Research Article

Wenxin Pan and Quan Chen*

Preparation and electroactuation of water-based polyurethane-based polyaniline conductive composites

<https://doi.org/10.1515/epoly-2022-0005>

received August 27, 2021; accepted October 15, 2021

Abstract: Ionic polymer-based conductive composite is a new type of ionic electroactive polymer smart material, which is composed of two electrodes, the ion-exchange polymer matrix film and the polymer surface and is a three-layer sandwich structure. The conductive composite material has the advantages of flexibility, portability, and biocompatibility, which has attracted a large number of researchers to study it in the fields of biomimetic flexible actuators and biomedical materials, but the conventional matrix film has the disadvantage of high preparation cost. In this study, using sulfonated waterborne polyurethane membrane as matrix membrane and aniline as monomer, polyaniline (PANI) was synthesized by *in situ* oxidation polymerization reaction, and the conductive composites with PANI as electrode were prepared. After applying alternating current electric field, a new brake with PANI as electrode is obtained. A low-frequency signal generator was used to study the electromechanical properties of the prepared materials. The results show that the waterborne polyurethane/PANI composite film produces a continuous and stable driving performance at 0.2 Hz and 20 V, and the maximum output displacement of the terminal is 40 mm. When the driving voltage and frequency are changed, the displacement output also changes, showing a good controllable performance. Its structure and morphology were characterized.

Keywords: electroactive polymer, sulfonation, ion-exchange membrane, electric brake, polyaniline

1 Introduction

Electroactive polymers (EAPs) refer to a kind of polymer materials that can change their shape under the action of an electric field; EAP is an intelligent material with special electrical and mechanical properties, and this kind of materials are often used in the field of actuators and sensors. At present, the application of EAP is in the stage of bold attempts, but its unique properties determine that this material has an inestimable application prospects and functions (1). Piezoelectric ceramic material is the main material that is often used to make actuators in the early stage. Piezoelectric ceramics have the characteristics of a large force, but their deformation capacity is very limited, and there are problems such as water loss (2). Therefore, people continue to explore new EAP materials and achieved breakthrough results. EAPs can be classified into electronic and ionic types according to their different mechanisms of action. Among them, the electrical EAPs are under the effect of electrostatic force in the electric field produced by entrainment electrostrictive, electrostatic, piezoelectric, and ferroelectric effects (3). The ionic EAP has advantages of low driving voltage (4).

Ionic polymer metal composite (IPMC) is a new type of ionic EAP intelligent material, but the conventional IPMC uses Pt metal nanoparticles as the electrode and Nafion film as the matrix, which has some defects such as high electrode rigidity (5).

Therefore, the research in the field of materials is no longer limited to hard materials, and people turn their eyes more to flexible materials. Compared with rigid materials such as traditional metals and ceramics, elastomer materials can produce deformation of different degrees under the action of external stimuli such as electric field, magnetic field, mechanical force, and temperature (6). Therefore, this kind of polymer material is made into a new type of electroactuating device with a green environmental protection and excellent performance,

* **Corresponding author: Quan Chen**, Chemical and Pharmaceutics Engineering School, Henan University of Science and Technology, Los Dragon Area, Luoyang 471023, China, e-mail: p18438612318@126.com

Wenxin Pan: Chemical and Pharmaceutics Engineering School, Henan University of Science and Technology, Los Dragon Area, Luoyang 471023, China

which can be often used in bionics, etc. (7). The development of artificial muscles in robotics is one of the most common applications of EAPs. Therefore, EAPs are often referred to as artificial muscles (8). Polyurethane elastomers in polymers have excellent properties, such as good mechanical properties, good wear resistance, high hardness, chemical resistance, and excellent aging resistance, and can be used as matrix membrane materials in a wide range of applications (9). The performance can be optimized by using sulfonate as chain extender. Sulfonic acid type waterborne polyurethane (WPU) can be used as matrix membrane material. Ionic polymers have gained much attention in recent years. Electrode materials are the key factors affecting its electrochemical performance (10). However, conventional IPMC has problems such as metal electrode shedding, high cost (11), and water loss, which limit its large-scale application. EAPs are usually conjugated systems with large π bonds, such as polyaniline (PANI), polypyrrole, and polythiophene (12,13). Since Anglonpols et al. (14) prepared a conductive PAN using protic acid doping, among many electrode materials, PANI is considered as an electroactive electrode material with a great potential for the development due to its advantages such as high doping stability, easy preparation, and good environmental stability (14), which can effectively overcome the above shortcomings.

2 Experimental

2.1 Experimental drugs

Polyadipate-1,4-butanediol ester diol (PBA) and polytetrahydrofuran ether diol (PTMEG) was purchased from chemical Xia (Chengdu Huaxia Chemical Reagent Co., LTD). Isophorone diisocyanate (IPDI) was purchased from chemical Xia. 2,2-Dihydroxymethylpropionic acid (DMPA) was purchased from Sane Chemical Technology (Shanghai) Co., Ltd. Analytical pure 1,4-butanediol (BDO) was purchased from Tianjin Komil Chemical Reagent Co., Ltd. Sodium sulfamate (A95) was purchased from Guangdong Wengjiang Chemical Reagent Co., Ltd. Analytical pure aniline ($C_6H_5NH_2$) was purchased from Tianjin Damao Chemical Reagent Factory. Analytical pure ammonium persulfate (APS) ($(NH_4)_2S_2O_8$) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Analytical pure hydrochloric acid (HCl) was purchased from Luoyang Haohua Chemical Reagent Co., Ltd.

2.2 Preparation of WPU matrix film

PBA 14 g, polytetrahydrofuran ether diol (PTMEG), $M_n = 2,000$ 14 g, and DMPA 1.5 g were added into a three-mouth flask equipped with an agitator, a condenser, and a thermometer. The flask was dehydrated at 120°C for 2 h in a vacuum. Dehydrated BDO 0.9 g was added at 80°C, stirred well, and IPDI 12.85 g was added, and allowed to react for some time. When the mass fraction of $-NCO$ reached the theoretical value, the prepolymer was obtained by cooling (15). The temperature was lowered to 60°C, and quantitative triethylamine was added to react for 10 min. Then an appropriate amount of acetone was added to reduce the viscosity of the system, and then a certain amount of sulfamic acid hydrophilic A95 was added to react for 30 min. The prepolymer was poured into the high-speed disperse water to emulsify, and ethylenediamine was added to expand the chain. Finally, the aqueous polyurethane product was obtained from acetone by vacuum distillation of the emulsion. Sulfonic acid waterborne polyurethane (SWPU) matrix film with an isocyanate radical index (R) = 1.7 (16) was prepared by the prepolymer method (17), and the average thickness of film is 0.51 mm.

2.3 Preparation of PANI composite electrode material (WPU/PANI)

A total of 5 mL of aniline after secondary vacuum distillation and 60 mL at a concentration of 1 mol·L⁻¹ of HCl were stirred at room temperature for 1 h, and then APS aqueous solution was added to the mixture while stirring, and the reaction gradually changed from light yellow to blue, blue-green, green, and dark green. The mixture was stirred continuously for 10 h at room temperature, and the dispersed solution was left standing overnight for reserve. The film obtained above is soaked in the PANI solution for 24 h, and then the soaked film is dried. After the above steps, the conductive composite material with the PANI electrode surface is obtained, and the composite film is sealed and preserved.

2.4 Testing and characterization

2.4.1 Fourier-transform infrared (FTIR) spectroscopy test

The Irttracer-100 FTIR spectrometer of Shimadzu Company, Japan, was used to characterize the dried WPU film and

WPU/PANI film samples in ATR mode by using the potassium bromide (KBr) compression method. The resolution was 4 cm^{-1} , and the scanning times were 32 times.

2.4.2 Scanning electron microscopy (SEM) morphology characterization

The surface and cross section of the PANI electrode composite film after spraying gold were observed using FlexSEM1000 scanning electron microscope of Hitachi.

2.4.3 X-ray diffraction (XRD) test

The XRD spectra of WPU/PANI were measured at a low temperature using the XRD instrument manufactured by the Dutch company. The test range is $5\text{--}95^\circ$.

2.4.4 Fluorescence spectral analysis

The fluorescence spectra of the samples were analyzed using F-4600 FL spectrophotometer.

2.4.5 Mechanical properties test

The sample was cut into a regular shape, and the tensile strength of the WPU film and WPU/PANI composite film was measured using a tensile machine. According to the method described in GB/T528-2009, the tensile speed is $10\text{ mm}\cdot\text{min}^{-1}$, and the experimental temperature is 26°C .

2.4.6 Electrochemical performance test

CHI604E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.) was used to test the electrode material in a two-electrode system, and its electrochemical performance was studied. Using platinum net and WPU/PANI as anode and cathode, saturated calomel electrode as reference electrode, and $0.5\text{ mol}\cdot\text{L}^{-1}$ sulfuric acid as electrolyte, the cyclic voltammetry (CV) test was carried out.

2.4.7 Electrical response performance test

Electrical performance testing system includes a low-frequency signal generator, laser displacement sensor (Keyence KG-80A), multifunction data acquisition card, oscilloscope, and signal amplifier. The signal generator can transform sinusoidal,

square, and triangular wave signals at $0\text{--}20\text{ V}$ voltage and $0.1\text{--}200\text{ kHz}$ frequency. The range of displacement sensor is 650 nm . Multifunction data acquisition card adopts the LapView (V14.0) supporting software; oscilloscope and signal amplifier are used to capture the electrical signals that may be generated when the film deflection occurs. The sample size of the PANI electrode composite membrane was $22\text{ mm} \times 5\text{ mm}$ and tested in air atmosphere.

3 Results and discussion

3.1 *In situ* oxidative polymerization of PANI

When polyaniline is treated with protic acid, good doping effect can be obtained, and the conductivity can be increased by more than ten orders of magnitude, when treated with proton acid, HA proton acid decomposition, the generated hydrogen protons (H^+) ten transferred to the PANI chain, the molecular chain of central Asia amine on the nitrogen atom of the protonation reaction, generate cation radicals. The positive charge of the imine nitrogen atoms is dispersed along the molecular chain to the adjacent atoms by conjugation, thus increasing the stability of the system. It is the migration of charge on the molecular chain or the interchain transition after doping that makes the PANI exhibit high conductivity. When $n = 0.5$ (Figure 1), the oxidation and reduction units on the molecular chain are equal, it is most conducive to the transfer of charge, so the polymerization product has the best electrical conductivity. When $n = 0.5$, PANI is called emerald green imine (18), which is an ideal structure for preparing conductive PANI. *In situ* polymerization, also known as adsorption polymerization, is used to prepare PANI conductive film; the synthesis reaction of PANI is carried out on the surface of the matrix film; using this method to prepare conductive composite film is relatively simple and easy; and it is to adsorb PANI as a conductive layer on the surface of the matrix to make it conductive. There are two key factors in preparing the conductive film by this method. One is to ensure that the generated PANI has an emerald green imine structure, so as to ensure its excellent electrical conductivity. Therefore, the appropriate oxidant and acidic medium are the two necessary conditions for the synthesis of an electroactive PANI. In addition, the type of medium acid, the concentration of aniline, and the dosage of oxidant have a great influence on the polymerization of PANI. The other is to ensure the effective adsorption of conductive PANI by a WPU membrane. For the sulfonated membrane with a better water

Figure 1: Oxidation-reduction (REDOX) unit of PANI.

Figure 2: Infrared spectra of WPU/PANI composite film matrix film.

absorption, the adsorption of doped PANI is relatively easy (Figure 1).

3.2 FTIR structure analysis

Figure 2 shows the FTIR spectrum of WPU/PANI conductive composite film. Where “a” is pure polyurethane, and

“b” is WPU/PANI composite film. In the spectrum curve, there is a typical characteristic absorption peak of PANI, and the characteristic absorption peak at 804 cm^{-1} is caused by the weak C–H in-plane bending deformation vibration on the aniline ring (19). The characteristic absorption peaks of $\text{N}=\text{Ar}=\text{N}$ and $\text{N}-\text{B}-\text{N}$ are $1,571$ and $1,496\text{ cm}^{-1}$, respectively. It can be seen from the structure of conjugated PANI that the conductive property is better because it contains the quinone structure (20). The absorption peaks of quinone ring and benzene ring unsaturated C–N bond are $1,300$ and $1,246\text{ cm}^{-1}$, respectively. There is a strong absorption peak at $1,082\text{ cm}^{-1}$, which is the characteristic absorption peak of sulfonates. The absorption peak at $1,496\text{ cm}^{-1}$ reflects the vibration of the benzene ring skeleton after HCl acidification. The absorption peak at $1,725\text{ cm}^{-1}$ is C=O stretching vibration in WPU. The infrared spectrum shows that the PANI electrode is covered on the WPU film.

3.3 Morphology and characterization of WPU/PANI

Figure 3 shows the surface SEM of the PANI electrode composite film. Figure 3a shows that the SWPU base film has a relatively flat and smooth surface with a good overall homogeneity. Figure 3b shows that the electrode layer is composed of a large number of nonuniform

Figure 3: SEM image of SWPU/PANI composites: (a) SWPU base film surface image, (b) surface diagram of the PANI electrode, and (c) base membrane and PANI composite cross section.

particles, and there are some gaps between the particles. Such a structure is more favorable for the composite film deflection. The reason is that when the SWPU/PANI composite film deflected, the particles stacked into the electrode layer would squeeze each other, resulting in a small resistance to the deflection, and the existence of a gap can appropriately reduce this resistance. At the same time, Figure 3c shows that the PANI particles that compose the electrode layer are larger in size, and the color of the base membrane and the electrode part of the lower layer is slightly different, which is due to the different electrical conductivity of the two, whereas the color of the PANI electrode distributed in the upper layer is slightly lighter. As can be seen from the SEM figures (Figure 3a–c), although the thickness distribution of the sample is slightly uneven, there is a good interface bonding between the PANI electrode layer and the SWPU matrix film.

SEM test further showed that the WPU/PANI electrically active conductive composite film was prepared.

3.4 XRD analysis

Figure 4 shows the XRD pattern of WPU/PANI, which appears as diffraction peaks, at $2\theta = 8.62^\circ$, 20.41° , 25.32° , and 26.92° . Among them, about 20° and 25° are, respectively, classified as periods parallel to the polymer molecular chain and periods perpendicular to the polymer molecular chain, indicating that the PANI doped by protic acid has an ordered orientation and has a wide peak near 28.88° , indicating that the doped PANI in the composite membrane has a good crystallinity. However, due to the

Figure 4: XRD patterns of WPU/PANI.

existence of rigid benzene ring on the molecular chain, the ordered crystalline structure is not perfect, and the peak shape is slightly wider.

3.5 Fluorescence spectra of composite films

When the WPU/PANI composite film is irradiated with ultraviolet light, fluorescence will be generated, and its fluorescence spectrum is shown in Figure 5. Because polyaniline is a conjugated polymer, when irradiated with the maximum absorption wavelength, the photon energy meeting the bonding of polymer-antibonding band gap, photons will be absorbed, absorbed photons rather than electrons from the bonding can stimulate the antibonding band, at the same time have a hole in the bonding energy band, hole excited electrons combining with the key, can emit fluorescence. The experimental results show that the composite membrane made of WPU and PANI can enhance the injection density of the carrier, suppress the nonradiation attenuation of PANI, and improve the luminous efficiency of the composite membrane. It is indicated that the conductive PANI has a slightly stronger fluorescence property, which provides an application prospect for making photoelectric devices.

3.6 Mechanical property analysis

Tensile strength can be obtained from the stress-strain curve as shown in Figure 6. The tensile strength of film A and composite film B is 2.38 and 0.30 MPa, respectively.

Figure 5: Fluorescence spectra of WPU/PANI.

Figure 6: Stress–strain curve: (a) WPU membrane and (b) WPU/PANI composite membrane.

The addition of PANI decreases the tensile strength, whereas the elongation increases, which is due to the formation of hydrogen bond reinforcement between the $-NH$ group of PANI and the $-NHCOO$ group of polyurethane, which increases the flexibility of the WPU film. The calculated Young's modulus is 1.18 times lower than that of matrix film A. The lower modulus is beneficial to produce larger bending deformation.

Figure 7: CV curves at different scanning speeds.

3.7 Electrochemical performance analysis of WPU/PANI composite films

Figure 7 shows the CV curves of WPU/PANI composite electrode materials in acidic electrolyte at different scanning speeds. As can be seen from Figure 7, at different scanning rates, the peak current of WPU/PANI composites increases with the increase of the scanning rate, indicating that the material has a good current response. When the scanning rate is low, a pair of REDOX peaks can

Figure 8: Deflection and displacement diagram of electric brake with a frequency of 0.2 Hz and a voltage of 20 V.

be observed. However, as the scanning rate increases, the REDOX potential difference gradually increases, the REDOX peak weakens, and the image begins to deviate and deform. This is because with the increase of the membrane surface scanning rate, there is not enough contact between the electrode material and the electrolyte, and the electrons in the electrode material have not yet had time to undergo REDOX reaction with the electrolyte solution.

3.8 Electromechanical properties test and analysis of WPU/PANI composite films

As shown in Figure 8, under the condition of 0.2 Hz frequency and 20 V driving voltage, the ion-exchange membrane has a particularly rapid deflection speed and a fairly large deflection angle, close to 90° vertical. After several electric cycles, the deflection angle can be changed by controlling the voltage output. The reasons are as follows: (1) the doping of sulfonates makes the water absorption of the composite membrane greatly increased, the flexibility of the hybrid membrane has been greatly improved, and the resistance of bending is smaller and (2) with PANI as the electrode, the conductivity of hybrid membrane increases, the current density in the membrane increases after adding voltage, and the ion migration rate is faster, and more hydrated cations gather in one side of the membrane at a faster rate per unit time, and the deformation is recoverable. As a result, the hybrid film is significantly deflected.

4 Conclusion

The electrode material of WPU/PANI composite membrane was prepared by using PANI solution with the WPU membrane as the matrix membrane. After introducing the electrical signal, the EAP electric driver was obtained. The results show that the electrode layer can be well combined with the matrix film, the thickness of the electrode layer is uniform, and there is a small gap on the surface of the electrode layer, which is more beneficial to the driving displacement output of WPU/PANI composite film. The driving displacements of the samples all increased with the increase of the driving voltage, and the maximum driving displacement was obtained at the driving voltage of 20 V, which also confirmed the conclusion characterized by the SEM morphology. The composite

products composed of SWPU and PANI can form synergistic and complementary effects, etc. Compared with traditional IPMC, it has the advantages of faster deflection speed, so the conductive composite products can be used to manufacture mechanical arms, cables, chemical/biological sensors, etc. (21). A hybrid ion-exchange membrane with a high solid content and high conductivity was prepared by using the sulfonate hydrophilic reagent and PU codoping, and a SWPU/PANI electroactuator with optimized electromechanical properties was obtained.

Funding information: This article was supported by the Key Scientific Research Program of Henan Universities (17A43016).

Author contributions: Wenxin Pan: writing – original draft, designed the experiment; and Quan Chen: writing – review and editing.

Conflict of interest: Authors state no conflict of interest.

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