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# Synthesis and characterization of foldable and magnetic field-sensitive, freestanding poly(vinyl acetate)/poly(vinyl chloride)/polyfuran composite and nanocomposite films

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ABSTRACT

In this study, polyfuran and poly(vinyl acetate)/poly(vinyl chloride)/polyfuran ternary composites were synthesized via the chemical polymerization method. The temperature and magnetic field–sensitive novel composites and the nanocomposite were obtained in the form of powders and films. It was observed that the prepared novel conductive films have superior properties at a certain temperature range (25–50 °C) such as bending and folding. The structural properties, thermal behavior, surface morphology, internal structure, and surface roughness of the prepared samples were investigated by various characterization techniques. The conductivities of the samples were measured at room temperature and different temperatures by the four-point technique. X-ray Diffraction analysis results demonstrated that the PF and composites have an amorphous structure, whereas the nanocomposite is in crystalline form. The saturation magnetization (Ms) values of the magnetite and nanocomposite were found to be 58.9 and 5.3 emu $g^{-1}$, respectively. It was found that magnetite-doped nanocomposite has superparamagnetic properties at room temperature.

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## 1. Introduction

In recent years, conducting polymers have attracted much attention in the scientific and technological fields, such as electrical, thermal, environmental, optical, chemical, and biological properties, due to their ease of preparation and potential for wide application. They have been used for various applications such as biosensors [1], rechargeable batteries [2], electrochromic display boards [3], electronic devices as resistor electronic circuits, capacitors, diodes [4], and electrorheology [5]. Polyfuran (PF) is an aromatic heterocyclic polymer that has the best properties redox capability, electrochromic effect [6], and humidity sensor [7].

In the literature, studies on the chemical synthesis of polyfuran are very limited due to its low stability and weak conductivity when compared to other conductive polymers. Many researchers have improved the weak mechanical and physical features of the PF by preparing its blend [8], composite/nanocomposite [9] and copolymers [10]. Nanocomposites composed with metal and metal oxides nanoparticles and conducting polymers have received special attention in various technological fields. Prepared in this way, nanocomposite materials showed optical, electrical, magnetic, or catalytic properties [11]. For instance, Reddy et al. [12] investigated the effect of dopant on the properties of $Fe_3O_4$/polyaniline nanocomposites. Kim et al. [13] prepared monodisperse $Fe_3O_4$-poly(styrene)/poly(thiophene) core/shell nanoparticles and investigated the sensor application. Zare et al. [14] have synthesized polyfuran/functionalized multiwalled carbon (PF/MWCNTs-COOH) nanocomposite and characterized. In another study, Amiri et al. [15] have synthesized magnetite nanoparticles modified with polyfuran (PFu/$Fe_3O_4$) and have suggested that it could be used as an adsorbent for the solid-phase extraction of the polycyclic aromatic hydrocarbons. The PVAc, PVC, and PF in the ternary composite structures were selected because they have superior properties. PVAc has a homogenous film-forming capacity and good adhesion properties. PVC has a good film-forming capacity that is easily processed and shows high adhesion to metal surfaces. PF has been used as a conducting content in ternary composites. This study describes the chemical synthesis of polyfuran, the preparation of the PVAc/PVC/PF ternary composites and magnetite-doped PVAc/PVC/PF/$Fe_3O_4$ nanocomposite. Their temperature-magnetic field–sensitive folding films were characterized. As a result of our research, the synthesis and characterization of the PVAc/PVC/PF ternary composites and nanocomposite have not been reported previously in the literature.

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## 2. Experimental

### 2.1. Materials

Furan (≥99% pure), ferric chloride ($FeCl_3.6H_2O$) ($M_w$ = 270.30 - g/mol, ≥97% pure), ferrous chloride ($FeCl_2{\cdot}4H_2O$) ($M_w$ = 198.93 g/mol, ≥99% pure), poly (vinyl acetate) (PVAc) ($M_w$: 83,000, d: 1.19 g/cm$^3$), poly (vinyl chloride) (PVC) ($M_w$: 80,700, d: 1.385 g/cm$^3$), chloroform ($CHCl_3$) (≥99% pure) were purchased by Sigma–Aldrich (Germany). Anhydrous iron (III) chloride ($FeCl_3$) ($M_w$: 162.21 g/mol, ≥98% pure), dimethylformamide (DMF) (≥99% pure) were purchased by Merck (Germany). Furan (F) monomer was distilled under reduced pressure before use. The others were used as received.

### 2.2. Synthesis of polyfuran

Furan (0.035 mol) was polymerized by using $FeCl_3$ as an oxidant in an anhydrous medium ($CHCl_3$) at 0 °C under $N_2$ via chemical oxidation polymerization. The ratio of monomer to oxidant was taken as 1:3. $FeCl_3$ (0.105 mol, 17.03 g) was dispersed in 50 mL of $CHCl_3$; the solution was stirred and refluxed at 0 °C under $N_2$ atmosphere for 10 min. Distillated furan in $CHCl_3$ was dropped on the $FeCl_3$ solution. The polymerization was carried out under $N_{2(g)}$ atmosphere at 0 °C for 1 h. Then, it was continued at room temperature for 24 h under the air atmosphere. After 24 h, the dark-brown precipitate was filtered, and washed with distilled hot water (70 °C). Then, it was dried in a vacuum oven at 70 °C for 24 h, and the yield was 95%.

### 2.3. Synthesis of PVAc/PVC/PF ternary composites

PVAc/PVC/PF ternary composites were prepared by a chemical oxidation polymerization technique at 0 °C using $FeCl_3$ as an oxidant in an anhydrous medium ($CHCl_3$). The ratio of monomer to oxidant was taken as 1:3. Initially, a known amount of $FeCl_3$ was dispersed in $CHCl_3$ contained in a tree-necked flask. PVAc and PVC were dissolved in $CHCl_3$ and then were added into the stirred oxidant medium. After 10 min of stirring, the furan monomer (dispersed in $CHCl_3$) was added drop-wise into this system under the $N_2$ gas atmosphere at 0 °C. The mixture was stirred by a magnetic stirrer for 1 day, and then, it was filtered and washed with distilled hot water and dried in a vacuum oven at 70 °C. Ultimately, the quantity of PF in ternary composite was calculated from the total mass of the composites. Hereby, PVAc/PVC/PF ternary composites with the inclusion of PF at different percentages (3, 10, 13 wt%) were synthesized.

### 2.4. Preparation of magnetite ($Fe_3O_4$) nanoparticles

$Fe_3O_4$ nanoparticles were synthesized according to the previously reported procedure with little change [16]. In deionized water, 1.99 g of $FeCl_2.4H_2O$ (0.01 mol) and 5.41 g of $FeCl_3.6H_2O$ (0.02 mol) were mixed by a mechanical stirrer (1000 rpm) under $N_{2(g)}$ at room temperature for 30 min. Then, 200 mL of 2 M of ammonia solution was quickly added into the solution of mixed iron salts. The resulting solution was stirred for 30 min under $N_{2(g)}$ until the pH value reached 10. After 30 min, the black precipitate was separated by a magnet. It was washed with distillated water and acetone three times, and dried in a vacuum oven at 60 °C.

### 2.5. Preparation of composite and nanocomposite films

While preparing films of the PVAc/PVC/PF ternary composites, 1.5 g of composite powder was dissolved in a chloroform ($CHCl_3$) and dimetylformamide (DMF) solvent mixture. This solution was constantly stirred at room temperature throughout 1 week. It was poured into a glass Petri dish, and the solvent evaporated from the films. The films were dried at room temperature for 48 h and was taken with pens; and uniform films were obtained. PVAc/PVC/PF/$Fe_3O_4$ nanocomposite film was prepared in the same method as the composite that was mentioned before. After the composite was dissolved, 0.25 g of magnetite was added into this solution and stirred mechanically at room temperature. Finally, the uniform film was obtained successfully.

### 2.6. Characterization techniques

The electrical conductivity of compressed pellets of polyfuran, composites, and nanocomposite were performed by a FPP 470 model of a four-probe instrument, at room temperature and between 10 and 50 °C. The magnetic susceptibility measurements of polymer and composites were achieved using a Sherwood Scientific Model MKI Gouy Scale (Sherwood, St. Louis, MO) at room temperature. Bulk densities of polymer, composites, and nanocomposite were measured using pellets (under the pressure of 5 tonne cm$^{-1}$ and a diameter of 1.3 cm). Heights and masses of these pellets were measured, and the corresponding densities (d) were calculated. Fourier transform infrared (FTIR) spectra of polymer, composites, and nanocomposite were recorded using a Nicolet 6700 FTIR spectrophotometer with the use of the KBr disc technique. The Thermogravimetric Analysis (TGA) was recorded with a Perkin Elmer STA 6000 model thermal analysis system at a heating rate of 10 °C min$^{-1}$ in a nitrogen atmosphere between 25 °C and 900 °C. X-ray diffraction (XRD) patterns were obtained at room temperature on a Rigaku Ultima-IV powder diffractometer with a scanning rate 0.02° min$^{-1}$, and the patterns were recorded in the 2θ range of 10–60°. The surface morphology of composite and nanocomposite films were observed with a scanning electron microscopy (SEM) using a Quanta 400F Field Emission SEM model instrument. During the transmission electron microscope (TEM) analysis, the magnetite was sonicated for 15 min in alcohol and dried on a carbon grid. The micrographs were taken with a JEOL 2100 HRTEM. A TEM image of the nanocomposite film was obtained by a FEI Tecnai G2 Spirit Biotwin CTEM. An atomic force microscopy (AFM) topography of the typical coatings was performed by a Veeco-Multimode V microscope using the tapping mode in an ambient condition. Silicon tips had a resonance frequency in the range of 241–336 kHz. The root mean square roughness (RMS) of the images was calculated using a commercial software. The magnetic property of nanocomposite films and magnetite at a magnetic field from ± 5 Oe were measured at a temperature of 298 K with a cooling rate of 1 K/min by a Cyrogenic Limited PPMS VSM magnetometer.

## 3. Result and discussion

### 3.1. Yield, electrical Conductivity, magnetic Susceptibility, and density results

Polymerization yield, conductivity, magnetic susceptibility, bulk density of ternary composites, nanocomposite, and polymers are seen in Table 1. The polyfuran was synthesized with 95% yield. The conductivity of polyfuran is $3.74 \times 10^{-5}$ S cm$^{-1}$ at room temperature. Table 1 shows that the polymerization yields decreased with the increase of PVAc and PVC in ternary composites. This can be attributed to the increasing intensity of the synthesis media with an increased amount of PVAc and PVC. Accordingly, the conductivities are also decreased. The conductivities of ternary composites PVAc/PVC/PF (13%), PVAc/PVC/PF (10%), and PVAc/PVC/PF

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