

The Role of Polypyrrole in Electrical Properties of ZnO-Polymer Composite Varistors

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ABSTRACT: Composite films on the base of ZnO with different weight percentages of polypyrrole have been prepared using the hot pressing method and their current-voltage characteristics have been studied. Results show that the films have nonlinear varistor behavior and can be used to protect sensitive circuits from 110V up to 350V over voltages. It is found that the higher the content of polypyrrole in the varistor, the lower the breakdown voltage. Samples with higher polypyrrole content have less nonlinearity. The interesting result is that, unlike semiconductor-polyaniline based varistors, varistor hysteresis decreases through increasing polypyrrole content. Results have been analyzed with respect to SEM micrographs and XRD patterns of the samples. Energy gaps of varistors are evaluated using their UV spectra analysis regarding Tauc relation, which show that increasing polypyrrole content in varistors causes their absorption to increase and the corresponding band gap to decrease.

KEYWORDS: Composite materials; Polymers; Scanning Electron Microscopy (SEM); X-ray scattering.

INTRODUCTION

Electronic equipment is faced to many hazards from over transient surges which have numerous sources. Among several protection technologies, the most practical one is to use varistors which, nowadays, are widely used in electric and electronic circuits and components as surge protecting devices against lightning or temporary over voltages of unwanted magnitudes [1]. Amongst possible choices, ZnO-based varistors show high nonlinearity when mixed with some other metal oxide additives [2, 3]. The nonlinear electrical behavior of polycrystalline ZnO ceramics make them well suited to protect electronic devices from surges [4]. The exceptional non-Ohmic characteristic in ZnO varistors is attributed to their grain boundaries because there are double schottky barriers between ZnO grains [5, 6].

Present technology is dependent on electrical power; so, there is high demand for manufacturing low-voltage varistors as scaling down electric and electronic equipment. Today, the new varistors -made of a low band gap semiconductor and polymers- have lower breakdown voltage than other varistors [7].

In this experimental work, ZnO varistors are studied as multi-component devices that composed of ZnO as filler and polymer, Polypyrrole and Polyethylene, as matrix. One of the most important semiconductors in protector's area is ZnO with an extra zinc ion at the interstitial site and/or oxygen vacancy as a donor [8]. ZnO is a wide-band gap semiconductor of the II-VI semiconductor group with a direct band gap of 3.437eV [9]. Polypyrrole (Ppy) is an important conducting polymer

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because of its relative ease of synthesis. Ppy has high electrical conductivity and environment stability [10, 11]. Because of low mechanical stability of ZnO- polypyrrole composites, it is inevitable to use a thermoplastic polymer. Polyethylene (PE) is a thermoplastic polymer with appropriate melting point. The role of PE in composite varistors is to increase the stability of the films as well as decrease their leakage current [12]. The aim of this study is to present the effect of polypyrrole amount in varistors, which has yielded some interesting results.

EXPERIMENTAL SECTION

In order to obtain powdered de-doped polypyrrole was synthesized from pyrrole monomer using chemical method we processed according to what follows. FeCl_3 was used as oxidant. The reaction was carried out in aqueous media (water) at 0°C for 3h .1.35gr of FeCl_3 dissolved in 50ml of distilled water and 30 min was placed in 0°C . After 30 min 1 mL of freshly distilled pyrrole was added. The mixture was stirred for 3h at 0°C then the solution was percolated and washed with ethanol. It was dehydrogenated using 2M Ammonia solution (NH_3) for 2h. Final product was dried at 80°C for 24h. Ordinary white powdered PolyEthylene (PE) was used in this experimental work. ZnO powder was ground and dried at 700°C for 3h to lose its dampness and have uniform sized ZnO grains. This way, the size of grains would become appropriate to cause well-behaved nonlinear films. All materials were sifted using a No. 200-mesh sieve so that the size of chosen particles was less than $70\mu\text{m}$. Since polymers do not have unique molar masses, values of ZnO, Ppy and PE were picked up according to their mass percentage. Five ZnO-polymer composite varistors with different weight percentage of each material were prepared as followed:

- 1) No. 1: 20% Ppy – 30% PE– 50% ZnO
- 2) No. 2: 25% Ppy – 25% PE– 50% ZnO
- 3) No. 3: 30% Ppy – 20% PE– 50% ZnO
- 4) No. 4: 35% Ppy – 15% PE– 50% ZnO
- 5) No. 5: 40% Ppy – 10% PE– 50% ZnO

The mixture was admixed in a ball mill for 2h to hand in a uniform mixed powder. Varistors, prepared in disk forms with 10mm diameters and $220\mu\text{m}$ thicknesses, were produced by hot pressing method at a temperature of 130°C and 60MPa pressure. Circulating current was then measured by applying voltage to disks at room

temperature. (I-V) characteristics were measured in a direct current mode. By increasing the voltage up to a voltage higher than the breakdown voltage and decreasing it to zero, it was possible to study the hysteresis of the sample.

Finally, microstructures of samples were analyzed by investigating SEM micrographs (MIRA3 TESCAN system) and X-ray diffractometer (D500 X-ray, Siemens Cu $\text{K}\alpha$ radiation). UV absorption spectra of the varistors were recorded using a PHARMA spectrophotometer, SHIMADZU model 1700. The UV absorption spectra, in the wavelength range of 300-1000 nm, were used to estimate the optical gap of each sample using $(\alpha h\nu)^2$ versus $h\nu$ diagram.

RESULTS AND DISCUSSION

Polymers are not completely flexible; at the length scale below persistence length, the polymer behaves more or less like a rigid rod. Because of its asymmetric chain, polypyrrole is a rigid polymer whose mechanical stability is weak (Fig. 1a). This may be the most important reason to classify polypyrrole as a semiconducting polymer due to probability of electron movement along the polymer chain. Studying (I–V) characteristic of pure dehydrogenated polypyrrole reveals that it has linear current-voltage characteristic and its measured electrical resistance is $\sim 10^3\ \Omega\cdot\text{m}$ (Fig. 2a). So, it can be classified as a semiconductor. This is the main reason of that pure dehydrogenated polypyrrole could be an appropriate choice as a binder which should have high resistivity (10^4 - $10^{10}\ \Omega\cdot\text{m}$) in composite varistors [13]. Polyethylene is a thermoplastic polymer with symmetric chain (Fig. 1b). It has linear current-voltage characteristic with measured electrical resistance of $\sim 90\ \text{M}\Omega\cdot\text{m}$ (Fig. 2b). Therefore, PE is a complete insulator. (I-V) characteristic of pure ZnO film is nearly linear which represents an Ohmic behavior, as well [14].

Despite linear electrical behavior of each component, a pressed disk of the composition of ZnO–Ppy–PE shows nonlinear (I-V) behavior at room temperature. This nonlinearity, which is called varistor nonlinearity, is determined by an electrical resistance of $\sim 36\text{k}\Omega\cdot\text{m}$ at pre breakdown zone which reduces to $0.6\text{k}\Omega\cdot\text{m}$ when the curve reaches upturn zone (Fig. 3).

It is noteworthy that (I-V) characteristics of both zones are linear. At nonlinear zone, current increases

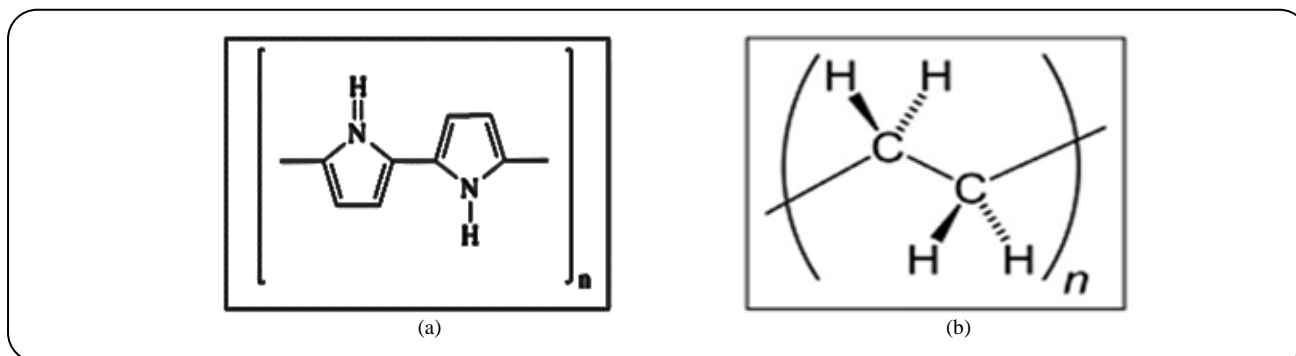


Fig. 1: a) Main polypyrrole structure, b) the repeating unit of polyethylene, showing its stereochemistry.

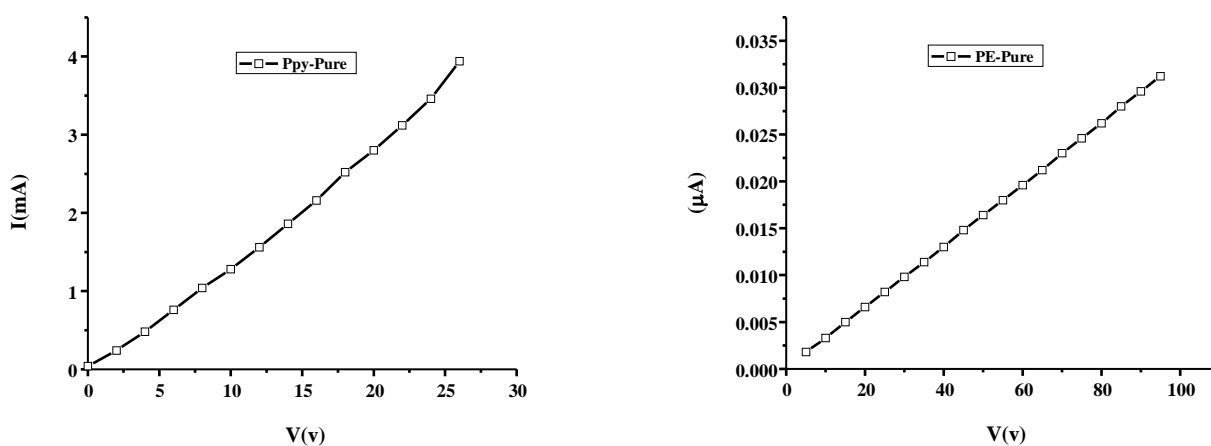


Fig. 2: a) Pure polypyrrole I-V characteristic, b) Pure polyethylene I-V characteristic.

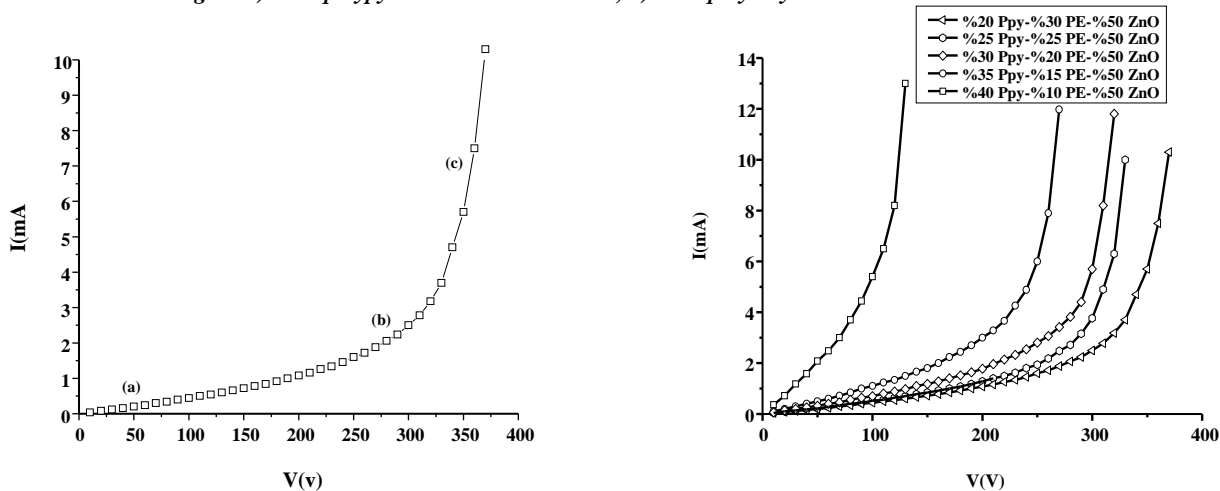


Fig. 3: (I-V) characteristic of ZnO-polymer composite varistor at room temperature, a) pre breakdown zone, b) breakdown zone, c) upturn zone.

Fig. 4: (I-V) characteristics of ZnO-polymer composite varistor at room temperature.

as a function of voltage as $I=kV^{\alpha}$, where α is nonlinear coefficient and k is a constant. Comparison of (I-V) characteristics of different samples shows that by

increasing Ppy percentage in varistor structure, breakdown voltage decreases where the corresponding leakage current increases (Fig. 4).

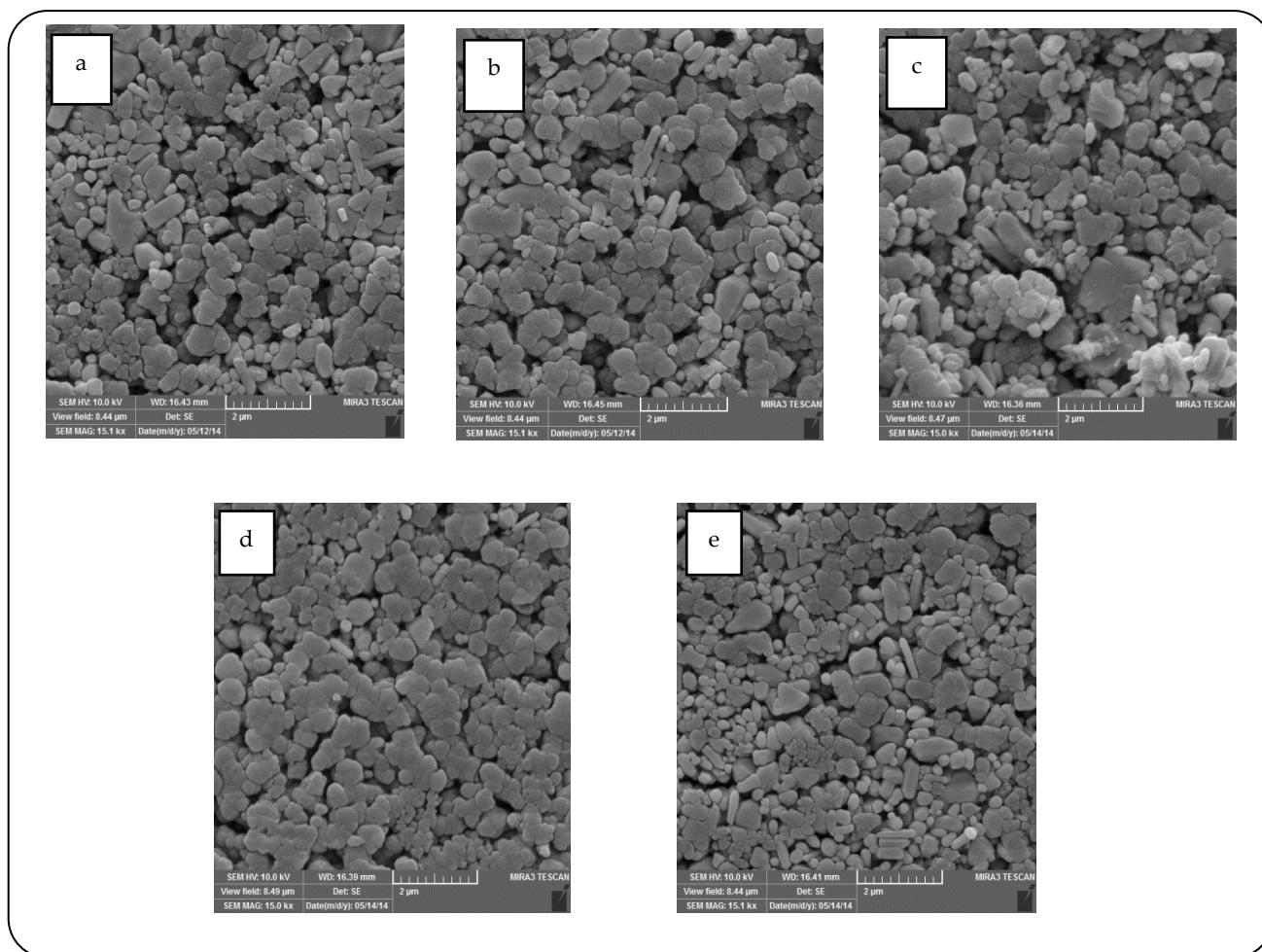


Fig. 5: The typical morphology of ZnO-polymer composites: a) 20% Ppy, b) 25% Ppy, c) 30% Ppy, d) 35% Ppy, e) 40% Ppy.

The samples can be used to protect sensitive circuits from 110V up to 350V over voltages, which is lower than similar ZnO-based ceramic varistors [15], but whose leakage currents are higher. Due to high leakage current, the system must have thermal evacuation capability to avoid the effects of Joule heating ($Q \propto RI^2$). Varistor behavior could be interpreted regarding grains and grain boundaries similar to what is done in ZnO-based ceramic varistor case [5]. The difference is that in present varistors, the phase between grains is made of polymer instead of metal oxides. The typical morphology of the ZnO- polymer composite varistors is shown in Fig. 5.

The figures show the ZnO grains on the polymer matrix background. The grains as well as grain boundaries are recognizable. This structure causes the varistors to show nonlinear behavior. Non Ohmic property of composite varistors is controlled by barrier

structures developed at grain boundaries by the incorporation of polymers which can be interpreted as regarding ZnO grains and their surrounded polymer matrix as back-to-back Zener diodes [5,16].

Regarding SEM micrographs of the prepared samples, it is clear that the size of ZnO grains is almost constant and it is found that the mean size of ZnO grains is about 200 nm, which confirms the fact that it is not dependent to material amount. On the other hand, Ppy has relatively high conductance in comparison with PE. So, it could be concluded that, as other sintering conditions are invariant, by increasing Ppy percentage in composite varistor conductivity of polymer matrix increases which results in higher leakage current and lower breakdown voltage as well. This behavior is due to the fact that the probability of electron tunneling via secondary phase increases. More increase in Ppy amount leads to linear behavior.

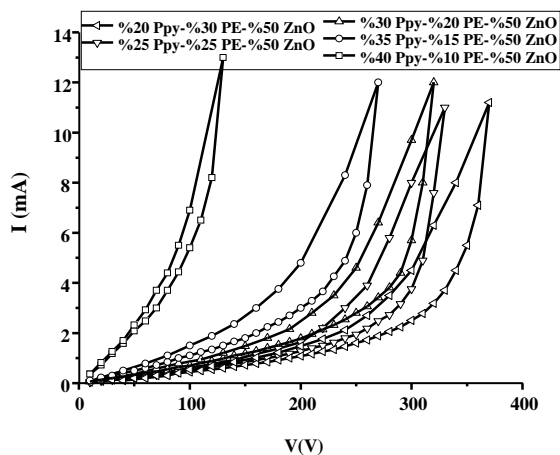


Fig. 6: Hysteresis diagrams of composite varistor at room temperature.

Nonlinear coefficient of a varistor, which is defined as:

$$\alpha = d(\ln I)/d(\ln V)$$

is determined by calculating the slope of $(\ln I - \ln V)$ curve. It is an estimate of varistor's response time. As shown in the Tab. 1, varistors with higher amount of Ppy have lower nonlinear coefficient.

Lifetime of a varistor is defined as the time required reaching a thermal runaway condition. Surge history, especially transient surges beyond rated maximums, are perhaps the greatest single contributor to reductions in varistor breakdown voltage, increased standby leakage current, and ultimate thermal runaway. Surge history is determined by hysteresis loop. If hysteresis loop is expanded, varistor degrades fast; so its lifetime is shorter. Fig. 6 shows hysteresis loops of the samples. By increasing the amount of Ppy, hysteresis loops get constricted leading to longer lifetime of the varistor. This is an interesting result. According to literature, when polyaniline is chosen as a component of polymer matrix, increasing its amount results in expanded hysteresis loop and lower lifetime [12]. As a result, Ppy could be a preferred choice to reach high quality composite varistors.

XRD analyses of ingredients and prepared composite varistors are shown in Fig. 7 and Fig. 8. As it is clear from Fig. 7a, Ppy is amorphous. The peaks shown in XRD pattern of PE emphasizes that it is a highly crystalline polymer (Fig. 7b). Also, ZnO has a crystalline structure (Fig. 7c). XRD analyses of prepared composite varistors confirm the fact that during synthesis, raw materials retain their chemical nature and

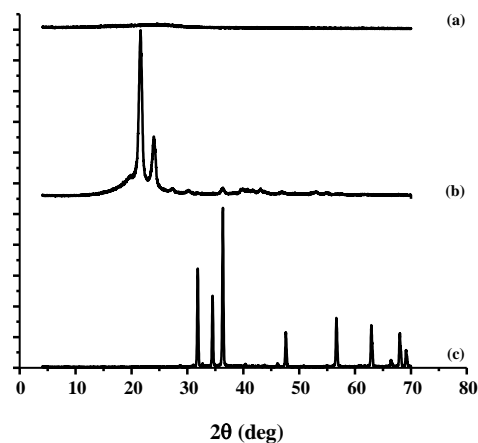


Fig. 7: XRD patterns of a) Ppy, b) PE and c) ZnO.

no new material arises during synthesis (Figs. 8a-e). Therefore, nonlinear varistor behavior relates to especial structure of samples, which, as mentioned before, includes grains and grain boundaries.

To calculate spacing between valance band and conduction band, E_g , absorption spectra of the samples are helpful. Absorption spectra analysis shows that due to high absorption of Ppy compared with PE, varistors with more Ppy content have higher absorption intensity (Fig. 9). As it is clear from Fig. 9, there is a peak in absorption spectra of each sample in the wavelength of ~ 364 nm, which is corresponded to energy of ~ 3.40 eV; Reported band gap for ZnO is ~ 3.43 eV at room temperature [17]. This reveals that a valance band-donor transition at ~ 3.40 eV exists, which can dominate the absorption spectrum when the bulk, as distinct from the surface, of a single crystal is probed. It is concluded that there should be a donor level with $\Delta E \sim 0.03$ eV. By applying the *Tauc* model [18], and the *Davis and Mott* model [19] in the high absorbance region:

$$\alpha h\nu = D(h\nu - E_g)^n$$

where $h\nu$ is the incident photon energy, α is absorption, and D is a constant, E_g - the optical band gap- can be calculated. For a direct transition, $n=1/2$ or $2/3$; the former value is found to be more suitable for ZnO since it gives the best linear curve in the band-edge region (Fig. 10) [20].

By plotting the relationship between $(\alpha h\nu)^2$ and $h\nu$, optical band gap of samples can be estimated; its value can be obtained by extrapolating the linear portion of the curve to the photon energy axis in the figure.

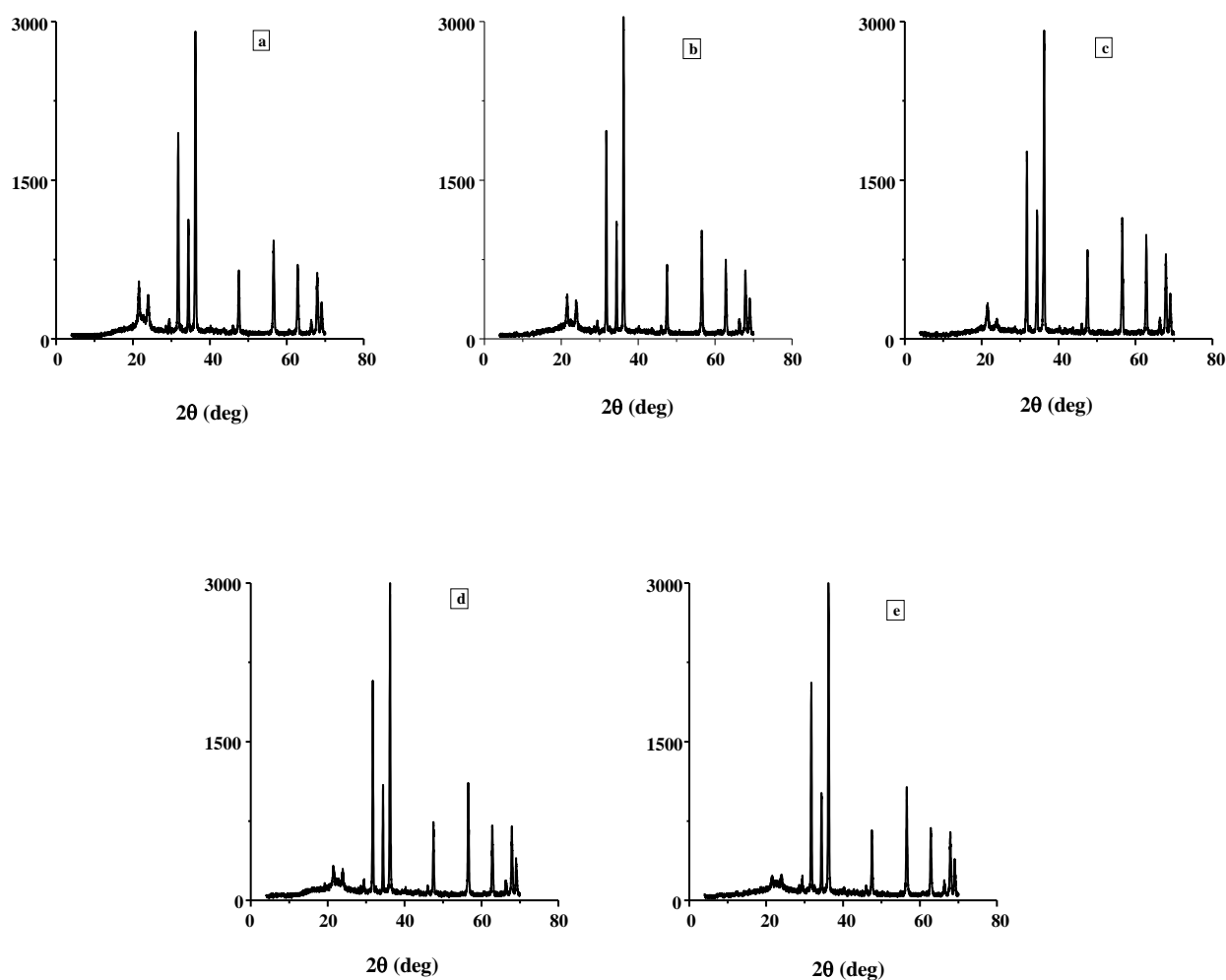


Fig. 8: XRD patterns of ZnO-polymer composites, a) 20% Ppy, b) 25% Ppy, c) 30% Ppy, d) 35% Ppy, e) 40% Ppy.

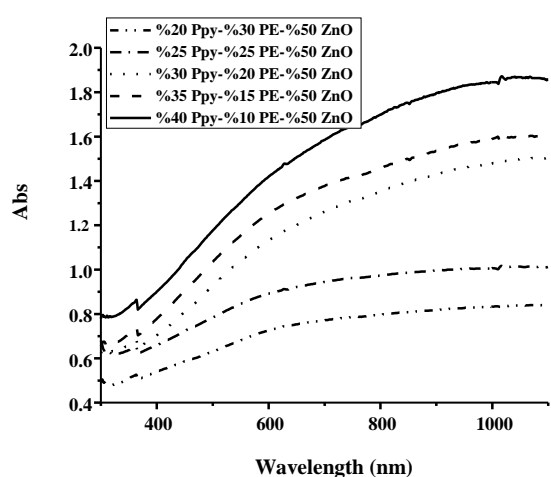


Fig. 9: Absorption spectra of the composite varistors.

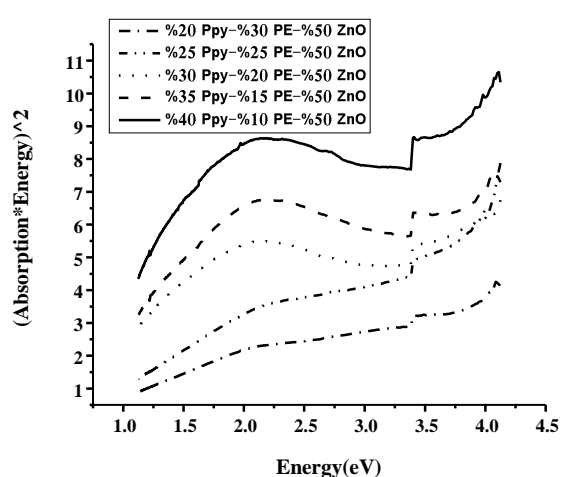


Fig. 10: $(\alpha hv)^2$ versus $h\nu$ diagram for estimating band gaps of samples.

Table 1: Abstracted information about sample.

Sample No.	Ppy content (%)	Breakdown voltage (V)	Nonlinearity coefficient	Optical band gap (eV)
1	20	350	5.05	280
2	25	310	4.95	260
3	30	300	4.71	245
4	35	250	4.38	210
5	40	110	3.26	190

Optical band gap differs from electrical band gap because of Burstein–Moss effect:

$$E_O = E_g + \Delta E_{BM}$$

Where E_O is optical band gap, E_g is electrical band gap, and ΔE_{BM} is Burstein–Moss shift. Absorption is measured at room temperature. At this temperature, the apparent band gap of a semiconductor is increased; this happens since the absorption edge is pushed to higher energies as a result of the population of all states close to the conduction band. Obtained optical energy gaps which are related to impurity levels are summarized in Table 1. It is noticeable that increasing Ppy content introduces impurity level farther from conduction band in energy gap.

CONCLUSIONS

ZnO-Ppy-PE composites varistors with higher amount of Ppy content have lower breakdown voltage, nonlinear coefficient, optical band gap and hysteresis. Nonetheless their leakage current is high. It is noteworthy that Ppy-based varistors have less degradation compared with corresponding polyaniline-based varistors. So, according to the need of low-voltage varistors in micro and nano technology with longer lifetime and higher nonlinear coefficient, proper ZnO-Ppy-PE composite varistor might be selected on the basis of our requirement.

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