Preparation, Characterization, Thermal and Electrical Conductivity Properties of PVDF Composites

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Abstract- Using PVDF and ZrO_2, polymer composites were prepared by sol gel method. Various measurements such as X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Differential Scanning Calorimetry (DSC) were used to characterize the composites. Thermal and electrical properties of the composite samples were studied. The conductivity of composites was found to increase with increase in temperature as well as with zirconia content. As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion.

Index Terms- PVDF; ZrO_2; T_g; conductivity; composites

I. INTRODUCTION

PVDF is a polar polymer with excellent chemical, mechanical and electrical properties [1-4]. It's strong piezoelectric response, chemical and mechanical durability make it a valuable material for sensors and actuators. Piezoelectrics are a class of materials that can transfer mechanical energy to electrical energy and vice versa. The piezoelectric effect consists of a linear coupling between an applied electric field and an induced strain. The response of the material is proportional to the electric field or change in dimension. This predictable material property is extremely valuable in sensing and actuation [5,6]. Zirconia (ZrO_2) is an oxide which has a high tensile strength, high hardness and corrosion resistance. Zirconia based ceramics are routinely used in structural applications in engineering, such as manufacture of cutting tools, gas sensors, refractories and structural opacifiers [7]. The properties of the polymers and the ceramics could be exploited in the corrosion and gas sensing studies. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures. Conductivity studies of $PVDF/TiO_2$ has been reported [8]. Multiwalled carbon nanotube/poly(vinylidene fluoride) (MWCNT/PVDF) composites dielectric properties were studied [9]. In the present study, $PVDF/ZrO_2$ composite was prepared, thermal and electrical properties of composites were studied.

II. EXPERIMENTAL

2.1 Preparation of PVDZr Composites

A definite quantity of PVDF was dissolved in dimethyl formamide followed by the addition of a known quantity of ZrO_2 and then it was made into a paste in an agate mortar and was subjected to heat at 80 °C for 30 minutes in a hot air oven and made into a powder. PVDZr composites were prepared in the following proportions of PVDF and ZrO_2: PVDZr 1 – 9:1, PVDZr 2 – 8:2, PVDZr 3 - 7:3, PVDZr 4 -6:4, PVDZr 5 – 5:5 and PVDZr 6 – 4:6.

2.2 Characterisation Techniques

XRD patterns of PVDF, ZrO_2 and PVDZr composites were recorded using Philips X'PERT PRO diffractometer with Cu Kα (λ= 1.54060 Å) incident radiation. The peaks were recorded in the 2θ range of 20°–80°. The SEM images of polymer and polymer composites were recorded using Hitachi Scanning Electron Microscope SU1510. The samples were gold plated before SEM observation. The DSC scans of polymer composite samples were carried out only to measure glass transition temperature (T_g). The DSC plots of polymers and polymer composites were recorded using METTLER-TOLEDO DSC1. The electrical conductivity of composites were measured using Hioki 3522-50 LCR Meter. Testing temperature ranged from 30 to 60 °C at frequency ranging from 50 Hz to 5 MHz. The measured conductance G, from 50 Hz to 5 MHz is used to calculate ac conductivity, $\sigma_{(ac)}$ using the following expression:

$$\sigma_{(ac)} = G \, d/A \qquad\qquad (1)$$

where d is the thickness of the sample and A is the cross sectional area of the electrode.

III. RESULTS AND DISCUSSION

3.1 XRD

The XRD pattern of pure PVDF has monoclinic structure. The peak positions (2θ = 18.48 (0 2 0), 20.18 (1 1 0), 26.60 (0 2 2), 34.91 (1 3 1), 38.81 (0 4 1) and 41.41° (2 2 1) and relative intensitites obtained for the polymer match with the JCPDS Card no. 38-1638 file, identifying it as PVDF with monoclinic structure with β phase Fig.1(a). The average crystallite size is found to be 0.1549 µm. The peak positions (2θ = 30.26 (0 1 1), 34.81 (0 1 1), 34.81 (0 0 2), 43.13 (0 1 2), 50.70 (0 2 0), 60.20 (1 2 1) and 74.53° (2 2 0) and relative intensitites obtained for ZrO_2 match with the JCPDS Card no. 50-1089 file, identifying it as ZrO_2 with tetragonal phase (Fig.1(b)). The average crystallite size is found to be 0.1756 µm. As the ZrO_2 content increases, the characteristic composite peaks at 30.26, 50.37, 50.70, 60.2 corresponding to the tetragonal phase ZrO_2, are obviously pronounced, and the peaks corresponding to PVDF diminish. The broad peak at region of of 2θ = 15-20°, showing the main crystalline property of PVDF disappears when ZrO_2 content increases. This shows that a small amount of PVDF may exist in the composite samples with higher ZrO_2 content(Fig.1(c) – (e)). The average crystallite size is found to be 0.1367 µm.
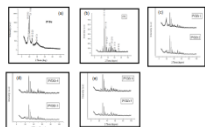
Fig. 3. SEM images of (a) PVDF (b) ZrO$_2$ (c) PVDZr 6

Fig. 1. XRD patterns of (a) PVDF (b) ZrO$_2$ (c) PVDZr 1 and 2 (d) PVDZr 3 and 4 (e) PVDZr 5 and 6

3.2 DSC

The T$_g$ of pure PVDF is found to be 38 °C whereas for PVDZr 1 and PVDZr 6 the values are found to be 35 and 31 °C respectively. The T$_g$ of polymer composites is decreased as compared to pure PVDF as shown in the figure. Probably, the mobility of PVDF chain is not constrained due to PVDF-ZrO$_2$ interaction. This interaction may be related to the dispersion of ZrO$_2$ in PVDF matrix. The incorporation of ZrO$_2$ considerably decreases the T$_g$ which enhances the polymer chain motion and increases volume fraction of the amorphous phase, which obviously increases the ionic transport process. It is also observed that composite with higher ZrO$_2$ content, possess low T$_g$ value. This may be attributed to highest conductivity of PVDZr 6 (Fig.2). It can be concluded that the cermic not only facilitates for ionic conductivity but also interacts with the polymer phase.
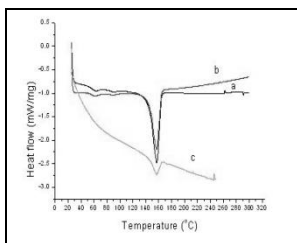

Fig. 2. DSC plots of (a) PVDF (b) PVDZr 1 and (c) PVDZr 6
3.3 SEM

The SEM images of PVDF, ZrO$_2$ and PVDZr 6 is shown in the Fig.3(a) – (c). SEM images reveal the porous nature of polymer composites, which inturn increases conductivity. Incorporation of ZrO$_2$ into the PVDF matrix, reduces the crystallinity and alters the orginial polymer structure and thus the conductivity of polymer composites increases. When the concentration of ceramic oxides are increased, the ceramic oxides are well dispersed and micropores distributed in part in the entire region of surface. It shows that the crystallinity of the composites decreases as the concentration of oxide is increases and it resembles the XRD pattern and also reponsible for higher conductivity. From the micrograph of composites, it can be seen that the addition of ceramic oxides increases the pore size, as a result of higher ionic conductivity [10]. It could be concluded that the presence of homogenous pore structure, leads to ion mobility, hence higher conductivity.
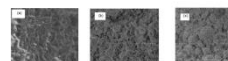
The room temperature AC conductivity and the temperature dependence of PVDZr composites are shown in Table 1. The conductivity increases with ZrO$_2$ content and temperature. The observed enhancement in the room temperature conductivity may be attributed to the incorporation of ZrO$_2$, gives rise to the possible change of chain conformation and it is confirmed by decrease in crystallinity and a relatively higher degree of amorphicity. The presence of higher levels of amorphicity is therefore expected to provide more free volume for the mobility of ions resulting in enhanced conductivity. from the temperature dependent conductivity values obtained for the composites, it is observed that the value of electrical conductivity increases with increasing temperature. This implies that mobile ions would migrate more easily through the conduction path formed by the modified network structure of PVDF chains. As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, inturn, favours hopping inter chain and intra chain movements, and, accordingly, the conductivity of the polymer composites becomes high. At low PVDF content, the semicrystalline nature of the PVDF may be hindered by the addition of higher content of ZrO$_2$, which results in higher segmental mobility in the amorphous phase and hence high ionic conductivity.

Table 1. AC conductivity of PVDF and PVDZr composites at different temperatures

	Conductivity(S/cm)			
System studied	303K	313K	323K	333K
PVDF	5.56X10^{-11}	7.85X10^{-11}	9.05X10^{-11}	3.78X10^{-10}
PVDZr 1	1.23X10^{-10}	1.573X10^{-8}	1.63X10^{-7}	1.12 X10^{-6}
PVDZr 2	2.66X10^{-10}	2.071X10^{-8}	2.57 X10^{-7}	2.01 X10^{-6}
PVDZr 3	3.74X10^{-10}	3.842X10^{-8}	3.22 X10^{-7}	3.85X10^{-6}

PVDZr 4	4.78×10^{-10}	4.979×10^{-8}	4.04×10^{-7}	4.628×10^{-6}
PVDZr 5	5.46×10^{-10}	5.504×10^{-8}	5.68×10^{-7}	5.88×10^{-6}
PVDZr 6	6.95×10^{-10}	6.438×10^{-8}	6.65×10^{-7}	6.68×10^{-6}

IV. CONCLUSIONS

PVDZr composites were prepared by sol gel method. The main crystalline property of PVDF disappears when ZrO_2 content increases. The incorporation of ZrO_2 considerably decreases the T_g which enhances the polymer chain motion and increases volume fraction of the amorphous phase, which obviously increases the ionic transport process.SEM images reveal the porous nature of polymer composites, which inturn increases conductivity. At low PVDF content, the semicrystalline nature of the PVDF may be hindered by the addition of higher content of ZrO_2, which results in higher segmental mobility in the amorphous phase and hence high ionic conductivity.

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