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Polypyrrole-Coated Woven Fabric as a Flexible Surface-Heating Element

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Abstract: Polypyrrole (PPy) was coated sequentially by chemical and electrochemical methods on a woven fabric, giving rise to a fabric having high electrical conductivity. We investigated the effects of the preparation conditions on the various properties of the resulting fabric. The PPy-coated fabric with optimum properties was obtained when it was prepared sequentially by chemical polymerization at the elevated temperature of 100 °C under a pressure of 0.9 kgf/cm^2 and then electrochemical polymerization with a 3.06 mA/cm^2 current density at 25 °C for 2 hrs with the separator plate. The surface resistivity of the resulting fabric was as low as 5 Ω/□.The PPy-coated fabric prepared under the optimum conditions showed practically applicable heat generating property. When electrical power was supplied to the fabric using a commercial battery for a mobile phone (3.6 V, LGL1-AHM), the temperature of the fabric increased very quickly from room temperature to ca. 55 °C within 2 min and was maintained for ca. 80 min at that temperature. The heat generating property of the fabric was extremely stable, exhibiting similar behavior over 10 repeated cycles. Therefore, we suggest that the PPy-coated fabric in this study may be practically useful for many applications, including flexible, portable surface-heating elements for medical or other applications.

Keywords: polypyrrole, electrically conducting fabric, heat generating property, flexible surface-heating element.

Introduction

The electrically conducting polypyrrole (PPy) has been extensively studied[1-6] since Diaz produced a free-standing PPy film with high electrical conductivity and good environmental stability through an electrochemical polymerization. Many limitations caused by poor processability or mechanical properties of the conventionally polymerized PPy have been successfully overcome by combining easy synthesis and high electrical conductivity of PPy with excellent mechanical strength and flexibility of various substrates such as polymer films or textile fabrics.[7-10] Therefore, researchers have made efforts to polymerize PPy on the textile substrates, observing that the resulting fabrics retained the mechanical properties of the textile as well as exhibited electrical conductivity high enough to be useful for several applications.[11,12] Potential applications of the electrically conducting textiles include anti-static conducting fabrics such as sanding belts and computer pad or electromagnetic interference (EMI) shielding materials.

The PPy-coated fabric with an appropriate electrical resistance can also be used as a flexible surface-heating element when an electrical current is applied to the fabric, while little attention has been paid on the heat generating property of the PPy-coated fabrics. PPy-coated fabric with heat generating property may have wide range of applications, including heating pad of outdoor leisure garments or medical blanket for maintaining patient's body temperature especially when the electrical power line is not available or restricted.

In this study, we report the methods to prepare the PPy-coated woven fabrics with fairly low electrical resistance, and investigated the effects of the preparation conditions on the properties of the resulting fabric such as surface resistivity, surface morphology, and heat generating properties.

Experimental

In order to provide the woven fabric with the electrical resistance suitable for heat generation, PPy was sequentially coated on a woven fabric by the chemical and the electrochemical polymerization following the procedures described below. Pyrrole (Aldrich) was distilled under a reduced pressure before use. For the chemical polymerization, dodecylbenzene

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sulfonic acid (DBSA, Acros) or 1-naphthalene sulfonic acid (NSA, Aldrich) as a dopant source and ammonium persulfate (APS, Sigma) as an oxidant were used as received. For the electrochemical polymerization, anthraquinone-2-sulfonic acid sodium salt (AQSA-Na, Aldrich) acting as not only the electrolyte but also the dopant source was used as received. Nylon fabrics (G/twill type, Kipoong Textile Company, Korea) were used as a textile substrate, whose typical size was about 20 cm × 30 cm.

PPy Coating through the Chemical Polymerization. PPy was coated on the fabric through the chemical polymerization using three different methods, which were the emulsion dipping method, the spraying method, and the polymerization at an elevated temperature and pressure.

In the emulsion dipping method, PPy was coated on the fabric by dipping the fabric into the PPy emulsion which was prepared by an emulsion polymerization of pyrrole. 0.15 mol of DBSA working as an emulsifier as well as a dopant source was dissolved in 800 mL of distilled water with vigorous stirring at 0 °C. To the DBSA solution, 0.15 mol of pyrrole was added with vigorous stirring, leading to a milky monomer emulsion. Polymerization was initiated by adding 0.15 mol of APS dissolved in 200 mL of distilled water and carried out at 0 °C for 6 hrs, producing a stable PPy emulsion. The fabric was then dipped into the PPy emulsion and was squeezed by a two-roller mangle to ensure uniform coating.

In the spraying method, PPy was polymerized directly on the surface of the fabrics. Poly(vinyl alcohol) (PVA) working as an emulsifier as well as a binder was firstly dissolved in 100 mL of distilled water. To the PVA solution, 0.15 mol of pyrrole was added with vigorous stirring and ultrasonification, resulting in a milky pyrrole emulsion. The amount of PVA was fixed at 10 weight percent to the weight of pyrrole. A certain amount of the monomer solution was sprayed on the fabric and the fabric was squeezed using a two-roller mangle to ensure uniform adsorption of pyrrole on the fabric. After a few minutes, polymerization was initiated by spraying the same amount of the mixture solution of the oxidant and the dopant as that of monomer solution. The mixture solution was prepared by dissolving 0.15 mol of APS and 0.075 mol of NSA in 100 mL of distilled water. Polymerization was carried out at room temperature for about 30 min.

In the polymerization at high temperature and high pressure (HTHP), PPy was coated on the fabric during polymerization of PPy in a reaction vessel at an elevated temperature and pressure. Before placing the fabric in the reaction vessel, 0.3 mol of pyrrole, 0.3 mol of NSA and 0.6 mol of APS were dissolved together in 300 mL of distilled water. Chemical polymerization was performed in the vessel containing the fabric at 100 °C and 0.9 kgf/cm^2, resulting in PPy coating on the fabric during polymerization of PPy. All the fabrics prepared by the three methods were dried and washed sequentially with distilled water, methanol and acetone, followed by final drying in an oven at 70 °C for 2 hrs.

PPy Coating through the Electrochemical Polymerization. Electrochemical polymerization was performed by applying constant current density using KEITHLEY 2400 SourceMeter (KEITHLEY Instruments Inc.). Figure 1 displays the schematic set-up for the electrochemical polymerization. The fabric coated with chemically polymerized PPy and a stainless steel (SUS 304) plate were used as the working and the counter electrodes, respectively. Another SUS 304 plate as the supporting electrode was stuck to the fabric in order to apply the electrical current uniformly to the fabric working electrode. A PVC mesh separator (thickness: 1.5 mm, mesh size: 4 mm × 4 mm) was used to separate the working electrode from the counter electrode and to form a good contact between the fabric working and supporting electrodes. The other side of the supporting electrode was completely protected only for the electrochemical polymerization of PPy on the fabric with chemically coated PPy. A vigorous stirring system was also installed to supply fresh electrolyte solution continuously to the working fabric electrode during the electrochemical polymerization.

The aqueous solution of AQSA-Na and pyrrole was used as the supporting electrolyte solution, whose concentrations were fixed at 0.05 and 0.3 M, respectively. After the electrochemical polymerization for the desired periods, the PPy-coated fabric was washed with distilled water and acetone, followed by drying in an oven at 70 °C for 2 hrs. We changed various electrochemical polymerization parameters

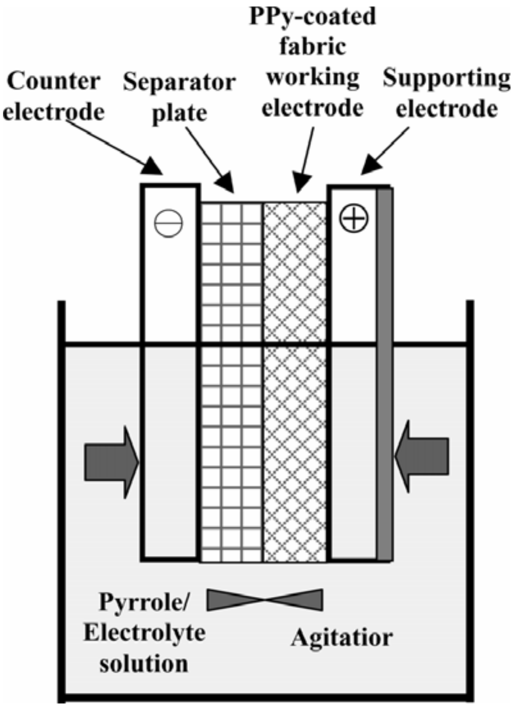


Figure 1. Schematic diagram of the electrochemical polymerization set-up.

such as stirring condition, polymerization time (0.5, 1, 2, 3 and 4 hrs), current density (0.59, 1.62, 3.06 and 5 mA/cm^2) and polymerization temperature (0, 25 and 50 °C) and investigated the effects of the parameters on the properties of the resulting PPy-coated fabric.

Characterization of the PPy-Coated Fabric. PPy content in the composite was determined as the ratio of the weight of PPy in the composite to the weight of the pristine fabric. Surface morphologies of the composites prepared under various conditions were observed by scanning electron microscopy (SEM, Hitachi S-2500C). Surface resistivity (Ω/□) was obtained by measuring the resistance between two platinum wire electrodes pressed on the surface of the fabric, where the distance between the electrodes and the length of the electrodes were 1 cm.

We investigated the heat generating property of the PPy-coated fabric by monitoring the temperature of the fabric surface upon applying an electrical current, where a commercial Li-ion battery (3.6 V, LGL1-AHM) for a mobile phone was used as the power supply. The temperature of the fabric surface was measured using a thermocouple mounted on the surface of the fabric under the atmospheric condition. We also studied the stability of the fabric by monitoring the heat generating property for repeated cycles.

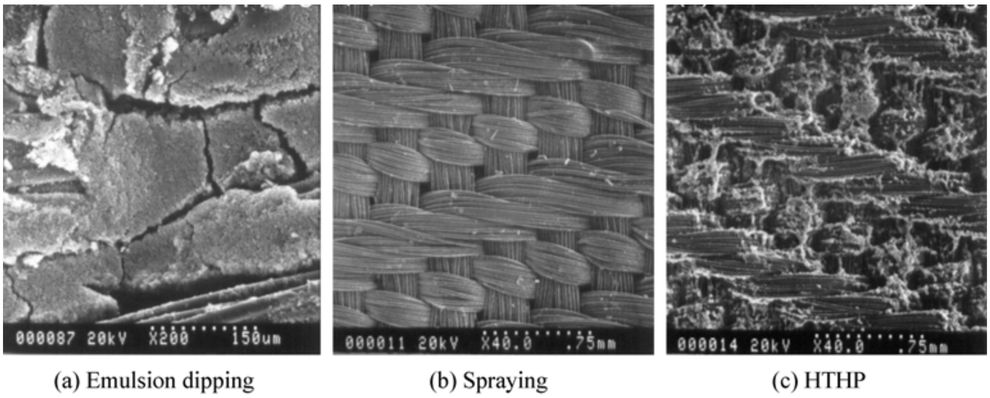
Results and Discussion

The amount of Joule's heat produced by an electrically resistant material is equal to the product of the voltage by the current supplied to the material. Since most of the portable batteries as the power source supply a constant voltage, the electrical current supplied to the PPy-coated fabric is inversely proportional to the resistance of the fabric. We must, therefore, recognize the fabric should possess the lower electrical resistance to generate the greater Joule's heat.

PPy Coating through the Chemical Polymerization. We confirmed the PPy coating through the chemical polymerization on the fabric produced the fabrics with fairly high electrical conductivity at relatively low PPy contents of 3 to 10%, even though the electrical conductivity strongly depended on the preparation method. We figured out the HTHP method yielded the fabric with the lowest surface resistivity among the methods in this study. The average surface resistivities of the fabric prepared by the emulsion dipping, spraying, and HTHP methods were 1.4×10^3, 9.7×10^2, and 1.6×10^2 Ω/□, respectively. We also observed the HTHP method produced the fabric with much more uniform surface resistivity across the whole area than the other two methods did.

The difference in the surface resistivity of the fabric must be due to the morphological difference as well as the content of the PPy coating, since the electrical conductivities of PPy itself prepared by the methods were little different. As shown in Figure 2(a), the emulsion dipping method gave rise to significantly thick PPy coating with many micro-cracks, showing PPy particles were physically coagulated on the fabric without any strong interaction. The relatively higher surface resistivity even at 10% PPy content was caused by the loose contact between the PPy particles on the fabric. In addition, when the emulsion method was employed, the adhesion of PPy coating to the fabric matrix was extremely poor, certainly because no binder polymer was involved.

On the other hand, the spraying and the HTHP methods produced a thin film-like PPy layer on the surface of fabric with fairly good adhesion as shown in Figures 2(b) and (c). The adhesion of the PPy layers was so excellent that even ultrasonification could not separate the PPy coating from the fabric. However, the PPy content of the fabric prepared by the spraying method was relatively low as about 3%, while the PPy content prepared by HTHP method was about 6%. The higher PPy content obtained by the HTHP method provided the fabric with the lower surface resistivity. We, therefore, used the HTHP method to prepare the fabric for the further electrochemical polymerization since the HTHP method gave rise to the best PPy coating with the lowest



(a) Emulsion dipping (b) Spraying (c) HTHP

Figure 2. Scanning electron micrographs of the PPy-coated fabrics chemically prepared by (a) emulsion dipping, (b) spraying, and (c) HTHP methods.

surface resistivity and good adhesion among the methods studied in this report.

PPy Coating through the Electrochemical Polymerization. Stirring of the electrolyte solution during the electrochemical polymerization was extraordinarily important to obtain the efficient polymerization of PPy on the fabric coated with chemically polymerized PPy. Figure 3 shows the surfaces of the fabrics prepared by the HTHP chemical method and the electrochemical polymerization at the current density of 5 mA/cm^2 for 3 hrs at room temperature. Electrochemical polymerization without any stirring produced a very thin PPy layer on the fabric even after 3 hrs as shown in Figure 3(a). On the other hand, the electrochemical polymerization with vigorous stirring produced an extremely thick PPy coating, exhibiting almost complete coverage of the fabric surface by PPy layer as shown in Figures 3(b) and (c). The electrochemical polymerization took place more efficiently with vigorous stirring, obviously because fresh electrolyte solution was continuously supplied to the surface of the fabric working electrode. The PVC mesh separator also played an important role in the electrochemical polymerization. When the fabric working electrode was well adhered to the supporting electrode with the aid of the PVC separator, the electrochemical polymerization proceeded much faster as shown in Figure 3(c), possibly because of more effective application of electrical current to the fabric working electrode.

We also figured out the electrochemical polymerization time had to be controlled to produce the fabric with the lowest electrical resistivity. In Figure 4, the variation in the surface resistivity of the fabric sequentially prepared by the HTHP chemical method and the electrochemical polymerization at the current density of 5 mA/cm^2 is plotted as a function of the polymerization time. The surface resistivity decreased steeply from about 90 to 15 Ω/□ within 1 hr, after which it gradually decreased to 5 Ω/□ until 2 hrs. It is obvious that the decrease of the surface resistivity resulted from more incorporation of PPy with the polymerization time as shown in Figure 5. However, further polymerization after 2 hrs resulted in the increase of the surface resistivity, possibly because of the overoxidation of the already polymerized PPy. In addition, the polymerization after 2 hrs proceeded very slowly, leading to a little increase of the PPy coating thickness with the polymerization time. We consider the slow polymerization results from the inhibition of PPy polymerization by the H^+ scavenger produced during the electrochemical polymerization of PPy. It was reported that the polymerization is inhibited by use of a buffer solution of pH higher than 7or by the presence of an H^+ scavenger.[13]

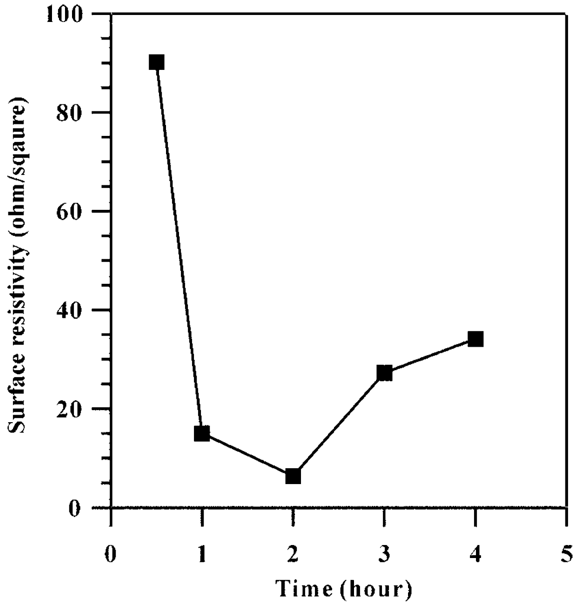
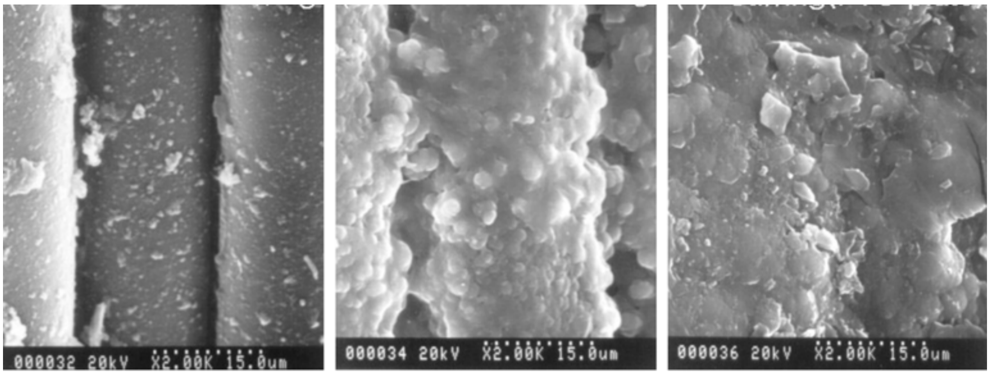


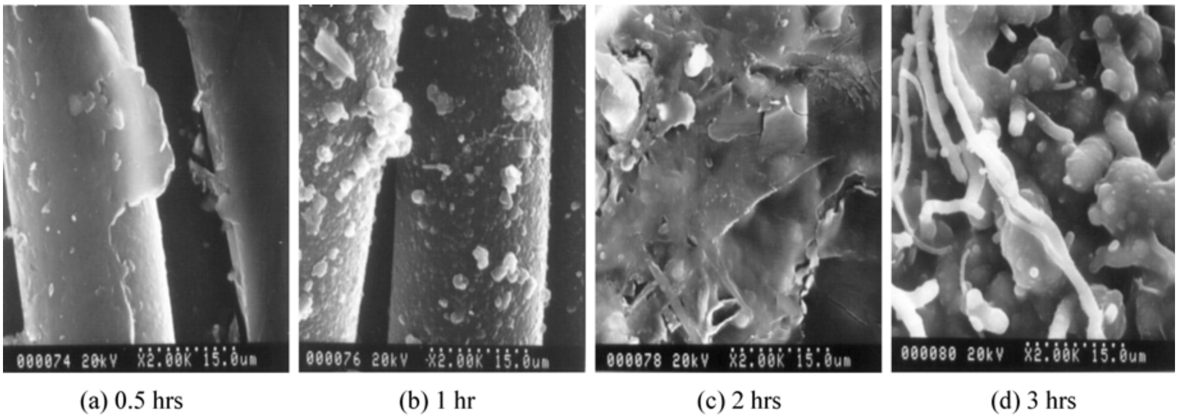
Figure 4. Change of the surface resistivity of the PPy-coated fabric as a function of the electrochemical polymerization time.

The current density of the electrochemical polymerization strongly affected the behavior of the electrochemical poly-



(a) No stirring (b) Stirring (c) Stirring with PVC plate

Figure 3. Scanning electron micrographs of the PPy-coated fabrics electrochemically prepared (a) without stirring, (b) with stirring, and (c) with stirring and a PVC contact plate.



(a) 0.5 hrs (b) 1 hr (c) 2 hrs (d) 3 hrs

Figure 5. Scanning electron micrographs of the PPy-coated fabrics electrochemically prepared for (a) 0.5, (b) 1, (c) 2, and (d) 3 hrs.

merization as well as the final properties as shown in Figures 6 and 7. Figure 6 shows the heat generating properties of the fabrics prepared by the electrochemical polymerization under various current densities for 1 hr at room temperature. The heat generating property became better with the increase of the current density up to 3.06 mA/cm^2. The temperature of the fabric prepared at 3.06 mA/cm^2 reached about 39 °C, while that of the fabric prepared at 0.59 mA/cm^2 reached only about 28 °C. It is obvious that the higher current density led to the faster polymerization of PPy, resulting in more incorporation of PPy and lower electrical resistance. Figure 7 confirmed PPy coating became thicker with the current density, showing almost complete coverage of the fabric as shown in Figures 7(c) and (d). However, the polymerization at 5.00 mA/cm^2 produced a discontinuous PPy coating with a number of pores and defects as shown in Figure 7(d), possibly because the high current density gave rise to a sudden polymerization with those defects, resulting in a little worse heat generating property.

The electrochemical polymerization temperature was also one of the important factors to produce the fabric with good

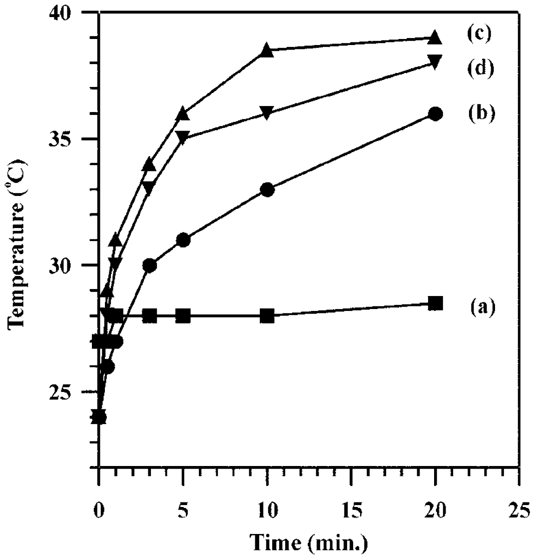
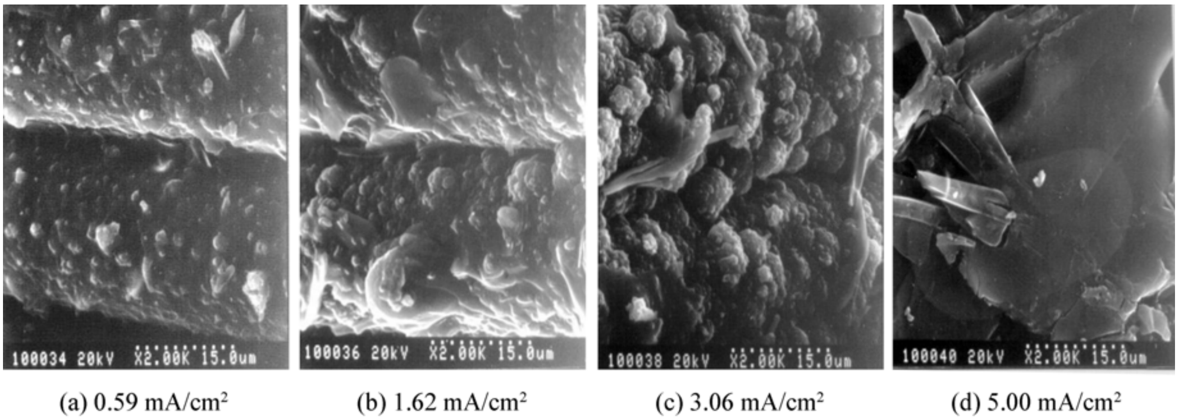


Figure 6. Temperature changes of the PPy-coated fabrics electrochemically prepared under applying the current densities of (a) 0.59, (b) 1.62, (c) 3.06, and (d) 5.00 mA/cm^2 for 1 hr.



(a) 0.59 mA/cm^2 (b) 1.62 mA/cm^2 (c) 3.06 mA/cm^2 (d) 5.00 mA/cm^2

Figure 7. Scanning electron micrographs of the PPy-coated fabrics prepared under applying the current densities of (a) 0.59, (b) 1.62, (c) 3.06, and (d) 5.00 mA/cm^2 for 1 hr.

heat generating property. In general, it is known that electrochemical polymerization at the lower temperature produces PPy with the higher electrical conductivity,[14] but proceeds much more slowly. The slow polymerization must give rise to much less PPy coating on the fabric, leading to much higher electrical resistance of the fabric. Therefore, the electrochemical polymerization temperature must be controlled to compromise the appropriate electrical resistance and polymerization rate. Figure 8 shows the heat generating properties of the fabrics prepared at various temperatures, indicating polymerization at 25 °C produced the fabric with the best heat generating property.

Heat Generating Property of the Fabric. We concluded from the above results that PPy-coated fabric with the optimum properties could be obtained when it is sequentially prepared by the HTHP chemical polymerization and the electrochemical polymerization with 3.06 mA/cm^2 of current density at 25 °C for 2 hrs with the separator plate. The surface resistivity of the resulting fabric was about 5 Ω/□ . Figure 9 shows the heat generating property of the PPy-coated fabric prepared by the optimum condition. The temperature of the PPy-coated fabric increased very quickly from room temperature to about 55 °C within 2 min and was sustained for about 80 min at the temperature as shown in Figure 9. The gradual decrease of the temperature after 90 min must be due to the discharge of the battery with the time. The heat generating period can be increased much longer when the temperature is controlled at a desired level such as 40 °C by applying an temperature controller. The heat generating property of fabric was so stable that exhibited the similar behaviors for at least 10 repeated cycles. We, therefore, suggest the PPy-coated fabric reported in this study may have wide range of applications including the flexible mobile surface-heating element for medical or other uses.

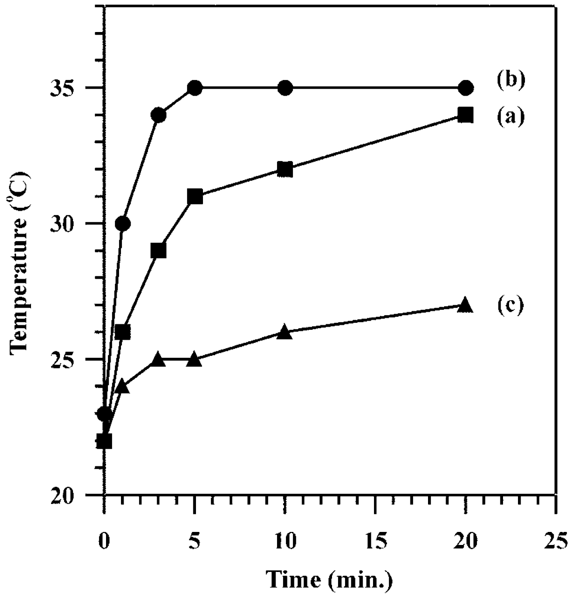


Figure 8. Temperature changes of the PPy-coated fabrics electrochemically prepared at (a) 0, (b) 25, and (c) 50 °C.

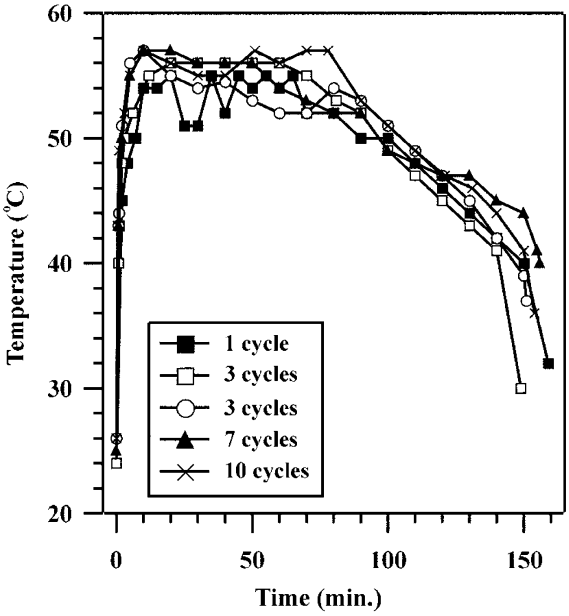


Figure 9. Temperature changes of the PPy-coated fabrics electrochemically prepared under applying the current density 3.06 mA/cm^2 with a PVC contact plate and vigorous stirring at 25 °C for 1 hr.

Conclusions

PPy-coated fabric with low electrical resistance was successfully prepared by coating of PPy on the fabric using both chemical and electrochemical polymerizations. We investigated the effects of the preparation conditions on the various properties of the resulting fabric, observing the PPy-coated fabric with the optimum properties could be obtained when it was sequentially prepared by the HTHP chemical polymerization and the electrochemical polymerization with 3.06 mA/cm^2 of current density at 25 °C for 2 hrs with the separator plate. The surface resistivity of the resulting fabric was about 5 Ω/□ .

The PPy-coated fabric prepared by the optimum condition showed an excellent heat generating property. When the electrical power was supplied to the fabric using a commercial battery (3.6 V), the temperature of the fabric was increased very quickly from room temperature to about 55 °C within 2 min and was sustained for about 80 min at the temperature. The heat generating property of fabric was pretty stable, exhibiting the similar behaviors for at least 10 repeated cycles. We, therefore, suggest the PPy-coated fabric reported in this study may be used for many applications including the flexible mobile surface-heating element for medical or other uses.

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