Polyaniline-modified Montmorillonite Nanocomposite as an Actuator

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Abstract: Polymer actuators have received much attention due to their vast potential applications. In this work the preparation of polyaniline nanocomposite actuator is studied. The main objective is to overcome the disadvantages of pristine polyaniline in thermal, mechanical and electroactive properties. Montmorillonite is the best candidate for this purpose. Various polyaniline/modified montmorillonite nanocomposite films were prepared using solution method. The properties of nanocomposites are characterized by X-ray diffractometry, transmission electron microscopy, thermal gravimetric analysis, dynamic mechanical analysis, conductivity measurement and cyclic voltammeter. The effects of actuator length and applied scan rate as well as the response of applied potential in actuating applications were investigated. The results show that the structure of nanocomposite is exfoliated. Adding organoclay to polyaniline matrix regardless of decreasing its conductivity; increases the stiffness of the actuator resulting in lower bending level in a linear manner. It reduces the required time to reach the maximum bending, also recovery bending time, i.e. actuator response. Increasing the applied scan rate decreases the actuator bending. Also increasing the length of actuator increases the amount of nanocomposite actuator bending in a linear manner.

Keywords: Nanocomposite, Montmorillonite, Electroactive, Conductive polymer, Polyaniline, Actuator

Introduction

In recent years, polymer actuators have received much attention due to their potential applications in advanced robotics, artificial muscles, and new medical devices [1]. Actuators based on conducting polymers, i.e. electroactive actuators, have some advantages over the other polymeric actuators [1].

They directly convert electrical energy to mechanical energy with a distinct response to the electrical stimuli [2]. These actuators can perform several exotic motions, such as; bending, twisting, and rolling which are performed weakly by or totally absent in conventional inorganic actuators [3]. The bending movements of these actuators resulting from the process of oxidation/reduction lead to reversible macroscopic volume changes in response to an even applied low voltage such as; 1-2 V [1].

A large number of electroactive actuators using conducting polymers such as polyaniline, polypyrrole and polythiophene have been proposed and developed by many researchers in the past decade [3]. Polyaniline is one of the most technologically important electroactive polymers because of its environmental
stability in a conducting form, the ease and low cost of synthesis, unique redox properties, and high conductivity [4]. Electroactive polyaniline actuators have been fabricated from both chemically and electrochemically synthesized polyaniline [5]. The behaviour of the actuator is discussed in terms of the changes in the oxidation and protonation states of polyaniline. A volume change in these samples causes electroactivity. Polyaniline is electroactive in acids below pH 3–4, at which it can undergo electrochemical reduction and oxidation (redox) between three states: leucoemeraldine (an insulator), emeraldine salt (a conductor), and pernigraniline (an insulator) [5].

To overcome the disadvantages of actuators based on pristine polymer, in their thermal, mechanical, and electroactive properties, the insertion of conductive polymers in the layered (two-dimensional) or microporous (three-dimensional) inorganic hosts has received extensive attention in recent years and many conductive polymer/inorganic host hybrid composites have been synthesized and studied such as polyaniline/MoO₃, polyaniline/HUO₂PO₄, polyaniline/V₂O₅, polypyrrol/mordenites, polythiophene/mordenites [6].

Progress in this field is extended to make organoclay polymer nanocomposites. Montmorillonite is one of the best candidates for this purpose. Several methods of preparation for polyaniline/organoclay nanocomposite have been reported by numerous researchers such as; Azevedo and Bae [4], Bissessur [7], Kim [8], Kim [9, 10, 11], Segal and Svelko [12], Wu [6], Yang [13], Yoshimoto [14], Zhu [15].

One of the reasonable ways to prepare the nanocomposite actuator using polyaniline cast-film is the solution method [1]. It is worth bearing in mind that exfoliated nanocomposites have better physical properties such as stiffness, strength, and barrier property with far less inorganic content than intercalative nanocomposites [4].

This paper presents a methodical production and characterization of the morphology, mechanical, thermal, conductivity and actuation properties of polyaniline/modified montmorillonite nanocomposite films involving different levels of organoclay. The morphology and properties of the nanocomposite actuators are characterized by X-ray diffraction, transmission electron microscopy [16], thermo gravimetric analysis [17, 18], dynamic mechanical analysis [19, 20]. The conductivity and actuation performance of the doped samples with (+)-10- camphor sulphonic acid (CSAC) (1M), are comprehensively characterized with four-probe technique [6, 9] and cyclic voltammetry (CV) [5, 21].

Results and discussion

Characterization of nanocomposites morphology

-X-Ray Diffraction (XRD)

Fig. 1 shows the result of XRD analysis performed on Cloisite 15A. As the figure and Table 1 show, there are three peaks in the range of 2° to 10°, the first peak is related to the basal spacing (d001) of the Cloisite 15A which appears at 2θ=2.97° (corresponding d-spacing is 3.15 nm). The second characteristic peak of the organoclay is observed as a shoulder beside the first one at 2θ=3.69° (corresponding d-spacing is 2.68 nm) and the last peak of the Cloisite 15A appears at 2θ=7.29° (corresponding d-spacing is 1.235 nm) which can be attributed to the portion of the organoclay that is not properly mixed by modifier.
XRD of pure polyaniline film is shown in Fig. 1, as well. It should be noted that the polyaniline polymer crystal plane peak is around $2\theta=20^\circ$, which is different from that of organoclay d-spacing. We have estimated the variation of d-spacing, which is induced from the angular position $2\theta$ of the observed peaks according to the Bragg formula; i.e. $\lambda=2dsin\theta$ [10]. It is of interest to determine d-spacing by monitoring the shifting of the corresponding peak at low angle for the actuator nanocomposites which have 0, 3, 5, 8 and 10% organoclay.

The XRD patterns of a series of polyaniline/modified montmorillonite nanocomposite films synthesized by solution method are shown in Fig.1.

![XRD](image)

**Fig. 1.** The X-Ray Diffraction (XRD) of polyaniline-modified montmorillonite.

As it is shown in XRD patterns, for all of the polyaniline-modified montmorillonite nanocomposite actuators, the d-spacing peak is no longer present in the detectable $2\theta$ range of XRD instrument, which suggests that organoclay has been exfoliated.

**Tab. 1.** d-Spacing of samples by WAXS techniques.

<table>
<thead>
<tr>
<th>Samples</th>
<th>d-Spacing (Å)</th>
<th>d-Spacing (Å)</th>
<th>d-Spacing (Å)</th>
<th>$2\theta$ (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First peak from left side</td>
<td>Second peak from left side</td>
<td>Third peak from left side</td>
<td></td>
</tr>
<tr>
<td>Cloisite-15A</td>
<td>31.5</td>
<td>20.68</td>
<td>12.35</td>
<td>7.29</td>
</tr>
<tr>
<td>Nanocomposite (3%)</td>
<td>-</td>
<td>-</td>
<td>27.37</td>
<td>3.225</td>
</tr>
<tr>
<td>Nanocomposite (5%)</td>
<td>-</td>
<td>-</td>
<td>27.5</td>
<td>3.21</td>
</tr>
<tr>
<td>Nanocomposite (8%)</td>
<td>-</td>
<td>-</td>
<td>29.62</td>
<td>2.98</td>
</tr>
<tr>
<td>Nanocomposite (10%)</td>
<td>-</td>
<td>-</td>
<td>27.5</td>
<td>3.21</td>
</tr>
</tbody>
</table>
Note that the galleries were expanded from 12.35 Å (at 2θ=7.29°) to ≥ 27.37 Å (at 2θ≤3.22°) and all peaks at 2θ=2.97° and 3.69° have been eliminated. The corresponding d-spacing values of the nanocomposites are summarized in Table 1.

To indicate the exact location of the eliminated peaks, a special setup was made. This setup comprised of a thin steel knife, a fixture and two screws. The first screw was used to align the edge of the knife with the X-ray generator and detector, while the second one was employed to adjust the position of the table in a manner to allow the sample to touch the knife. Great care was taken in adjusting the alignment of X-ray equipment, upper surface of the sample and the edge of the knife. The exact peak locations are shown in Table (2).

**Tab. 2.** d-Spacing of samples by modified-WAXS techniques.

<table>
<thead>
<tr>
<th>Samples</th>
<th>d-Spacing (Å) - 2θ(°)</th>
<th>d-Spacing (Å) - 2θ(°)</th>
<th>d-Spacing (Å) - 2θ(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First peak from left side</td>
<td>Second peak from left side</td>
<td>Third peak from left side</td>
</tr>
<tr>
<td>Nanocomposite(3%)</td>
<td>Eliminated</td>
<td>Eliminated</td>
<td>27.37-3.225</td>
</tr>
<tr>
<td>Nanocomposite(5%)</td>
<td>Eliminated</td>
<td>67.38-1.31</td>
<td>35.73-2.47</td>
</tr>
<tr>
<td>Nanocomposite(8%)</td>
<td>Eliminated</td>
<td>52.38-1.68</td>
<td>29.62-2.98</td>
</tr>
<tr>
<td>Nanocomposite(10%)</td>
<td>Eliminated</td>
<td>61.51-1.43</td>
<td>27.5-3.21</td>
</tr>
</tbody>
</table>

- Transmission electron microscopy (TEM)

TEM micrographs provide a visual image of the expansion of organoclay gallery and total exfoliation (Fig. 2). In the TEM micrograph of polyaniline/modified montmorillonite nanocomposite, it can be observed that the distance between the lines are expanded randomly, which indicate exfoliation of polyaniline into montmorillonite organoclay gallery. This is in agreement with the XRD data.

**Fig. 2.** TEM of nanocomposite actuator with 5% modified montmorillonite.
Electroactivity behaviour of nanocomposite actuator

-Conductivity

The low conducting state of nanocomposite actuators originates from the insertion of the organoclay layer, which weakens the interchain interaction. Also it is proposed that in the nanocomposite systems the organoclay layers interrupt the effective doping process and induce weak interchain and intrachain interactions, resulting in increased localization of charge carriers [11]. Also organoclays are electrical insulators so adding this reinforcement to polyaniline matrices decreases their conductivity regardless of increasing electroactivity which is discussed in the next section. Fig. 3 shows decreasing conductivity with increasing the percentage of organoclay in three types of doping acids. (+)-10-camphor sulfonic acid is the best doping acid because it creates crystals region in polyaniline chains and improves the conductivity of the samples [22].

![Fig. 3. Conductivity of nanocomposites versus percentage of organoclay in three types of doping acid.](image)

-Electroactivity; bending

Before starting the electroactivity tests all of the samples were doped in (+)-10-camphor sulfonic acid (1M), and the effective lengths of the samples were kept in HCl electrolyte (pH=0) for 10–15 min to ensure that the samples were completely protonated.

-The effect of organoclay

![Fig. 4. Bending of nanocomposite of 5 mm length versus percentage of organoclay at different scan rates.](image)
Mechanism of electroactivity in these actuators is based on oxidation-reduction reaction in electrolyte solution. Input or output ions in or from actuator nanocomposite films cause bending of the films, but organoclay restricts the motion of ions [10]. Decreasing amount of nanocomposite actuator bending of the samples is due to the presence of insulating nanofiller in polyaniline matrices. The decreasing amount of nanocomposite actuator bending is about 64% in nanocomposite with 10% organoclay in comparison with pure polyaniline films. The bending of nanocomposite actuator with a fixed length decreases in a linear manner with increasing percentage of organoclay at different scan rates. This behaviour is typically shown in Fig.4.

- **The effect of actuator length**

By increasing the effective length of actuators, oxidation-reduction reaction will be increased around actuators in electrolyte solution. Increasing the length of actuators is more effective than increasing their widths, being fixed at 0.1 cm. Therefore, the bending of nanocomposite actuator (with a fixed percentage of organoclay) increases in a linear manner with increasing the length of samples at different scan rates. This behaviour is typically shown in Fig.5.

**Fig. 5.** Bending of typical nanocomposite of 5% organoclay versus length at different scan rates.

- **The effect of scan rate**

**Fig. 6.** Bending of nanocomposite of 5mm length versus scan rate at different percentage of organoclay.
The scan rate was varied to probe the response speed of the actuators. Scan rates were considered in four levels, i.e. 5, 10, 50 and 200 mV/s. Actuator bending (with a fixed length) decreases in a non-linear manner with increasing the scan rate at different percentages of organoclay. These data reflect the dependence of response time on mass transport. Actuator nanocomposite films need suitable and optimized time for oxidation-reduction reaction. For this reason, increasing the scan rate would decrease the time length of reactions, so bending decreases. This behaviour is typically shown in Fig. 6.

-Electroactivity; recovery

-The effect of organoclay

Elasticity of nanocomposite films will be increased with increasing percentage of organoclay. Also bending and residual bending of nanocomposite actuator films with a fixed length decrease with increasing percentage of organoclay at different scan rates [5]. The typical results are shown in Figs. 6 and 7.

Fig. 7. Residual bending of nanocomposite of 5mm length versus percentage of organoclay at different scan rates.

-The effect of length

Fig. 8. Residual bending of polyaniline nanocomposite of 5% organoclay versus length at different scan rates.
Bending and residual bending of nanocomposite actuators with a fixed percentage of organoclay increase with increasing length of actuators at different scan rates for the reason mentioned already. Typical results are shown in Fig.8.

*The effect of scan rate*

Nanocomposite actuator deflection due to bending decreases with increasing the scan rate. Also residual deflection increases in a non-linear manner with increasing the scan rate at fixed length with different percentages of organoclay for the reason mentioned already. The results are typically shown in Fig. 9.

![Residual bending of polyaniline nanocomposite of 5mm length versus scan rate at different percentage of organoclay.](image)

**Fig. 9.** Residual bending of polyaniline nanocomposite of 5mm length versus scan rate at different percentage of organoclay.

*Bending time and recovery time*

Dynamic mechanical analysis was performed to characterize the elastic and loss modulus of pure polyaniline and its nanocomposites, Figs. 10 and 11. A sharp drop is observed around 150°C which is attributed to the glass transition temperature, Fig.10.

![Elastic modulus curves of nanocomposites.](image)

**Fig. 10.** Elastic modulus curves of nanocomposites.

The presence of organoclay increases the elastic modulus of actuator, so the response rate and the recovery rate of actuator increase, [5, 20]. For this reason, the bending time and recovery time of nanocomposite actuator at fixed length decrease...
in a non-linear manner with increasing percentage of organoclay with different scan rates. The results are typically shown in Figs. 12 and 13.

**Fig. 11.** Loss modulus curves of nanocomposites.

**Fig. 12.** The bending time of nanocomposite of 5mm length versus percentage of organoclay at different scan rates.

**Fig. 13.** The recovery time of nanocomposite of 5mm length versus percentage of organoclay at different scan rates.
Thermal behaviour of nanocomposites actuator

- Decomposition temperature

In Fig. 14 the corresponding thermogravimetric curves for a pure polyaniline and its nanocomposites with different percentages of organoclay are shown.

![TGA curves of nanocomposites.](image)

Fig. 14. TGA curves of nanocomposites.

In general, the thermal behaviour of the pure polyaniline shows a three-step weight loss process indicating the majority weight loss for respective steps. The first weight loss just below 100 °C is attributed to the loss of water and the second weight loss ranging from 200-400 °C is believed to be due to the elimination of doping acid (HCl) and alkylammonium chains in organoclay as a modifier. The third weight loss starting at around 400 °C is assigned to the thermal decomposition of polyaniline backbone chains [17, 18, 20].

This result suggests that the exfoliated nanocomposite system is more thermally stable than the pure polyaniline system. An enhancement of thermal stability of polyaniline nanocomposites is clearly indicated by an increase of about 40 °C of the decomposition temperature. This enhanced thermal stability of the polyaniline nanocomposite was attributed to the restricted thermal motion of the polyaniline in the gallery of organoclay [18].

- Glass transition temperature (T_g)

Fig. 15 shows damping (\tan \delta) curves for a pure polyaniline and its nanocomposites with different percentages of organoclay. Increasing percentage of organoclay as reinforcement reduces damping effect. It is observed that the T_g which is the glass transition temperature or temperature of maximum damping shows a shift of 21 °C in the polyaniline nanocomposite with 10% organoclay [19, 20].
Conclusions
Polyaniline nanocomposite actuators have an exfoliated morphology. It was observed that bending and residual bending of nanocomposite actuator at fixed length decrease in a linear manner with increasing percentage of organoclay at different scan rates. Residual bending of nanocomposite actuator at fixed percentage of organoclay increased in a linear manner with increasing length of samples at different scan rates. Bending and recovery of nanocomposite actuator at fixed length showed increase in a non-linear manner with increasing the scan rate at different percentages of organoclay while bending time and recovery time at fixed length decreased in a non-linear manner with increasing the percentage of organoclay at different scan rates. The glass transition temperature and the degradation temperature of polyaniline nanocomposites showed a shift of 21°C and 40°C, respectively.

Experimental

Materials
Polyaniline powder has been made in Chemistry Department of Tabriz University with a molecular weight of 90000 g/mol. Modified montmorillonite (cloisite-15A) was purchased from Southern Clay, Inc, USA. The cation exchange capacity (CEC) is 125 meq/100g. The modifier is di-hydrogenated tallow ammonium chloride (HTAC). All of the essential chemicals such as; (+)-10-camphor sulfonic acid (CSAC), hydrochloride acid, sulfuric acid, dimethyl acetamide (DMAC), and potassium hydroxide were purchased from Merck.

Preparation of samples
Six grams of polyaniline was added into 240 ml DMAC, stirred for 4 h at room temperature and filtered for making polyaniline solution. Various percentages of cloisite-15A (0, 3, 5, 8 and 10%) was added into 10 ml DMAC separately and stirred for 3 h at room temperature. To make polyaniline/modified montmorillonite
nanocomposite, a suspension of organoclay-solvent was added to polyaniline solution and stirred for 3 h at room temperature.

To prepare films, the nanocomposite was placed on a glass plate which had been washed with potassium hydroxide solution (1%). After 24 h stayed at room temperature, the samples were transferred to an oven at 65-70 °C for further 24 h. Then, polyaniline/modified montmorillonite nanocomposite films were removed from the glass plate with deionized water. All of the films with a thickness of 80µm; surface areas of: 0.1 cm×0.5 cm, 0.1 cm×1cm and 0.1cm×15cm, were doped with CSAC (1M) for 50 min.

**Instruments**

**-Structural analysis**

X-ray diffraction (XRD) patterns were obtained by using a modified X'pert-Philips Diffractometer. Transmission electron microscopy (TEM) was used to observe the structure of the polyaniline/modified montmorillonite nanocomposite using a CEM902-a electron microscope.

**-Physical-mechanical properties**

For dynamic mechanical analysis (DMA) test a NETZSCH-242c was used. This test was performed in the tension mode, under a steady force of 0.712 N and a dynamic force of 0.6 N, under a nitrogen flow of 50 ml/min. The sweepings were made in at temperature interval of 25 °C to 250 °C at a heating rate of 2 °C/min and a frequency of 5 Hz. The dimensions of the sample used in the characterization by DMA were 5 mm × 10.0 mm × 0.08 mm.

**-Thermal analysis**

The thermal gravimetric analysis (TGA) was obtained on a PL-STA 1500. A heating rate of 10 °C/min was used with an argon flow of 15 ml/min from room temperature to 800 °C [20].

**Electroactivity behaviour**

![Image](Fig. 16. Special setup to determine the bending angle of the specimens.)
To determine the conductivity of samples, a four-probe technique was used. Actuation performance were obtained on an EG & G PRINCETON 273A cyclic voltammeter at 0-1.2 V with four levels of scan rates such as; 5, 10, 50 and 200 mV/s. The electrolyte was 1 M HCl (pH= 0) unless otherwise specified. The electrical connection of these samples in cyclic voltammeter was based on polyaniline-modified montmorillonite nanocomposite film as a working electrode, calomel as a reference electrode and Pt foil as a counter electrode [5]. The bending of the samples was determined by a special setup shown in Fig. 16. This setup includes four parts: electrodes of CV, degree detector, electrolyte and sample protector.

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References