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Material Properties

Dielectric properties of graphene oxide doped P(VDF-TrFE) films

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The samples of polyvinylidene fluoride/trifluoroethylene with different amount of graphene oxide dopant 5, 10, 15, 20 and 25% were fabricated and their phase situation were estimated. Moreover the para–ferroelectric phase transition was studied using the dielectric spectroscopy technique. The results of dielectric measurements allowed to perform Cole–Cole analysis and to estimate the activation energy of the films. On the basis of these results the influence of graphene oxide dopant on structure and properties of polyvinylidene fluoride/trifluoroethylene was discussed.

1. Introduction

The lack of the symmetry center in crystalline materials is of particular interest because it has been well recognized to be a prerequisite for many technologically useful properties such as ferroelectricity, pyroelectricity, piezoelectricity and nonlinear optical (NLO) function (especially second harmonic generation, SHG) [1–5].

Recently very intensive research has focused on the exploration of piezo active organic crystals and polymers [6–12]. One of the most promising is poly(vinylidene fluoride)(PVDF) and it is used as transducers, sensors etc. Moreover PVDF can be easily spun into fibers [13] and therefore may be incorporated into textiles and fabrics what substantially increases its potential applications.

PVDF can form several different phases in the solid state. Each of them is built up of polymer chains in a specific molecular conformation, and these phases are denoted in literature as α (or so called phase II), β (phase I), γ (phase III) and δ (phase IV) [14–17]. The phase usually obtained when PVDF is crystallized from melt is α–phase. This phase is non–polar due to its trans–gauche–trans–gauche' (TGTG′) torsion conformations of chains [14]. The most interesting, taking into account its piezoelectricity, is phase β. It is polar because in its structure all chains are in trans conformation (TTTT) and all dipole moments are oriented in the same direction. There are many methods developed to transform PVDF from phase α to β. The review paper of Bohlén and Bolton [18] enumerates them and they are as follows: drawing and poling of PVDF, processing conditions (pressure, temperature and cooling rates), copolymerization with trifluoroethylene (TrFE), addition of carbon nanotubes. Another one method of obtaining β phase is polymerization of PVDF with graphene oxide (GO) [19].

Although the copolymerization with trifluoroethylene (TrFE) yields the lower piezoelectric effect compared to pure PVDF [20], the ease of obtaining polar structure makes this method often applied [21]. The studies of Dargavilleet [22], Dietze and Es-Souni [23] or Belovickis et al. [24,25] have showed improvement of piezoelectric, dielectric and elastic properties of the polymers by mixing ferroelectric copolymers like P(VDF-TrFE) with electroactive fillers. There were also other successful attempts to tailor the physical properties of polymers by using the reduced graphene oxide [26] or barium titanate [27].

Recently, the graphene oxide (GO) is of great interest due to its large surface area, porous structure, and chemical stability which provide a capable platform for anchoring the nanoparticles to enhance the properties of nanocomposite structures [28,29]. One of the most attractive property of GO is that the plane of carbon atoms is modified by oxygen–containing groups. It expands the interlayer distance what makes the layers hydrophilic, which provides favorable sites for bonding the foreign molecules. Moreover, GO is water–dispersible and therefore can be easily synthesized by chemical methods, which result in eco–friendly materials [30–32]. Thus GO served as a building block of many nanocomposites such

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as GO/$Zn_xFe_{12x}Fe_2O_4$ [33], GO/polyimide resin [34] and aforementioned composites, just to name a few.

In this work we have studied the dielectric and thermal stability of P(VDF-TrFE) copolymer doped with large amount of GO – from 5% up to 25% what to our best knowledge was not encountered in literature. This is supposed to set further the way of tailoring the properties of P(VDF-TrFE) copolymer.

2. Experimental

Graphene oxide (GO) was prepared by the chemical exfoliation of graphite (graphite powder, $<45\mu$ m, $\geq$ 99.99%, Sigma–Aldrich). Briefly, it is the reaction of graphite flakes with concentrated H_2SO_4 and $KMnO_4$ in order to obtain individual sheets of graphene in an oxidized state. The resultant suspension was extensively washed with distilled water by filtration and centrifugation and finally subjected to dialyses to remove ionic contaminants. The resulting GO was dried by lyophilization to avoid aggregation.

For the composite sample preparation, poly(vinylidene fluoride–trifluoroethylene) $P(VDF-TrFE)$ copolymer with a TrFE content of 30% was used. The $P(VDF-TrFE)$ copolymer was chosen because it favors crystallization from a solution or melts directly to the ferroelectric phase without additional stretching in comparison to the pure PVDF polymer. 4 g weight of the copolymer powder was added to 100 ml of a dimethyl sulfoxide (DMSO) and acetone mixture in 80/20 ratio. The powder was dissolved within 2 h at a temperature of 100 °C. The solution was then carefully filtered to remove impurities. Dry graphene oxide was added to the solution at various concentrations of GO and then stirred magnetically for 30 min at 50 °C. For a homogeneous distribution of GO in the solution, this mixture was subjected to ultrasonic vibration for 1 h and stirred again for 3 h at 50 °C. The resulting $P(VDF-TrFE)-GO$ solution was used to produce the thin composite films on the base of copolymer $P(VDF-TrFE)$ as the matrix. Composite with different concentration of GO: pure $P(VDF-TrFE)$ (hereafter abbreviated as PG00), 5% (PG05), 10% (PG10), 15% (PG15), 20% (PG20) and 25% (PG25) were prepared by a crystallization from the solution with thickness of 1 μm. Note that the later on used abbreviation PGXX stands for all samples, i.e. from PG00 to PG25.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed on a Setaram SETSYS 16/18 instrument in nitrogen atmosphere with heating rate of 5 $\text{deg} \cdot \text{min}^{-1}$ in the temperature range 298–900 K. Samples mass (mg) were: 14.374 (0% GO), 14.662 (5% GO), 14.270 (10%), 11.846 (15%), 11.490 (20%) and 15.018 (25%). TGA analysis was carried out also for the pristine graphene oxide in nitrogen atmosphere with heating rate of 5 $\text{deg} \cdot \text{min}^{-1}$ in the temperature range 298–1200 K. The sample mass was 16.733 mg. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC 8500 in the temperature range of 300–440 K in the case of no doped $P(VDF-TrFE)$ film and from 300 to 405 K in the case of the samples doped with GO with a scan rate of 5 $\text{deg} \cdot \text{min}^{-1}$.

The complex electric permittivity, $\varepsilon^* = \varepsilon\prime + i\varepsilon''$, was measured using an E4980A Precision LCR Meter within the frequency range of 20 Hz–2 MHz and in the temperature range of 260–400 K. Each sample was the piece of foil of 70 μm thickness with the Al electrodes sputtered of the area of 78.5 mm^2. The overall error for the real and imaginary parts of the complex electric permittivity was less than 5% and 10%, respectively.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 presents the results of the thermogravimetric measurements for all films in the full temperature range, i.e. from room temperature to 900 K. Since the phase transitions in the lower temperature region observed in DTA are much less pronounced than the energetic effect associated to the decomposition of the films the temperature range up to 600 K is in different scale than the rest of the graph.

It is worth noting that all the measured compounds decompose completely to the gaseous products reaching the final temperature of 900 K. Generally speaking the thermogravimetric behavior of the PG00 is typical for $P(VDF-TrFE)$, see for example that recorded by Erh-Chiang Chen and Tzong-Ming Wu [35]. Another interesting feature of the films is the existence of the exoenergetic peak taking place just above the melting temperature. This peak is associated with the mass loss and, since it is not observed for PGO00, must correspond to the reaction of part of GO leading to the gaseous products. This feature is related to the decomposition of oxygen containing groups in the GO, which are CO_2 and H_2O [36].

In order to check the thermal behavior of the pristine GO TGA analysis was also performed and is presented in Fig. 2. One may observe just one exothermic thermal anomaly related to detaching the oxygen containing particles, as mentioned above. It is worth of note that the exothermic peak appears at the same temperature as in the $P(VDF-TrFE)$ doped with GO films. One may observe one difference on TGA scans of GO and other samples, which is the higher stability of graphene oxide than polymer samples. In the case of GO sample there still remains about 40% of initial mass even at 1200 K whereas GO doped polymers decompose to gaseous products almost completely already at 900 K. The different behavior of bulk GO and incorporated into $P(VDF-TrFE)$ is most probably due to higher granularity of GO in $P(VDF-TrFE)$. It should be emphasized that the thermogravimetric measurements' result of pristine GO is identical to those presented in literature [37,38].

The endoenergetic thermal anomalies observed at lower temperatures than that mentioned above point at the phase transitions (PTs) – the ferro–paraelectric one and then melting of the film. The temperature of melting of the film is almost constant and does not depend on the content of GO. In order to perform the detailed analysis of ferro–paraelectric phase transition the temperature dependence on amount of GO DSC measurements were carried out. The results are presented in Fig. 3. Since the decomposition process in the doped films starts just after the melting the liquid phase was reached only in pristine $P(VDF-TrFE)$. In all the cases the thermal anomalies on heating are very diffused therefore determining the phase transition temperature as well as the heat of each transformation was difficult and unreliable. That is why the heating scans are presented only for the no doped and 5% doped samples. The cooling scans are showed for all films and the parameters of the phase transitions (T and Δ H) are collected in Table 1. Note that the temperature of the phase transition is taken from the onset (i.e. the temperature where the change of energetic anomaly is the biggest) on cooling scans. Thus it is representative for the higher temperature thermal anomaly i.e. the higher temperature PT. The presented Δ H is the sum of enthalpies of both PTs on cooling runs as well.

It is clearly visible that the lower temperature PT does not shift with increasing of GO amount beside the pure $P(VDF-TrFE)$ whose phase transition takes place ca. 12° lower than those in the doped films. It should be noted that the PT is manifested by two peaks what indicates the presence of either some intermediate phase or two ferroelectric phases with different arrangements as suggested by Tanaka et al. [40]. Subsequent studies of Gregorio Jr. and Botta [39] carried out by means of XRD measurements suggest an existence of two ferroelectric phases as the origin of double peak observed in the DSC technique. It should be added that the properties depends on the crystallization temperature, especially