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Polymeric varistor based on PANI/ABS composite

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ABSTRACT

In this work, we present a new class of materials with non-linear electrical behaviour: the Organic Polymeric Varistors. These devices were built using a conducting polymer, polyaniline, and a conventional low-cost dielectric polymer, acrylonitrile–butadiene–styrene copolymer. The apparatus has low-voltage varistor behaviour with a breakdown field of around 10 V, and a non-linear coefficient of 5.0. They also remain stable after several voltage–current cycles and its preparation procedure is easy and inexpensive.

1. Introduction

The manufacturing of high-performance electronic devices with micrometer or sub-micrometer dimensions lead to the necessity of low-voltage varistors to protect these systems against transient overvoltages [1]. Varistors, until now, have been built using ceramic materials, such as SnO_2 or ZnO doped with CoO, NbO_5 [2], TiO_2 [3], V_2O_5 [4], or Bi_2O_3 [5]. They present a non-linear electric behaviour upon polarization, which is attributed to the formation of double Schottky barriers at the grain boundaries [6]. These devices are prepared in a very specific configuration where the conductivity of the grain boundary layer is several orders of magnitude lower than the bulks grain conductivity. Therefore, from a physical view, the nonlinearity in the *I–V* characteristics originates from the *bias* dependence of the grain boundary electrical charge, which controls the barriers height, and the current flow across the junction. The non-linear current–voltage properties of an oxide varistor comes from the formation of a double Schottky barrier, which is described by the empirical relation $J = KE^{\alpha}$, where J is the current density, E is the applied electric field, α is the coefficient of non-linearity and K is the constant of proportionality [7]. Their typical nonlinear coefficient, α value, ranges from 30 to 50, and the electrical field breakdown exceed 100 V mm^{-1} [2]. This last parameter determines the application of the devices. The values described above cannot be used in low voltage applications, such as electronic equipments protection against overvoltage. Therefore, it was necessary to modify these devices in order to decrease the breakdown field. Two different ways of doing this are by increasing the grain size or using different oxide materials, such as TiO_2, WO_3, ZnO or SnO_2 containing small amounts of other metal oxides, such as, Bi_2O_3, CoO, Sb_2O_3 and Cr_2O_3 [8]. Those varistors were reported, in the literature, to present a nonlinear coefficient of 4–7, and breakdown voltage below 15 V mm^{-1} [3].

In general, ceramic varistors are built of n-type semiconductor grains surrounded by insulating electrical barriers at the grain boundary. Important drawbacks on the preparation and usage of these devices include high temperature processing, the use of non-environmentally friendly chemicals, its non-flexible mechanical behaviour and its high density. Thus, to overcome these problems, we present in this study a new class of materials with non-linear electrical behaviour: the Organic Polymeric Varistor (OPV). The OPV, in the present case, has been built using a conducting polymer, polyaniline (PANI), and a conventional low-cost dielectric polymer, acrylonitrile–butadiene–styrene copolymer (ABS). The same reasoning used to build ceramic varistor devices was applied in this work, i.e., the conducting polymeric grains (PANI) were embedded in a dielectric matrix (ABS).

2. Experimental

All reagents used were of analytical grade. All solutions were prepared with deionized and purified water (resistivity 18 MΩ cm^{-1}). Aniline monomer and $(NH_4)_2S_2O_8$ were supplied by Mallinckrodt. DBSA and NH_4OH were purchased from Aldrich and HCl, m-cresol, and chloroform from VETEC. The aniline had to be purified, it was distilled under reduced pressure, before use. The other reagents were used as received.

The PANI emeraldine-salt form (PANI-ES) underwent a chemical oxidative polymerization synthesis in which 6.0 mL of aniline in the presence of an inorganic protonic acid, such as, 1.0 mol/L HCl,

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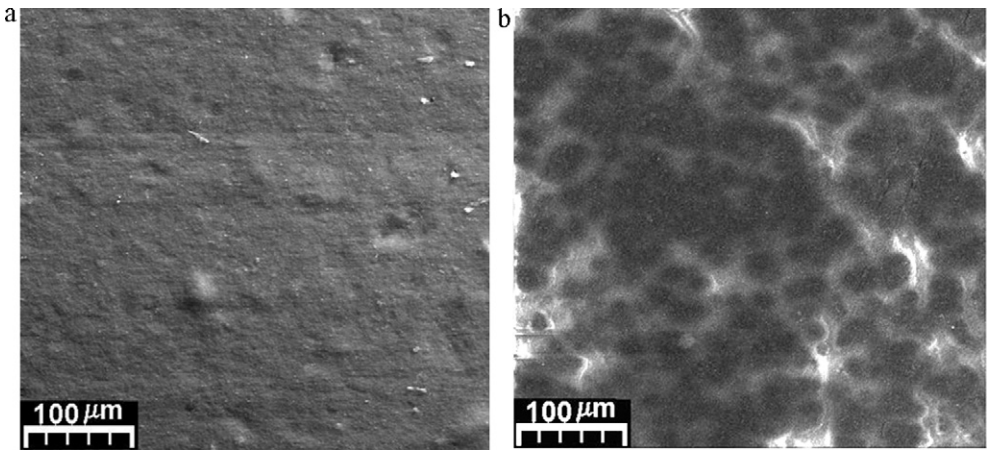

Fig. 1. SEM micrographs of PANI–DBSA/ABS blend (a) and PANI/ABS varistor composite (b), both with 20 wt% of PANI.

was used combined with 3.756 g of $(NH_4)_2S_2O_8$, as an oxidant, at 0 °C. The synthesis was carried out for 2 h with continuous stirring. The PANI emeraldine-base form (PANI-EB), was obtained by stirring the PANI-ES in 0.1 mol/L of NH_4OH aqueous solution for 24 h to obtain a material which can be solubilised in chloroform. Finally, the PANI-EB was filtered and dried under vacuum for 48 h.

The PANI-ES with ABS composite was prepared by dissolving the required amount of ABS into chloroform. PANI-ES particles were added into the solution and stirred together for 4 h until a uniform dispersion of PANI-ES particles was formed in the ABS solution. The PANI amount in the composites changed from 1 to 30% (w/w). The films were casted on a glass plate for a complete solvent evaporation in the ambient condition, and then deployed as a self-sustained film.

We also prepared PANI–DBSA/ABS blends (20% (w/w) in conductive PANI) to compare its electrical behaviour with the PANI-ABS composites behaviour. Details of the synthesis and electrical properties of these blends were reported elsewhere [9,10]. In order to prepare PANI-ABS blends, PANI-EB and ABS were dissolved separately in a mixture of *m*-cresol and chloroform (1:4, v/v) and stirred for 4 h. Afterwards the PANI-EB was doped with dodecylbenzenesulfonic acid (DBSA), and stirred for 2 more hours. When the mixtures were ready the PANI–DBSA and the ABS solutions were mixed together and stirred for 5 h to obtain the blended solution. The films were casted from the solution on a glass plate, and the solvent was left to evaporate at 40 °C for 24 h. Finally, the blended film was detached from the glass plate in order to obtain the self-sustained sample.

The DC polarization experiments of the blends and varistors were performed using a Keithley 2400 source meter and the usual two-probe method. The contacts used were made of thin gold films, deposited on both sides of the samples by sputtering (BOC Edwards, Six Scan Coat), producing a Metal–Polymer–Metal structure. The blend and varistor SEM micrographs were obtained using a Zeiss Supra 35VP microscope. The Fourier transform infrared spectra (FTIR) were recorded from a KBr sample pellet using a Bruker spectrometer, EQUIXOX 55 model. The OPV sample was grounded for this purpose. The samples for the UV–Vis absorption spectra analysis were sampled out of OPV and ABS films. The UV–Vis absorption spectra analysis was recorded using a VARIAN spectrophotometer, CARY model 500.

3. Results and discussion

The varistor device consists of a polymer composite of PANI-ES with ABS. The conductive polymer, PANI-ES, acts as a conductor of particles (or grains) in analogy to conventional ceramic varistors. As described in the experimental section, PANI particles were dispersed in a dielectric polymer matrix of ABS. ABS was chosen because of its mechanical and thermal properties [11,12], and also because it can be recycled. ABS has an additional advantage, its composition ratio among acrylonitrile, butadiene and styrene can be changed and thus lead to different physical and chemical properties. In the present, this polymeric dielectric matrix involves PANI particles. They form a great number of core–shell particles in series where the engineering polymer acts like the grain boundary layer, due to its low conductivity, therefore, providing a series of Schottky barriers between the conductive polymer particles and dielectric polymer [12].

Fig. 1 shows SEM micrographs of the PANI–DBSA/ABS blend (Fig. 1a) and of the OPV composite (Fig. 1b), both of which contain 20% (w/w) of PANI. It is easy to observe that the PANI–DBSA/ABS blend micrograph presents a homogeneous phase. However, the varistor sample shows that PANI grains are loosely packed and distinguishable; in other words, PANI particles are dispersed in the ABS matrix.

Infrared spectroscopy was used to detect the interaction between PANI-ES and ABS. Fig. 2a shows the FTIR-transmittance spectra of PANI-ES, ABS and OVP PANI/ABS with 20% (w/w) PANI. In the PANI-ES spectra it is possible to observe bands at ~1580 cm^{-1} and ~1481 cm^{-1} which correspond to quinoid and benzenoid ring stretching deformations, respectively. The absorption band at 1304 cm^{-1} corresponds to a π-electron delocalization induced in the polymer by protonation [13]. The band at 1235 cm^{-1} is characterized as a conducting protonated form, this band is interpreted as a C–N^{+*} stretching vibration in the polaron structure [14]. The prominent band at 1135 cm^{-1} corresponds to a vibration of the –N^{+*}= structure [15]. The FTIR ABS transmittance spectra were observed between the 3150–300 cm^{-1} and 3000–2840 cm^{-1} range, respectively, the aromatic and aliphatic C–H stretches. The intense and well-defined C≡N stretch from acrylonitrile units at 2238 cm^{-1}, the ring modes of styrene, which are clearly seen at 1600 and 1496 cm^{-1}, and the peaks at 964 and 911 cm^{-1} were taken as a representative of the butadiene component [16]. In the OVP PANI/ABS with 20% (w/w) PANI FTIR spectra solution, an enlargement in all ABS bands was observed. This occurs due to the interaction of PANI-ES with the ABS matrix, in other words, the –NH group of PANI possibly interacts with any of the three components from the ABS matrix. Nevertheless, the C≡N group is the most reactive, this group can interact strongly with –NH of PANI [17]. Fig. 2b shows the UV–Vis absorption spectra of ABS and OVP PANI/ABS with 20% (w/w). ABS practically has no absorption in the 800–400 nm range. In the 400–300 nm range there is an increase in the absorption from the aromatic rings of styrene. In the OVP PANI/ABS with 20%