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# Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

# Improved electroactive phase content and dielectric properties of flexible PVDF nanocomposite films filled with Au- and Cu-doped graphene oxide hybrid nanofiller

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## ARTICLE INFO

Article history: Received 26 July 2016 Received in revised form 10 August 2016 Accepted 12 August 2016 Available online 21 August 2016

Keywords: Poly(vinylidene fluoride) Graphene oxide Copper nanoparticles Gold nanoparticles Electroactive phase Dielectric constant Dielectric loss

#### ABSTRACT

In the present work, new and flexible poly(vinylidene fluoride) (PVDF) based nanocomposites containing Au- and Cu-doped graphene oxide (GO/Au and GO/Cu) nanosheets were prepared by solution casting. The resulting nanocomposites present a high content of electroactive phases and high dielectric constant accompanied with low dielectric loss which make them interesting for possible applications in sensors and electronic devices. Fourier transformed infrared spectroscopy (FTIR) was used to study the crystalline structure of nanocomposites which showed no absorption band related to non-polar  $\alpha$  phase. FTIR confirmed an enhancement of the electroactive phase with the increase in nanofiller concentration due to the electrostatic interactions among the CH<sub>2</sub>-CF<sub>2</sub> dipoles of PVDF and nanofiller. Electroactive phase content as calculated from FTIR spectra presented a maximum value of about 95% for PVDF filled with 1% GO/Au nanofiller. This value is about 2.5 times higher than that of neat PVDF. For a given filler concentration, nanocomposites filled with GO/Au showed a higher increase of electroactive phase in comparison with those containing GO/Cu. This trend was also confirmed by X-ray diffraction (XRD) spectra. From inductance, capacitance, and resistance (LCR) measurement, nanocomposites display high dielectric constant, increasing with the nanofiller content, and low dielectric loss which is favorable to fabricate flexible and simple high performance nanodielectric materials.

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## 1. Introduction

The most well-known ferroelectric polymer, poly(vinylidene fluoride) (PVDF) has attracted increasing attention due to its amazing electroactive properties such as piezoelectricity and pyroelectricity [1–3]. Due to these properties combined with its low cost, ease of processing and flexibility, applications of PVDF have been increased enormously in various fields such as sensors and actuators [4–7]. However, PVDF exhibits piezoelectric properties only in its  $\beta$  and  $\gamma$  electroactive polar crystalline phases as compared to the nonpolar  $\alpha$ -phase. In fact, PVDF is a thermoplastic semicrystaline polymer that can crystallize in four different phases;  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  depending on the macromolecular chain conformations. Among these phases,  $\beta$  and  $\gamma$  phases play a special role due to their peculiar piezoelectric properties, although

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http://dx.doi.org/10.1016/j.synthmet.2016.08.008 0379-6779/© 2016 Elsevier B.V. All rights reserved. the  $\beta$  phase is more polar than the  $\gamma$  phase. Unfortunately, the more common form of PVDF crystals is the nonpolar  $\alpha$  phase, because it is thermodynamically more stable in PVDF than the other phases and it is therefore relatively easy to obtain  $\alpha$  phase dominant PVDF films. The polar phases cannot naturally form although the  $\gamma$  phase is more thermodynamically stable than the  $\beta$  phase. However, the nonpolar phase can be converted into polar phases [8–10]. As a consequence, so far numerous research works have published on the possible methods to transform nonpolar phase to polar phases in PVDF, including mechanical stretching, polarization, electrospinning and several others [11,12]. However, these methods have obvious limitations that make them undesirable to prepare cost effective material especially at a large production scale.

In more recent years, another possible approach to induce electroactive phases in PVDF based on the dispersion of proper nanofillers in the polymer matrix has been investigated [13]. In particular, much attention has been paid to increase the amount of electroactive phases by the addition of carbonaceous nanofillers





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such as carbon nanotube (CNT), graphene, graphene oxide (GO), reduced graphene oxide (rGO), etc. [14–16].

PVDF possesses outstanding dielectric properties that makes it a material having great potential for applications in MEMS devices and in high charge-storage capacitors [17]. For PVDF polymer to be employed as a functional material in these fields, it is required an enhancement of its dielectric constant. Dielectric constant can be enhanced by adding high dielectric permittivity ferroelectric ceramics such as BaTiO<sub>3</sub> [18,19], but the resulting material suffers from low flexibility, and poor mechanical performance [20]. The best way to increase the dielectric constant along with preserving its mechanical flexibility is by adding a conductive nanofiller, especially carbon based nanomaterial to the polymer matrix [21]. The dielectric constant of composites can be significantly improved by adding only a small amount of expanded graphite nanoplatelets (xGnP) and rGO as reported in literature [22,23]. However, the enhanced dielectric constant of these composite is simultaneously accompanied with high dielectric loss, which is not desirable for practical applications. Some research works have been reported on the enhancement of dielectric constant with low dielectric loss by adding carbon based filler to PVDF matrix [21,24] but the electroactive properties of PVDF, which is the most important property of PVDF, has not been considered in those reports. From a practical point of view, to preserve the applications of PVDF, it is important to consider both the electroactive and dielectric properties. Yang et al. [20] investigated the effect of TiO<sub>2</sub>/ multiwalled carbon nanotubes (MWCNT) on ferroelectric and dielectric properties of PVDF, but only 3% change in polar phase content was reported.

In this study we report new, flexible, low cost and light weight GO/Au-PVDF and GO/Cu-PVDF nanocomposites having high content of electroactive phase and high dielectric constant along with low dielectric loss, which were prepared through a simple solution casting method. Graphene oxide have been chosen as a filler due to its high surface area and aspect ratio and its versatile functionality attributed to the different attached functional groups [25]. Since GO is an electrically insulating material, due to its disrupted sp<sup>2</sup> bonding networks, two different metal nanoparticles, Au and Cu, separately have been attached on GO surface to increase the electrical conductivity of the filler. These nanofillers were added to PVDF matrix at various concentrations. The microstructure, electroactive and dielectric properties of nanocomposites were investigated and the effect of the two nanofillers was compared. Since the electroactive properties of PVDF mainly depend on the crystalline structure of the polymer, the effects of the selected nanofillers on crystallization process and crystallinity of the samples were also investigated.

# 2. Experimental

### 2.1. Materials and sample preparation

All chemicals and solvents were purchased from Merck and Sigma Aldrich and were used without further purification. Synthesis of graphene oxide, Au nanoparticles and Cu nanoparticles and also the preparation of nanofillers (GO/Au and GO/ Cu) used in present work have been described in detail in our previous works [26,27]. In the present work, GO/Cu was dispersed in *N*,*N*-dimethylformamide (DMF) using ultrasonication for 60 min. Separately PVDF was dissolved in DMF with a mass ratio of 10/90 and stirred for 3 h to obtain a homogeneous and transparent solution. The PVDF solution was then mixed with the GO/Cu solution and the resulting solution was kept under ultrasonication for 1 h. Afterwards, the well dispersed solution was poured onto Petri dish and kept in an oven at 120 °C for 2 h for a complete removal of the solvent. Finally, dried GO/Cu-PVDF nanocomposite films were obtained. GO/Au-PVDF nanocomposite films were prepared in the same way. Likewise, composite films with different GO/Cu and GO/Au loading (0.5, 1.0 and 5.0 wt.%) were prepared and coded as 0.5GO/Cu-PVDF, 1.0GO/Cu-PVDF, 5.0GO/Cu-PVDF, 0.5GO/Au-PVDF, 1.0GO/Au-PVDF and 5.0GO/Au-PVDF, respectively.

#### 2.2. Testing methods

The chemical information and modifications have been assessed by FT-IR (Fourier transformed infrared) spectroscopy. Measurements were carried out using Varian 4100 FTIR (Excalibur series) in transmittance mode with a resolution of  $4 \text{ cm}^{-1}$  and spectra wavenumber range between 4000 and 500 cm<sup>-1</sup>.

X-ray diffraction (XRD) data were acquired by an Italstructures IPD3000 instrument equipped with a multilayer monochromator. Spectra were collected by means of an Inel CPS120 detector over the omega + 120° two-theta range. Different incidence angles were tested to maximize the signal coming from the deposition layer, with a final choice of 1°; acquisition time was 1800 s per diffractogram.

Differential scanning calorimetry (DSC) analysis was performed by a Mettler DSC 30 calorimeter. All experiments were performed at a heating rate of  $10 \,^{\circ}$ C/min under a constant nitrogen flux of 100 mL/min maintained during the tests in the temperature range from 0 to 200  $^{\circ}$ C.

Thermogravimetric analysis (TGA) was performed with a Mettler TG 50 thermobalance in the temperature range from 25 up to 750 °C at a heating rate of 10 °C/min under a of nitrogen flux of 100 mL/min.

The morphology of films was investigated by field emission scanning electron microscopy (FESEM) with a Zeiss SUPRA 40 microscope. A layer of platinum and gold was deposited on samples prior to FESEM observations.

The measurement of relative permittivity and dielectric loss of the nanocomposite film were performed by an Agilent 4284A impedance analyzer in the frequency range from 20 up to  $10^{6}$  Hz.

#### 3. Results and discussion

### 3.1. Fourier transformed infrared spectroscopy

FTIR spectroscopy provides information about the structure of PVDF matrix that enables us to distinguish between the various possible crystalline forms. FTIR spectra of PVDF and related nanocomposites are reported in Fig. 1. In the FTIR spectrum of neat PVDF, the peaks located at  $530 \text{ cm}^{-1}$ ,  $615 \text{ cm}^{-1}$ ,  $763 \text{ cm}^{-1}$ ,  $795 \text{ cm}^{-1}$ , and  $975 \text{ cm}^{-1}$  represent the characteristic bands of the  $\alpha$  phase, the absorption band at  $510 \text{ cm}^{-1}$  is related to  $\beta$  phase and the peak at  $838 \text{ cm}^{-1}$  is associated to  $\gamma$  phase [5,8]. The peaks in the range  $833 - 840 \text{ cm}^{-1}$  can be related to both  $\beta$  and  $\gamma$  phase and is often difficult to distinguish. As both of these phases correspond to the polar electroactive phases of PVDF, for simplicity, it can be considered as a single polar phase [14]. However, in the present work the combination information coming from XRD analysis allowed used to establish that they are related to the  $\gamma$  phase. The peaks at 873, 1066 and 1163 cm<sup>-1</sup> are not reported in the literature.

In PVDF films loaded with GO/Au nanofillers whose FTIR spectra are reported in Fig. 1a, all characteristic bands related to  $\alpha$ -phase completely disappear and the absorption intensity of peaks related to  $\gamma$  phase increase. Moreover, also a new peak at 1232 cm<sup>-1</sup> related to  $\gamma$  phase appears. These results reveal that the addition of GO/Au nanoparticles to PVDF can induce a transition from nonpolar  $\alpha$ -phase to polar  $\gamma$  phase. In fact, none of the characteristic  $\alpha$ -phase absorption bands can be observed in the GO/Au-PVDF nanocomposite films. A decrease of the the intensity



Fig. 1. FTIR spectra of pure PVDF and PVDF nanocomposite containing various amounts of (a) GO/Au and (b) GO/Cu nanofillers.

of all peaks of 5.0GO/Au-PVDF is related to an increase in the thickness and opacity of nanocomposite films at the maximum percentage of nanofiller loading and does not reflect changes in the crystalline structure of PVDF.

FTIR spectra of GO/Cu-PVDF nanocomposites are shown in Fig. 1b. For low filler concentration, no appreciable changes have been found for absorption intensity of nonpolar  $\alpha$  phase of nanocomposites as compared to neat PVDF spectrum. Increasing nanofiller loading led to a conversion of the nonpolar  $\alpha$  phase to  $\gamma$ electroactive phase. In fact, the 5.0GO/Cu-PVDF nanocomposite exhibited predominantly the polar phase as documented by a peak centered at  $\sim$ 838 cm<sup>-1</sup>. Compared with the GO/Cu nanoparticles, GO/Au nanoparticles show a higher efficiency in promoting the polar phase at the same amount of nanofiller. The transformation of  $\alpha$  phase into electroactive  $\gamma$  phase can be explained by the electrostatic interactions between surface charge of nanofillers and CF<sub>2</sub> dipoles of PVDF. Indeed, due to the presence of charge dissimilarity in the surface of nanofillers, some CH<sub>2</sub>-CF<sub>2</sub> dipoles are attracted and some of them are repelled, that results in the formation of  $\gamma$  phase. It may be also possible that, the functional groups presents in GO/Au and GO/Cu can interact with the F and H atoms of PVDF via hydrogen bonding [8,14].

FTIR spectroscopy can also be used to determine the relative amount of  $\gamma$  phase using the following equation [5,28]:

$$F(\gamma) = \frac{A_{\gamma}}{(K_{\gamma}/K_{\alpha})A_{\alpha} + A_{\gamma}}$$
(1)

where  $A_{\alpha}$  and  $A_{\gamma}$  are the absorbance at 763 cm<sup>-1</sup> ( $\alpha$ -form) and 838 cm<sup>-1</sup> ( $\gamma$ -form),  $K_{\alpha}$  and  $K_{\gamma}$  are the absorption coefficient at the respective wavenumbers, with the value of 0.365 and 0.150  $\mu$ m<sup>-1</sup>. Using Eq. (1), the  $\gamma$  phase content of the nanocomposites were calculated. The relative  $\gamma$  phase content of neat PVDF was 41%. For GO/Cu-PVDF nanocomposites, this amount increased to reach a maximum of  $\approx$ 95% for nanocomposite loaded with 0.5% and 1.0% GO/Au. Also, in nanocomposite filled with GO/Cu,  $\gamma$ -phase content was calculated to be 66% and 90% for 5.0GO/Cu-PVDF and PVDF-1% GO/Cu respectively. This increase of polar phase due to such low filler loading has not been reported yet in literature.

## 3.2. X-ray diffraction

The XRD patterns of neat PVDF and PVDF nanocomposite films are reported in Fig. 2. The peaks of neat PVDF appear at 2 $\theta$  of  $\approx$  17.8°, 18.4°, 19.93° and 26.9° which correspond to the diffraction



Fig. 2. X-ray diffraction patterns of neat PVDF and PVDF nanocomposites containing various amounts of (a) GO/Au and (b) GO/Cu nanofillers.

planes of (100), (020), (110) and (021) generally attributed to nonpolar  $\alpha$  phase [5]. These indicate that  $\alpha$  phase is predominantly formed during the crystallization process of neat PVDF. From Fig. 2a it can be seen that by adding GO/Au nanoparticles to PVDF, two diffraction peaks at  $2\theta$  of  $\approx 17.8^\circ$ ,  $18.4^\circ$ , related to  $\alpha$  phase, completely disappear and a single peak at 20.6° is seen, which corresponds to the diffraction from (100) plane indicating the stabilization of polar  $\gamma$  phase in the nanocomposite. All  $\alpha$ ,  $\beta$  or  $\gamma$ phases have an intense peak around 20°, thus it is difficult to distinguish from each other by only XRD analysis. In general, the  $\beta$ phase can be characterized by the presence of only one peak at 20° in the whole XRD spectra [5]. The combination of XRD result with FTIR technique (explained in previous section) confirms the remarkable transformation of nonpolar  $\alpha$  phase to polar electroactive  $\gamma$  phase induced by the addition of GO/Au to the PVDF and also indicates a good interaction between nanofiller and matrix. The peaks at  $2\theta$  values of  $38.1^{\circ}$  (111),  $44.3^{\circ}$  (200),  $64.5^{\circ}$  (220),  $77.5^{\circ}$ (311) and 81.7° (222), that are observable only in 5.0GO/Au-PVDF spectrum, are consistent with the standard XRD data for Au (JCPDS 89-3697). From Fig. 2b, by increasing Cu/GO amount in the nanocomposite, the peak intensity of the nonpolar  $\alpha$  phase (at  $\approx$ 17.6 and 26.6°) gradually decreases and finally in nanocomposite with 5.0% nanofiller, these two peaks completely disappear. Also the peak at 19.93°, which is related to the  $\gamma$  phase, shifted to 20.4°. The peaks of Fig. 2b located at 36.2°, 42.6° and 61.7° are attributed to copper oxide [29].

By comparing Fig. 2a and b, it can be seen that in PVDF nanocomposite films filled with GO/Au nanoparticles, even by the inclusion of 0.5 wt.% of nanofiller, significant changes in the crystal structure of the polymer phase can be observed while these changes are less pronounced in GO/Cu-PVDF nanocomposite films.

## 3.3. Differential scanning calorimetry

As mentioned, the electroactive property of PVDF strongly depends on the crystalline structure of the polymer, as well as on the electroactive polar phase formation in the nanocomposite [8]. Hence, the crystallization process of the neat PVDF and GO/Au- and GO/Cu-PVDF nanocomposite films was also investigated by DSC. The DSC thermograms under heating and cooling conditions of neat PVDF and its nanocomposites are presented in Fig. 3. The crystallinity content ( $X_c$ ) of samples was calculated using the

#### Table 1

 $T_m$ ,  $T_c$  and  $X_c$  values of PVDF and GO/Au-PVDF and GO/Cu-PVDF nanocomposite film at different nanofiller loadings.

Sample	T <sub>m</sub> (°C)	$T_c(^{\circ}C)$	$X_{c}(%)$
Neat PVDF	161.1	130.0	58
0.5GO/Au-PVDF	166.3	131.3	56
1.0GO/Au-PVDF	167.5	132.5	52
5.0GO/Au-PVDF	166.3	133.0	52
0.5GO/Cu-PVDF	161.0	130.5	55
1.0GO/Cu-PVDF	161.0	130.7	52
5.0GO/Cu-PVDF	164.7	131.5	53

following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 \times \omega} \times 100 \tag{2}$$

Where,  $\Delta H_m$  is the melting enthalpy of the nanocomposite,  $\Delta H_m^0$  is the melting enthalpy of the 100% crystalline PVDF (104.7 J/g [13])



**Fig. 4.** TGA thermograms of neat PVDF and relative nanocomposites with various amounts of GO/Au and GO/Cu nanoparticles.



Fig. 3. DSC thermograms under (a) heating and (b) cooling conditions of pure PVDF, GO/Au-PVDF and GO/Cu-PVDF nanocomposite films at different nanofiller loading.

and  $\omega$  is the weight fraction of PVDF in the nanocomposites [13].  $X_c$ values are listed in Table 1 along with the melting temperature  $(T_m)$ and crystallization temperature  $(T_c)$ . It can be seen that the melting temperature and crystallization temperature gradually shifted to higher temperature in the nanocomposites by the increase of filler loading. This is related to well-dispersed nanofillers in the polymer matrix that acts as nucleating agent and inhibits the movement of polymer chain segments, resulting in improvement of the crystallization temperature of nanocomposite films. Moreover, it is observed that by adding GO/Au and GO/Cu, no remarkable changes in the crystallinity percentage of PVDF was observed. These observations indicate that the addition of nanofiller has little influence on the crystallization process of PVDF. Furthermore, electroactive properties of the PVDF depend on promotion of polar crystalline phases (i.e.  $\beta$  and  $\gamma$  phases) in polymer matrix. By addition of nanofillers, the relative percentage of  $\gamma$  phase in PVDF progressively increases, and a maximum extent of  $\gamma$  phase formation was achieved at 1.0 wt.% of the GO/Au loading [8].

#### 3.4. Thermogravimetric analysis

TGA was performed to investigate the thermal stability of the neat PVDF and PVDF nanocomposites and the related thermograms are reported in Fig. 4. As evidenced in the figure, a major weight loss occurs in the range from 450 °C to 550 °C which can be ascribed to the degradation of PVDF matrix. The onset degradation temperature, Tonset, was 490 °C for neat PVDF, while the introduction of the nanofillers slightly increased the onset degradation temperature. In case of 0.5GO/Cu-PVDF, 1.0GO/Cu-PVDF and 5.0GO/Cu-PVDF, the degradation temperature onset shifted to 491, 496 and 492 °C respectively, while the degradation temperatures for nanocomposite containing GO/Cu were found to be 494 °C, 499 °C and 501 °C for nanocomposites filled with 0.5, 1.0% wt and 5.0% wt. respectively. The enhancement of thermal stability can be explained by the better packing of the polar crystallites in PVDF composites compared to the non-polar  $\alpha$  phase of neat PVDF. Moreover, the interaction between the nanofiller and PVDF may



Fig. 5. SEM observations on the cross section of (a) neat PVDF, (b) 0.5GO/Au-PVDF, (c) 1.0GO/Au-PVDF, (d) 5.0GO/Au-PVDF e) 0.5GO/Cu-PVDF, (f) 1.0GO/Cu-PVDF and (g) 5.0GO/Cu-PVDF.

result in the enhancement of the thermal stability of nanocomposites compared to neat PVDF [30].

## 3.5. Scanning electron microscopy

The fracture surfaces of GO/Au- and GO/Cu-PVDF nanocomposite films were analyzed using field emission scanning electron microscopy. Fig. 5 reveals the fracture surfaces of the neat PVDF and respective GO/Au and GO/Cu nanocomposite films. It is interesting to note that in case of GO/Au-PVDF films (Fig. 5b–d), the nanofiller cannot be visualized thus indicating a good adhesion level between matrix and the filler. On the contrary, PVDF and GO/ Cu have poor adhesion between each other (Fig. 5e–g).

### 3.6. Dielectric properties

Plots of relative permittivity (commonly known as dielectric constant) of the neat PVDF and PVDF nanocomposites measured at room temperature in a frequency range between 10<sup>2</sup> and 10<sup>6</sup> Hz are shown in Fig. 6a and b. As it can be seen in Fig. 6a, a remarkable improvement in relative permittivity in comparison to neat PVDF is observed even when only 0.5% wt of GO/Au nanoparticles are added to PVDF. It is worthwhile to observe that the increase of the dielectric constant values is proportional to the filler content. In

fact, the dielectric constant measured at  $10^3$  Hz increases from about 5 (neat PVDF) to about 23 for 0.5GO/Au-PVDF, to about 31 for 1.0GO/Au-PVDF, to about 39 for 5.0GO/Au-PVDF nanocomposites. A similar behaviour can be observed in Fig. 6b for the dielectric constant of nanocomposite thin films with 0.5, 1.0 and 5.0% wt. of GO/Cu nanoparticles. In this case, at a frequency of  $10^3$  Hz the dielectric constant of neat PVFD is increased to about 12 for 0.5GO/ Cu-PVDF, to about 27 for 1.0GO/Cu-PVDF, to about 45 for 5.0GO/Cu-PVDF nanocomposites. The observed behaviour is consistent with what previously observed by He et al. on the effect of graphene oxide on the relative permittivity of PVDF nanocomposites films obtained using solvent *N*,*N*-Dimethylformamide (DMF) and cosolvent comprising deionized water/DMF combination [31].

In general, an increment of relative permittivity may occur for several reasons. One of them is the formation of a network of micro-capacitors in the nanocomposite due to the presence of nanofillers. This mechanisms has been reported by He et al. in a study on the effect of expanded graphite nanoparticles (xGnP) on the dielectric permittivity of PVDF nanocomposites [23]. In fact, when GO/Au and GO/Cu nanofillers are incorporated into the PVDF matrix, they could play the role of micro-capacitors thus resulting in an overall increase of the dielectric constant of the nanocomposites with respect of that of neat PVDF.

Another possible mechanisms responsible for the observed increase of the dielectric constant in nanocomposites could be the



Fig. 6. Frequency dependence of dielectric constant and dielectric loss tangent (tan  $\delta$ ) of pure PVDF and nanoocomposites with various amount of a, c) GO/Au and b, d) GO/Cu.

Maxwell-Wagner-Sillars (MWS) polarization effect, often observed in heterogeneous systems [19,32]. In fact, the MWS effect, which is associated to an entrapment of free charges at an interface between two heterogeneous materials, can significantly enhance the permittivity. This effect has been frequently observed in composites filled with a conductive filler and it has been previously reported also for PVDF nanocomposites filled with carbon nanofibers [33], graphene [21,24] and nano silver-anchored reduced graphene oxide sheets [34]. The MWS effect is generally characterized by a frequency dependence of the dielectric constant, particularly in the low-frequency range where interfacial polarization effects are more intense [23]. In addition, polymorphism of PVDF may also play a remarkable effect on the dielectric constant. In fact, it is well known that  $\beta$ - and  $\gamma$ -phases of PVDF manifest the largest spontaneous polarization [35]. Therefore, part of the observed effects could be attributed to the ability of GO/Au and GO/Cu nanofillers to promote the formation of electroactive phases in PVDF, as discussed in previous sections.

Fig. 6c and d shows the changes of dielectric loss of neat PVDF and PVDF nanocomposites with frequency in a range between  $10^2$ and  $10^6$  Hz at room temperature. The dielectric loss is a measurement of the energy dissipation from the movement or rotation of the molecules in the alternating electric field. It is interesting to observe how for all the investigated nanocomposites the dielectric losses are suppressed in the low frequency range with respect to neat PVDF. Thus, these nanocomposites show relatively high dielectric constant with relatively low loss at low frequency range (below 10 KHz) which is basically the requirement of a material for its usage in devices for the energy storage.

## 4. Conclusions

A simple solution casting method was used to prepare new and flexible PVDF nanocomposite films filled with GO/Au and GO/Cu nanofillers. The electrical interaction between charged surface of the nanofiller and CH<sub>2</sub>-CF<sub>2</sub> groups of the PVDF chains was responsible for the formation of the electroactive  $\gamma$ -phase. Nanocomposites filled with GO/Au showed higher increase in amount of polar phase compared to GO/Cu in same concentration. Dielectric measurement showed that by increasing nanofiller loading nanocomposites showed the higher dielectric constant compared to the neat PVDF accompanied with low dielectric loss. Maximum dielectric constant was achieved for 5.0GO/Cu-PVDF nanocomposite which is about 9 times greater than that for neat PVDF at 10<sup>3</sup> Hz. All these results suggest that the PVDF nanocomposites containing GO/Au and GO/Cu are promising candidates for the preparation of high performance flexible nano-dielectric materials used in electronic and electric industry.

#### Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## Acknowledgements

Parisa Fakhri gratefully acknowledges Bu-Ali Sina University for the scholarship that partly supported her stay at the University of Trento.

The support of prof. Gian Franco Dalla Betta for the measurement of dielectric properties is kindly acknowledged.

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