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Structural Morphological and Electrical Study On PI/ ITO/ PVDF Ternary Composite Thin Films

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Abstract: Studies of polymeric ternary composite thin films incorporating inorganic materials are of immense importance for current technological applications. Polyimide (PI) composite thin films incorporating indium tin oxide (ITO) and poly (vinylidene fluoride) (PVDF) at various weight ratios were processed using an in situ generation approach with the spin coating unit. The resultant product was oxidized up to 350° C to test the ability of the material to endure high temperatures without affecting the host matrix. The structural and morphological behavior of the PVDF/ ITO/ PI composite films was investigated using Fourier Transform Infrared, Scanning Electron Microscopy and Atomic Force Microscopy characterization techniques. The degrees of crystallinity and PVDF/ ITO particle size within the PI matrix were studied using X-ray diffraction. The electrical properties were analyzed using Differential Scanning Calorimetry, UV-visible spectroscopy, and the four-probe technique. An overall improvement in the properties of the composite films was observed in comparison to those of pure PI. The synergistic improvement in the composite films is associated with the interaction mechanism between ITO/ PVDF with PI, where ITO becomes dispersed and interacts within the PI and PVDF compound matrix. This leads to a decrease in available free-space volume and increases the surface enrichment providing reinforcement to the matrix.

***Keywords:** Polyimide, PVDF, ITO, Composite Thin Films, Structural, Morphological and Electrical.*

INTRODUCTION

Polymer composite thin films incorporating metal oxides are of great interest because oxides within polymer matrices display a very wide range of physical and chemical properties for many applications, such as flexible thin-film solar cells and conducting flexible thin-film transistors [1-4]. The control of inorganic particle size and dispersion of particles within organic matrices using solution synthesis processes is currently a frontier field of research with far-reaching implications for new technologies [5-9]. In previous studies of hybrid composites, it was demonstrated that the properties of the polymer matrix are strongly influenced by the presence of inorganic materials [10-14]. The synergism in properties could be attributed to a very high surface/volume ratio of the particle and as well very different inter-phase between nanoparticle and matrix.

Inorganic comprising polyimide (PI) composites are revolutionary materials, which play a significant role in today's technology revolution. Aromatic polyimide, a condensation product of the reaction of pyromellitic dianhydride and oxy dianicline containing aromatic heterocyclic fused rings finds use in myriad of technical and industrial field such as dielectric materials for microelectronics, high temperature adhesives, photoresists, non-linear optical materials, membranes for separation technology, atomic oxygen resistant polymers for low earth oxygen resistant polymer for low earth orbit spacecraft and Langmuir-Blodgett (LB) films. These applications arise as polyimides are associated with excellent mechanical properties, low relative permittivity, high breakdown voltage, low losses over a wide range of frequency, good planarization, good processability, wear resistance, inertness expansion, good hydrolytic stability, and long-term stability [3, 4]. The pioneering studies in metal incorporated polyimide have been conducted by L.T. Taylor et al [5] in the laboratories of NASA.

The control of compositions, size and shape mean control of new structure and macroscopic properties. Poly (vinylidene difluoride) PVDF is a semi-crystalline polymer exhibit isomorphic characteristics in nature with a melting point of about 170^0C. It has good mechanical strength properties i.e. tensile strength (s) of 48.35 Mpa. and resists distortion and creep at both high and low temperatures. PVDF shows very good weather ability and solvent resistant [10–11]. Indium tin oxide (ITO) $In_2O_3 \bullet SnO_2$ is a ternary composition of indium, tin, and oxygen in varying proportions. Depending on the oxygen content, it can either be described as a ceramic or alloy. Indium tin oxide is typically encountered as an oxygen-saturated composition with a formulation of 74% In, 18% O_2, and 8% Sn by weight. Oxygen saturated compositions are so typical, that unsaturated composition are termed oxygen deficient

ITO. Indium tin oxide is one of the most widely used transparent conducting oxides because of its two main properties, its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film [7].

Since the key of the synthesis of poly (vinylidene fluoride) (PVDF) and indium tin oxide (ITO) polyimide (PVDF/ ITO/ PI) composite thin films lies on the fact of the modification of PVDF and ITO with polyamic acid (PAA) in micro level quantities, this aspect has been given a re-look and the investigation was made for knowing the size, shape and the structural feature of the micro modified PI composite. It is visualized that the modification of PAA with PVDF and ITO will result in a macroparticle as very lightly cross-linked will be produced and a further increase in size will be prevented. In this research paper, a deeper insight into the formation of PVDF and ITO particles within PI matrix is discussed and the causes of unusual characteristics exhibited by these functionalized PVDF and ITO material.

S. No.	wt % (g) of ITO/ PVDF in PAA	Sample designations	Thermal imidization (°C)	Color	Flexibility	Transparency
1.	(Nil)	PI	350	Light Yellow	Bendable	Color Transparent
2.	(0.1) & 1	PPVITO-1	350	Light yellow reddish	Bendable & Foldable	Color Transparent
3.	(0.075) & 5	PPVITO-2	350	Light yellow reddish	Bendable & Foldable	Color Transparent
4.	(0.050) & 10	PPVITO-3	350	Light yellow reddish	Bendable & Foldable	Color Transparent
5.	(0.025) & 15	PPVITO-4	350	Light yellow	Bendable	Color Transparent

The present paper reports the synthesis of PI/ PVDF/ ITO ternary composite thin films prepared by incorporating ITO and PVDF in various concentrations within the PI matrix using an in situ generation approach, to facilitate the study of structure morphological and electrical property relationships. Study of the water absorption behavior of ternary composite thin films is of great importance because of the hygroscopic nature of PI; a fraction of moisture within a composite thin film can alter its whole set of properties. The moisture absorption characteristics of the composite films developed were evaluated by constructing water absorption isotherms, which involves immersion of films in water from 24 h to a maximum of 144 h. The structure and Surface morphology relationship were studied using Fourier Transform Infrared (FTIR) spectroscopy, SEM, and AFM. The thermal stabilities of pure and composite films were analyzed using DSC technique. Also, the electrical properties of the pure and composite films were investigated in the light of band-gap determined using UV-visible spectroscopy and the four-probe technique

EXPERIMENTAL

Material Used

For the preparation of pure and ternary blend specimens, commercially available polymers; Benzene-1,2,4,5-tetracarboxylic-1,2,4,5-dianhydride or pyromel-litic dianhydride (PMDA), 4,4'-diaminodiphenyl ether or oxydiani-line (ODA) and analytical-grade tetrahydrofuran were used supplied by M/S Merck Chemicals, Germany, while ITO (powder) was used supplied by Sigma-Aldrich Chemicals, USA. PVDF was used supplied by Aldrich, USA. The chemical was used as received.

Synthesis of PAA

In a 500mL three-necked round-bottom flask fitted with mechanical stirrer, nitrogen inlet and $CaCl_2$ drying tube was added 0.05mol of ODA in 188g of dry dimethylacetamide. Then, 0.05 mol of PMDA was added slowly to the solution and vigorously mixed. The solution was again stirred for a further 2 h in a nitrogen atmosphere. The concentration of the solution was 10% having an intrinsic viscosity of 29.37dL g^{-1} at 26º C and was stored at −10º C.

Preparation of PAA/ PVDF/ ITO ternary composite thin films blends

For preparing the ternary composite thin films Polyimide (PI) chosen as a host matrix in which poly vinylidene fluoride (PVDF) and indium tin oxide (ITO) will be incorporated. In PAA, ITO and PVDF were incorporated using solution cast technique to form PI/ITO/PVDF ternary composites thin films of desirable percentage using In-situ Generated Macro/ Nano Phase Structure (IGM-NPS) and with the help of spin coating unit.

Various appropriately calculated concentrations of ITO and PVDF were added to fixed quantities of PAA. The concentration of metal oxide and polymer depends upon its mass density and free surface volume of the host material, i.e. PAA. The blends were stirred for 30 min with a magnetic stirrer in a dust free environment. The concentrations and designations of the various samples are given in Table 1. For preparation of PI/ PVDF/ ITO composite thin films PAA/ PVDF/ ITO blends were weighed onto clean and dry glass plates and spread evenly using a spin-coating unit in a dust and moisture free chamber and cured at 350°C for 2 h using heavy duty oven. The cure cycle involved conditioning at 70°C for 24 h and thereafter for 30 min each at 100, 150, 200 and 300°C. This first step partially imidized the reactants. Subsequently, the films were heated at 350°C for 2h. The films were then allowed to cool slowly to room temperature. The pure PI film was also cured under identical conditions. The films were of 15 cm^2 in area and 25μm in thickness, and the same were used for all the characterizations. Table 1 gives the physical and optical characteristics of the composite films formulated.

Table 1. Thermal, medication, the physical and optical appearance of PI/PVDF/ITO ternary composite thin films.

Calculation of PVDF/ ITO particles within PI matrix

Presuming the division of PI chain in the domain of 100 by 100 nano meter cube, the volume occupied by PVDF and ITO is calculated. Moreover, the calculation of particles is based on the concentration used and the interaction of particles with the polymeric chain, shown in Table 2.

Measurement of film thickness

For measurement of film thickness, micrometer gauge was used. This is one of the simplest ways of measuring the thickness of a film sample. A highly accurate micrometer screw gauge of least count I μm manufactured by Mitutoyo Mfg. Co. Ltd., Japan, was used. Measurements were taken at different positions on each sample and the average thickness of the sample was obtained.

Sample designation	Number of molecules of PI and PVDF	Number of molecules of ITO	Number of particle in a domain attached to polyimide chain
PI	$1.434x10^{21}$	0	0
PPVITO-1	$1.567x10^{21}$	$2.605x10^{21}$	~1 domain contains 12 particle
PPVITO-2	$1.786x10^{21}$	$1.345x10^{21}$	~1 domain contains 15 particle
PPVITO-3	$1.890x10^{21}$	$2.56x10^{20}$	~1 domain contains 8 particle
PPVITO-4	$1.987x10^{21}$	$1.428x10^{20}$	~1 domain contains 3 particle

Table 2. Calculated numbers of molecules of PI/ PVDF and number of ITO particle within a domain connected to PI chain.

CHARACTERIZATIONS

Water Sorption

The water sorption behavior was performed using ASTM D570 method. Samples were dried at 100°C for 1 hr. and dipped in methanol to leach out residual solvent (DMAc). These samples were dried at 120°C for 2 hrs and then dipped in 100 ml of water. The water uptake at different intervals of time was recorded till it reaches the equilibrium condition. The Perkin-Elmer's Microbalance (Model-AD-4) having accuracy up to 1 microgram was used for the purpose. The water sorption was calculated using equation (1):

Water Uptake (%) = $[(W_0-W_1)/ W_1] \times 100$

where, W_1 and W_0 are the initial and final weight, respectively.

Sample designation	Water absorption %					
	24 h	48 h	72 h	96 h	120 h	144 h
PI	2.41	2.43	2.44	2.45	2.45	2.45
PPVITO-1	1.82	185	1.86	1.88	1.88	1.88
PPVITO-2	1.78	1.81	1.83	1.85	1.86	1.86
PPVITO-3	1.81	1.82	1.83	1.84	1.85	1.85
PPVITO-4	1.92	2.02	2.03	2.04	2.05	2.05

Table 3. Water absorption (%) of PI and PI/ PVDF/ ITO ternary composite thin films for different intervals of time.

Fourier Transform Infrared Spectrum (FT-IR)

The Fourier Transform Infrared Spectrum (FT-IR) of pure PI and PI/ PVDF/ ITO ternary composite thin films were obtained using Lambda BX instrument, Perkin Elmer, Singapore. Mostly, FT-IR applications are based on the correlation between IR frequency and chemical functional group. IR group frequencies may vary considerably for a given functional group (e.g., stretch frequency can vary from $1100cm^{-1}$ to $2300cm^{-1}$). Thus, group frequency can be a useful aid in identifying an unknown compound (by comparison to the same group frequency in a molecule of closely related structure).

Differential Scanning Calorimeter (DSC)

Modulated DSC (TA Instruments model 2910) was used to characterize Tg of the pure and ternary composite thin films.

X- Ray Diffraction (XRD)

The X- ray diffraction technique has been utilized to detect the degree of crystallinity and crystallite size within composite thin films. Samples were kept in the aluminum sample holder in such a way that upper surface is smooth and was exposed to X-rays in vertical goniometry assembly. The scan was taken between (10 to 80°) 2θ with scanning speed of 20° 2θ per min., the operating target voltage was 35kV, with a current of 20mA and radiation used is FeK alpha with wavelength of 1.93735 Å on Rigaku Rotating anode mode RU-H3R (18 kW), X-ray powder diffractometer and to evaluate the crystalline size K_α line of copper (λ =1.5418 Å) irradiation source was used.

In the present work, the degree of crystallinity has been measured on the premise that increasing amorphousness tends to broaden the line width whereas increasing crystallinity increases the intensity. The degree of crystallinity can also be estimated by comparing the intensity vs width of the line for obtaining crystallinity index. Accordingly, the scan is resolved into a crystalline peak, amorphous peak and the background. The following assumption is made: (i) The total scattering from the sample is divided between crystalline peaks from the crystallites and amorphous peak from the remaining amorphous regions. (ii) The total scattering from the sample is that included in the resolved crystalline and amorphous regions. (iii) The relative areas of the crystalline and the amorphous peak are respectively proportional to the mass of polymer in the crystalline and amorphous regions. Within these assumptions, the crystallinity index, X_c, is calculated for each sample from the resolved peak area using the equation:

$$X_c = \frac{A(C_r)}{A(C) + KA(A_m)_r} = \frac{1}{(1+KR)}$$

Where A (C_r) is the area of the crystalline peak, An (A_m) is the area of the amorphous peak, (R) is the ratio of amorphous to crystalline peak areas and (K) is constant. For comparison, (K) is set to unity.

Scanning Electron microscopy (SEM)

SEM micrographs help to study the complete chain formation with texture and other features of developed nano–domain structures, if any, in the pure and poly blend specimens. Study of polymer blends under the SEM can thus yield useful data on the surface morphology and phase distribution within a blend, which helps in predicting the final properties of the blend.

Atomic Force Microscopy (AFM)

AFM topography of PI, PVDF, ITO and PPVITO-1 film were imaged using (DIAFM-4 instrument) in tapping mode. Generally AFM works on two modes contact mode and tapping mode, however, due to the softness of the polymeric blends, AFM topography was taken out in tapping mode, which is more suitable for soft polymeric materials.

UV-Visible Spectroscopy

UV-visible spectra of the pure and composite thin films were recorded using a PerkinElmer Lambda 3B spectrophotometer in the wavelength range 190–1100 nm. The air was taken as reference for the characterization; the transmittance of the bare substrates was also measured for comparison. The band-gap energy (E_g) was calculated from the UV-visible spectra using

$E_g = hc / \lambda$

Where (h) is Planck’s constant (6.6×10^{-34} J s), (c) is the speed of light

(3×10^{8} ms^{-1}) and λ is the starting absorption wavelength.

Four Probe Technique

DC electrical conductivity of the PI and PPVITO ternary composite thin films was measured using a four-in-line probe. DC electrical conductivity, σ (in S cm^{-1}), was calculated using

$\rho = \rho^0 / G(W/S)$

$\sigma = 1 / \rho$

Where, ρ and ρ^0, W and S are the resistivity (Ω cm), thickness of the film (cm) and probe spacing (cm), respectively. G (W/S) is a correction divisor, which is a function of the thickness of the sample as well as probe spacing.

RESULT AND DISCUSSION

FTIR has been utilized to analyze the physical/chemical blending of PI, PVDF and ITO ternary composite thin films. Figure 1 shows the FT-IR absorption spectra for pure PI and composite films. A close examination of physical appearance of PPVITO-1 film reveals a uniform and smooth texture. It is clear that characteristic peak of PI, PVDF and ITO are present in PPVITO-1 film confirming the presence of PVDF polymer and ITO metal oxide in ternary system. The absorption spectrum of pure PI in figure clearly indicates the presence of aromatic moieties possibly the phenoxy or amino substituents at 1777, 1500 and 1020 cm^{-1}. The characteristic absorption band of pure PVDF shows the band of α- phase at 488.63-1072.74 cm^{-1} and β- phase at 414.82-1403 cm^{-1} [7, 8]. The vibrational band at 512 cm^{-1} corresponds to bending vibration mode of CF_2 dipoles, characteristic of TT (trans trans) conformation of the ferroelectric β–phase of PVDF. The absorption band appearing at 854 cm-1 is assigned to the characteristic frequency of vinylidene compound. The presence of indium and tin compounds was clearly identified at 770 and 725 cm^{-1} (absorption bands) in the figure. In figure PPVITO-1 ternary composite thin film the H-bonds was noticed on introducing PVDF with phenoxy or amino substituents present in PI. The CH_2 group of PVDF and indicates the formation of homogeneous blending with PI. The FTIR spectra of the PPVITO-1 film also revels the α- and β- phase of PVDF. The FTIR spectrum of the PPVITO-1 ternary composite thin film indicates the presence of 1, 4-disubstitution in aromatic (benzinoid) moieties between 1000 and 1500 cm^{-1}. The band corresponding to the out-of-plane bending vibration of C–H bonds of p-disubstituted benzene rings appears at 824 cm^{-1}. A few other moieties with either mono-substitution or other forms of disubstitution may occur as a result of the influence of the substituents, i.e. phenoxy or aryl carboxy substituent at 2723 cm^{-1}. The stretching frequency at 1775 cm^{-1} shows the interaction of C–O bonds. The bands corresponding to stretching vibration of In–O–O–Sn appear at 1497 and 1585 cm−1. The band close to 1130 cm $^{-1}$ describes the behavior of conducting composite films, which is due to delocalization of electrical charges caused by deprotonation.

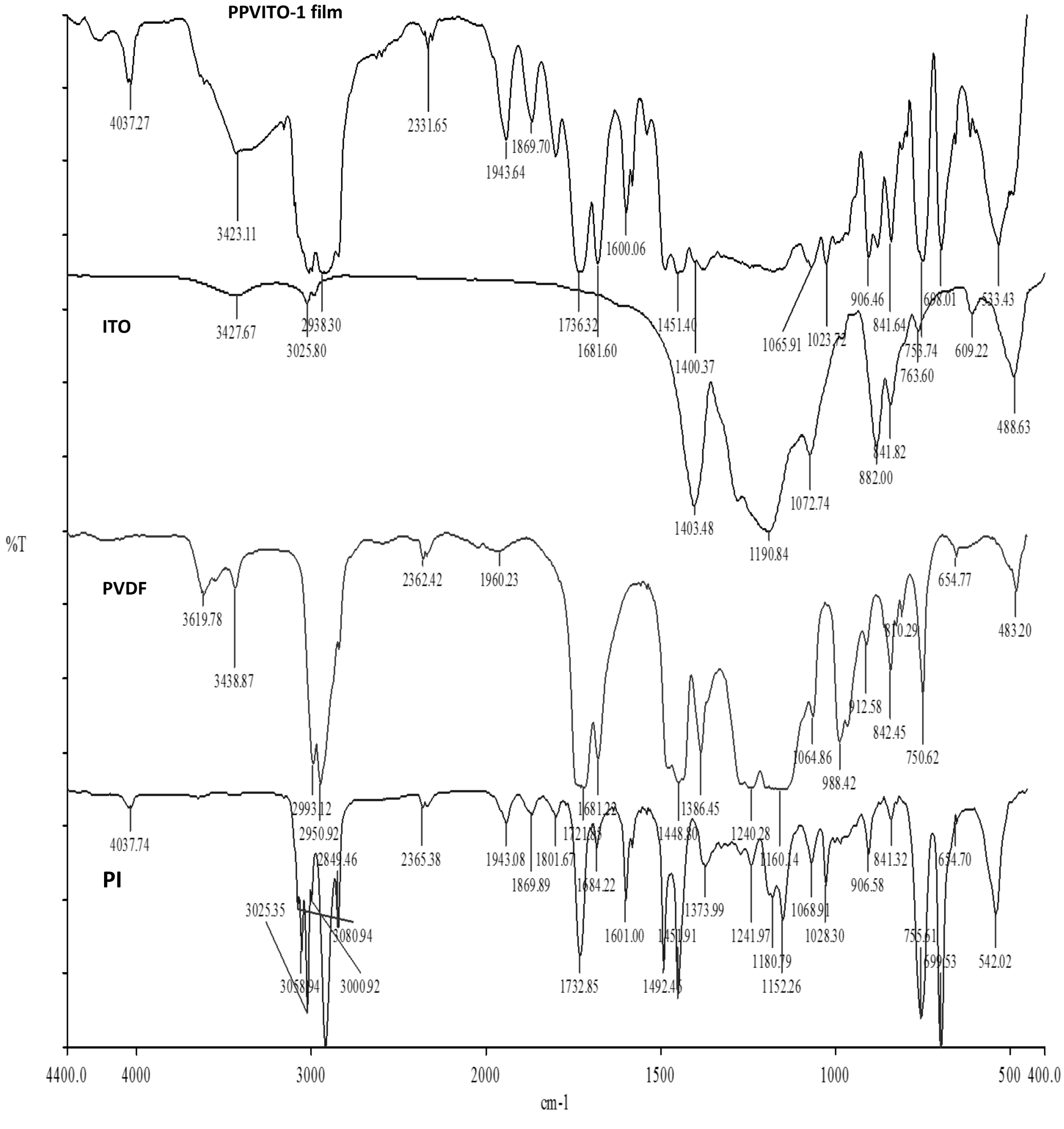
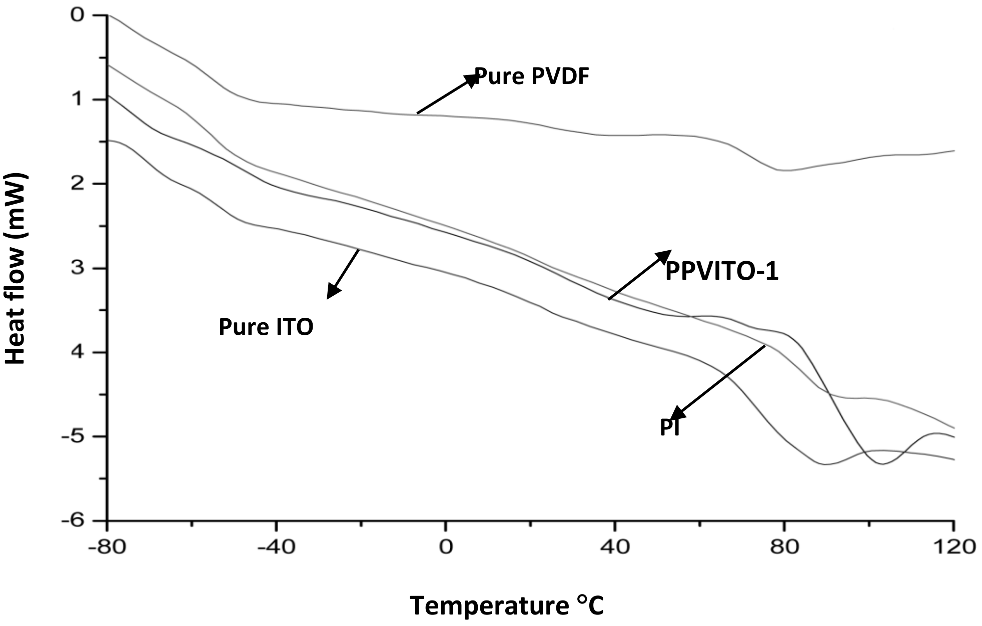


Figure 1. FT-IR spectrum of PI, PVDF, ITO and PPVITO-1 film.

Figure 2 shows the glass transition temperature, T_g, of pure PI, PVDF and ITO films along with the FEMA-1 film. Study related to T_g helps to understand the phase compatibility, morphology, degree of cross-linking etc. of ternary composite thin films. On observing the DSC thermograph, Fig. 2, the occurrence of an endothermic process is indicative. Close examination of DSC thermograph reveals a single T_g for PPVITO-1 film and shifting of T_g towards higher side shows the miscibility of three component with single phase and greater crystallinity. Thus shifting of T_g towards the higher region shows the presence of crystalline particle and crosslinking between them, which results in the hardening of ternary films in comparison to the individual. This also is inferred from the microhardness and mechanical analysis. A most interesting feature which is observed is that the vinylidene group of PVDF α- phase and β- phase forms a crystalline particle and gets embedded within the ITO. Thus, the surface enrichment in PPVITO films is strongly affected by the interaction parameter rather than the surface free energy difference.



XRD technique has been used to study the degree of crystallinity and to calculate the embedded crystalline particle size of ITO in the compound matrix of PI/PVDF. Crystallization depends on the degree of miscibility and mobility of crystallizable and non-crystallizable components of the ternary blend. Crystallinity can be estimated by comparing the intensity and width of lines [15]. Figs. 3 exhibit the XRD patterns of PI, PVDF, ITO and PPVITO-1 ternary composite thin film. In the present work, the crystallinity has been measured on the premise that increasing amorphousness tends to broaden the line width whereas increasing crystallinity increases the intensity. The degree of crystallinity can also be estimated by comparing the intensity vs width of the line for obtaining crystallinity index. The approach of Hermans and Weidinger has been utilized for obtaining crystallinity index, (Table 4), from XRD patterns of samples.

S. No.	Sample Designation	Calculated Crystallinity Index (X_c)
1.	PI	0.00
2.	ITO	3.56
3.	PVDF	2.96
4.	PPVITO-1	3.12
5.	PPVITO-2	2.37
6.	PPVITO-3	1.34
7.	PPVITO-4	Large Particle

XRD patterns in Fig. 3 shows the crystalline behavior of pure PI, PVDF, ITO and PPVITO ternary composite thin films, respectively. A higher value of the degree of crystallinity in the case of the PPVITO-1 film is observed in comparison to other PPVITO films. This is also supported by the calculated value of X_c as shown in Table 4 and 5.

The nanocrystalline particle size of ITO within the PI/ PVDF compound matrix was ablated by using the infinite three-dimensional crystal lattice defect X-ray in a manner analogous to the reflection of visual light from a ruled grating when the particle size is the of order of the wavelength of the incident beam. The diffraction beam becomes diffused as crystallite size decreases; the diffraction beam becomes more and more diffused until it is lost in the general background as for amorphous material. Thus the width of X-ray diffraction line is able to give crystallite size. The relationship between crystallite size and diffraction ray line broadening is given by Scherrer [15-16] equation:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where (K) is constant which depends upon the crystalline and diffractometer set up, **(**λ) is the wavelength of monochromatic radiation, (β) is full width at half maxima [FWHM], (θ) is the Braggs diffraction angle.

The value of K = 0.9 and, λ = 1.518 Å which are equipment parameters and the value of β and θ can be obtained from the diffraction pattern. The calculated value of crystallite particle size for PPVITO films with different composition is reported in Table 4 and 5.

Table 4. Calculated value of crystallinity for PEMA, PMMA, PVDF and their ternary blend films.

S. No.	Samples Designation	D (Å) nm
1.	Pure PI	Particles not present
2.	Pure PVDF	6.78
3.	Pure ITO	9.24
4.	PPVITO-1	1.34
5.	PPVITO-2	4, Particle size are too large due to agglomeration
6.	PPVITO-3	6, Particle size are too large due to agglomeration
7.	PPVITO-4	9, Particle size are too large due to agglomeration

Table 5. Particle size calculations of PI, PVDF, ITO and their ternary composite thin films from XRD Analysis.

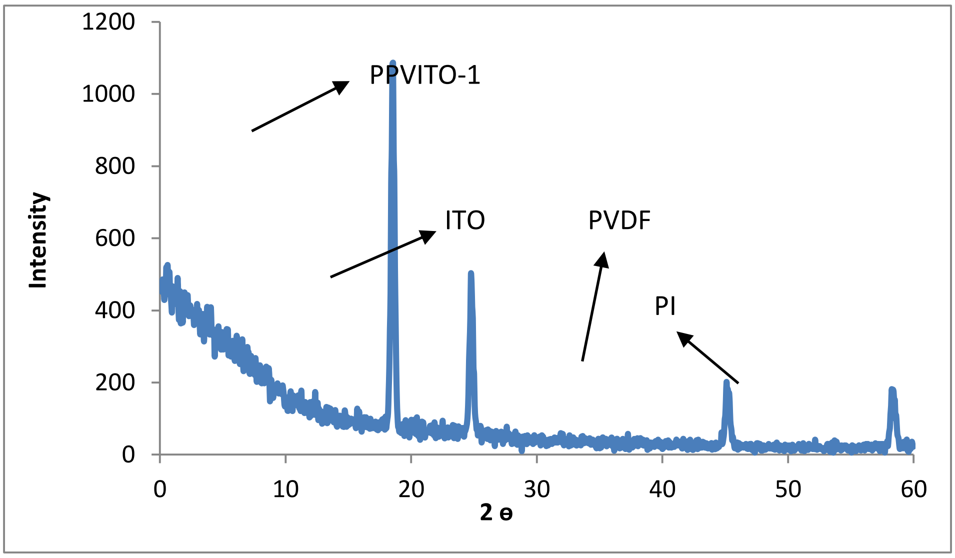


Figure 3 XRD graph for PI, PVDF, ITO and PPVITO-1 Films film.

SEM micrographs help in understanding the morphology and also the phase domain structure within the blend system. The SEM micrographs of specimens exhibit interesting trends related to physical properties such as phase structure, chain interpenetrating network, and mechanical strength. SEM micrographs shown in Figs. 4-7, help to understand the nanophase structure, chain interpenetrating network, morphological feature etc. of PI, PVDF, ITO and PPVITO-1 film. For PI amorphous morphology with complete unidirectional chain entanglement and with a smooth surface is observed. In the case of ITO rough morphology was observed. SEM photograph of PVDF shows a globular structure with some empty space between globules is evident. The sizes of these globular structures are found to be approximately 55 nm. Ternary composite thin film i.e. PPVITO-1 illustrate the presence of crystallite particles of ITO at nano/ micro regime within the compound matrix of PI/ PVDF. The presence of crystalline particles within the matrix leads to decrease in the surface enrichment for specific interaction between matrix and filler to form homogeneous ternary system.

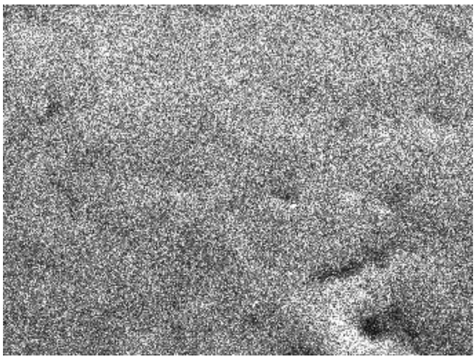


Figure 4. SEM micrographic image of ITO.

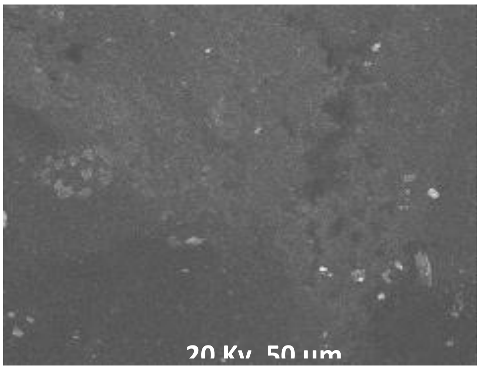


Figure 5. SEM micrographic image of PI film.

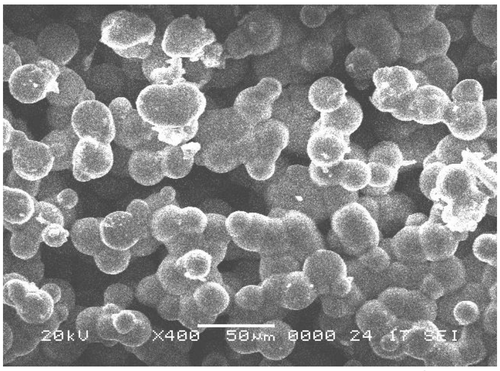


Figure 6. SEM micrographic image of PVDF.

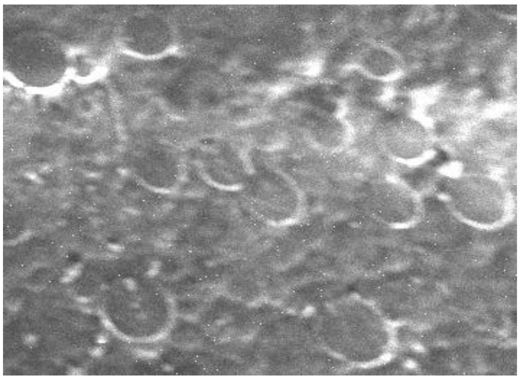


Figure 7. SEM micrographic image of PPVITO-1 film.

Figs. 8 to 11 show the micrograph image of PI, PVDF, ITO and PPVITO-1 ternary composite film, respectively. Figure 8-9, define the bulk characteristics indicating amorphous morphology of PI and ITO. Fig. 10 represents the topographic image for pure PVDF film, where spherical domains are observed. Ternary composite thin film PPVITO-1 film, shown in Fig. 11, illustrates the presence of crystalline particles of ITO at nano/ micro regime within the complex matrix of PI/ PVDF. Moreover, in addition, the role of PVDF blending with PI confirmed, the α- and β- particles of PVDF get embedded in micro/ nano level in spheroidal form. The presence of crystallite particles within the matrix leads to decrease in the surface enrichment for a specific interaction between matrices and filler to form homogeneous ternary system. The result suggests that the surface enrichment in this study is more strongly affected by the interaction parameter. Therefore, it should be noted that the degree of surface enrichment is controlled by the magnitude of interaction. The most significant outcome of the proposed work is that better miscibility with a greater degree of cross-linking between an amorphous and crystalline material having uniform texture can be found when PI, PVDF, and ITO are mixed in calculated proportion.

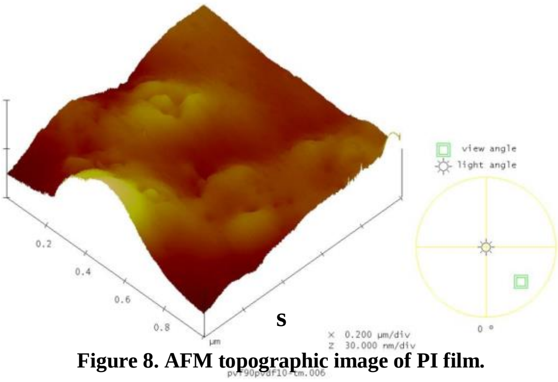


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Figure 8. AFM topographic image of PI film.

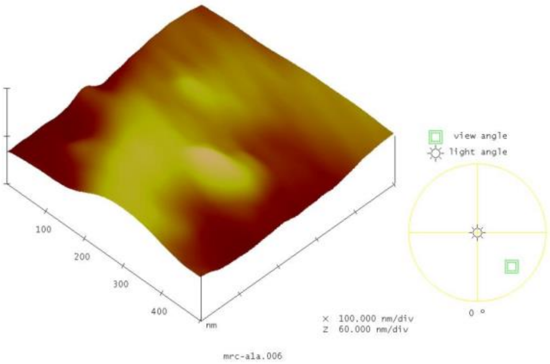

Figure 9. AFM topographic image of ITO film.

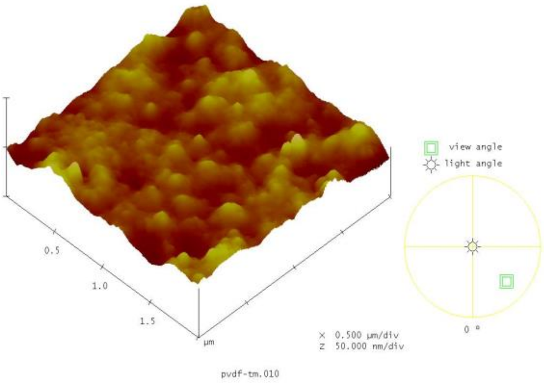

Figure 10. AFM micrographic image of pure PVDF film.

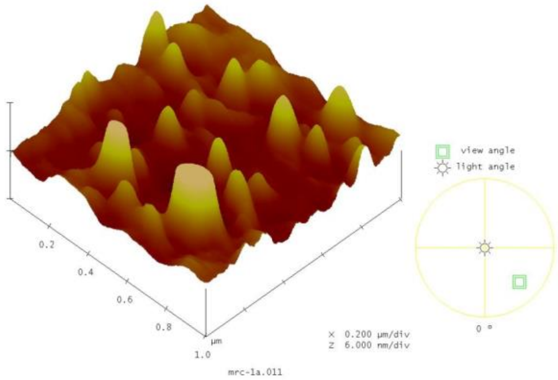

Figure 11. AFM micrographic image of the FEMA-1 film.

The UV-visible spectra shown in Figure 12 allow an analysis of the transparency and a calculation of the band-gap of the pure PI and PI/ITO composite films. The results are summarized in Table 6. From Fig. 12 it is evident that the transparency of the composite films is not affected adversely on ITO and PVDF incorporation into the PI matrix. Moreover, the compatibility of the composite films is found to be increased markedly, which is due to better dispersion of ITO particles within PI and PVDF matrix and also the chain compatibility of PVDF with PI. This is also confirmed by SEM and AFM analysis. On comparing with PI film, it is found that the ternary composite thin films have stronger absorption in the band near the UV region. It is also found that the band gap decreases as the amount of ITO increases. Best result was fond in the PPVITO-1 ternary composite thin film. The variation of electrical properties is summarized in Table 6. The resistivity of the thin films significantly decreases when PVDF and ITO were added in a calculated amount in PI; hence, the conductivity of the films increases. The change in the band-gap strongly depends on the amount of incorporated material, which may possibly be due to the formation of additional energy levels near the conduction band formed by incorporated material. The decrease in the resistivity of the composite films as the percentage of ITO increases could be related to the increase in the free carrier concentration as the number of oxygen vacancies in the material increases. In general, the electrical conductivity of the ITO incorporated composite thin films is determined by the oxygen vacancies which are responsible for the carrier density and hence the conductivity.

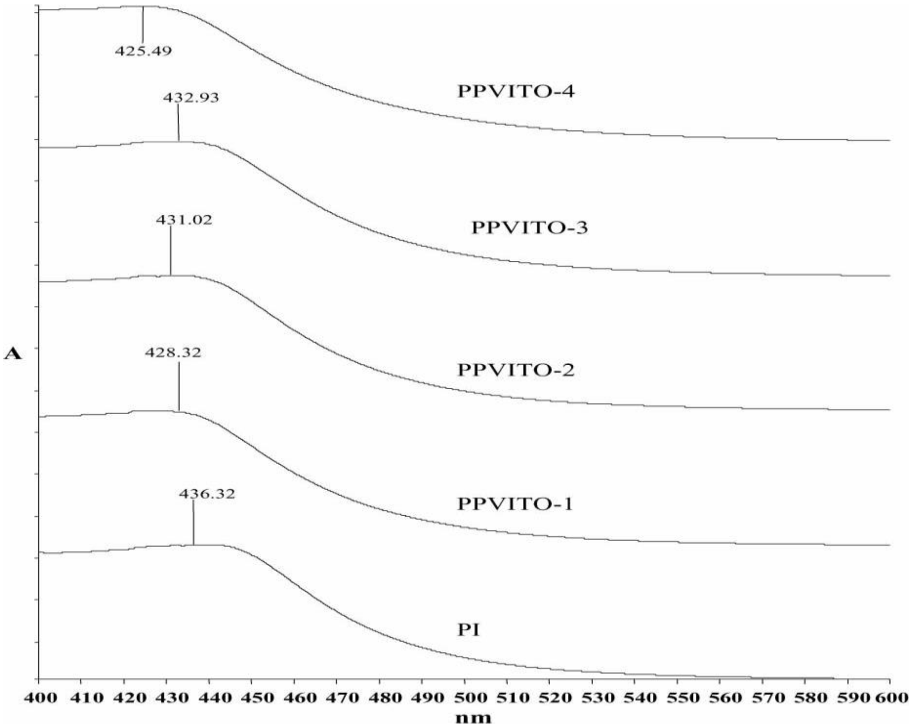

Figure 12.UV-visible spectra of PI and PPVITO ternary composite thin films

Table 6. Calculated value of band-gap, resistivity and conductivity of PI and PPVITO

ternary composite thin films. (-^{a} no conductivity)

Composition (%)	Band-gap (eV)	Resistivity (Ω cm)	Conductivity (S cm^{-1})
PI	2.7	1.01×10^{-15}	-^{a}
PPVITO-1	2.20	0.05×10^{-14}	0.05×10^{-7}
PPVITO-2	2.51	0.08×10^{-14}	0.08×10^{-13}
PPVITO-3	2.60	0.09×10^{-14}	1.02×10^{-13}
PPVITO-4	2.69	1.01×10^{-14}	1.04×10^{-13}

CONCLUSION

A series of PVDF/ ITP/ PI ternary composite thin films were prepared using an in-situ generation approach. The composite films obtained were characterized to facilitate the study of morphology structural property relationships and electrical behavior of developed ternary composite thin films. The resultant products were found to exhibit an unusual synergistic change in macroscopic properties by micro-modification realized by the formation of PVDF and ITO particles within the PI. The overall improvement in the properties of the composite films is attributed to the presence of crosslink network structure and dense packing of dispersed PVDF/ ITO particles within the PI matrix. The PVDF/ ITO/ PI high-temperature resistive conducting composite films are useful products for a wide spectrum of uses in solar cells, thin-film transistors, and microelectronics applications.

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