

Optical and Micro structural Studies on films of Pb (NO₃)₂ filled PVA-PVP composite

Preeti B Hammannavar, Blaise Lobo

Department of Physics, Karnatak Science College, Karnatak University, Dharwad 580 001, Karnataka, India

Corresponding author: Blaise Lobo

Abstract: Lead Nitrate (Pb(NO₃)₂) filled polyvinyl alcohol (PVA)- polyvinyl pyrrolidone (PVP) composite films were prepared by solution casting method, with filler levels varying from 7.6 wt% up to 39.8 wt%. These films were characterized by using UV-Visible spectroscopy, fluorescence spectroscopy and fluorescence microscope. The UV-Visible spectra showed incorporation of additional bands in the HOMO-LUMO bandgap, with increment of filler (Pb(NO₃)₂) content in the polymeric blend (PVA-PVP) matrix. Fluorescence microscope images reveal hexagonal patterns in the low and moderate range of filler concentration, varying from 7.6 wt% up to 19.9 wt%, and further increment of filler concentration leads to exaggeration of filler in the polymer matrix, for which fluorescence microscope images show no pattern. Width of absorption bands, as well as the edge of the optical absorption in the polymer films is measured from the optical spectra of the composite polymeric blends and their values are listed separately. Fluorescence spectra of composite films, with filler level varying from 7.6 wt% up to 24.8 wt% show decrease in intensity of photo-luminescence, whereas a further increase in filler content increases the fluorescence intensity. Surface morphology of the prepared Pb(NO₃)₂ filled PVA/PVP composite show significant variation; as the filler concentration in the polymer matrix increases, the surface roughness increases.

Keywords: UV-Visible; Fluorescence; Fluorescence microscopy; Atomic force microscope; Lead nitrate; Doping; PVA-PVP blend; Composite.

I. Introduction

Research on development of radiation shielding materials has gained vital importance in recent times, due to large number of applications of ionising radiation, like for example, medical diagnosis and treatment, food preservation and radiation induced modification of materials. Personnel handling equipment using high activity ionising radiation sources, as well as users have to be protected from the dangerous effects of radiation. In this direction, the use of polymers as radiation shielding materials shows promise, especially when they have a high atomic number (Z) component, like for example, lead (Pb), bismuth (Bi) or tungsten (W) incorporated as filler [1-3]. Therefore, preparation and characterization of high Z metal salt incorporated polymers and polymeric blends assumes relevance. A correlation between structural changes and modified properties of the resulting material (composite) helps to tailor it, for potential applications. The metal salt incorporated polymer composites need to be properly characterized, using different techniques. Another field involving application of metal salt doped polymeric blends is its use as solid polymeric electrolytes (SPE) [4]. Application as energy storage devices can also be explored [5].

Polyvinyl alcohol (PVA) is a linear, semi-crystalline vinyl polymer wherein a rotation of chain segments is restricted or aided by neighbouring segmental molecules. The hydroxyl group is responsible for interesting chemical and physical properties of PVA. High water solubility, crystallinity and other desirable properties of PVA, like for example, its non-toxic nature makes it widely applicable to linear and non-linear optical components, sensor applications, as well as a host of optoelectronic systems, magneto-optical recording devices and bio-medical uses [6]. PVA doped with iodine/ potassium iodide (KI), ferric chloride, potassium permanganate and other inorganic salts has been studied by researchers [7-13].

Polyvinylpyrrolidone (PVP) is a high molecular weight polymer which is soluble in water and some polar solvents; it is an amorphous vinyl polymer. PVP contains a rigid pyrrolidone group (proton accepting carbonyl group). PVP is a tasteless and odourless white powder, which forms various complexes with other polymers. PVA and PVP are found to be miscible in different proportions, and have interesting properties and applications [14-16]. PVA-PVP blends have been doped with different chemical agents, including inorganic salts; composites have been prepared by incorporating inorganic salts in PVA-PVP blend [17-20]. Many polymers (non-conjugated polymers) do not have intrinsic charge carriers; hence, in order to enhance charge carrier content in the system, doping, either by oxidation or reduction is necessary. The dopant induced change in properties of the resulting composite can be studied by various known techniques like UV-Visible spectroscopy, fluorescence spectroscopy, x-ray diffraction, x-ray fluorescence and thermal analysis, among

many others [21-27]. However, structure and properties of the host polymeric material are altered due to incorporation of a filler or doping species. This change in the properties of a doped or filled polymeric material or composite depends on how the incorporated chemical species interacts with the polymer matrix as well as the nature of the filler. In this paper, lead nitrate (Pb(NO₃)₂) has been chosen as the filler, which has been incorporated in PVA-PVP blend, because this inorganic salt (Pb(NO₃)₂) contains the high – Z component, Pb, which makes the resulting composite a good radiation shielding material [3, 19, 25].

First, the effect of Pb(NO₃)₂ on optical properties of PVA-PVP blend was studied, using UV-Visible spectroscopy. UV-Visible absorption spectroscopy involves molecules undergoing electronic transitions on absorption of electromagnetic (EM) radiation of suitable frequency in UV (200 nm – 400 nm) or visible (400 nm-800 nm) range. Optical absorption spectroscopy (UV-Visible spectroscopy) is one of the necessary tools required to understand effect of filler on the band-structure of a polymer matrix. Incorporation of filler in a polymer matrix alters its energy band gap. UV-Visible absorption spectrometer records the degree of absorption in a sample at different wavelengths and the resulting plot of absorbance (*A*) versus wavelength (λ) gives a UV-Visible spectrum. Most significant quantities that can be determined from UV-Visible absorption spectra are the wavelength at which there is a maximum absorption (λ_{max}) and the absorption edge.

Fluorescence (or photo-luminescence) spectroscopy records the emission spectrum, when the sample (target material) absorbs light of suitable frequency (which is chosen after studying UV-Visible absorption spectrum of the same target material). Fluorescence spectroscopy is used to investigate emission of light from a sample (polymer/ organic-inorganic compounds), after it is excited by incident EM radiation by using a beam of visible or UV light of proper frequency required to excite electrons (from HOMO to LUMO) in molecules of the material (and causes them to emit light of lower frequency). Fluorescence spectroscopy is applicable in biochemical, medical and chemical (materials science) research fields, for analyzing organic compounds. Atomic force microscopy (AFM) is applicable to visualize conducting, non-conducting and insulating surfaces, and permits resolution of individual atoms.

II. Experimental

2.1 Materials:

PVA (of molecular weight 140,000), PVP (of molecular weight 50,000) and lead nitrate Pb(NO₃)₂ were purchased from HiMedia Laboratories Pvt. Ltd., Mumbai.

2.1 SAMPLE PREPARATION:

Sample preparation was done using solution casting method. Two grams of PVA and two grams of PVP are taken in a cleaned beaker and mixed thoroughly with a glass rod. Later, to obtain a homogeneous solution, 100 ml of double distilled water was added and the mixture was continuously stirred for eight hours, by using a magnetic stirrer. Eight such identical PVA-PVP homogeneous solutions were prepared in different glass beakers. A known amount of standard Pb(NO₃)₂ aqueous solution was prepared in 100 ml of double distilled water. Different volumes of this standard aqueous solution of Pb(NO₃)₂ was added to homogeneous solution of PVA-PVP already prepared, and then the resulting mixture was stirred again, using magnetic stirrer, for half an hour so that Pb(NO₃)₂ which acts as a filler is evenly mixed in homogeneous aqueous solution of PVA-PVP blend. These identical solutions were then poured into glass petridishes and kept in a hot air oven maintained at 40°C, in order to get films by solution casting. After a week, the films were peeled from the glass substrate, carefully labelled and stored in a desiccator, for further characterization.

2.2 CHARACTERIZATION

Hitachi U 3310 UV-Visible spectrometer was used to obtain optical spectra of the prepared Pb(NO₃)₂ filled PVA-PVP composite samples, the wavelength of incident EM radiation on the prepared films was varied from 200 nm up to 700 nm, and the intensity of transmitted EM radiation was recorded at each wavelength. Obtained UV-Visible absorption spectra have been analysed, to study optical properties of the prepared samples. F-7000 FL spectrophotometer (scan speed of 1200nm/min) was used to obtain the photoluminescence (fluorescence) spectra of composite films, with excitation wavelength fixed at 380 nm, and PMT voltage fixed at 500V. Fluorescence microscope was used to obtain images with different types of reflectors, namely, AF 488 (green image), DAPI 49 (blue image) and Rhod 29 (red image). 40X sensitivity was used for all images. Nanosurf Easyscan 2 instrument was used to record the Atomic Force Microscopy (AFM) images. Specifications of operating mode are 200mV of free vibration amplitude and 8 μ m/s speed of the tip.

III. Results And Discussion

UV-Visible (optical) spectra of Pb(NO₃)₂ filled PVA-PVP composite films, with filler level (FL) varying from 7.6 wt% up to 39.8 wt% are shown in Fig. 1.

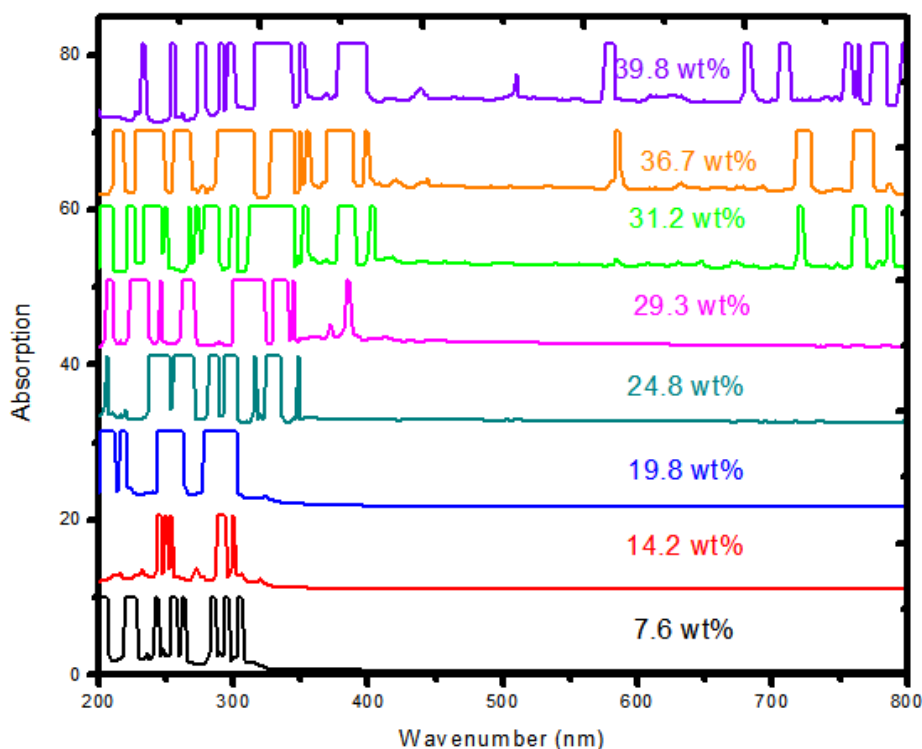


Figure 1. UV-Visible spectra of Pb(NO₃)₂ filled PVA-PVP composite films.

UV-Visible spectra of Pb(NO₃)₂ filled PVA-PVP composite films, with filler levels varying from 7.6 wt% up to 39.8 wt% show incorporation of additional absorption bands in the LUMO-HOMO band gap of the polymeric host (PVA-PVP blend), as illustrated in Fig. 1. As the filler content is increased from 7.6 wt% to 29.3 wt%, there is red shift in absorption bands, along with increase in width of these bands. UV-Visible spectra for composite samples with FL varying (from 7.6 wt% to 29.3 wt%) show additional bands, as well as their superposition. Further increment of the filler, Pb(NO₃)₂ in PVA-PVP matrix reveal presence of additional absorption bands in the higher wavelength region, which could be due to complex formation. Thus, UV-Visible spectra reveals significant modification in band structure of PVA-PVP blend, on incorporation of Pb(NO₃)₂ as filler. It is important to note that the extent of modification in band-structure of the composite films depends on the filler level.

UV-Visible spectra, at different filler levels of Pb(NO₃)₂ in PVA-PVP blend were analyzed to yield important parameters about additional bands introduced on incorporation of filler. The parameters thus determined are listed in table 1. The values of start (rising edge), absorption peak (apex) and end (falling edge) of each absorption band are listed in table 1, for different filler levels. From fig. 1 and table 1, it can be noted that additional bands are introduced in the forbidden band gap [HOMO-LUMO band gap] in the band structure of PVA-PVP blend, due to the incorporation of filler (Pb(NO₃)₂) in the polymeric host (PVA-PVP blend).

Table 1. List of number of bands in the UV spectra of Pb(NO₃)₂ filled PVA-PVP composite films for filler levels varying from 7.6 wt% up to 39.8 wt% .

Absorption Band 7.6 wt %				
Sl.No.	Start (eV)	Apex (eV)	End (eV)	width (eV)
1	3.76	4.19	4.52	0.76
2	4.52	4.84	5.34	0.82
3	5.34	5.49	5.85	0.51
Absorption Band 14.2 wt%				
1	2.25	4.13	4.40	2.15
2	4.40	4.56	4.63	0.23
3	4.63	4.96	5.58	0.95
4	5.58	5.74	6.20	0.62
Absorption Band 19.9 wt%.				
1	1.80	3.83	3.97	2.17
2	3.97	4.16	4.59	0.62
3	4.59	4.80	5.34	0.75
4	5.34	5.74	6.20	0.86
Absorption Band 24.8 wt%.				
1	1.55	3.56	3.65	2.10

2	3.65	3.76	4.03	0.38
3	4.03	4.16	4.52	0.49
4	4.52	4.66	5.49	0.97
Absorption Band 29.3 wt%.				
1	1.55	1.58	1.60	0.05
2	1.60	1.66	1.69	0.09
3	1.69	3.01	3.12	1.43
4	3.12	3.21	3.56	0.44
5	3.56	3.69	3.80	0.24
6	3.80	3.89	4.46	0.66
7	4.46	4.63	4.84	0.38
8	4.84	5.34	5.69	0.85
Absorption Band 31.2 wt%.				
1	1.55	1.58	1.60	0.05
2	1.60	1.62	1.68	0.08
3	1.68	1.72	1.79	0.11
4	1.79	1.84	1.88	0.09
5	1.88	3.07	3.15	1.27
6	3.15	3.21	3.41	0.26
7	3.41	3.65	4.03	0.62
8	4.03	4.37	4.73	0.70
9	4.73	5.12	6.20	1.47
Absorption Band 36.7 wt%.				
1	1.55	1.61	1.68	0.13
2	1.68	1.71	1.77	0.09
3	1.77	1.79	1.81	0.04
4	1.81	1.82	1.86	0.05
5	1.86	1.88	1.91	0.05
6	1.91	1.96	1.99	0.08
7	1.99	2.12	2.16	0.17
8	2.16	2.21	2.25	0.09
9	2.25	2.33	2.40	0.15
10	2.40	2.45	2.49	0.09
11	2.49	2.79	2.87	0.38
12	2.87	2.95	3.00	0.13
13	3.00	3.09	3.16	0.16
14	3.16	3.23	3.41	0.25
15	3.41	3.48	3.87	0.46
16	3.87	3.99	4.52	0.65
17	4.52	4.69	4.88	0.36
18	4.88	5.08	5.53	0.65
19	5.53	5.74	6.19	0.66
Absorption Band 39.8 wt%.				
1	1.55	1.554	1.61	0.06
2	1.61	1.75	1.78	0.17
3	1.78	1.81	1.93	0.15
4	1.93	1.98	2.07	0.14
5	2.07	2.14	2.19	0.12
6	2.19	2.43	2.53	0.34
7	2.53	2.82	3.04	0.51
8	3.04	3.15	3.42	0.38
9	3.42	3.52	3.58	0.16
10	3.58	3.67	3.97	0.39
11	3.97	4.46	4.66	0.69
12	4.66	4.84	5.08	0.42

Fluorescence or photo-luminescence (PL) spectra of PVA-PVP samples filled with Pb(NO₃)₂ is shown in Fig. 2. The peaks obtained are identified by multiple Gaussian fitting (fig. 3 and listed in table 2). Fluorescence peak intensity decreases for PVA-PVP samples doped with Pb(NO₃)₂ in dopant range varying from 7.6 wt% up to 24.8 wt%. Fig. 3 reflects the increased interaction between filler (Pb(NO₃)₂) and host polymer molecules (PVA-PVP). The decrease in fluorescence intensity is due to fluorescence quenching. However, the fluorescence intensity increases for samples with filler level equal to 29.3 wt% and 31.2 wt%. Further incorporation of Pb(NO₃)₂ in the polymer matrix, that is, for filler levels varying from 31.2 wt% up to 39.9 wt%, there is again a decrease in fluorescence intensity.

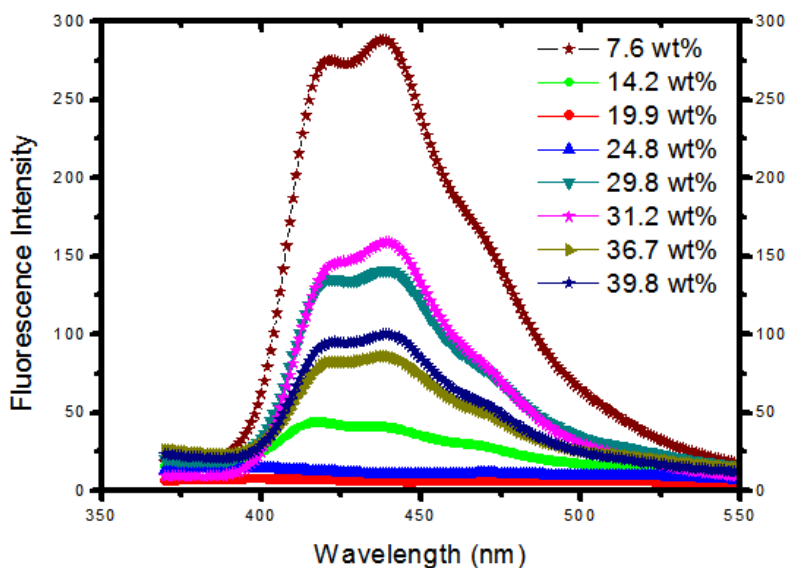


Figure 2. Fluorescence spectra of $Pb(NO_3)_2$ filled PVA-PVP composite, with filler levels from 7.6 wt% up to 39.8 wt%.

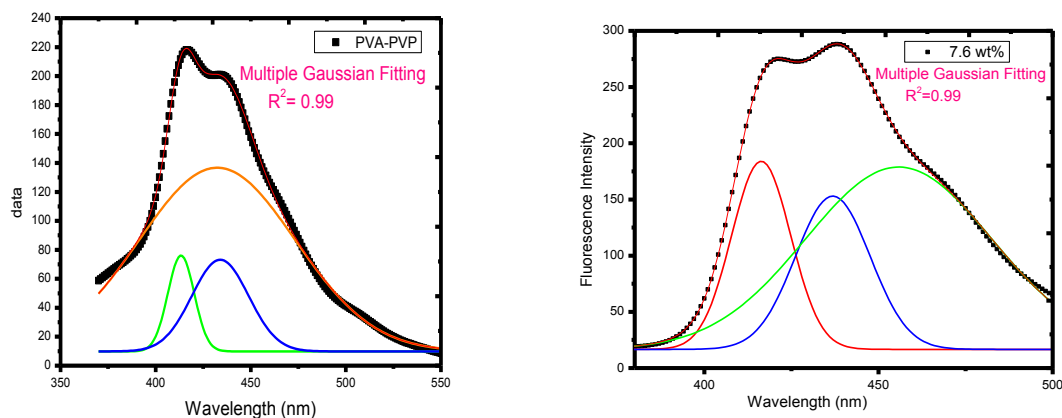


Figure 3. Fluorescence spectra of un-doped PVA-PVP blend, showing multiple Gaussian fitting (figure on left). The plot on right side shows Gaussian fitting for fluorescence spectra of $Pb(NO_3)_2$ filled PVA-PVP composite film, at filler level 7.6 wt%.

Table 2. Area under peak (A), Center (X_c), width and the height of the acquired fluorescence spectra of $Pb(NO_3)_2$ filled PVA-PVP composite films, after Gaussian fitting ($R^2 = 0.99$)

Filler Level FL (wt%)	Emission Band No.	Area	Center λ_p (nm)	Peak energy E_p (eV)	FWHM $\Delta \lambda$ (nm)	Width of energy band, ΔE (eV)	Height (Counts)
0.0	1	13038.7	432	2.9	82.0	15.1	127
	2	1149.4	413	2.3	13.8	89.6	66
	3	2366.6	433	2.9	29.8	41.6	63
7.6	1	47949.3	414	2.9	15.9	77.9	2403
	2	55118.6	435	2.8	22.1	56.0	1986
	3	130802.5	455	2.7	55.2	22.5	1892
14.2	1	11914.6	416	2.9	27.3	45.4	348
	2	2534.5	440	2.8	14.5	85.3	139
	3	7944.9	461	2.7	33.4	37.2	190
	4	1058.1	500	2.5	21.6	57.3	39
19.9	1	5874.8	395	3.1	75.8	16.4	62
	2	441.7	458	2.7	28.8	43.1	12
	3	4859.1	506	2.5	73.3	16.9	53
29.8	1	26894.7	415	2.9	16.9	73.5	1273
	2	19124.8	436	2.8	17.4	71.3	877
	3	70557.4	452	2.7	52.5	23.6	1072
31.2	1	5172.4	417	2.9	15.9	77.6	258
	2	6621.9	436	2.8	21.2	58.4	249

	3	12462.3	455	2.7	49.9	24.8	199
36.7	1	16689.9	416	2.9	17.1	72.7	781
	2	12082.5	437	2.8	18.3	67.9	528
	3	40325.9	449	2.8	49.5	25.0	649
39.8	1	25812.9	416	2.9	17.7	70.0	1163
	2	17968.5	437	2.8	17.9	69.5	803
	3	47469.5	452	2.7	46.4	26.7	815

Fluorescence microscopy imaging is done with three different reflectors, namely, DAPI 49, AF 488 and Rhod 20. The fluorescence microscope images of PVA-PVP samples filled with $Pb(NO_3)_2$ are shown in Fig. 4 – Fig. 12, for composite samples with filler levels varying from 7.6 wt% up to 39.8 wt%. The blue image is from the reflector DAPI 49, the reflector AF 488 results in green image and the red image is the effect of the reflector Rhod 20. Significant changes are observed in the fluorescence microscope images of PVA-PVP samples filled with $Pb(NO_3)_2$, when compared to that of un-doped PVA-PVP blend. In the lower concentration region, for composite films with filler levels varying from 7.6 wt% up to 19.9 wt%, hexagonal patterns and other shapes are seen in these images, due to surface structural features caused by the filler. Increase of filler content in the polymer matrix, from 24.8 wt% up to 29.3 wt%, results in complete interaction of filler and PVA-PVP blend, so the fluorescence microscope image reflects uniform deposition of filler in the polymer matrix. This is complemented from fluorescence spectra, which show very less fluorescence intensity at higher filler levels in the composite.

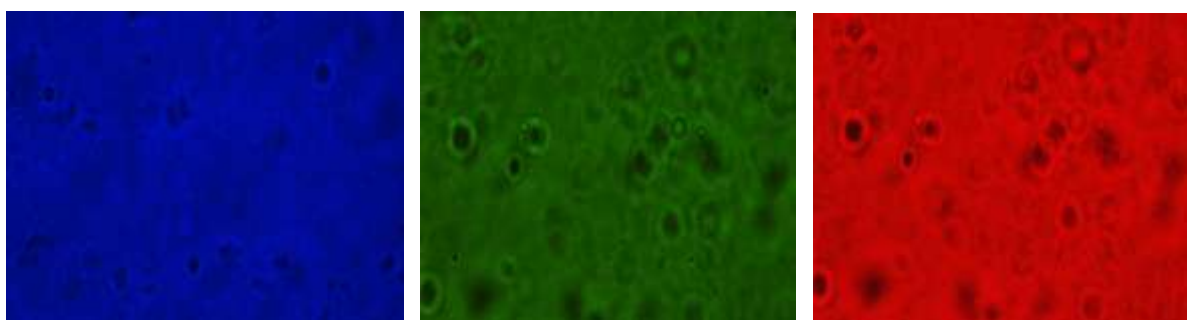


Figure 4. Fluorescence microscope images of un-doped PVA-PVP blend, with different filters; The blue image (left) is from the reflector “DAPI 49”, the reflector “AF 488” results in green image (middle) and the red image (on right) involves use of reflector “Rhod 20”.

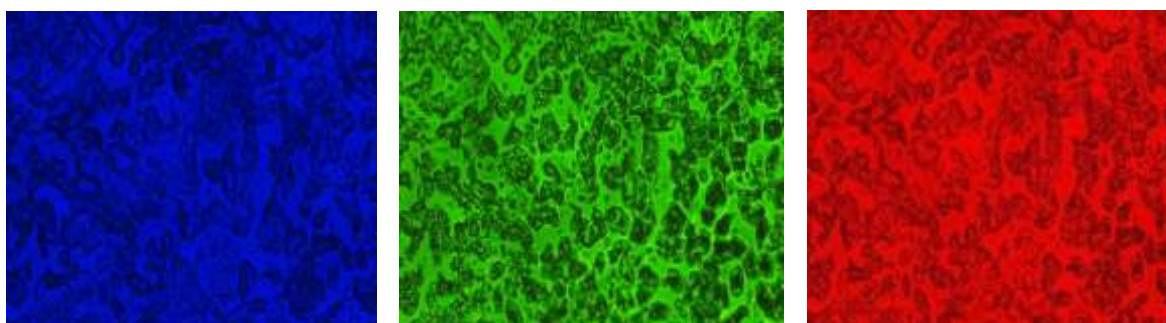


Figure 5. Fluorescence microscope images of $Pb(NO_3)_2$ filled PVA-PVP composite film of filler level (FL) 7.6 wt%.

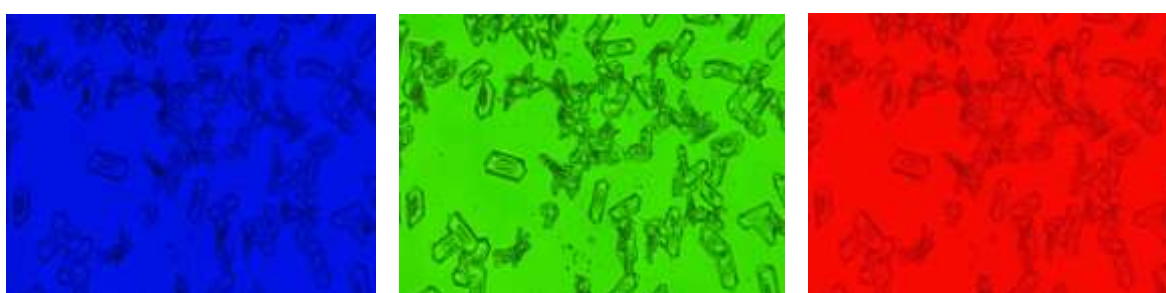


Figure 6. Fluorescence microscope images of $Pb(NO_3)_2$ filled PVA-PVP composite film of FL 14.2 wt%.

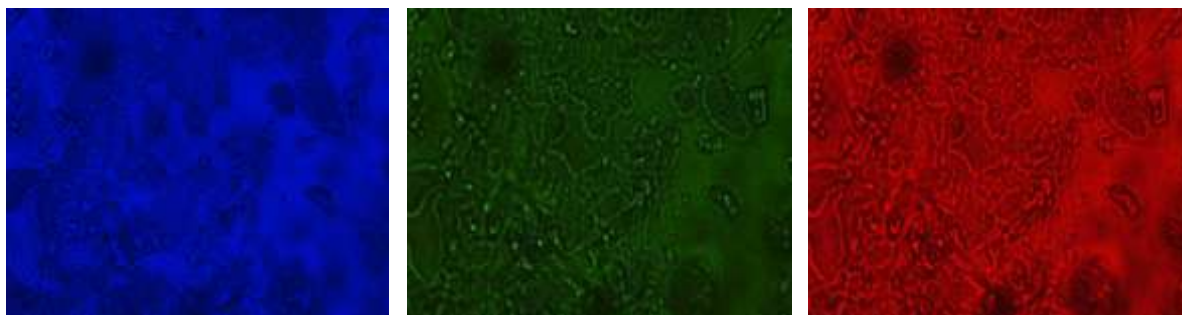


Figure 7. Fluorescence microscope images of Pb(NO₃)₂ filled PVA-PVP composite film of FL 19.9 wt%.

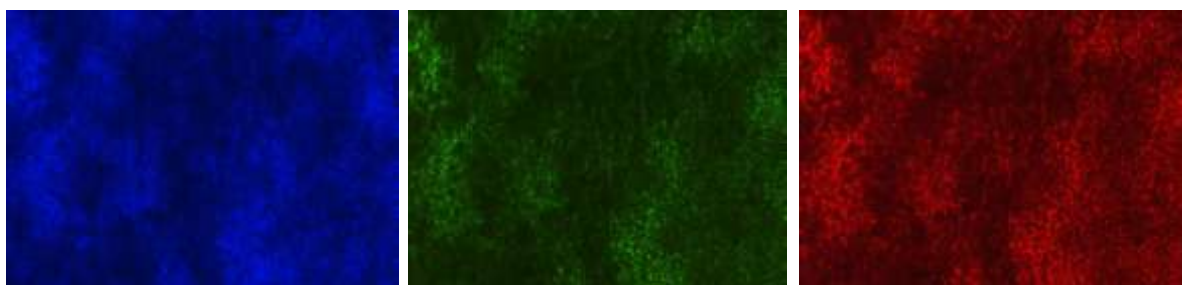


Figure 8. Fluorescence microscope images of Pb(NO₃)₂ filled PVA-PVP composite film of FL 24.8 wt%.

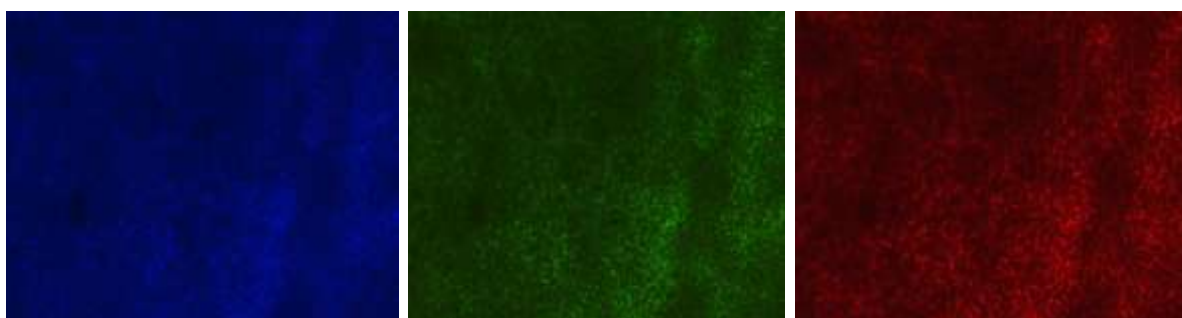


Figure 9. Fluorescence microscopic image of Pb(NO₃)₂ filled PVA-PVP composite film of FL 29.8 wt%.



Figure 10. Fluorescence microscope images of Pb(NO₃)₂ filled PVA-PVP composite film of FL 31.2 wt%.



Figure 11. Fluorescence microscope images of Pb(NO₃)₂ filled PVA-PVP composite film of FL 36.7 wt%



Figure 12. Fluorescence microscope image of $Pb(NO_3)_2$ filled PVA-PVP composite film of FL 39.8 wt%.

Atomic Force Microscopy relates to surface modifications in the polymeric material. The scanned images with respective scan of graph are as shown in Fig. 13 – Fig. 21. Each sample (composite film) for this study was cut to dimension of 10 mm × 10 mm. Bright regions and spikes observed in the images are due to the effect of filler, $Pb(NO_3)_2$, on the morphology of the polymeric blend (PVA-PVP). Morphological variations observed in the obtained images is due to inter/intra molecular interaction between PVA-PVP blend and ions of the filler (Pb^{2+} and NO_3^- ions). Measured surface roughness parameters, namely, arithmetic mean height (S_a), root mean square height (S_q), maximum peak height (S_p), maximum pit height (S_v) and material ratio (S_m) are listed in the table 3.

Table 3. List of area roughness parameters (100 μm^2) arithmetic mean height (S_a), root mean square height (S_q), maximum peak height (S_p), maximum pit height (S_v) and material ratio (S_m), for $Pb(NO_3)_2$ filled PVA-PVP composite film of different filler levels (FL).

FL (wt%)	S_a (mV)	S_q (mV)	S_p (mV)	S_v (mV)	S_m (nV)
0.0	3.7	5.7	40.4	73.9	3.3
2.7	1.30	1.85	8.41	12.88	3.3
14.2	7.10	10.38	40.35	811.16	3.3
19.9	0.50	0.653	4.29	4.92	3.3
24.8	3.40	4.37	21.30	14.40	3.3
29.8	8.90	11.59	28.29	82.70	3.3
31.2	19.10	26.62	95.34	93.30	3.3
36.7	2.75	3.92	12.61	23.26	3.3
39.8	14.50	20.48	65.33	92.23	3.3

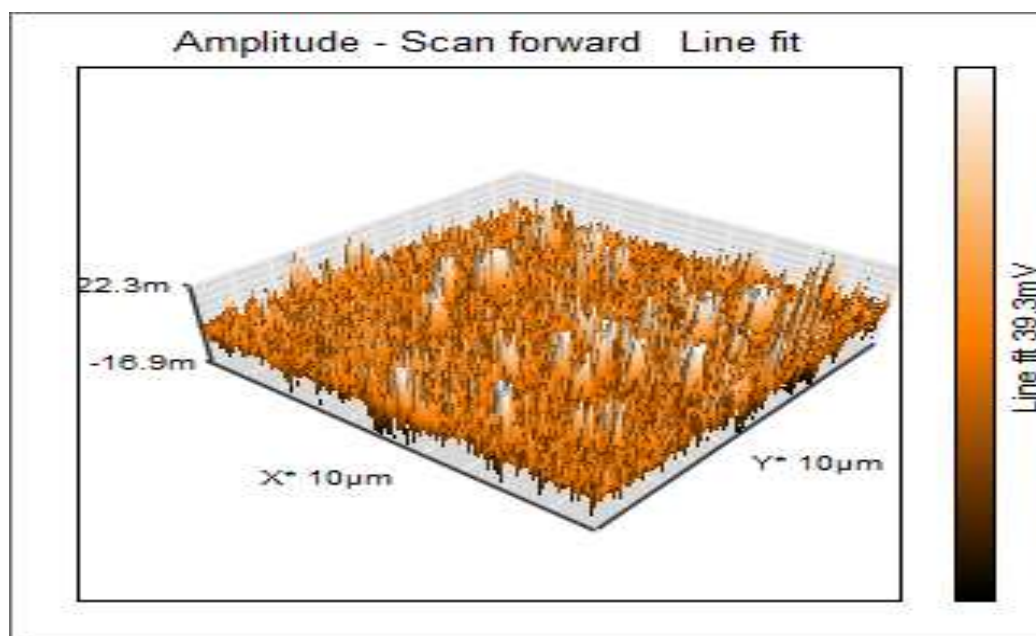


Figure 13. AFM image of 0.0 wt% (un-doped) PVA-PVP blend film.

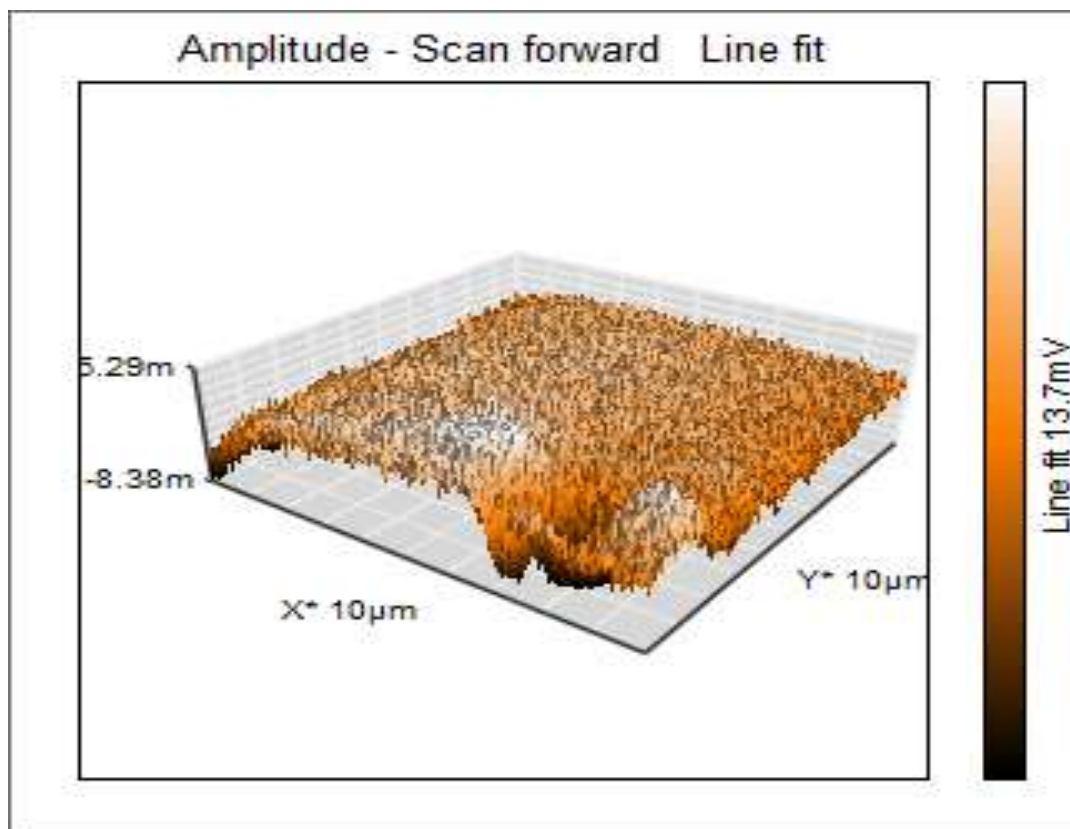


Figure 14. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 7.6 wt%.

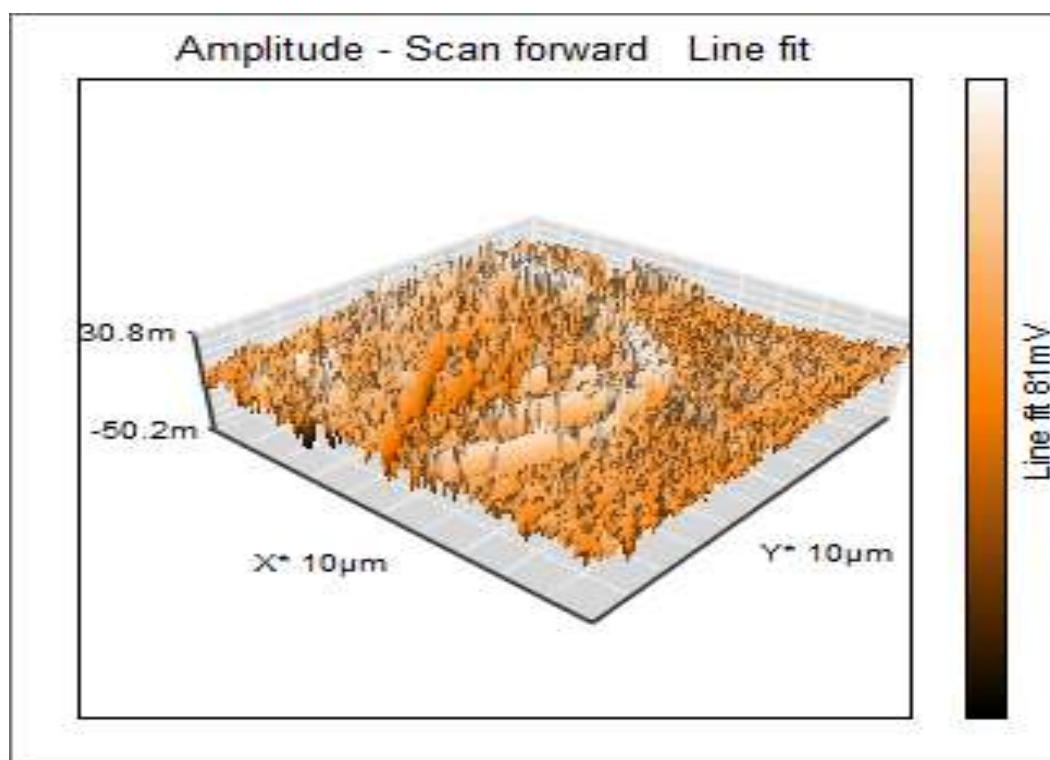


Figure 15. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 14.2 wt%.

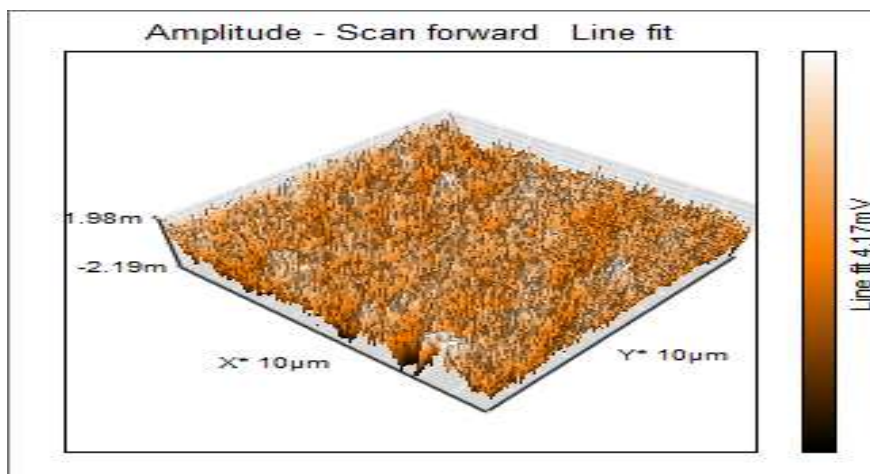


Figure 16. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 19.9 wt%.

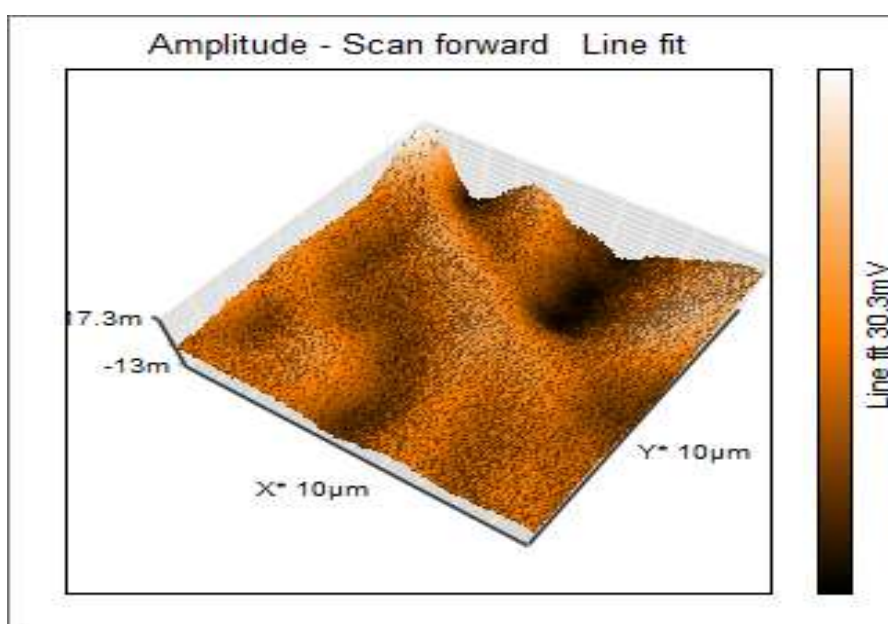


Figure 17. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 24.8 wt%.

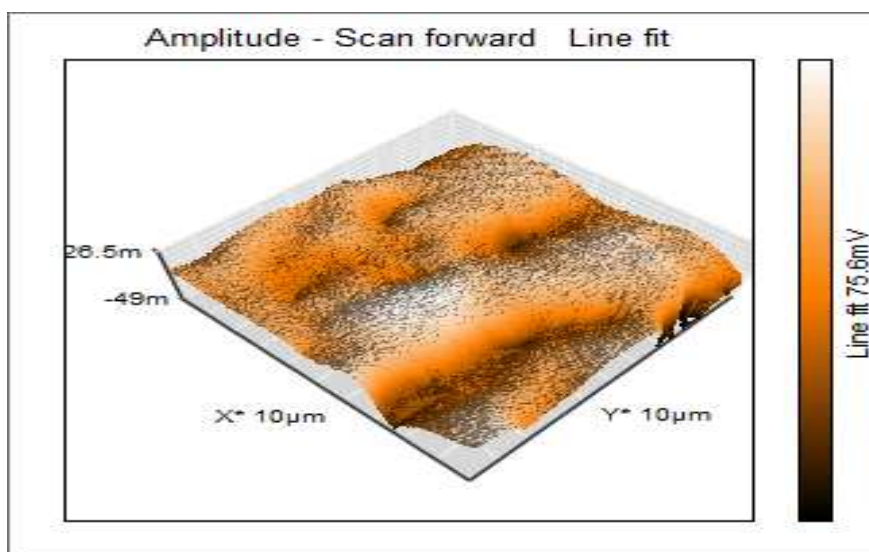


Figure 18. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 29.8 wt%.

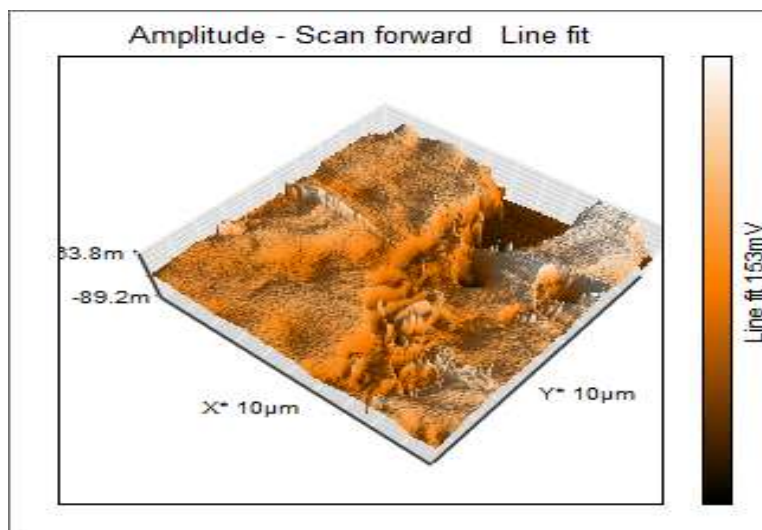


Figure 19. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 31.2 wt%.

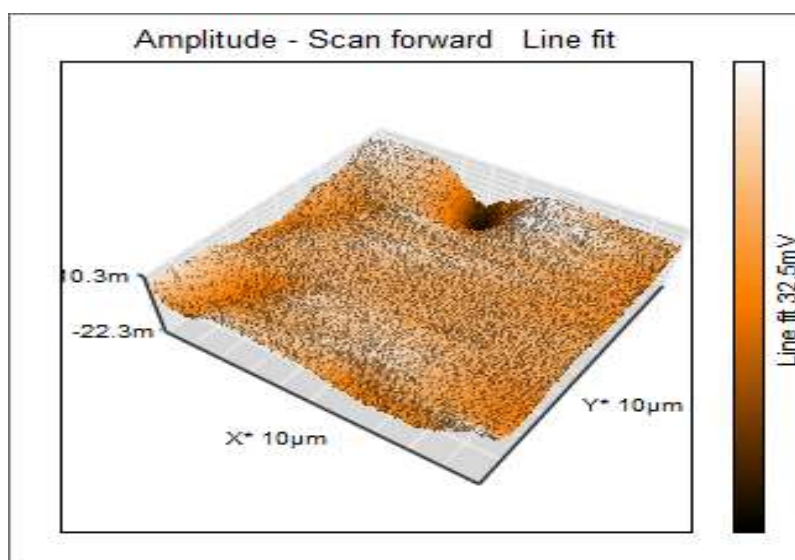


Figure 20. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 36.7 wt%.

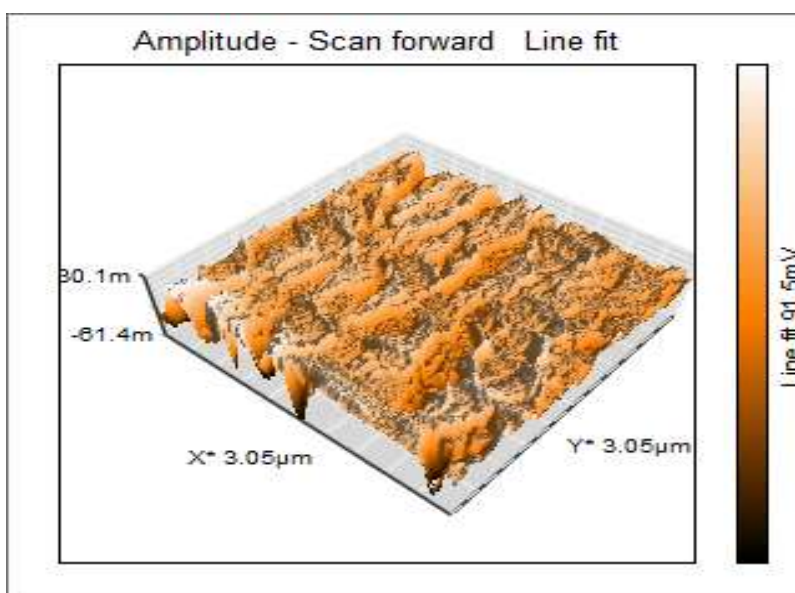


Figure 21. AFM image of $Pb(NO_3)_2$ filled PVA-PVP composite film, with FL 39.8 wt%.

IV. Conclusions

Pb(NO₃)₂ filled PVA-PVP composite films prepared by solution casting method were characterised by UV-Visible spectroscopy which revealed the effect of the filler in the polymer matrix on the band structure of the polymeric blend. As the concentration of the filler in the polymer matrix increases, the UV-Visible spectra showed multiple additional absorption bands, with a red shift. The fluorescence microscopy images shows formation of hexagonal structures, when observed in different reflectors (DAPI 49, AF 488, Rhod 20). The variation in fluorescence intensity is the effect of filler in the polymer matrix wherein, fluorescence quenches at lower dopant concentration from 7.6 wt% to 24.8 wt%. On increasing the filler concentration in the polymer matrix, the fluorescence intensity also increases at the moderate doping levels from 7.6 wt% to 39.8 wt% AFM images show roughness of the surface.

Acknowledgements

The authors are thankful to University Science Instrumentation Centre (USIC), Karnatak University Dharwad (KUD), for providing facility to record UV-Visible spectra, fluorescence spectra and fluorescence microscope images. One of the authors (PBH) is thankful to KUD for financial assistance in the form of UPE fellowship.

References

- [1] V. Harish, N. Nagaiah and H. G. Harish Kumar, Lead oxides filled isophthalic resin polymer composites for gamma radiation shielding applications, *Indian J. Pure Appl. Phys.* 50 (11), 2012, 847 - 850.
- [2] R. Mirji and B. Lobo, Computation of the mass attenuation coefficient of polymeric materials at specific gamma photon energies, *Rad. Phys. Chem.* 135, 2017, 32 - 44.
- [3] R. Mirji and B. Lobo, Radiation shielding materials: A brief review on methods, scope and significance, *Proc. National Conference on Advances in VLSI and Microelectronics*, P.C. Jabin Science College, Huballi, India, 27 January 2017, ISBN: 978-81-931806-8-6, p 96 - 100.
- [4] F. Croce, G.B. Appetecchi, L. Persi and B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, *Nature* 394, 1998, 456 - 458.
- [5] L. Nyholm, G. Nyström, A. Mhryan and M. Strømme, Toward flexible polymer and paper – based energy storage devices, *Advanced Materials*, 23 (33), 2011, 3751 – 3769.
- [6] C. M. Hassan and N. A. Peppas, Structure and applications of polyvinylalcohol hydrogels produced by conventional crosslinking or by freezing/thawing methods, *Advances in polymer science*, 153, 2000, 37-65.
- [7] B. Lobo, M. R. Ranganath, T. S. G. Ravi Chandran, G. Venugopal Rao, V. Ravindrachary and S. Gopal, Iodine – doped polyvinylalcohol using positron annihilation spectroscopy, *Phys. Rev. B* 59 (21), 1999, 13693- 13698.
- [8] B. Lobo and M. R. Ranganath, Analysis of the optical spectra of UV irradiated Fe:PVA, *Proc. 53rd DAE Solid State Physics Symposium*, BARC and TIFR, Mumbai, 16-20 December 2008, ISBN 978-81-8372-044-1, *Solid State Physics (India)* 53, 2008, 589-590.
- [9] B. Lobo, B. M. Baraker, P.B. Hammannavar, R. F. Bhajantri, M. R. Ranganath, M. Hurkadli, and V. Ravindrachary, DBAR investigation on films of polypyrrole incorporated polyvinylalcohol doped with ferric chloride, *J. Phys: Conf. Ser.* 618 (1), 2015, 012026 (1-4).
- [10] M. R. Ranganath and B. Lobo, Thermal analysis of potassium permanganate oxidized poly (vinyl alcohol) films, *Proc. Int. Conf. on Nanotechnology: Materials and Composites for Frontier Applications*, Bharati Vidyapeeth Deemed University, 14-15 October 2010, p 56-57.
- [11] R. F. Bhajantri, V. Ravindrachary, A. Harisha, V. Crasta, S. P. Nayak and B. Poojary, Microstructural studies on BaCl₂ doped poly(vinyl alcohol), *Polymer* 47 (10), 2006, 3591 – 3598.
- [12] S. Kramadhathi, and K. Thyagarajan, Optical Properties of Pure and Doped (KNO₃ & MgCl₂) Polyvinyl Alcohol Polymer Thin Films, *International Journal of Engineering Research and Development* , 6 (8) , 2013, 15-18.
- [13] R. T. Abdulwahid, O. G. Abdullah, S. B. Aziz, S. A. Hussein, F. F. Muhammad, and M. Y. Yahya, The study of structural and optical properties of PVA/PbO₂ based solid polymer nanocomposite, *J. Mater. Sci: Mater. Electron.*, 27 (11), 2016, 12112-12118.
- [14] J. Lu, Q. Nguyen, J. Zhou, and Z. H. Ping, Poly(vinyl alcohol)/Poly(vinyl pyrrolidone) Interpenetrating Polymer Network: Synthesis and Pervaporation Properties, *Journal of Applied Polymer Science*, 89 (10), 2003, 2808–2814.
- [15] A. B. Seabra, and M. G. de Oliveira, Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blended films for local nitric oxide release, *Biomaterials*, 25 (17), 2004, 3773-3782.
- [16] A. Bernal, I. Kuritka, and P. Saha, Poly(vinyl alcohol)-poly(vinyl pyrrolidone) blends: Preparation and characterization for a prospective medical application, *Proc. 13th WSEAS international conference on mathematical and computational methods in science and engineering, Catania, Sicily, Italy — November 03 - 05, 2011; ISBN:978-1-61804-046-6*, 431-434.
- [17] K. Hemalatha, Mahadevaiah, G. K. Gowtham, G. Thejas Urs, H. Somashekarappa, and R. Somashekar, Microstructural and electrical properties of PVA/PVP polymer blend films doped with cupric sulphate, *AIP Conf. Proc.*, 1731 (1), 2016, 070007.
- [18] B. M. Baraker and B. Lobo, Analysis of electrical measurements on cadmium chloride doped PVA-PVP blend, *Mapana: Journal of Sciences* 16 (1), 2017, 45 – 65.
- [19] P. B. Hammannavar and B. Lobo, Study of lead nitrate doped PVA/PVP blend films using EDXRF and complementary techniques, *Macromol. Symp.* 376 (1), 2017, 1600198 (1-6).
- [20] N. Rajeswari., S. Selvasekarapandian, C. Sanjeeviraja, J. Kawamura, S. A. Bahadur , A study on polymer blend electrolyte based on PVA/PVP with proton salt, *Polymer Bulletin*, 71 (5), 2014, 1061-1080.
- [21] R.F. Bhajantri, V. Ravindrachary, B. Poojary, Ismayil, A. Harisha, and V. Crasta, Studies on fluorescent PVA + PVP + MPDMAPP composite films, *Polymer Engineering and Science*, 49 (5), 2009, 903-909.
- [22] V. Krishnakumar, and G. Shanmugham, Electrical and optical properties of pure and Pb²⁺ ion doped PVA-PEG doped polymer composite electrolyte films, *Ionics*, 18 (4), 2012, 403-411.

- [23] S. Nagalingam, S. Monohorn, H. S. Min, and A. Kassim, Synthesis of PbSe thin film by chemical bath deposition and its characterisation using XRD, SEM and UV-Visible spectrophotometer, *Makara Seri Sains*, 14 (2), 2010, 117-120.
- [24] B. M. Baraker and B. Lobo, Spectroscopic analysis of CdCl₂ doped PVA-PVP blend films, *Can. J. Phys.* 95 (8), 2017, 738 – 747.
- [25] P. B. Hammannavar and B. Lobo, Investigation of high Z components doped in polymeric films, using 2π configuration X-ray fluorescence technique, *Macromol. Symp.* 376 (1), 2017, 1600212 (1-5).
- [26] O. W. Guirguis, and M. T. H. Moselhey, Thermal and structural studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends, *Natural Sciences*, 4 (1), 2012, 57-67.
- [27] G. Attia and M.F.H. Abd El-Kader, Structural, optical and thermal characterization of PVA/2HEC polyblend film, *Int. J. Electrochem. Sci.*, 8, 2013, 5672-5687.

IOSR Journal of Applied Physics (IOSR-JAP) (IOSR-JAP) is UGC approved Journal with SI. No. 5010, Journal no. 49054.

Preeti B Hammannavar, Blaise Lobo "Optical and Micro structural Studies on films of Pb (NO₃)₂ filled PVA-PVP composite." IOSR Journal of Applied Physics (IOSR-JAP) , vol. 9, no. 6, 2017, pp. 13-25.