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Chromic-thermal sensitivity response of the PVDF/PDA/GO composite nanofibers

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ABSTRACT

In this research, the composite nanofibers of polyvinylidene fluoride/polydistylene/graphene oxide (PVDF/PDA/GO) have been produced and their thermal and choromic properties have been investigated.

For this purpose, samples of PVDF/PDA/GO were produced. The results of examining the morphology of the produced nanofibers shows that the diameter of nanofibers is significantly decreased and the uniformity of the nanofibers increased by adding GO to the nanofibers. The decrease in nanofiber diameter causes increase in specific surface area of them. The increase of nanofibers specific surface area helps to improve the sensitivity of them. This was confirmed by reflective spectrophotometric test and their high color response to methanol solvent. Also, by heating the sample, it was observed that the produced samples are sensitive to 60 ° C and therefore, they are thermochromic. Because of choromic-thermal properties of PVDF/PDA/GO composite nanofibers, they can be used as a type of chromic sensors and/or thermal sensors. In PVDF/PDA/GO composite nanofibers, graphene oxide enhances the chromic sensitivity responses of polyvinylidene fluoride/polydiacetylene nanofibers.

Keywords

Composite, Nanofiber; Graphene Oxide, Polyvinylidene Fluoride, Polydiacetylene, Choromic sensor, Thermal Sensor.

1. Introduction

Smart materials and systems have the ability to feel and respond predictably and usefully to their environment stimulus [1]. In fact, smart materials are materials that memorize situations and, like a thinking brain, store information and respond intelligently by creating external stimuli. Smart materials are part of intelligent systems. These systems have the ability to sense the environment or external stimuli and if they are truly intelligent to respond to these external stimuli and coordinate their behavior with them [2].

Due to the widespread use of sensors in various industries, any effort to improve them can be very effective. These improvements can be enhanced using additive nanoparticles such As carbon or graphene nanotubes and their derivatives such as graphene oxide. With very little use of these nanoparticles in the production of materials can lead to significant improvements in their properties.

A category of smart materials that has received a lot of attentions is called color changeable material or chromic material. Chromic material refers to materials that change their color, clean or shine is caused by external stimuli such as heat, light, pressure, flow, etc. [3,4].

They are used as a main component in a number of sensors, monitors, switches and memory devices. Among the stimulus-responsive chromic materials that have been investigated so far, conjugated polymers have received a great deal of attention due to their unique optical properties due to the presence of

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an unstable electron-pie system [5,6]. Among the conjugated polymers with various physical, chemical and optical properties, polydystylenes have unique structural properties that distinguish them from other conjugated polymers. Diacetylene monomers can be polymerized by ultraviolet radiation and self-assembled resulting supermolecules [7,8,9,10]. Although fluorescence and color change of polydystylenes after exposure to environmental stimuli have been used to detect important chemical and biological targets, the true mechanism for changing blue to red and the corresponding fluorescence has not yet been determined.

Most of the polydystylenes sensors are prepared as thin films on solid layers. In order to overcome the limitations of these conventional films, electrospinning is a method of producing polydystylenes sensors to overcome the limitations of these conventional films. This simple method in the production of polydystylenes encapsulating nanofibers has led to the discovery of a new and interesting way in polydystylenes-based sensors.

The procedure begins with diacetylene monomers in the presence of a polymer-bedding that is randomly distributed in an organic solvent prior to electrospinning. During the fiber formation process and when the solvent evaporates, the self-assembly of diacetylene monomers is happened. Ultraviolet radiation of nanofibers containing self-assembled diacetylene monomers results in the formation of polydystylenes supermolecules embedded in the polymer fiber substrate. Polydystylene sensors based on electrospun nanofibers with high surface-to-volume ratio have several advantages over films [11,12].

Graphene oxide is a two-dimensional material that is made in a single layer, with a crystalline hexagonal structure in which there are oxygen groups on the plates.

Advances in the dispersion of graphene oxcide nanoparticles in polymer matrices have opened a new and attractive window in materials science. These nano-hybrid materials show significant improvements in properties that pure polymers and conventional composites cannot normally achieve. The improvement in properties is directly related to the degree of diffusion of the filler nanoparticles in the polymer matrix.

In 2016, ISA et al. Reported the production of PVC polymer nanofibers by the addition of graphene oxide leading to increased piezoelectric dielectric properties, increased mechanical strength, dynamic modulus, and thermal stability [13].

In 2017, Abbasipour and his colleagues performed a comparison between the two by producing hollow electrospun nanofibers and adding graphene and graphene oxide as nanoparticles. The results showed that the addition of graphene oxide increases the beta property and dielectric coefficient and thus improved the piezoelectric property of PVDF/GO compared to pure PVD [14]. Graphene oxide improves the electrochemical properties and fluorescence properties of PDA/GO hybrid nanosheets that is very important in production of biosansors [15].

The choromic properties of PVDF/PDA sensor, can be improverd by adding GO to the composite. The chromic-piezoelectric sensitivity responses of polyvinylidene fluoride/polydiacetylene nanofibers using graphene oxide have been studied in our erliar work [8]. In this research, we study the choromic-thermal sensitivity response of PVDF/PDA/GO composite nanofibers.

2. Experimental

2.1. Materials

In this study, 10 and 12 pentacosadionic acid (PCDA) was used as the monomer of DA and polyvinylidene fluoride (PVDF) with a molecular weight of 275,000 (g/mol) was used as the substrate polymer to produce the PVDF/PDA layer. GO nanoparticles were used as additive in

PVDF/PDA/GO composite nanofibers. The PVDF and PCDA were purchased from Sigma Aldrich and GO purchased from nanoscience and nanotechnology institute of Sharif university of technology [16].

2.2. Methods

Electrospinning method was used to provide conditions for self-assembly of diacetylene monomers in polyvinylidene fluoride nanofibers. To produce the solution, the DMF and acetone solvents were added to the desired amount of PVDF and stirred at 50 ˚ C until the PVDF was completely dissolved (Figure 1). The desired amount of graphene oxide nanoparticles was dispersed separately in a certain amount of DMF solvent by an ultrasonic mixer and GO homogenous solution was achieved. Then the DA powder and GO solution were added to the PVDF solution and stirred on the stirrer to be completely dissolved. The solution was homogenized using ultrasonic mixer for 2 minutes before electrospinning. The solutions were prepared by PVDF content of w/v23%, solvent of DMF/acetone with the volume ratio of 6:4, mass ratio of 3:1 for PVDF/PDA and various contents of 0.1, 0.5, 1, 1.5 and 2.5% of GO.

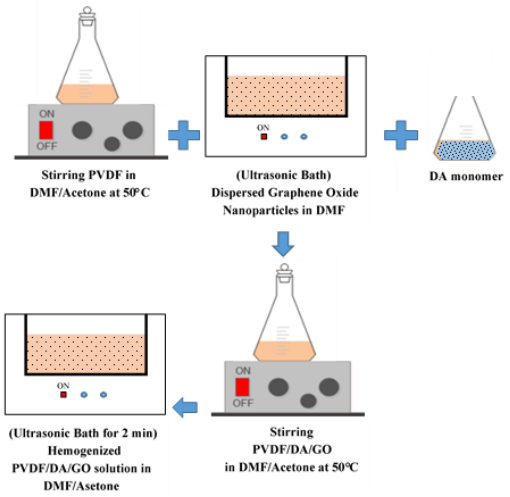

Fig1. Schematic of PVDF/DA/GO electrospinning solution preparation.

In electrospinning process, 1 ml of the produced solution of PVDF/DA/GO was feed into a 1 ml syringe mounted on a feed pump with a feed rate of 0.5 ml/h. The electrostatic voltage of 22 kV and spinning distance of 18 cm were applied to electrospin the PVDF/DA/GO composite nanofibers [17].

Due to the application of manufactured nanofibers in sensors, the uniformity of the diameter of nanofibers and the thickness of the nanofiber layers are very important. For this purpose, the rotating collector was used with an auxiliary electrode on a needle with dimensions of 5.3 × 5.3 cm at a distance of 10 mm from the tip of the needle. Placing an auxiliary electrode on the needle contributes to the uniformity of the electric field created between the needle and the collector, and provides further regular nanofiber flow. Random nanofibers collected on a low-speed rotating collector have more uniform thickness than those produced on a fixed collector. Therefore, the rotating collector was used in electrospinning.

Self-assembly of diacetylene monomers occurs during the fiber formation process and during solvent evaporation. The electrospun layers were then subjected to optical polymerization using ultraviolet radiation for one minute. The ultraviolet radiation self-assembls DA monomers and forms polydiacetylene supermolecules embedded in a PVDF substrate. Before ultraviolet irradiation, the PVDF/DA/GO nanofiber layer is white and its color is changed to blue after irradiation.

3. Results and Discussion

The results of measuring 100 random samples of nanofibers diameters showed that the diameter of PVDF/PDA/GO composite nanofibers is smaller than that of PVDF/PDA nanofibers [8]. The diameter of PVDF/PDA/GO composite nanofibers

shows better uniformity and smaller coefficient of variation than that of PVDF/PDA nanofibers (Figure 2). As this figure shows, PVDF/PDA/GO composite nanofibers with GO contents of less than 1% (0.1%, 0.5% and 1%) show the optimum condition in therm of uniformity. Also, this figure shows that 1% of GO is the enough content to obtain the nanofibers with highest diameter uniformity. According to the studies, the reason for better uniformity and smaller coefficient of variation of PVDF/PDA/GO composite nanofibers is due to the presence of GO and its effect on increasing the electrical conductivity of the electrospinning solution.

One of the charactristics of PVDF/PDA/GO composite nanofibers is their ability to be sensitive to some solvents. Due to the presence of PDA in the structure of these nanofibers, their response to the exposure to solvents is indicated by a noticeable color change. When they are exposured to the solvents, their color changes from blue to red with absorption spectrum of 540 nm and 640 nm, respectively, that is visible to the human eyes. This change in adsorption is a result of the rotation of the π conjugate PDA structure after the presence of solvent.

The GO nanoparticles in the structure of PVDF/PDA/GO composite nanofibers increase their sensitivite and the color change intensity. This is due to reducing the diameter of nanofibers and increasing the specific surface area and thus improving the sensory properties of PVDF/PDA/GO nanofibers.

In order to evaluate the color sensitivity of PVDF/PDA/GO composite nanofibers against solvents, the amount of color reflection was measured before and after exposure to methanol solvent using reflective electrophotometry. As Figure 3 shows, the colorimetric response percent of the PVDF/PDA/GO composite nanofibers in creases as the GO percentage increases. Also, this figure shows that the PVDF/PDA/GO sample of 1.5% GO has highest color absorption than the graphene oxide-free sample and other samples against the methanol solvent.

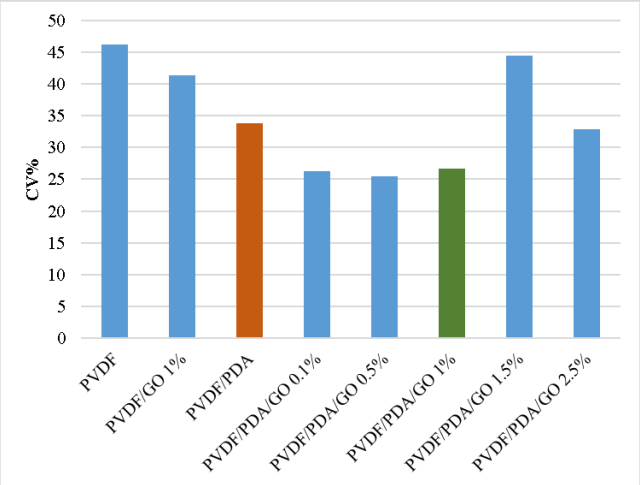

Fig2. Coefficient of variation of nanofibers diameter**.**

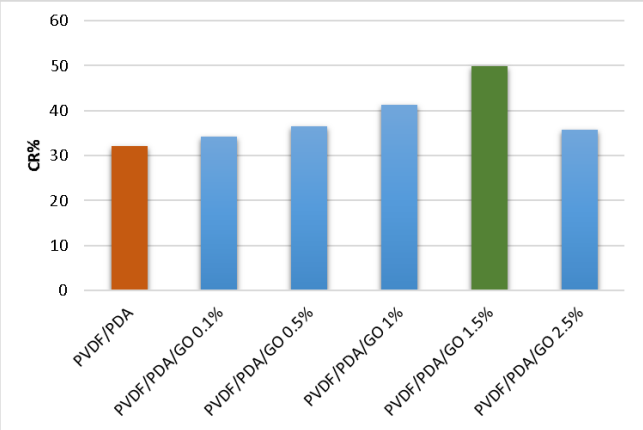

Fig 3. Color response of PVDF/PDA/GO composite nanofibers against methanol.

In order to check the thermochromicity of the produced PVDF/PDA/GO composite nanofibers, we placed them under heat by increasing the temperature by 10 °C interval from 40 to 110 ° C in the oven. Color change from blue to red was observed at a temperature of 60-70 °C for all samples (Figure 4). As this figure shows, as the tempreture increases, the intensity of color change change increases till 90 ˚C. The tempreture higher than 90 ˚C does not change the intensity of color

change, significantly. This figure also shows that the samples containing GO do not show a significant difference with those samples of without GO in regard to color change.

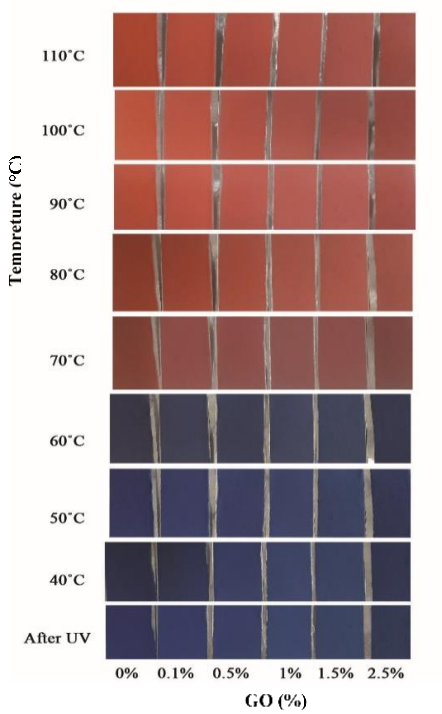

Fig4. Image of color response of PVDF/PDA/GO composite nanofibers produced with different percentages of graphene oxide against heat between 40 to 100 °C.

4. Conclusions

In order to improve the sensory properties of PVDF/PDA composite nanofiber sensors, we produced PVDF/PDA/GO composite nanofibers by adding GO nanoparticles to the electrospinning solution.

SEM images showed that the GO nanoparticles decrease the diameter and increases the uniformity of nanofibers in comparison with the sample without GO. The results showed that 1% of GO is the enough content to obtain the nanofibers with highest diameter uniformity.

The results of reflective spectrophotometric test on color sensitivity of PVDF/PDA/GO composite nanofibers against exposure of methanol solvents show that the sample with graphene oxide has a higher color response. Therefore, the GO nanoparticles in the structure of PVDF/PDA/GO composite nanofibers increase their sensitivite and the color change intensity.

Color change from blue to red was observed at a temperature of 60-70 ˚C for all samples. The intensity of color change increases till 90 ˚C. Consequently, the PVDF/PDA/GO composite nanofibers can be used as a type of chromic sensors and/or thermal sensors.

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