

Introduction Sensors are key components in an overwhelming wealth of systems for industrial and consumer applications. The new sensor device concepts will emerge to improve performance, e.g. sensitivity, and so on. Wearable instrumented garments, capable of recording body kinematic maps with no discomfort to the subject and showing negligible motion artifacts caused by sensor-body mechanical mismatch, are crucial in several fields of application. These sensors are “smart” because of their capacity to adapt to the specific mechanical properties of textile structures that are lightweight, highly flexible, stretchable, elastic, etc. Because of these properties, textile structures are continuously in movement and easily deformed, even under very low stresses. A normalized relative resistance is defined in order to characterize the electrical response of the sensor. Previous approaches to develop wearable monitoring systems have been made using traditional technologies such as accelerometers, gyroscopes, strain gauges [1], piezoelectric materials [2], fiber-optics [3] and pressure sensors [4], strapping the sensors to the body, adhering them to the skin, or integrating them into skin-tight garments [5, 6]. Conducting electro active polymers (CEPs), such as polypyrrole (PPy), polyaniline and polythiophene constitute a class of polymeric materials which are inherently able to conduct charge through their conjugated polymeric structure. PPy, in particular, has attracted much interest, as it is easily prepared in a number of forms, films, powders and composites and it has a relatively high conductivity and stability in its conducting state. When applied as a coating to soft flexible substrates, PPy has little effect on the mechanical properties of the substrate, but renders the entire structure electro active. Therefore, it is possible to make a conducting material that retains the desirable properties of a textile or other soft structure. PPy-coated textiles have been used in previous wearable sensing applications [7-10]. Integration of conducting polymer molecular template into textiles is similar to dyeing process and requires optimization of reaction conditions. The objective of this paper is studying the effect of quality and quantity of oxidant agent used in chemical deposition process on development of Polypyrrole coated fabrics as piezoresistive sensors. Experimental Materials Lycra/Polyester fabric provided by pooshineh baft Co, Iran. – Pyrrole monomer purchased from sigma-Aldrich, was distilled before use and stored in a freezer – Naphtalen disulfonic acid (NDSA), Ferric chloride, Sulfuric acid, Ammonium peroxodisulfate, Hydrochloric acid, Hydrogen peroxide, Silver nitrate, Ferric nitrate, Sodium nitrite, Trichloroacetic acid, Acetate vinyl, Copper nitrate. All of them were purchased from Merck and used without further purification – Deionized water. Sample preparation Lycra/Polyester fabrics were first pretreated in sulfuric acid (1M) for 30 minutes, at room temperature. All samples were then chemically polymerized in an aqueous solution containing 0.015M Pyrrole, 0.005M NDSA, and 0.04M of various oxidant agents at room temperatures for 2 hours. The effect of various oxidant agents in polymerization process have been investigated: (1) Ammonium peroxodisulfate, (2) Hydrochloric acid, (3) Hydrogen peroxide, (4) Silver nitrate, (5) Ferric nitrate, (6) Sodium nitrite, (7) Trichloroacetic acid, (8) Ferric chloride,

(9) Acetate vinyl, (10) Copper nitrate. Polypyrrole deposited on the fabrics surface. Then the black conductive fabrics were washed with deionized water and dried in desiccators, at room temperature (in order to avoid oxidative reaction in the air)

**Instrumentation** Electrical conductivity and morphology assessment

Electrical conductivity of prepared samples was measured by four-probe method (According to ASTM F43-93). The morphology of samples for detection of shape, size and distribution of coated particles were performed with scanning electron microscope (XL30 Philips model) in different magnifications.

**Results and discussion**

**Electrical conductivity analysis**

Electrical conductivity ( $\sigma$ ) of samples have calculated by the formula, given in equation (1):

$$\sigma = \frac{L}{Wt} \frac{I}{V} \quad (1)$$

where, L – space between inner probes; I – current passed through outer probes; V – voltage drop across inner probes; W – width of sample; t – thickness of sample.

Figure 1 shows the electrical conductivity of Polyester/Lycra PPy coated fabric prepared with different oxidants in polymerization reaction.

**Figure 1 – Typical electrical conductivity of Polyester/Lycra PPy coated fabric prepared with different oxidants in polymerization reaction:**

(1) Ammonium peroxodisulfate, (2) Hydrochloric acid, (3) Hydrogen peroxide, (4) Silver nitrate, (5) Ferric chloride, (6) Sodium nitrite, (7) Trichloroacetic acid, (8) Ferric nitrate, (9) Acetate vinyl, (10) Copper nitrate

According to investigations, Ferric chloride is a common oxidant and deionized water is a useful solvent in polymerization process of Pyrrole monomer. If Ferric chloride uses as oxidant agent, Clion with good moving ability causes production of unstable polymer (Polaron) (Fig. 2). In this condition, adding dopant (with negative charge) in reaction solution causes a mixture of opposed ions produces (Fig. 3) and electrical conductivity increases.

**Figure 2 – Chemical oxidation mechanism of Pyrrole monomer**

**Figure 3** shows the schematic of reciprocal interaction between Polypyrrole and dopant agent in chemical polymerization process when oxidant agent ( $\text{FeCl}_3$ ) exists in reaction compartment. It is not possible to ignore the importance of the best oxidant concentration. So the experiments continue to determine optimum concentration of  $\text{FeCl}_3$ .

**Fig. 4** shows the electrical conductivity of samples prepared with different concentration of  $\text{FeCl}_3$ . In chemical oxidation process of Pyrrole monomer, concentration of monomer is distinguished value in reaction solution, so lower or upper than the optimum value (the value needed to interference all of the monomer in chemical oxidation reaction) will have negative effect on electrical conductivity. If concentration of  $\text{FeCl}_3$  is lower than the optimum value, the chemical oxidation reaction and coating process will accomplish defectively, that will result decreasing of electrical conductivity. Results show that using oxidant agent upper than the value needed to oxidation of Pyrrole, does not have positive effect on electrical conductivity of coated sample how much decreases it. This reality may be related to increasing the number of growing chains in constant concentration of monomer that will result shortage of polymeric chains and demolition of charge transition route perform finally, because of deformation of long polymeric chain with no defect.

**Figure 3 – Reciprocal interaction between Pyrrole monomer and NDSA in polymerization reaction**

**Figure 4 –**

Typical electrical conductivity versus  $\text{FeCl}_3$  concentration (1) 0.02M, (2) 0.04M, (3) 0.08M, (4) 0.1M. Dwindle in longitude of chain with increasing concentration of reaction active portion in polymerization process, is a recognized subject. During oxidation of Polypyrrole, neutral polymeric chain, with losing an electron, will be oxidized and a couple radical will be obtained. This radical ionic is established on assistant region of polymer back bone, and a structure defect will be produce. This defect that consists of spin and positive charge is "Polaron island". In this state two processes are probable. 1) The second oxidation reaction performs on polaron directly and a double cationic bipolaron be produced. 2) The second oxidation process performs in other region of neutral polymeric chain and because of penetration of two polaron in together, a bipolaron part will be obtained. These islands on polymer back bone are charge bearers and control the electrical conductivity value. The effect of oxidant preparation conditions on electrical conductivity In polymerization process of Polypyrrole, three fundamental parts consists of Pyrrole (monomer), 1,5Naphtalene disulfonic acid(dopant) Ferric chloride (Oxidant) interference in produce of electro active composite particles. About this, one of the important points in the controlling of coating particle size, that effect on fabric electrical behavior and its final application certainly. Taking into the role of oxidant agent on growing process of polymer, it seems particle size has sensible effect on electrical and morphological behavior. Therefore the effect of pretreatment process on oxidant agent in constant conditions of polymerization reaction has been studied. In first experimental Ferric chloride powder added to reaction solution during 20 minutes. In second experimental Ferric chloride in deionized water (50cc) prepared in form of solution with magnetic stirrer and then was added to reaction solution during 1 hour drop by drop. In third experimental Ferric chloride in deionized water (50cc) prepared in form of solution with Ultrasonic homogenizer then was added to polymerization solution during 1 hour, drop by drop. Results show sensible effect of pretreatment process of oxidant agent on increasing the electrical conductivity. This change may related to oxidant particle size, certainly. The size of Ferric chloride in solid state is equal to 5-10 micrometers approximately; that when add into polymerization solution after pretreatment process, mixture in aqueous solution is requestable, and the particle size may be equal to 1-5 micrometers. By using prepared mixture with magnetic stirrer, particle size will be equal to 1 micron (Fig. 5a) and by using Ultrasonic waves horn, the particle size will be smaller than previous states and can be reported equal to 50-100 nanometers (Fig. 5b). Figure 5 – Comparison of prepared particles with (a) Magnetic stirrer and (b) Ultrasonic homogenizer Electrical conductivity values of samples prepared with various preparation conditions of oxidant agent is shown in Fig. 6. Figure 6 – Electrical conductivity values of samples prepared with various preparation conditions of oxidant agent: (1) Ferric chloride powder; (2) Ferric chloride solution prepared with magnetic stirrer; (3) Ferric chloride solution prepared with Ultrasonic homogenizer. Decreasing of oxidant particle size in constant value of Ferric chloride mass fraction causes

increasing volume fraction of particles. This action facilitates suitable distribution of polymeric nanoparticles that organize in growing process and penetration of particles in fabric surface will increase. Fig. 7 shows Scanning electron microscope (SEM) graphs of Polypyrrole coated fabric prepared with mentioned methods. Gathering of particles in micro and nano scale is clear. d c b a

Figure 7 – Fibers morphology of Polypyrrole coated Lycra/Polyester fabric obtained with different preparation conditions of oxidant agent (in two magnifications): (a, b) sample 1 and (c, d) sample 3, given in Fig. 6.

Suitable distribution of particles on surface in form a monotonous film and in fabric structure in nano scale is recommender of undesirable effect of initial material conditions on final product specification.

Conclusion Results of the study show that the samples obtained with the ratio of monomer to oxidant equal to 0.375, have the best electrical conductivity, gauge factor and response time equal to  $6.9 \times 10^{-3}$  S/cm, 5.2, 3s, respectively.