

Experiments on the Molecular Mechanism and Interface Structure of Pure and Doped Polymer Nanocomposites Used in Microelectronics

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Polyvinylcarbazole (PVK) exhibits excellent interface properties despite its structural properties playing a dominant role in nanocomposites. In the present work, we attempted to identify the interface and the molecular mechanism in pure and nano ZnO doped PVK samples. The performance of solution-cast foil samples of pure and nano ZnO sensitized PVK samples with similar (Al-Al) electrode combinations was studied by varying temperature from 30 to 170 °C. Polymer samples exhibit dielectric loss maxima around 100±10 °C. The peak is shifted towards lower temperatures, and variation is found in short circuit thermally stimulated discharge current (TSDC) study. The results show that the polymer interface and matrix behavior are suitable for microelectronic device applications. The location of the TSDC α -peak is found to be comparable with the α -peak obtained by dielectric relaxation spectroscopy. The results obtained by TSDC, XRD, and EDX analysis are in good agreement with the results of TSDC and charge transfer interface of the polymer matrix.

Keywords: TSDC, XRD, Activation energy, PVK, ZnO, Dipole orientation, Glass transition temperature.

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1. INTRODUCTION

Polymers are known to be good electret forming materials. Polymer electrets have several applications in modern solid-state devices. In recent years, a huge amount of literature has appeared on electret forming characteristics of polymers, but the mechanisms responsible for charge storage in polymers are far from being clear. Studies on polymers have attracted particular attention due to their useful properties, unique disordered structure, and potential applications in many technological and engineering areas [1-5]. Polyvinylcarbazole (PVK) is a polar polymer, and comparatively little attention has been paid to understand its charge storage capability.

With the progress in the field of materials science, the use of insulating materials in solid state devices of engineering and microelectronics has become very common [6-8]. The problem of selecting a suitable insulator for a particular use has become complicated due to their operation in abnormal conditions of high environmental humidity, very low and very high temperatures, electrical and mechanical stresses, etc. [9-12]. It has been shown that electret forming characteristics of polymers can be greatly improved by doping them with suitable impurities. With this view, the PVK matrix has been sensitized with nano ZnO under suitable conditions [13, 14].

2. EXPERIMENTAL DETAILS

Films of pure and nano ZnO doped PVK samples were formed using solution cast technique by taking 1,

2, 3 and 4 mg of DMF and nano ZnO, respectively. Pure and nano ZnO doped PVK films in our study were 7.4 cm in diameter with circular aluminum electrodes 5.5 cm in diameter deposited on them. The relatively large diameter of the sample ensured that the remaining barren annular polymer film provided insulating edges between the two electrodes. For short circuit TSDC measurements, the samples were coated with aluminum electrodes on both sides, while for open circuit measurements, the samples had an aluminum electrode on the side which had to be given positive polarity during polarization. This circular aluminum foil acted as a patch electrode for the uncoated side of the one-sided aluminum deposited samples. Patch electrode was removed during depolarization [15].

For both polarization and depolarization processes, the bottom electrode was surrounded by a Teflon ring. This Teflon ring's internal diameter was 5.7 cm and the outer diameter was 9.0 cm, the height of the Teflon ring was 1 mm less than that of the fixed bottom electrode. This prevented the sample edges from curling during the polarization and depolarization process, especially at and above the glass transition temperature T_g .

3. RESULTS AND DISCUSSION

The thermally stimulated discharge currents of pure and nano ZnO doped PVK samples were measured at different field and temperate parameters. Details are given below: polarizing field strength is 300 and 900 V, polarizing temperature is 45 and 75 °C, heating rate is 3 °C/min, electrode material is aluminum.

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Fig. 1 and Fig. 2 display the thermally stimulated discharge current (TSDC) spectra for pure and nano ZnO doped PVK samples polarized with 300 and 900 V at 45 and 75 °C, respectively. The TSDC thermograms for different ratios of ZnO sensitized PVK samples (i.e., PVK + 1 mg nano ZnO, PVK + 2 mg nano ZnO, PVK + 3 mg nano ZnO, and PVK + 4 mg nano ZnO represented by M₁, M₂, M₃, and M₄, respectively) with comparative TSDC thermogram of pure PVK samples poled with (A) 300 and (B) 900 V at a constant polarizing temperature of 45 °C are shown in Fig. 1, and TSDC thermograms of sensitized PVK samples poled at (A) 45 and (B) 75 °C with a constant voltage of 900 V are shown in Fig. 2.

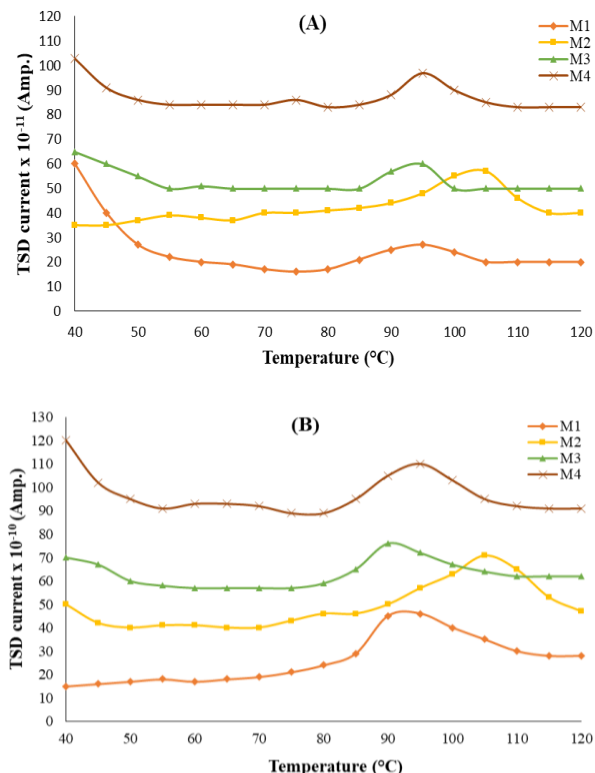


Fig. 1 – Comparative TSDC thermogram of pure PVK samples poled with (A) 300 and (B) 900 V at a constant polarizing temperature of 45 °C

Since PVK is a polar polymer, the contribution to polarization may come from the field and different parameters of relaxation and interfacial mechanism. The TSDC thermograms exhibit a broad peak which is centered around 100±10 °C. The magnitude of the peak increases with field strength and polarization effect depending on the influence of the reaction mechanism. In some cases, a large current is observed in TSDC thermograms, which gradually decreases to a certain temperature and further with an increase in the polarizing field or temperature due to the polarization mechanism. Saturation current is visible at the end of the thermograms. The peak is attributed to the interface, and at higher temperatures, charge carrier injection enhances the charge storage mechanism. This process is followed by a shift in the current maximum temperature (T_m) with E_p [16].

The presence of a peak in the high-temperature area in this case indicates that ion injection may play an

important role in this polymer interface. Prior to field treatment, it is likely that PVK often has a large number of impurity molecules, which dissociate under the action of a combination of strong internal and external fields on different ionic species. In a polymer, charge trapping occurs in the main molecular chain, side chains, and at the interface between the crystalline and amorphous regions [17, 18]. Any additional trapping sites can be generated in a strong field during the selected formation.

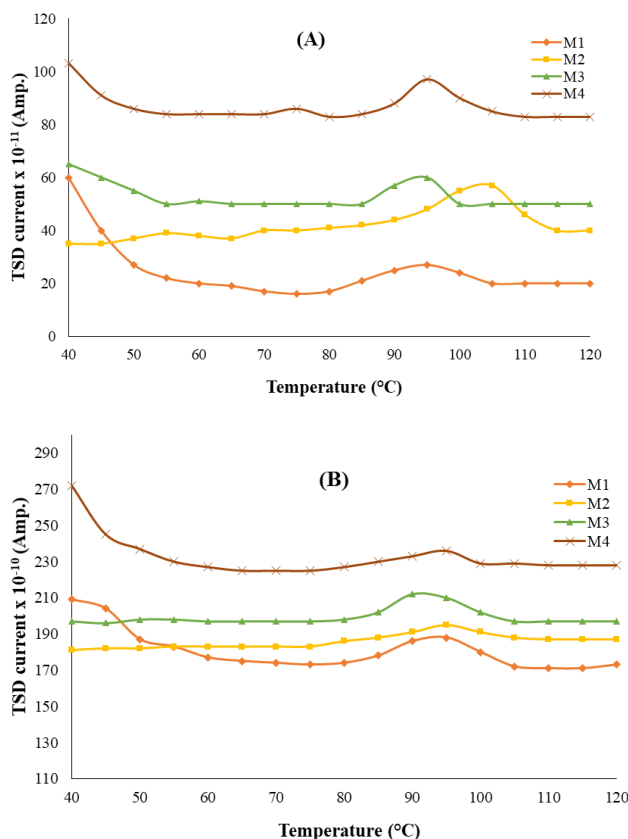


Fig. 2 – TSDC thermogram of sensitized PVK samples poled at (A) 45 and (B) 75°C with a constant voltage of 900 V

TSDC study shows that due to polarization, uniform structural forms and charge carriers play a dominant role. The complete process is controlled by the electric field, and the total charge accumulation is calculated from the activation energy. In this way, TSDC gives excellent results for microelectronic device applications.

3.1 Structural Analysis

The XRD diffractograms of pure and nano ZnO sensitized (in different ratios) PVK samples are shown in Fig. 3. These spectra exhibit a broad peak for pure as well as nano ZnO sensitized PVK samples. The addition of nano ZnO does not result in a new peak or a shift relative to PVK [19, 20]. The XRD trend reveals that as the sensitizer increases, the full width at half maximum (FWHM) increases. The observed increase in FWHM is usually associated with a decrease in the polymer matrix crystallinity. The average crystallite size L is measured using the Scherrer formula:

$$L = k\lambda/(\beta\cos\theta), \tag{1}$$

where β is the full width at half maximum (FWHM) of the peak (in radians) and k is the shape factor whose value is equal to 0.9. The crystallite sizes of pure and nano ZnO sensitized (in different ratios) PVK samples are calculated and listed in Table 1. In the present study, X-ray analysis shows that sensitization does not change the phase of PVK and increases peak intensity and crystallite size.

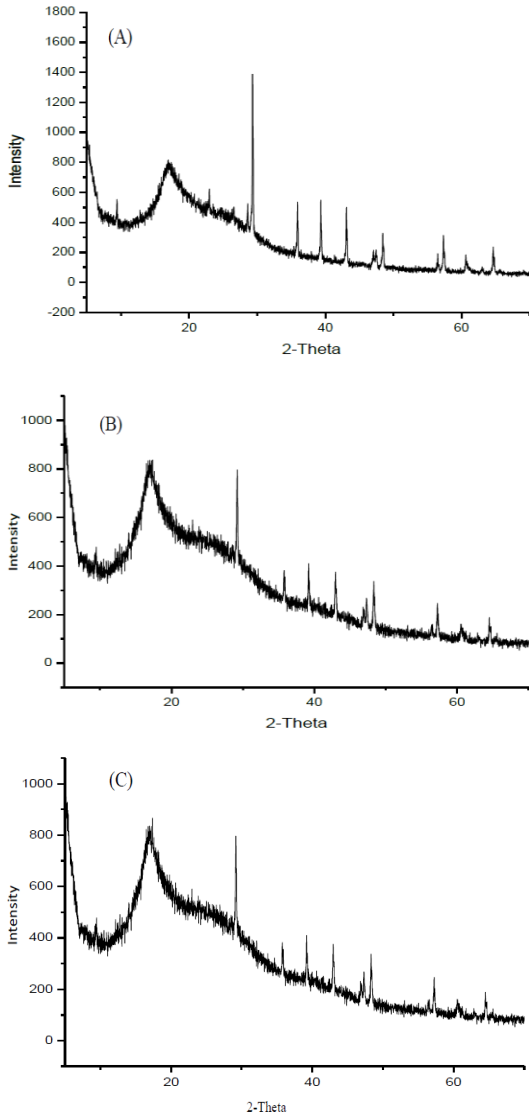


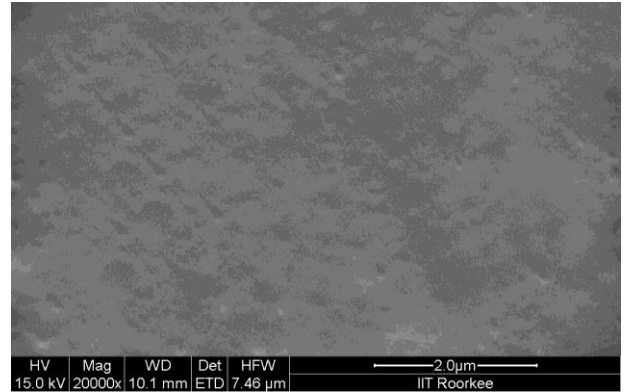
Fig. 3 – XRD spectra of (A) pure and nano ZnO sensitized PVK samples: (B) M₁ and (C) M₄

Table 1 – Structural parameters of pure and nano ZnO sensitized PVK samples obtained from XRD patterns

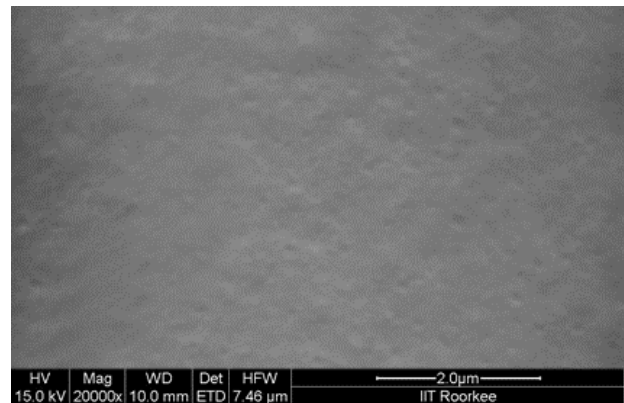
Samples	2θ	Intensity	FWHM	L (Å)	D
M ₁	16.88	727.31	θ ₁ = 15.57	0.49	5.31
			θ ₂ = 18.40		
M ₂	16.88	730.58	θ ₁ = 15.57	0.46	5.31
			θ ₂ = 18.61		
M ₃	16.88	759.45	θ ₁ = 15.47	0.45	5.31
			θ ₂ = 18.51		
M ₄	16.99	802.56	θ ₁ = 15.47	0.35	5.22
			θ ₂ = 19.37		

M ₅	17.00	809.47	θ ₁ = 15.80	0.34	5.31
			θ ₂ = 18.73		

FESEM micrographs of pure and nano ZnO doped PVK films are shown in Fig. 4. The surface roughness and crystalline texture tend to be reduced, assisting in the development of a smooth surface texture on nano ZnO doped film.



a



b

Fig. 4 – FESEM micrographs of (a) pure and (b) nano ZnO doped PVK samples

Fig. 5 and Fig. 6 depict Energy Dispersive X-ray (EDX) study of pure and nano ZnO doped PVK samples, respectively. These statistics and Table 2 reveal that the polymer interface raises the percentage of C, N₂, and O₂ and shows the existence of Cl.

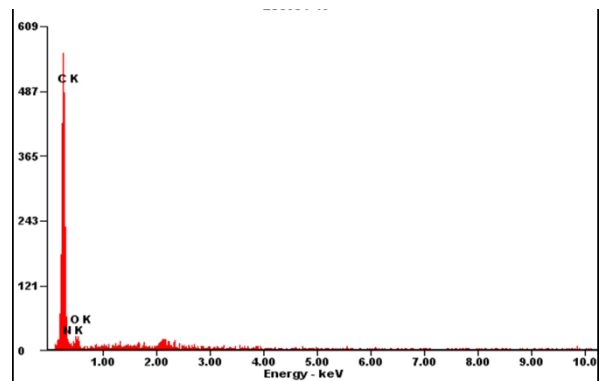


Fig. 5 – PVK samples presented graphically utilizing the EDX methodology

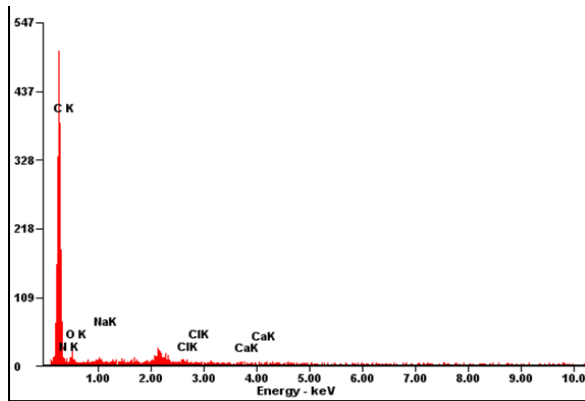


Fig. 6 – Graphical representation of nano ZnO sensitized PVK sample (M₁) using EDX

Table 2 – Compositional analysis of nano ZnO sensitized PVK sample

Element	wt. %	at. %
CK	81.09	84.18
NK	09.73	08.66
OK	09.18	07.15

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Експерименти із молекулярним механізмом та структурою інтерфейсу чистих і легованих полімерних нанокompatивів, що використовуються в мікроелектроніці

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Полівінілкарбазол (PVK) демонструє чудові властивості інтерфейсу, незважаючи на його структурні властивості, які відіграють домінуючу роль у нанокompatивах. У роботі ми спробували ідентифікувати інтерфейс та молекулярний механізм у зразках чистого PVK та PVK, легovanого nano ZnO. Дос-

4. CONCLUSIONS

The charge storage and transport mechanisms in pure and nano ZnO sensitized PVK samples have been investigated in detail. Various information obtained from the studies undertaken is sufficiently important for understanding the manifestation of the electret state by this polymer interface. It would be worthwhile to study the decay mechanisms of injected homo-charges. The broad relaxation behavior exhibited by PVK in TSDC and XRD studies has been investigated in detail to resolve the overlapping relaxations. We concluded that impregnation with different ratios of nano ZnO of the PVK polymer matrix interface forms charge-transfer complexes. The following conclusions can be drawn from the above studies.

- XRD study reveals that nano ZnO sensitization does not change the PVK phase, reducing the crystallite size.
- FESEM study shows the formation of a smooth texture with a decrease in surface roughness and crystal structure.
- EDX study confirms an increase in the percentage of C, N₂ and O₂ after nano ZnO sensitization in the PVK matrix.

The results of the present investigation can be considered as an addition to our current understanding of the charge storage and transport properties of pure and nano ZnO PVK in particular, and other polymers in general.

лджено експлуатаційні характеристики зразків литої фольги з чистого PVK та PVK, сенсibilізованого нано ZnO, з подібними (Al-Al) комбінаціями електродів шляхом варіювання температури від 30 до 170 °C. Полімерні зразки демонструють максимуми діелектричних втрат близько 100 ± 10 °C. Пік зміщений у бік нижчих температур, і зміни виявлені при дослідженні термічно-стимульованого розрядного струму короткого замикання (TSDC). Результати показують, що інтерфейс полімеру та поведінка матриці підходять для застосування у пристроях мікроелектроніки. Положення α -піку TSDC виявилось порівнянним з α -піком, отриманим методом діелектричної релаксаційної спектроскопії. Результати, одержані за допомогою TSDC, XRD та EDX аналізу, добре узгоджуються з результатами TSDC та інтерфейсом перенесення заряду полімерної матриці.

Ключові слова: TSDC, XRD, Енергія активації, PVK, ZnO, Дипольна орієнтація, Температура склування.