Optical, Electrical and Morphological Response to Thermal Annealing by Poly (N-vinylcabazole) - Polyaniline Blend Thin Films

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We present a fundamental study of the opto-electrical response of poly (N-vinylcabazole) (PVK) - polyaniline (PANI) blend thin film as measured by the sheet resistance and some morphological features due to thermal annealing. The optical absorbance and the sheet resistance were not significantly affected by annealing at temperatures of 100°C, 160°C and 210°C. A weak characteristic absorption peak that was found to exist in the 635 – 680 nm range in PANI disappeared after blending. In the visible range, the transmittance of the blend was found to be significantly higher than that of PANI alone. The average particle size of the blend was about 34% less than that of PANI indicating an improved miscibility due to the presence of PVK. The observed morphological features of the blend suggest improved intermolecular reassembly and alignment of the polymer chains due to blending with possible implications on the interfacial charge transfer efficiency.

1. Introduction

Blends of aniline based in another conjugated polymers have become important in practical applications to diverse fields [1] such as electromagnetic shielding [2], microwave absorption [3], sensor materials, and other optoelectronic devices [4,5] among others. A self-assembled interpenetrating network can be obtained by physical blending of a previously polymerized conjugated polymer. Also, a majority of conjugated polymers tend to preferentially transport one type of charge carrier (electrons or holes), which makes it possible to take advantage of blending different polymers together in creating device-applicable materials having improved electronic properties [6,7].

PANI has received greater attention among conducting polymers due to its ease of preparation and well behaved electrochemistry [8]. Several improvements have been reported in the performance and lifetime of organic light-emitting diodes (OLEDs) with the use of PANI (a hole emitting layer) as anode [9]. PANI absorbs light strongly in the deep blue region, making it unsuitable for blue OLEDs [10]. This absorption problem can practically be solved by blending PANI with PVK.

Various coating technologies, ranging from laboratory-scale spin-coating or spray-coating to large-scale fabrication technologies such as inkjet Thermal annealing is often used in conventional polymer processing as an effective method that increases crystallinity and improves the phase segregation of donor and acceptor domains in conjugated polymer blends. Annealing also tends to affect the surface morphology thereby producing coarser surfaces with phase separation. The continued interest in the study of conjugated polymer blends [14] with respect to the understanding of annealing [15-17] and the film morphology [17-19] is founded on their possible contribution to device efficiency enhancement when used as active layers [11]. However, the chosen blend for this investigation could be said to be a system consisting of rodlike chains as in most conducting polymers [6].

This study investigates the optical and electrical characteristics of poly (N-vinylcabazole) (PVK) - polyaniline (PANI) blend thin films due to thermal annealing. The effect of different dopants on the optical transmittance of different blends is also investigated alongside some morphological features of polymers and their blends.

printing, slot-die coating, and flexographic printing [11] can then be used in characterizing the blend morphology and the level of interaction and degree of phase segregation among its components [12,13].

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2. Material and Methods

A 2% by weight, each of pristine emeraldine salt of polyaniline (PANI), HCl-doped and ptoluenesulfonic acid (pTSA)-doped PANI (Alfa Aesar, USA), were prepared by dissolving 0.1 g of each PANI sample in 5 ml of m-cresol (Fluka, Sigma-Aldrich, Germany) and stirring continuously for 2 hrs at room temperature followed by filtering with a 0.2 µm Fisherband nylon filter to remove particulates. The resulting solutions were darkgreen and appeared to be smooth and uniform with some visible particulates despite vigorous stirring for 8 hrs. m-cresol is one of the best known of the available solvents for dissolving PANI but solubility is still not 100%. After characterizing the three PANI types, the pristine emeraldine salt of PANI (un-doped) was used for the comparative property studies of prepared resulting blends.

50 mg of poly (vinylcabazole) (PVK) was dissolved in 5ml of chloroform to obtain a 1% by weight (w/w) solution at room temperature. The resulting solution was covered air tight to avoid evaporation of the solvent within a reasonable time after dissolution prior to use. PVK completely dissolved in chloroform to obtain a highly vaporizing colorless solution.

Blend of PVK - PANI (un-doped) solution was prepared by mixing 10% by volume of PANI with PVK, making PVK the host material. 10% by volume of PANI was used based on earlier reported work [10], which found 10% concentration as the optimal concentration for OLEDs performance. ITO-coated glass (Colorado Concept Coatings, USA) substrates were cleaned successively by use of acetone, glass detergent, distilled and de-ionized water and ethanol with each applied for 10mins in a Branson ultrasonic cleaning bath. Each resulting specimen was subsequently blow-dried with nitrogen gas [20].

The three solutions namely, PANI, PVK and PVK - PANI blend were spin coated onto precleaned ITO substrates to cast the thin films. PANI was spin coated at a speed of 1000rpm and acceleration of 200rpm/s for 30 sec., while those of PVK and PVK - PANI blend were spun at an acceleration of 255rpm/s for the same period and speed. This was because of the high evaporating chloroform used in the preparation of PVK and the blends in order to reduce the effect of phase segregation, though evidence of residual solvent content has been reported [19]. The coated PVK thin films showed excellent transparent surface finish. All the films were subsequently annealed in a vacuum oven (Sheldon Inc, USA) at temperatures of 100°C, 160°C and 210°C for 30 min. The film thickness was measured by profilometry using a Veeco Dektak 150 surface profiler (Bruker Instruments, Santa Barbara, CA, USA), which averaged 200nm for each blend sample of PANI, PVK and PVK-PANI.

A four-point collinear probe (Signatone, Gilroy, CA, USA) was used for measuring the sheet resistance of the films. The optical transmittance T and reflectance R were obtained with a UV-Vis spectrophotometer (Jenway 6405, UK) in the wavelength range of 300nm -900nm. The Surface morphology of selected films was observed with a high resolution Optical Microscope (AP2000 MTI), whereas 3-D surface plots and average particle sizes of the films were obtained with IMAGEJ [21] image analysis software package on the optical micrographs.

3. Results and Discussion

3.1. UV-visible spectroscopy

Fig. 1 presents the transmittance plots of the three different PANI grades considered before the choice used for this study was made: pristine, HCl-doped and pTSA-doped, annealing of the PVK, all the PANI grades and their blends with PVK - PANI blend films at the three annealing temperatures of 100°C, 160°C and 210°C. There appears to be no noticeable significant changes in the bands of absorption spectra when compared to un-annealed samples. The transmittance peaks, though weak at around 400nm, informed the choice of pristine PANI rather than HCl and pTSA-doped varieties.

Fig. 2 shows the absorbance plots of PVK, pristine PANI and PVK – pristine PANI blend thin films in which sharp characteristic absorption peaks are observed at wavelengths of 300nm, 330nm and 345nm for PVK film. This is consistent with previously reported works [22-24] reiterating the non-existence of strong absorption in the visible region (beyond 400 nm) of PVK spectra with strong absorption only in the ultraviolet region. The absorption peak around 300nm of PVK corresponds to that of the ligand center with other peaks representing a transition from the ground state [24].



Fig.1: Transmittance spectra of the three PANI specimens: pristine, HCl-doped and pTSA-doped polyaniline (PANI)



Fig.2: The absorbance spectra of PVK, pristine PANI and pristine PANI-PVK blend

The absorption bands, due to the polymer moiety in the UV-Vis spectra of the pristine PANI film, showed four weak bands at 285nm – 300nm, 415nm – 495nm, 635nm – 665nm, and 800nm – 815nm. These bands are quite similar to 305 nm – 315nm, 425nm – 480nm and 805nm – 820nm ranges referred to as peaks I, II and III in the UV, visible and near infra-red regions, respectively [25]. The peaks I and II were attributed to characteristic absorption peaks due to π - π * transition of

benzenoid and quinoid ring in the PANI structure while peak III was said to be due to polaron lattice resulting from transition of exciton.

In this study, we have observed an additional band, though weak, a characteristic absorption band peak the range 635 nm - 665 nm, which is in the visible to near infra-red region 'bridge'. A more detailed study of chemical and electronic structures would be required to identify this observed peak. A close look at these bands shows that a wavelength shift (averaged 15 nm) occurs when compared to that reported by Kim et al. (2007) [25].

However, upon blending pristine PANI with PVK, peak I band remained strong in the ultraviolet region while all other absorption bands peaks in the visible region varnished or were probably suppressed. The dominance of the PVK absorption in the range of 300 nm - 345 nm in the UV region after blending remained unchanged. This is an indication of an overwhelming dominance and control of the blend morphology by PVK as it affects the optical response.

Fig. 3 shows the transmittance plots for PVK, pristine PANI and PVK - pristine PANI blends at approximate film thickness of 200nm. It shows that the transmittance of the blend lies between the low PANI and the high PVK transmittance spectra. The transmittance of the PVK – pristine PANI blend film (49% – 76%) is significantly higher than that of pristine PANI film (23% – 30%) in the visible region compared to 88% and 20% for PVK films.



Fig.3: The transmittance spectra of PVK, pristine PANI and pristine PANI-PVK blend

It is useful to briefly consider the comparative effect of blending the doped PANI on their transmittance characteristics. Fig. 4 shows respective plots of pristine PANI, pristine PANI-PVK blend, HCl-doped PANI-PVK and pTSA-doped PANI -PVK blends. The four peaks on the pristine PANI specimen reduced to three after blending with the peak in the UV region either disappearing or suppressed. The pTSA-doped PANI blended with the PVK retained two peaks while none remained on the PVK-HCl-PANI blend. The difference in the transmittance spectra may have been caused by the fact that pTSA is an organic acid compared to HCl. There may have been organic-organic interactions at the molecular level that appeared to have favored the retention of two of the original peaks, though weak, observed in the pristine PANI. Again, this observation requires a more in-depth and detailed investigation that would give a better explanation of this optical response due to blending doped PANI with PVK.



Fig.4: The transmittance spectra of PANI-PVK blends with the differently doped PANI

PANI is an established hole injection material while PVK is a hole transport material [10] in an OLED device. Blending is capable of eliminating the PVK buffer layer thereby achieving the required good transmittance and hole injection due to the presence of PANI. This strongly suggests that the PVK - PANI blend is a potentially suitable hole emitting material with excellent transmittance that needs further investigation for visible light in OLED applications.

3.2. Sheet resistance measurement

The sheet resistance R_s was obtained from the standard expression [26]

$$R_s = \frac{\pi}{\ln 2} \left(\frac{V}{I} \right)$$

Where, V is the potential drop across the 2 inner contact points of the four-point contact and I is the current injected at the 2 outer contact points of the probe head.

In contrast to other parameters, the electrical resistance of the films, as measured by the surface sheet resistance, decreased for all the films after thermal annealing (Fig. 5). As the annealing temperature increased, a comparatively more significant decrease was observed in PVK compared to other films. At room temperature (un-annealed samples), the sheet resistance of $23.11 \times 10^6 \Omega/cm$ was recorded in PVK, whereas upon annealing at the highest temperature under consideration, 210° C, it had decreased to $20.22 \times 10^6 \Omega/cm$, a 12.5 % reduction. In pristine PANI, however, the sheet resistance reduction was less marked as it dropped to $18.71 \times 10^6 \Omega/cm$ from $19.66 \times 10^6 \Omega/cm$, a mere 4.8% decrease.

With PVK as the host, the sheet resistance of the PVK – pristine PANI blend showed no significant changes through the chosen annealing temperature range, suggesting that annealing in this temperature range had no significant effect on the sheet resistance of the blend. A close look at each annealing temperature under consideration, even before annealing, the presence of pristine PANI within the PVK matrix had no significant impact on the sheet resistance at the annealing temperatures of 160°C and 210°C. This may be attributed to the effect of phase segregation within the pristine PANI-PVK blend continuous network [27].



Fig.5: Plots of surface sheet resistance of thin films of PVK (), PANI () and PANI-PVK Blend (), and the percentage difference in the changing resistance (secondary axis)

3.3. Film morphology

Fig. 6(a) shows the high resolution optical micrograph of a PVK thin film annealed at the maximum temperature of 210°C obtained at a magnification of 400x. The equivalent surface plot obtained with the aid of an image-analysis software is presented in Fig. 6(b). Figs. 7(a) and 7(b) respectively represents the micrograph of pristine PANI thin film at 400x magnification and the equivalent surface plot obtained using the IMAGEJ software. Also, Figures 8(a) and 8(b) show the micrograph of an annealed thin film of PANI-PVK blend at the same magnification of 400x alongside the equivalent surface plot.

The morphology of PVK film (Fig. 6(a)) revealed an inter-connected fibrous feature with uniform and well ordered arrangement. This seeming self-assembled structure may have been promoted by the complete solubility of PVK in chloroform and the subsequent thermal annealing. The micrograph also suggests absence of visible phase segregation on the microstructure. It has previously been reported that the absence of phase segregation in chloroform-cast film was attributable to significant time reduction during spin coating, due to solvent volatility [28]. The image analysis of the PVK micrograph (Fig. 6(b)) demonstrated the uniformity and smoothness of the surface showing the consistency of the morphology obtained in Fig. 6(a).

Figs. 7(a) and 7(b) respectively show the micrograph and the equivalent surface plot of pristine PANI thin film indicating morphologies suggesting entities with rough surface structures and aggregates that appeared to suggest possible phase segregation and incomplete dissolution of the particles, despite the filtering stage during thin film preparation.

The micrograph in Fig. 8(a) and the surface plot in Fig. 8(b) represent features obtained for the PVK - PANI blend thin film. This is a honeycomb-like, cell-like and grain-like structure (Fig. 8(a)) with clear boundaries that appeared to suggest ordered PANI and PVK blend structure. It is not possible to be definite about what these features are until a more quantitative investigation is carried out. However it can be suggested that the dominance of the PVK matrix in the blend may have promoted self-assembled ordered structure with well-ordered pristine PANI boundaries. The surface plot also revealed a less coarse topology compared to that of pristine PANI shown in Fig. 7(b). This appears to be consistent with the morphology as shown by the micrograph in Fig. 8(a) and the corresponding imaging in Fig. 8(b).



Fig.6: Optical micrograph of a typical PVK thin film (a) and the equivalent surface plot (b) obtained with IMAGEJ analysis software



Fig.7: The high resolution optical micrographs of a PANI thin film (a) obtained at 400x magnification, and the equivalent surface plot (b) obtained with an8 IMAGEJ software



Fig.8: The high resolution optical micrographs of PANI-PVK blend thin film (a) obtained at 400x magnification, and the equivalent surface plot (b) obtained with an IMAGEJ software

The blend thin film appears to consist of inhomogeneous surface with localized globular-like conglomerates with significant number of voids suggesting that incompletely dissolved PANI may still be present in the blend since PVK dissolved completely in the blend. These features are characteristic of phase segregation as revealed on the micrograph and the surface plot.

A close look at the pristine PANI film surface plot (Fig. 7(b)), qualitatively suggests a relatively higher film roughness when compared to the other films (Figs. 6(b) and 8 (b)). However, it can be seen that blending pristine PANI with PVK resulted in significant textural changes as suggested by the relative differences in the surface smoothness due to improved solubility offered by PVK components, which 'smoothened out' part of the pristine PANI giving a grain boundary-like structural organization.

This is a likely continuous morphological evidence that appears to give credence to possibly each component of the blend independently perimprovement. Fig. 9 shows the plot of the average particle size of each film as obtained by section analysis and particle size estimation of the images as obtained with IMAGEJ. As expected, the size distribution shows PVK with the lowest particle size (204 μ m) while the pristine PANI has the highest (713 μ m). However, the particle size reduction in the blend was about 34% when compared to that of PANI showing a significantly improved miscibility of the blend brought about by the PVK. This would have implications on the overall hole injection and transport effectiveness and efficiency of the blend when used in, for example, an OLED fabrication.



Fig.9: The plot of average particle size for PVK (Film 1). PANI (Film 2) and PANI-PVK blend (Film 3)

This is premised on interface contact reduction in a typical multilayer structured device. Meanwhile, blended thin films of conducting polymers poly(3-octylthiophene-2,5-diyl) P3OT and (6,6)-phenyl C_{71} butyric acid methyl ester (PC₇₁BM) was used in a previous study [16] in which the effect of solvent and annealing on the morphology of bulk hetero-junction solar cell was investigated.

4. Conclusion

In search for materials that are conducting and highly transparent in the visible range, which is required for anode enhancement of light emitting diodes (LEDs) and PVK – PANI blend, appears to be a suitable candidate for further detailed optical, electronic and morphological investigations in order to have a better understand of the detail mechanisms that control the features observed in this study. This study suggests that blending of PVK with PANI overcomes absorption in the visible spectrum while thermal treatment showed no significant effect on the sheet resistance of the blend thin films, whereas the individual polymer showed marginal improvement. However, a more detailed quantitative analysis of this effect is required by innovative combination of different conducting polymers for charge transport studies at the interface. The film morphology study suggested improved intermolecular reassembly and alignment of the polymer chains in the blend suggesting 'grain' boundary-like structural organization with the PANI at the boundaries and obvious possible implications for independent interfacial charge transfer by each component in the blend when used in device fabrication.

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