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Thermal properties and dielectric permittivity of PVDF/reduced graphene oxide nanocomposite film

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ABSTRACT

In this study, the nanocomposite films of polyvinylidene fluoride (PVDF) / reduced graphene oxide (RGO) were prepared by mixing of reduced graphene oxide in a solution of dimethyl formamide and polyvinylidene fluoride. The prepared nanocomposites were investigated by X-ray diffraction (XRD) analysis, showed an obvious α - to β -phase transformation compared to pure PVDF. SEM images showed spherulitic crystal structure of PVDF. The spherulitic morphology of the pure PVDF is maintained for the PVDF nanocomposites. Also the thermal behavior of PVDF/RGO nanocomposite films have been investigated by employing thermogravimetric analysis (TGA) which showed higher thermal stability of PVDF nanocomposite after loading of RGO than pure PVDF.

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1. Introduction

Polyvinylidene fluoride (PVDF) is a widely studied semicrystalline polymer due to its piezoelectric and pyroelectric properties [1]. Consequently, PVDF finds widespread applications in transducers, sensors, actuators and MEMS [2–8]. Piezoelectric properties of PVDF are strongly related to its crystalline structure.

PVDF crystallizes into five different polymorphs which include α , β , γ , δ , and ε , depending upon crystallization conditions. The α phase is the most common and stable polymorph of PVDF [9]. Among all the PVDF polymorphs, the β -phase is responsible for piezo- and pyroelectric properties of PVDF [10].

PVDF films often form the α -phase and β -phase can be obtained by stretching, applying high pressure nd high electrical field to the α -phase. Recently, the combination of PVDF with nanomaterialssuch as Cu [11], graphenenanosheets [13, 14], graphite [15], TiO₂ [16],ZnO [17], ferrite [18], graphene–CuS [19], Pb(Zr0.53Ti0.47)O₃ [20], nanoclays [21], MgCl₂ [22], MWNTs [23, 24], zeolite [25], polypropylene [26], BaTiO₃ [27], P(VDF-TrFE)[28], polystyrene [29] and poly(3-[30]to alkylthiophenes) form polymer nanocomposites has been an attractive approach to promote β -polymorph within the polymer, improveing its piezoelectricity and modify its properties.

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In the present work, reduced graphene oxide was added into PVDF with two purposes. The first one is to investigate of the effect of RGO addition on the polymorph changing of PVDF; the second one is to study the effect of RGO on the dielectric permittivity and thermal properties of PVDF. As one cansee, in this work we prepared PVDF nanocomposite films with relatively higher β phase content than some works done before, also improve thermal which the stability makes this nanocomposite an interesting material for using in specific applications. For graphenebasedcomposites, the dispersion of graphene sheets in a polymer matrix is a tricky issue because graphene layers are not compatible with some polymer materials.

Several techniques such as physical absorption and chemically linking between functional groups and graphene sheets have been developed to solve the problem [13]. In this paper, we describe the facile and effective preparation of PVDF/reduced graphene oxide nanocomposite by reduction of graphene oxide to disperse it better in polymer matrix due to its functional groups on the edge, top, and bottom surface of each RGO sheets. The dielectric properties were studied. The high dielectric constant in the PVDF/RGOnanocomposites might come from two aspects: the homogeneous dispersion of RGO in PVDF and the strong interactions between the two components.

2. Experimental Procedure

2.1 Materials and methods

PVDF (Mw = 534,000), in powder form, was purchased from Sigma Aldrich. Dimethyl formamide (DMF) (Merck) of purity 99.5% was used as solvent. RGO and RGO-ZnO were synthesized by following procedures described below.

2.2 Preparation of graphene oxide (GO)

Graphite oxide was synthesized from commercial graphite by modified Hummers method [31]. The commercial graphite powder (10g) was put into 230mL concentrated H₂SO₄ that had been cooled to bellow of 20°C with a circulator. Then 300g potassium permanganate (KMnO₄) was added with stirring, so that the temperature of the mixture was fixed at bellow of 20°C. Later, the temperature of the reaction was changed to 40° C and mixture was stirred at this temprature for 1h. Then 500 mL de-ionized water was added to the mixture, causing an increase in temperature to 100° C and 2.5 mL H₂O₂ (30 wt.%) was slowly added to the mixture supplementary this solution was diluted by addition 500mL deionized water. For purification, the suspension was washed with 1:10 HCl solution (200 mL) in order to remove metal ions by filter paper and funnel. The suspension was washed with much de-ionized water at several times, until the filtrate became neutral to remove remaining salt impurities. Exfoliation was performed by sonication for 1hour. The resulting product, denoted graphene oxide (GO), was reduced by following procedure.



Fig.1.TEM image of reduced graphene oxide

2.3 Synthesis of reduced graphene oxide (RGO)

Chemical reduction of graphene oxide to reduced graphene oxide was done according to following procedure. Suspension aqueous colloids of GO were prepared from the dried graphene oxide (GO) bymechanical stirring and heat treatment with a circulator. In the experiment, 10g of graphene oxidewas stirred into 1L of distilled water. This dispersion was stirring using a Fisher mechanical stirring until it became a clear solution with no visible particulate material. After that the pH of the solution was increased to 10 by adding NaOH solution and 20mL of hydrazine monohydrate was added to the solution at 95°C and stirred for 4h, subsequently the reaction was completed, the reduced graphene oxide was collected by filtration as a black powder. The obtained powder was washed with distilled water several times to remove the excess hydrazine. The final product was dried in a vacuum oven at 100°C for 24h. Figure 1 shows

TEM image of reduced graphene oxide. The lightgray thin films are the RGO nanoplates. It can be clearly seen in Fig.1 that the thickness of exfoliated RGO sheet is nanosize.

2.4 Preparation of the PVDF/RGO nanocomposite 1%

PVDF solution was prepared by dissolving the PVDF powder into Dimethyl formamide (DMF) with a mass ratio of 10/90 and stirred for 2 h to obtain a homogeneous and transparent solution. In order to get a homogeneous dispersion of the reduced graphene oxides inside the polymeric matrix, the following procedure was applied: first, the desired amount of reduced graphene oxide and DMF were mixed then this mixture was placed in an ultrasound bath for 5 min to ensure that the reduced graphene oxide was well dispersed in the DMF and to avoid aggregates; then the corresponding amount of PVDF solution was added. The obtained mixture was placed in a stirrer to complete dissolution of the polymer and then was dried on a petri dish inside the oven for 2 h at 120°C toensure the complete crystallization of the nanocomposite and complete removal of the solvent.

2.5 Characterization

The X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 20 range (5°-65°) with scanning speed of 2°/min. Thermogravimetric analysis (TGA) was used to determine the thermal stability of polymers. TGA provides quantitative information on the weight change process. TGA was carried out on both PVDF (reference) and PVDF/RGO nanocomposite samples using Perkin Elmer system. The sample was heated under nitrogen atmosphere (70 cm³/min) at a rate of 10°C/min in 200 - 900°C. Precision LRC meter Agilent 4258A with 16451b dielectric testfixture at various frequencies 75 kHz to 30MHz with 1MHz stepswas exploited to determine dielectric constants for PVDF and PVDF/RGO nanocomposite film.

3. Results and Discussion

3.1. XRD

To reveal the crystal phase in the hybrid films, X-ray diffraction experiments are preformed and the results are given in Fig.2. The neat PVDF sample displays three peaks at 2θ =18.3° and 26.5°, corresponding to the (1 0 0), (0 2 0) and (1 1 0) reflections of α phase, respectively [10, 11]. Whereas, the peak appears at 2θ =20.4° corresponding to the (1 1 0) and (2 0 0) β planes, implying the existence of the β -phase [30]. To evaluate the relative quantity of the different phase in the PVDF and PVDF hybrids, the peak fitting step is processed via the area of the peaks. Also we can calculate the quantity ratio between α and β phase with the following equation [10]:

$$F(\beta) = S\beta / [S\alpha + S\beta]$$
(1)

where S_{α} and S_{β} are the integral area of α and β phase in XRD patterns after the peak-fitting of superposition of the α and β phase, respectively.

It is observed that the β -phase content increased in compare with pure PVDF. The amount of 78% β for PVDF/RGO nanocomposite film 1% was resulted, which is a good achievement. The formation of β -polymorph in (RGO)-filled PVDF solvent casted films is attributed to the strong and specific interaction between the carbonyl group (-C=O) found in graphene oxide and the CF₂ segments of the PVDF polymer.



Fig.2. XRD patterns of PVDF (a) and PVDF/reduced graphene oxide (b) nanocomposite films

3.2. SEM images

SEM images of pure PVDF and PVDF/RGO nanocomposite surface are shown in Fig.3. SEM graphs show spherulitic crystal structure for both pristine PVDF and PVDF/RGO nanocomposite films; it's clear that the size of the spherulites decrease after loading of reduced graphene oxide nanocomposite.

3.3. TGA

Thermogravimetric analysis (TGA) and its derivative (DTG) were widely used to characterize the thermal stability of polymer nanocomposites. In Fig.4 (a) and (b), the TGA and DTG thermograms of pure PVDF and its RGO nanocomposite are compared. It is apparent from the figure 4(a) that PVDF exhibits three-step degradation although PVDF mainly degrades in two steps and the last step is inconsequential compare with the other steps. The first one occurs at 419-480°C, and the second one occurs at 480-560°C. The decomposition mechanism of the first degradation step is chain-stripping process. In this stage carbonhydrogen and carbon-fluorine bonds scission occurand different species, such as HF, with the destruction of the pristine polymer structure and formation of a conjugated system have been formed [32]. This process leads to a weight loss observed in the first degradation step.





Device: MV2300 School of Metallurgy, University of Tehran School of Metallurgy, University of Tehran Fig.3.SEM image of PVDF (a) andPVDF/reduced graphene

oxide (b) nanocomposite film

The second step is a kind of poly (aromatization) process. In this step the polyenic sequence formed previously on the first degradation step is unstable and, therefore, the macromolecules formed undergo further reactions leading to scission followed by the formation of aromatic molecules [18]. In addition the onset temperature of degradation usually used to investigate the thermal stability of composite and evaluated as the temperature at which 10% degradation occurs (T10) showed in Fig.4 under nitrogen gas at ramp rate of 10°C/min. Table1gives a summary of all the data collected.

From the Table 1, it can be observed that the pure PVDF decomposed at temperature of 440.1°C whereas for PVDF/RGO nanocomposite, decomposition temperature increased about 20°C by adding of 1wt.% RGO filler. Therefore, the presence of the RGO filler modifies slightly the thermal stability of the polymer matrix.

The resistance of nanocomposites toward thermal degradation may be related to the interaction between PVDF and RGO filler. The strong interaction between nanofillerand the PVDF matrix is indicated by the XRD patterns too. In order to increase the resolution of TGA analysis, the first derivative of the mass loss versus the degradation temperature has been analyzed. It is noticed from Fig. 4(b) that the temperature at which the mass loss rate is maximum (named also inflection temperature-TI) rises as adding RGO to pure polymer. The shift of TI to higher temperature after adding of RGO demonstrates the enhancement of the thermal stability and confirms the formation of PVDF-RGO interface.

The rate of thermal decomposition of polymers and influence of RGO nanocopmosite in the polymer thermal degradation can be modeled by three different methods. First of all is the Ozawa– Flynn–Wall method [32].

$$Ln\beta = Ln(AE/R) - 5.33 - Ln(1-\alpha) - 1.05(E/RT)$$
 (2)

where A is the exponential factor, β is the heatingrate (dT/dt), E is the activation energy, R is the gas

Table 1.Thermal data obtained from TGA thermograms of PVDF/RGO nanocomposite films.

Sample name	Weight loss temperature(±2°C)
	T_{10}
Pure PVDF PVDF/RGO	440.1 458.6

constant (8.314 J/K mol-1) and

$$\alpha = (w0 - w(t))/(w0 - w\infty)$$
 (2.1)

where w_0 is the initial mass of the sample, w(t) is the mass of the sample at temperature t and w_{∞} is the final mass at a temperature at which the mass loss is approximately unchanged. In this method, plots of Ln[$\beta(1-\alpha)$] versus 1/T were drawn. The slope of these lines gives the activation energy, as seen from equation 2.

In the second molel, Broido method was used, assuming n=1 [18, 33]:

$$Ln[-Ln(1-\alpha)] = -E/RT + const$$
(3)

In this method, plots of $Ln[-Ln(1-\alpha)]$ versus 1/T with a slope of (-E/R) were drawn, from which the activation energy is determined. Further, the Coats–Redfern method was also used, considering a constant heating rate [18, 33]:

$$Ln[[-Ln(1-\alpha)]/T^2] = -E/RT + Ln(AR/BE)$$
(4)

where A is constant, β is the heating rate and α represents the degree of conversion. In an analogous way, analysis of the TG curves was performed with the Coats–Redfern method by plotting Ln[-Ln(1- α)/T2] versus 1/T and determining the activation energy of the nanocomposites. The kinetic parameters obtained from Ozawa–Flynn–Wall (Eq.2), Broido (Eq.3) and Coats–Redfern (Eq.4) methods are listed in Table 2.

It's obvious that for PVDF/RGO nanocomposite, the activation energies, increase compare with pure PVDF. It shows that PVDF/RGO nanocomposite film is more stabilized than pure PVDF. In most of the cases addition of nanofillers can lead to thermal stabilization of polymers during their decomposition.

In the present work, thermal stability of polymer increases afterembedding of RGO. The higher thermal stability of PVDF/RGO nanocomposite is because of the β -phase has a higher thermal stability than α -form due to the better packing of the zigzag β -PVDF chain than that of the TGTG α -PVDF chain [11, 20].

3.4. Dielectric permittivity

The effects of the RGO content on the dielectric permittivity of the PVDF/RGO composite films are illustrated in Fig.5 Resistivity of the materials were calculated using equation $\rho = A/(2\pi f C_p D t)$ (Ωm) and

dielectric permittivity, $\varepsilon = C_p/C_0$, where C_p is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and the C_0 the vacuum capacitance = $\varepsilon_0 A/t$, A and t are the crosssectional area of the electrode and thickness of the sample, respectively. ε_0 is the permittivity of vacuum to be equivalent to 8.85×10^{-12} F/m. As expected, the effective dielectric permittivity increased by adding of the RGO content in PVDF at all frequency ranges (0 - 3×10^7 Hz). The increased Dielectric permittivity can be attributed to the formation of various nanocapacitors consisting of RGO sheets separated by dielectric PVDF film [34].



0.00E+00 5.00E+06 1.00E+07 1.50E+07 2.00E+07 2.50E+07 3.00E+07 Frequency/Hz

Fig.5.Dielectric permittivity of pure PVDF and PVDF/RGO nanocomposite films

Sample name	Degradation stage	Activation energy (KJ mol ⁻¹)		
		Broid method	Coats-Redfern method	Ozawa-Flynn-Wall method
PVDF	First step	317	313.3	348.9
	Second step	21.6	12.05	12.14
	Third step	4.18	1.79	2.32
Average		114.26	109.04	121.12
PVDF/RGO	First step	573.88	512.16	589.15
	Second step	31.13	26.27	35.62
	Third step	5.49	3.83	1.43
Average		202 99	180 73	208 73

Table 2.Calculated activation energy

4. Conclusions

The PVDF/reduced graphene oxide nanocomposite was prepared by mixing of 1wt.% reduced graphene oxide in DMF and PVDF solution. The nanocomposite films were studied by various methods. The results of XRD exhibited the polymorph transformation from α - to β -phase as a result of insertion of reduced graphene oxide. The amount of 73% ß for PVDF/RGO nanocomposite film 1% was resulted. The presence of the RGO modifies the thermal stability of the polymer matrix. The observed enhancement of the thermal stability of PVDF by the loading with RGO is a direct proof for the existence of interface between polymer (PVDF) and fillers (RGO). In addition dielectric permittivity increased after adding of 1wt.% reduced graphene oxide to pure PVDF because of the homogeneous dispersion of RGO in PVDF and the strong interactions between the two components.

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