sequentially with CSA, DBSA, and GCT in solution phase to yield intrinsically conductive polymer adhesives. As a solvent, NMP was chosen since it is commonly used to dissolve binder polymers. First, the electrical conductivity of PANI was measured at each stage to examine the effect of the organic additives (or dopants). For the solubility, CSA/DBSA was introduced into PANI, followed by the addition of GCT, resulting in stable PANI solutions. PANI solutions were coated on glass substrate, and then their four-probe conductivities were measured. Figure 1 shows the dependence of PANI conductivity on the type and

concentration of the additives. The PANIs treated with CSA and DBSA exhibited 7.3×10^{-2} and 6.5×10^{-3} S cm⁻¹ as the maximum conductivity values at the concentrations of 4.6 and 2.7 wt%, respectively (Figure 1a and 1b). Although the conductivity of PANI/CSA was higher than that of PANI/DBSA, the conductivities were as low as 10⁻² S cm⁻¹. However, enhancement in conductivity was achieved by treating PANI with both CSA and DBSA (Figure 1c). The conductivity of PANI/CSA/DBSA (max. 9.1×10^{-1} S cm⁻¹) was found to be approximately one order of magnitude higher than that of PANI/CSA. Owing to the large molecular size, CSA decreases the interaction among PANI chains. DBSA endows PANI chains with a solvating effect derived from the inherent amphiphilic molecular structure. Thus, it is considered that the two sulfonic acids contribute to the conductivity and solubility of PANI through complementary cooperation. The conductivity of PANI/CSA/DBSA increased with increasing CSA weight fraction in the mixed sulfonic acid, which was consistent with the results obtained when individual sulfonic acids were used. It seems clear that CSA contributes more to the conductivity of PANI than DBSA. The maximum conductivity of PANI/CSA/DBSA would originate from a fully doped state. Therefore, PANI/CSA/DBSA (0.35 w/w) with extra room for further doping or interaction was chosen, although the conductivity was slightly lower than the maximum value. Treatment with GCT was then applied. The resulting products exhibited 45% improvement in conductivity at 0.3 wt% GCT content, whereas the conductivity gradually decreased at higher GCT contents (Figure 1d). The electrical conductivity of PANI depended on the GCT content. GCT is a linear sugar alcohol (or polyol) and bears a high dipole moment (ca. 3.3 Debye) due to the hydroxyl groups in its molecular structure.

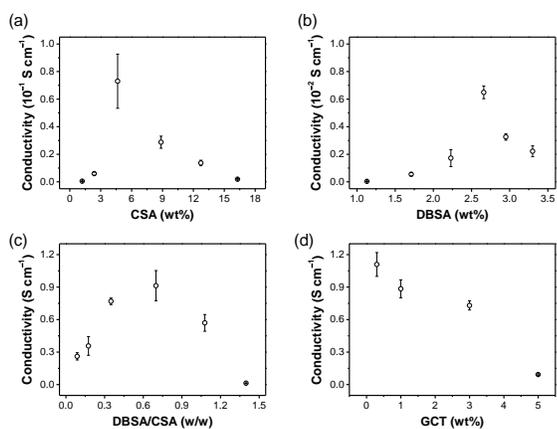


Figure 1: Electrical conductivities of PANIs treated with (a) CSA (b) DBSA (c) both CSA and DBSA (3.1 wt% CSA, 3.0 wt% PANI), and (d) GCT (3.1 wt% CSA, 1.5 wt% DBSA, 3.0 wt% PANI). PANI was treated with the additives in NMP and then coated on glass for the measurement of conductivity.

3. CONCLUSION

An intrinsically conductive quaternary polymer adhesive consisting of PANI, CSA, DBSA, and GCT was successfully prepared. The three organic additives were found to efficiently act as a ternary dopant for conducting and gluing properties of PANI, and thus, the resulting Q-PANI could have excellent conductivity and adhesive properties without the use of additional conductive fillers or heat-treatment processes. It is believed that the synergistic effect of the additives inside a conducting polymer plays a pivotal role in achieving the electrical and adhesive properties of interest. Q-PANIs were demonstrated as an excellent binder to enhance the electrode performance of both pseudocapacitive and electric double-layer capacitive nanomaterials. Since Q-PANIs are solution-processable and require no thermal annealing process, it is expected that they will be suitable for emerging all-organic flexible or wearable devices after optimization.

4. REFERENCES

- [1] M. Kang, J. E. Lee, H. W. Shim, M. S. Jeong, W. B. Im, H. Yoon, Intrinsic Conductive Polymer Binders for Electrochemical Capacitor Application, *RSC Adv.*, 4, 27939-27945, 2014.
- [2] H. -W. Park, T. Kim, J. Huh, M. Kang, J. E. Lee, H. Yoon, Anisotropic Growth Control of Polyaniline Nanostructures and Their Morphology-Dependent Electrochemical Characteristics, *ACS Nano*, 6, 7624-7633, 2012.
- [3] O. S. Kwon, T. Kim, J. S. Lee, S. J. Park, H. -W. Park, M. Kang, J. E. Lee, J. Jang, H. Yoon, Fabrication of Graphene Sheets Intercalated with Manganese Oxide/Carbon Nanofibers: Toward High-Capacity Energy Storage, *Small*, 9, 248-254, 2013.
- [4] J. E. Lee, S. J. Park, O. S. Kwon, H. W. Shim, J. Jang and H. Yoon, Systematic Investigation on Charge Storage Behaviour of Multidimensional Poly(3,4-ethylenedioxythiophene) Nanostructures, *RSC Adv.*, 4, 37529-37535.