Electrochemically Synthesized Polypyrrole and Cu-Plated Nylon/Spandex for Electrotherapeutic Pad Electrode

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ABSTRACT: Electroconductive fabrics were prepared to improve the properties of conductive electrode pad material used for electrotherapy when it is subjected to various movements of the human body. Highly stretchable and conductive fabrics were prepared by *in situ* electrochemical polymerization of polypyrrole (PPy) on nylon/spandex stretchable fabric in aqueous solutions with 0.05*M* pyrrole and 0.05*M* anthraquinone-2-sulfonic acid, sodium salt monohydrate (AQSA) at room temperature for 2 h. Electroless Cu plating was also applied after chemical polymerization of PPy to improve the conductivity of the fabric pad. Performance of prepared stretchable conductive fabric pad was evaluated in terms of conductivity changes as a function of extension and continuous current application time, and clinical test. As a result, the fabric conductivity was well maintained with extension up to 60% and prolonged treatment time over 30 min. The effect of transcutaneous electrical nerve stimulation (TENS) was observed with prepared TENS pad in this study and conventional TENS pad for medical use. The significant effect of TENS was observed with a pad made of conductive fabric by Cu plating and a conventional TENS pad ($P < 0.05$, respectively). Even though the efficiency of an experimental pad made of fabric composite with electrochemically polymerized PPy was not as good as conventional TENS pad for medical use in this experiment, it can possibly be used for other applications where relatively low-strength electrical pulse is required. J Appl Polym Sci 91: 4064–4071, 2004

Key words: polypyrrole; electrochemical polymerization; electroless copper plating; electrotherapy; electrode

INTRODUCTION

Medical textiles are a major growth area within technical textiles and are used as textile materials for medical and healthcare products. They range from simple gauze or bandage materials to scaffolds for tissue culturing and a large variety of prostheses for permanent body implants such as artificial heart, heart valve, blood vessel, and skin.[1,2] Moreover, intelligent biomedical clothing and textiles have the potential to substantially change the provision of health and health care services for large population groups (e.g., those suffering from chronic diseases such as cardiovascular and respiratory disease, diabetes, neurological disorders, and rehabilitation, and the elderly with specific needs).[3]

Among the various medical treatments, electrotherapy using voltage or current pulses is increasingly used in physiotherapy and rehabilitation to reduce pain, to enhance healing, and to improve motion.[4] However, in the case of conventional electrotherapy, there are problems related to the surface electrode placed on the skin or needle electrode inserted into the living body. In general, neurostimulation electrodes are attached to the skin by adhesive or suction, or with an elastic band. Therefore, patients cannot move freely during treatment because the electrodes are not tightly attached to skin. Furthermore, because the material for the electrode must provide constant current with low resistance, it should be flexible and closely adhered to the human skin. Therefore, the interest in manufacturing pad electrode material has grown to improve their electroconductive and physical properties. Textiles became a focus because of its unique properties such as flexibility, durability, and ease of use.

Generally, conductive materials used for electric stimulation electrode can be manufactured by the posttreatment or during spinning of blend. Specifically, the posttreatment is mainly used because it is easy to apply for fabric step. The posttreatment is classified into many techniques such as metal coating, resin processing with conductive materials, metal plating, and coating with polymer-containing conjugated π-electron backbone. Among them, conductive polymer coating gives the flexibility and durability on fabric. Therefore, the pad electrode materials can be

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prepared by using the π-conjugated polymer such as polypyrrole (PPy), polyaniline (PANI), and polythiophene (PT) on the fabric.[5] Among them, PPy has excellent environmental stability and facile synthesis, and higher conductivity than many other conductive polymers.[6–8] Electrochemically synthesized PPy particularly was suitable for use in electronic devices because of the direct formation of conducting polymer with control of film thickness and morphology.

In this research, therefore, a study to prepare electroconductive material for electrotherapeutic pad electrodes was primarily conducted. Changes in conductivity with extension were investigated to improve the properties of conductive electrode pad material used for electrotherapy when it is subjected to various movements of the human body. PPy was *in situ* polymerized chemically and electrochemically on nylon/spandex stretch fabric to provide flexibility and elasticity as well as good conductivity. Moreover, electroless Cu plating was additionally continued on the composite to increase its conductivity to the extent where the application area required a high electrical strength. To establish optimum process conditions and to investigate composite properties with extension, the conductivity and physical and mechanical properties were measured with various polymerization conditions, degrees of extension, and multiple extensions. In addition, behavioral observation with experimental rats was conducted to test the practical utility of the textile pad electrode prepared in this study. Mechanical allodynia and heat hyperalgesia was compared with conventional transcutaneous electrical nerve stimulation (TENS) pad for medical use.

EXPERIMENTAL

Materials

Nylon/spandex (95/5) stretch fabrics (140 denier, warp 184, weft 256 in 25 cm^2, twill weave, Taewoo Fabrics Co., Korea) were washed with aqueous solution of scouring agent and sodium hydroxide for 1 h to remove spinning oil used for the weaving step before polymerization. Then the fabrics were completely rinsed and dried. Pyrrole (Aldrich Chemical Co.) was purified with vacuum distillation.

Ferric chloride ($FeCl_3$, Duksan Pure Chemical Co., Korea), benzene sulfonic acid (BSA, Lancaster Synthesis, UK), and anthraquinone-2-sulfonic acid, sodium salt monohydrate (AQSA, Aldrich Chemical Co.), tin (II) chloride ($SnCl_2$, Junsei Chemical Co., Japan), palladium (II) chloride ($PdCl_2$, Kojima Chemical Co., Japan), cupric sulfate ($CuSO_4 \cdot 5H_2O$), Rochelle salt [potassium sodium tartrate, $KOOCCH(OH)CH(OH)COONa \cdot 4H_2O$] (Kanto Chemical Co., Japan), formaldehyde (HCOH) (Duksan), NaOH, citric acid [$C_3H_4(OH)(COOH)_3 \cdot H_2O$] (Yakuri Pure Chemical Co., Japan), and sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) (Duksan) with special reagent grade were used without further purification.

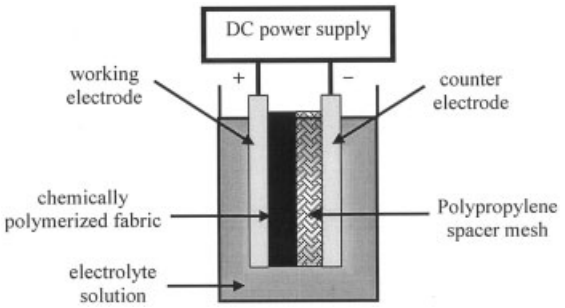


Figure 1 Schematics of electrochemical polymerization apparatus.

Preparation

Electrochemical polymerization

Conductive fabrics were prepared by using electrochemical polymerization on the top of the *in situ* chemically polymerized fabric. In chemical polymerization, a diluted pyrrole solution was diffused in fabric at room temperature for 1 h to synthesize conducting polymer on the substrate. During the diffusion step, ultrasonic treatment (Bransonic 3510R-DTH, 42 kHz) was employed for 20 min to improve the diffusion of pyrrole monomer into the fabric. *In situ* chemical polymerization was performed by adding the mixture of oxidant ($FeCl_3$) and dopant at 5°C for 1 h. BSA was used as a dopant and the molar ratio of pyrrole : oxidant : dopant was determined to be 1 : 2.33 : 0.33 by referring to precedent research.[9,10]

Composite fabrics polymerized with chemical polymerization were well washed with flowing water and dried *in vacuo* at 40°C for 24 h. For the electrochemical polymerization, to aid circulation of reactive solution, the composite fabrics were immersed in solution for 1 h and polypropylene mesh was inserted between the fabrics prepared by chemical polymerization and electrode. Then, the electrochemical polymerization was carried out in a dopant solution, where two stainless steel plates were used as the working and the counter electrodes, at room temperature under a constant power source of 1.3 V. Conductive fabrics obtained from the working electrode connected with anode were washed with distilled water and dried. A schematic of the electrochemical polymerization apparatus is shown Figure 1.

Electroless Cu plating

Nylon/spandex fabric covered with chemically synthesized PPy was used as a substrate. For surface catalyzation, composite fabric was dipped into a cata-

lyzation solution of pH 12.4 containing $SnCl_2$, $PdCl_2$, and HCl at room temperature for 10 min. The catalyzed fabric was then rinsed in a large amount of distilled water to prevent contamination of the plating bath. The acceleration step was performed to remove Sn^{2+} ions over the catalytic Pd nuclei with the HCl solution. It was then immersed in a bath containing the mixture of cupric sulfate, Rocelle salt, formaldehyde, and NaOH. The plated sample was then treated in a posttreatment solution.[11]

Performance of conductive fabric

The conductivity of conductive stretch fabric was measured by four straight line probes and equidistant points, taking the thickness as that of the fabric with Keithley 238 at 65% relative humidity (RH) and 25°C. Constant pressure was applied to improve the contact between fabric and line probe. In this device, current is applied between the outer probes, and the voltage difference between the inner probes is measured and then the conductivity of fabric was calculated.

The conductivity measurement of the conductive fabrics with extension of the conductive fabrics was performed by using the two line probes under loading of the specimens in the tensile testing machine (Instron Co., Ltd., UTM Instron 4465) by standard test methods for coated fabrics at RH 65% at 25°C, because of poor contact from loaded sample state in the Instron.[12] After the fabric was stretched to a certain degree, the machine was stopped and the electrode was then placed and clamped over the fabric mounted in the tensile tester under constant pressure to keep good contact between fabric and electrode. Pressure was adjusted to give a constant conductivity and the modified electrode was calibrated with standard for probes.

The morphologies of each fiber were investigated with field emission scanning electron microscopy (FE-SEM), JSM-6330F (JEOL Co.), in a stress-relaxed state (i.e., after extension without stress).

Clinical test

Surgery

Adult male Sprague–Dawley rats weighing 250–300 g were used in this study. Experiments were approved by the Animal Care Committee of Seoul National University. The animals were housed in plastic cages with wood chip bedding and maintained on a 12/12 h light/dark cycle. Experiments were conducted during the light component of the cycle. The rats were kept for at least 3 days under these conditions before surgery.

The rats were prepared under isoflurane/oxygen anesthesia for a surgical neuropathy model, according to the method devised by Kim and Chung.[13] The rats were placed in a prone position and the left paraspinal muscles were separated from the spinous process at the L_4–S_2 levels. The L_6 transverse process was carefully removed with a fine rongeur to visually identify the L_4–L_6 spinal nerves. The L_5 and L_6 spinal nerves were isolated and tightly ligated with 6-0 silk thread. Animals with the inability to flex the left hindlimb postoperatively, indicating damage to the L_4 nerve, were discarded. Sham-operated rats underwent the same surgical procedure as described above but without ligation of the designated spinal nerves.

Behavioral observation

Mechanical allodynia was measured by using von Frey hairs (0.41, 0.70, 1.20, 2.00, 3.63, 5.50, 8.50, 15.10 g) (Stoelting Inc., Wood Dale, IL). Rats were placed in a plastic cage with a wire mesh bottom, which allowed full access to the paws. The test was performed after 15 min of habituation or as soon as the rat stopped exploring and appeared acclimatized to the testing environment. The 50% paw withdrawal threshold was determined by using the up–down method.[14] In this paradigm, the test was initiated with the 2.0 g hair, in the middle of the series. Stimuli were always presented in a consecutive fashion, whether ascending or descending. The area tested was the mid-plantar left hind paw, avoiding the foot pads. The von Frey hair was applied for 3 s perpendicular to the plantar surface with sufficient force to cause slight buckling against the paw. Each trial was repeated at 10-s intervals. A positive response was noted if the paw was sharply withdrawn. Flinching immediately upon removal of the hair was also considered a positive response. Animals that did not display a 50% threshold with less than 2.0 g Frey hairs by postoperative day 14, when wound healing was essentially completed, were considered to be failed preparation and excluded.

Heat hyperalgesia was assayed with the paw withdrawal test. As described previously,[15,16] the rats stood upon an elevated glass floor and a movable radiant heat source beneath the floor was aimed at the mid-plantar hind paw (Hugo Basile Inc.). The light intensity was adjusted at the beginning of experiment in order for the rat to feel the stimulus by 15 s; the light intensity was held constant thereafter. We express the data as difference scores, computed by subtracting the latency of the control side from that of the operated side. The heat stimulation was repeated three times at an interval of 5 min for each paw and the mean calculated.

Electrical pads were prepared by cutting the electrical fabric into a 1 × 2 cm size pad, which was connected with a TENS stimulator via copper wire. Under isoflurane anesthesia, TENS of 80 Hz was applied to the involved paws for 30 min. The intensity was ad-

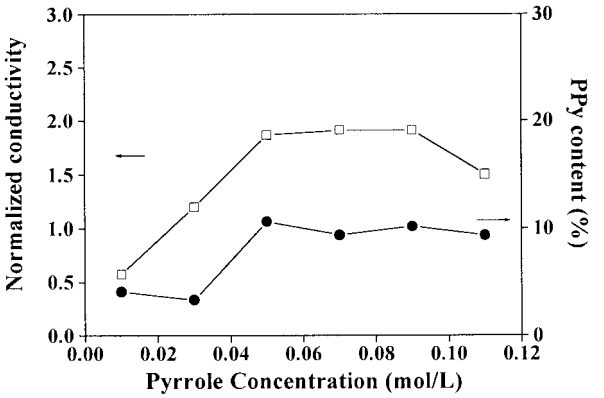


Figure 2 Change of conductivity with pyrrole concentration.

justed just to induce withdrawal reflex on the normal paws. Mechanical allodynia (decreased mechanical sensitivity) and heat hyperalgesia, two representing symptoms and signs of the neuropathic pain, were evaluated to check the competence of the pain model and to evaluate the effect of TENS.

RESULTS AND DISCUSSION

Electrochemical polymerization

To prepare conductive fabric, PPy was electrochemically polymerized on the chemically synthesized PPy on nylon/spandex stretch fabric, because electrochemical polymerization offers a distinct advantage in that the materials can be produced *in situ* on the electrode without the need for intermediate treatment and to provide much higher conductivity. To determine optimum polymerized condition, conductivity and PPy content were measured with variation of monomer concentration, dopant concentration, and polymerization time. Chemical oxidative polymerization was carried out under the optimum conditions determined in our previous study before electrochemical polymerization.[17]

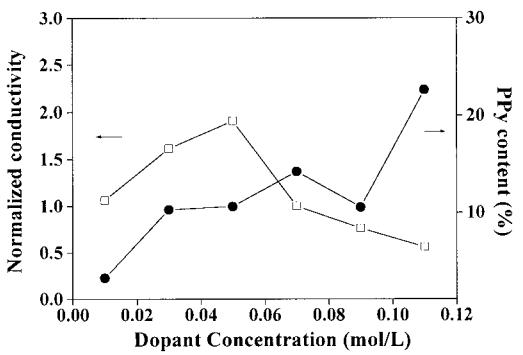


Figure 3 Change of conductivity with dopant concentration.

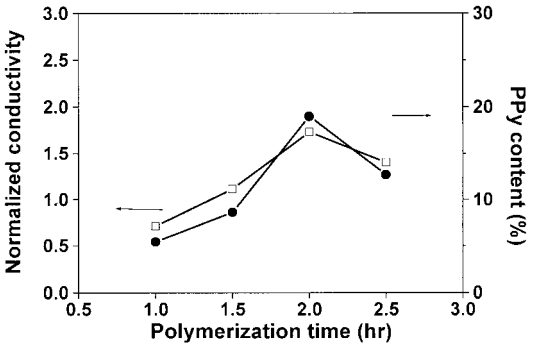


Figure 4 Change of conductivity with polymerization time.

To decide optimum conditions for electrochemical polymerization, therefore, the experiment was carried out with varying pyrrole and dopant (AQSA) concentrations and polymerization times. The conductivity of electrochemically polymerized fabrics were normalized against the conductivity of *in situ* chemically polymerized fabric. The changes in the normalized conductivity and PPy content with polymerization conditions are shown Figures 2, 3, and 4. As the pyrrole and dopant concentrations were increased up to 0.05*M*, the fabric conductivity was increased and then tended to reduce with further addition. The optimum polymerization time was determined as 2 h. The overall optimum polymerization condition is given in Table I.

Electroless Cu plating

Recently, the metallization of polymer materials has attracted intensive attention. Among the various metallization processes, electroless metal plating is probably a preferred way to produce metal-coated materials because of the attractable advantages such as uniformity of coverage, excellent conductivity, the possibility of metallizing nonconductors, and flexibility.

Electroless metal plating is a nonelectrolytic method of deposition from solution, which is explainable by mixed potential theory, a combination and reduction process.[11] The driving forces for these reactions arise from the potential difference that exists between the metal solution interface and the equilibrium electrode potential for these half-reactions. In a typical system,

TABLE I
Optimum Electrochemical Polymerization Condition

Factor	Optimum condition
Pyrrole concentration	0.05*M*
Dopant concentration	0.05*M*
Polymerization time	2 h

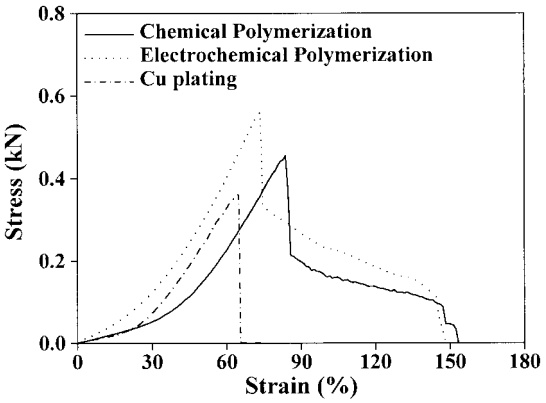


Figure 5 Change of tensile property with extension up to 80% strain.

copper reduction and formaldehyde oxidation are the cathodic and anodic reactions, respectively. The catalytic sites on the surface to be metallized are usually palladium nuclei chemisorbed in solution. From the previous studies,[11] it was found that the presence of N atoms on the nonconductors improved the chemisorption of Pd. Therefore, it was expected that the deposition of PPy on the surface of nylon/spandex fabric possibly improved the chemisorption of Pd ions on the surface. Therefore, the Cu plating process was performed after chemical polymerization of PPy on the nylon/spandex fabric in this study. Changes in tensile property and the surface morphology were studied and are shown in Figures 5 and 6.

The tensile property of the fabric was measured with an Instron 4465 to investigate the physical changes and maximum extension of the stretchable fabrics. The change of tensile stress with strain is shown in Figure 5. From the tensile test data, it was found that nylon/spandex core-spun yarns that were decrimped during the fabric were stretched up to 20% extension and then extended as the level of extension was further increased. Spandex core fiber was elongated up to nearly 80% and then broken beyond that point. Therefore, the extension limit of chemically polymerized composites was determined to be 80%, but it reduced to about 70% with additional electrochemical polymerization, which is probably due to the formation of a thicker layer of PPy on the surface of fiber. However, the tensile strength of this fabric increased. On the other hand, breaking strength and strain of composite prepared by additional electroless Cu plating after chemical polymerization were further reduced. It may due to the degradation of substrate by acid treatment during the catalyzation process. However, the conductivity of Cu-plated fabric increased by more than 70 times.

The surface morphology of fabric electrodes was examined by FE-SEM, as shown in Figure 6. Figure 6(a) represents the surface of fabric electrodes made after chemical polymerization. A thin layer of PPy was formed over the fiber surface. With the sample prepared by both chemical polymerization and electrochemical polymerization represented in Figure 6(b), it was found that the thicker layer of PPy could be formed with additional electrochemical polymerization. It has a globular form similar to a crocodile-skin surface. On the other hand, uniform deposition of Cu

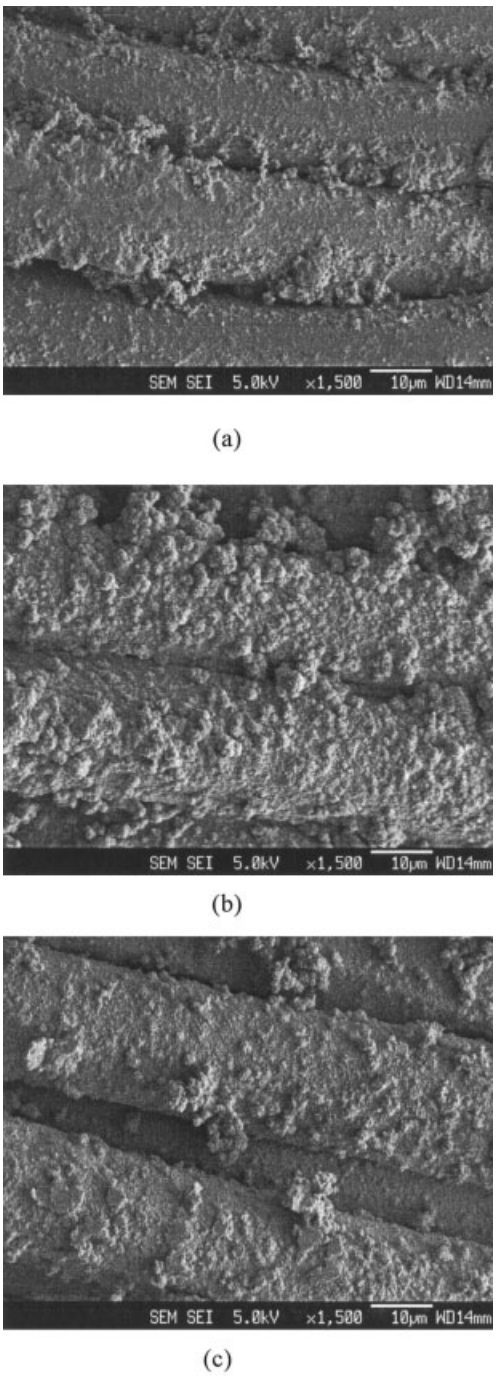
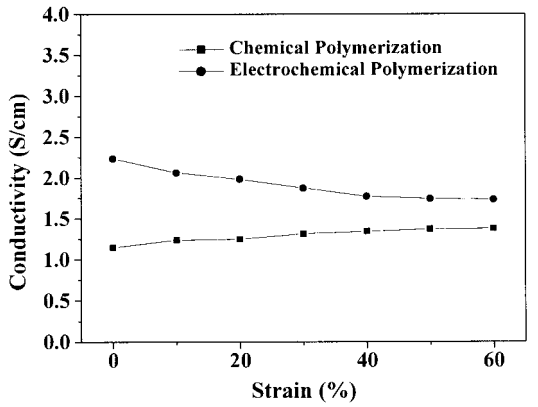
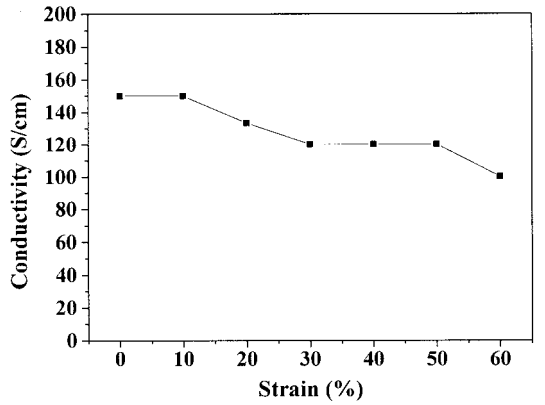


Figure 6 FE-SEM images (×1500) of fabric electrode prepared by (a) chemical polymerization; (b) chemical polymerization–electrochemical polymerization; and (c) chemical polymerization–Cu plating.



(a)



(b)

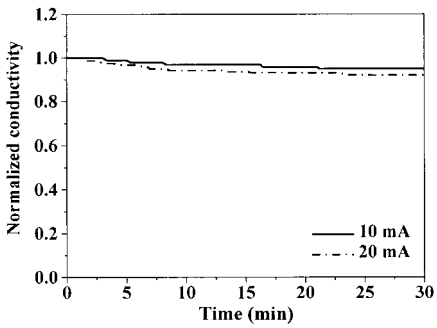
Figure 7 Change of conductivity with extension up to 60% strain: (a) chemical and electrochemical polymerization and (b) Cu plating.

particles in small size over the PPy layer was found in the sample prepared by both chemical polymerization and Cu plating, as shown in Figure 6(c).

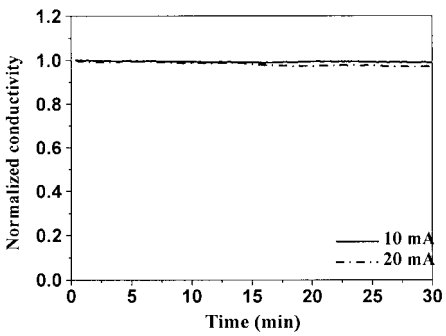
Conductivity changes with extension

Changes in conductivity with extension were investigated to test whether prepared electrode pad material can be used for electrotherapy when it is subjected to various movements of the human body, because the material for electrode should be flexible and closely adhered to the human skin to improve comfort wearability during treatment. In general, circumference of body skin can be increased up to 20% with muscle contraction where no joint is, and percentage of skin extension is up to 50% with bending at a joint in the longitudinal direction.[18] Therefore, a conductivity test was conducted with extension up to less than 60%. As shown in Figure 7, the measured fabric conductivity values increased as the fabric covered with chemically polymerized PPy was stretched up to about 40% extension and then leveled off. An initial increase in conductivity is probably due to a progressive increase in the number of contacts in the area contacting the bundles of fibers as the applied load increased.

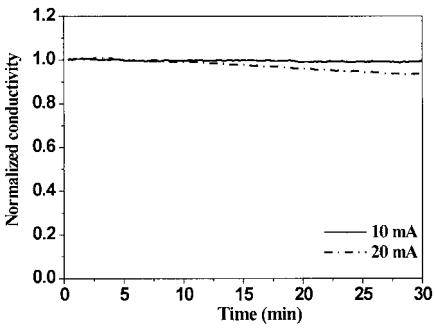
However, the conductivity of the fabrics covered with electrochemically polymerized PPy and Cu particles tend to decrease slightly as the strain increases. It may be due to an increase in the rigidity of fabric after electrochemical polymerization. It is possible that cracks occur over the thick layer of PPy and partial separation of Cu particles on the surface of composite fabric. However, the change in the conductivity is relatively small to be considered.



(a)



(b)



(c)

Figure 8 Changes of conductivity with treatment time: (a) electrochemical polymerization (2 h); (b) Cu plating; and (c) self-adhering neurostimulation electrodes for TENS or EMS.

Conductivity changes with treatment time

Currents for medical use are generally classified into the direct current, induction current, and the alternating current. The direct current of medical use is electrified to nerve or muscle with the range of voltage from 4.5 to 45 V and the current ranges from 0.1 to 10 mA; the induction current for TENS has the current from 2 to 10 mA. It is possible that generating heat when currents flow on electrode for electrotherapy changed conductivity. To investigate conductivity change with treatment time for electrotherapy, therefore, the experiment was performed at 10 mA for generally used treatment and 20 mA for the purpose of prevention of electrode damage subjected an excessive current.[3,19] The normalized conductivity variation in measuring current of conductive stretch fabric is shown in Figure 8. Changes in the conductivity of the prepared fabric were compared with that of commercial TENS pad material. As a result, the conductivities of all tested materials were slightly decreased and then maintained more than 95% of initial value with time over 30 min at the same current. However, the decrement of conductivity was so small that conductivity changes for conductive fabric were negligible. During electrotherapy, therefore, the effect of prolonged current applied on an electrical resistance developed on the substrate can be negligible. Thus, it was found that the effect of charging during the electrotherapy treatment on current flow through the prepared electrode pad was negligible.

Clinical effect

After recovering from anesthesia, mechanical allodynia and heat hyperalgesia were tested as described above. For comparison, the same procedure was repeated on the sham-operated rats. Heat hyperalgesia was expressed as difference scores (Δ) computed by subtracting the latency of the control side from that of the operated side. Statistical analyses were done by using paired *t*-test or unpaired Student's *t*-test. *P* values less than 0.05 were considered to be significant.

In the sham-operated rats, TENS with all the three electrical pads did not show any effects, as presented in Table II. In the spinal-injured rats, 50% threshold of mechanical sensitivity decreased and thermal latency increased ($P < 0.05$, respectively), which proved that the spinal nerve injury model was successfully made. In rats of the spinal-injury model, the significant effect of TENS was observed with pad made of conductive fabric by Cu plating and conventional TENS pad for medical use ($P < 0.05$, respectively). As shown in Table II, mechanical sensitivity was reduced after TENS treatment, indicated by an increase in 50% threshold value. Thermal hyperalgesia latency time was also reduced by TENS treatment. Because we express the data as difference scores, computed by subtracting the latency of the control side from that of the operated side, a reduction of this value indicates remedy of injury.

Even though the efficiency of experimental pad made of fabric composite with electrochemically polymerized PPy was not as good as conventional TENS pad for medical use in this experiment, slight decreases in 50% threshold of mechanical sensitivity and thermal latency were observed with it. Therefore, it could possibly be used for other applications where relatively low-strength electrical pulse is required.

CONCLUSIONS

Electroconductive stretchable fabrics were prepared by coating of conductive PPy and electroless copper plating on nylon/spandex stretchable fabric to pursue feasibility of the conductive electrode pad materials for electrotherapy. Highly stretchable and conductive fabrics were prepared by *in situ* electrochemical polymerization of PPy on nylon/spandex stretchable fabric. Electroless Cu plating was also applied after chem-

TABLE II
Change in Mechanical Sensitivity and Thermal Hyperalgesia Latency after TENS

Electrical pads	Sham-operated ($n = 8$)		Spinal nerve-injured ($n = 8$)	
	Pre-TENS	Post-TENS	Pre-TENS	Post-TENS
Mechanical sensitivity (g) (50% threshold)				
Fabric pad prepared by electrochemically polymerized PPy	2.1 ± 0.4	2.0 ± 0.3	1.2 ± 0.3*	1.7 ± 0.2
Fabric pad prepared by Cu plating	2.3 ± 0.3	2.2 ± 0.3	1.3 ± 0.2*	2.0 ± 0.2†
Conventional TENS Pad for medical use	2.2 ± 0.3	2.1 ± 0.2	1.2 ± 0.1*	2.2 ± 0.3†
Thermal hyperalgesia latency (s)				
Fabric pad prepared by electrochemically polymerized PPy	1.2 ± 0.2	1.3 ± 0.1	5.1 ± 0.4*	3.7 ± 0.6
Fabric pad prepared by Cu plating	1.1 ± 0.2	1.2 ± 0.3	4.7 ± 0.3*	2.3 ± 0.4†
TENS Pad for medical use	1.4 ± 0.1	1.3 ± 0.2	5.6 ± 0.3*	2.5 ± 0.2†

Mean ± SE.
* $P < 0.05$ versus sham-operated animal.
† $P < 0.05$ versus Pre-TENS.

ical polymerization of PPy to improve the conductivity of fabric pad. Performance of prepared stretchable conductive fabric pad was evaluated in terms of conductivity changes as a function of extension and continuous current application time, and clinical effect.

Overall results showed that the conductivity of the stretchable fabric prepared in this study was well maintained with extension up to 60% and prolonged treatment time over 30 min. Therefore, it is expected that the prepared pad material can be closely adhered to the human skin, improving comfort wearability during treatment. In addition, we found that electrotherapy by TENS stimulator with prepared electrode pad could reduce symptoms of the neuropathic pain such as mechanical sensitivity and thermal hyperalgesia. Therefore, the prepared TENS pad in this study can be practically useful for electrotherapy.

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