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Image profiling of poly-(diamino naphthalene) doped poly-(vinyl alcohol) film by time of flight secondary ion mass spectrometry

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ABSTRACT

Due to its high mass resolution and high sensitivity with low surface damage under static limit, ToF-SIMS has acquired great importance in the past few years. In complex systems where the films are made up of more than two polymers, it is quite difficult to identify image profiles with great contrast. In this paper, the comparative study of image profiles of poly-(diamino naphthalene) (PDAN) doped poly-(vinyl alcohol) (PVA), monomer doped PVA and pure PVA films have been studied. Without much higher consideration of parameter "static limit", the image profiling of all three films with higher resolution are obtained with ToF-SIMS technique. The image profiling results show that for going towards higher mass species, the intensity i.e. contrast of images decreases as well as the ions count also decreases. The primary ion dose of the ion beam from ToF-SIMS becomes 62.25, which is under limit to avoid surface damages.

Keywords: Time of flight secondary ion mass spectrometry, poly-(diamino naphthalene), poly- (vinyl alcohol), Static limit, Image profile

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INTRODUCTION

It is well known fact that due to high mass resolution with high sensitivity under low surface damage in static conditions, ToF-SIMS technique produces good results for the wide applications in studying surface morphology of organic polymer films [1-5]. The binding energy between monomer species applied large impact in the image profiling of a samples, with ToF-SIMS technique. In the imaging mode this technique collects the data for each point of the surface as well as constructs the images of each species distributed over the surface and the interfaces. But for the organic polymers it is quite difficult to identify all the species and the relation between them because these species are countless. At the same time for higher mass fragments, though much more important, may produce weaker signal due to the static limit condition of the SIMS. The static limit or static condition maintains the integrity of the surface layer within the timescale of the analytical experiment. This limit, expressed as the number of ions per square cm, ensures that the probability of bombarding a previously damaged area is extremely low. For simplicity, if analyst knows the chemical formula or structure of organic polymers than, for specific species present inside or the surface, can obtain the images and analyze the imaging profile.

For obtaining the image profile accurately with maintaining adequate signal/noise ratio, parameter "static limit" plays the important role. To determine the static limit, the surface area which has been imaged, individual scan time and primary beam current are known and then primary ion dose (ions/cm^2) will be calculated for each scan [6]. If there is change in the contrast in the ion images, the static limit will vary and on the basis of this concept the description of image profile can be observed or analyzed [7]. Normally, intensity of the secondary ion decreases as the surface density of the species increases and therefore in the mass spectrum, going towards the higher mass fragments, the intensity is largely affected by surface density [8]. In this paper the image profile of PDAN doped PVA film, without much consideration of parameter static limit, has been analyzed.

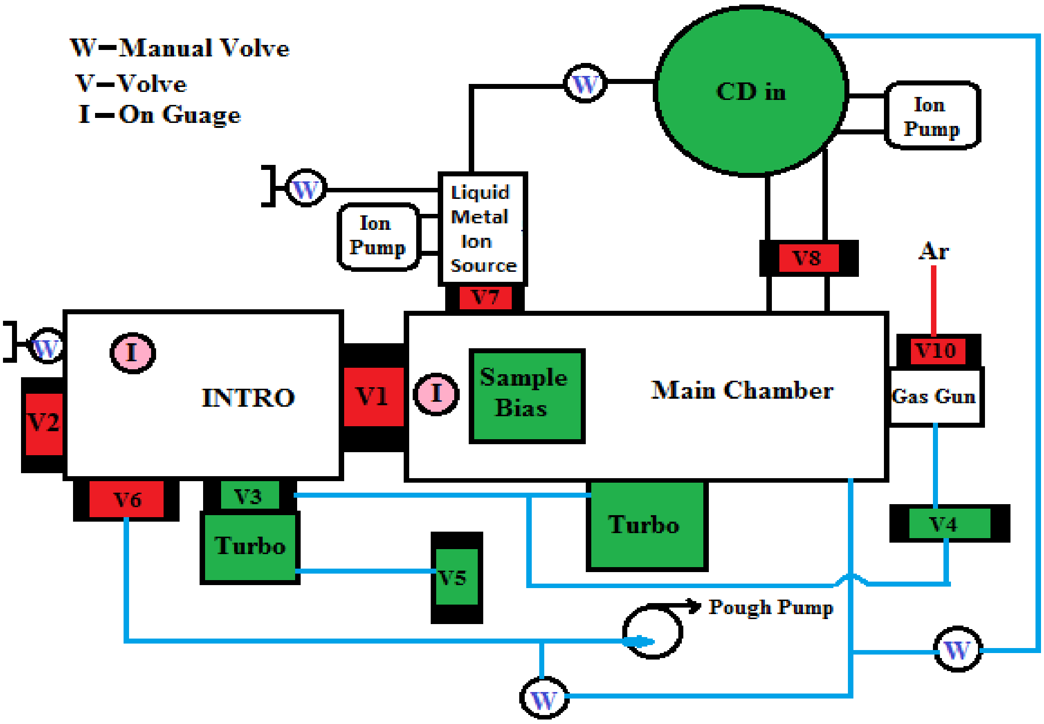


Fig.1 Block Diagram of ToF-SIMS

MATERIALS AND METHODS

2.1 Materials and Methods

PVA (99% hydrolyzed, MW 85,000) was purchased from Hi Media Chemicals, Mumbai, India. The monomer DAN was purchased from Merck Chemicals, Mumbai, India. Solvent acetonitrile (MW 41.05) was purchased from Hi Media Chemicals, Mumbai, India with a maximum limit of impurities of water (KF) of 0.1% and non-volatile substances of 0.005%. All other reagents were of high purity grade.

In a typical experiment, 5 g PVA was dissolved in 100 mL of hot distilled water and to this solution pre-calculated amount of glutaraldehyde was added as cross-linking agent. Now, the whole mixture was kept in a Petri dish (Corning glass, 2.5" diameter) at oven at 50°C for 48 h. After 48 h, the whole mass was in the form of semi transparent film. The dry film was equilibrated in distilled water for a week to leach out toxic chemicals. The swollen gel was than dried at room temperature, cut into rectangular size pieces and stored in air tight plastic bags.

Required quantity of DAN was dissolved in acetonitrile and the PVA gel was allowed to soak in the DAN solution for 48 h. The DAN containing swollen gel was dried and dipped into oxidizing reagent. As the polymerization proceeds, the semi transparent gel turns into black and when seen in white light its color looks dark brown.

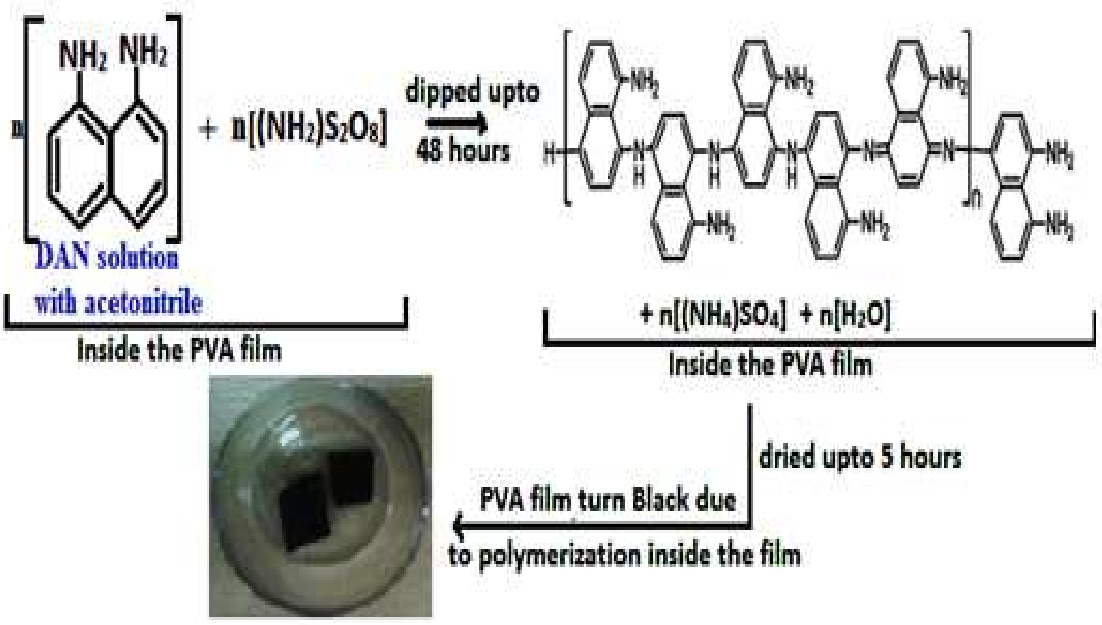


Fig.2 Proposed mechanistic pathway for synthesis of the PDAN-based PVA film

2.2 About the instrument

Time-of-Flight Secondary Ion Mass Spectroscopy (ToF SIMS) is a surface sensitive spectroscopy that uses a pulsed primary Ion beam to induce desorption and ionization of atomic and molecular species from a solid sample surface. The instrument have PHI TRIFT V nanoTOF model. This is surface analysis instrument manufactured by Physical Electronics, USA. The primary ion beam which is used to ionize the surface molecules is Gallium ion source with maximum ion beam energy of 30 KeV. Therefore, for mass data acquisition Ga_3^+ cluster ion was implemented which produces secondary ion of molecules of different masses, lying at the upper surface of the sample. The Gallium beam current was 3 X 10^{-9} Amps and Raster size 60 X 60 µm^2. Mass data acquisition was performed by raster scanning over a 200 X 200 µm^2 area. Surface spectra acquisition for 5 min. was employed for mass data at delivering rate of 4 nA current. An oxygen ion source was employed as the sputter/etch tool with 3 KeV sputter ion energy and the oxygen beam current was 8.4 X 10^{-7} Amps. Therefore, the depth profiling experiments were performed by singly charged oxygen ions. The oxygen ion sputter/etch area was 600 X 600 µm^2. A sputter/etch interval of 10 sec. was used in this analysis. The data acquisition obtained by two frame method of interval of 0.26 min. and the whole apparatus works on the phase profile mode.

RESULTS AND DISCUSSION

The molecular formula and polymeric structure of PDAN and PVA are expressed in Figure 3. As per experimental method, the polymerization of DAN will take place well inside the PVA film.

Molecular mass of glutaraldehyde $[CH_2(CH_2CHO)_2]$ = 100

Molecular mass of monomer of poly-(vinyl alcohol) $[(CH_2CHOH)]$ = 44

Molecular mass of monomer of poly-(diamino naphthalene) $[C_{10}H_{10}N_2]$ = 158
It is well known fact that each impact physically affects an area of 10 nm^2 which implies that 10^9 impacts/cm^2 influence all the atoms in the surface. Therefore, the static limit is defined to be $\leq 10^9$ ions/cm^2 without much considering the parameter "sputter yield". Any primary ion dose lower than this value is accepted in the static regime of SIMS analysis.

The primary ion dose is calculated by using the formula:

$$\text{Primary ion dose} = \frac{I_p t}{A} \qquad (1)$$

where I_p is primary ion flux (A/cm^2), t (sec.) is the analysis time and A (cm^2) is the bombarded surface area [9].

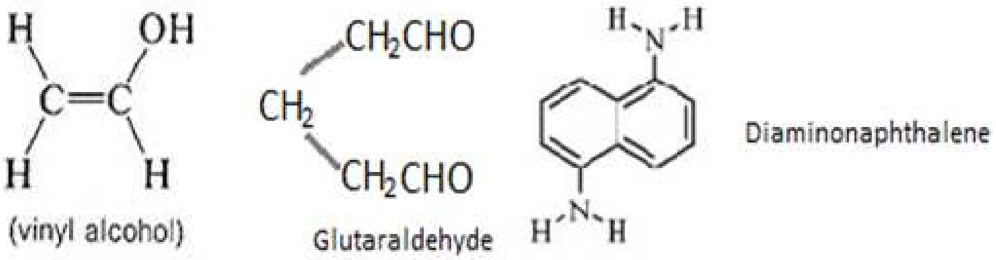
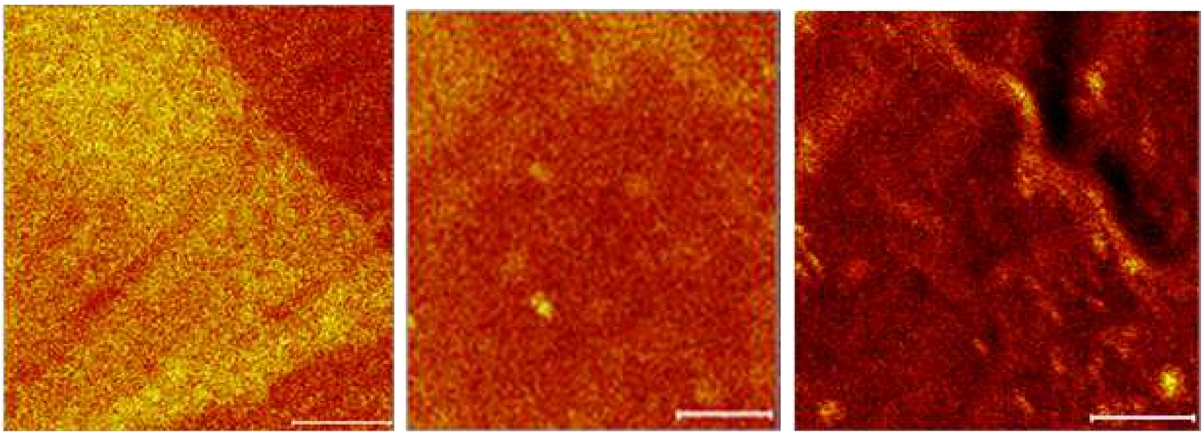


Fig.3 Molecular formula with molecular mass and their structure

As given earlier that the primary ion current is 3 X 10^{-9} Amps with raster size 60 X 60 µm^2, therefore the primary ion flux becomes 8.3 X 10^{-5} A/cm^2. The analysis time becomes 5 min. and data acquisition area was 200 X 200 µm^2, which gives the value of primary ion dose from Eq. 1 is equal to 62.25 which was very low from the static limit and was accepted in the static regime of SIMS analysis.

Within static limit, the total ion image of topmost surface of (i) PVA (ii) DAN doped PVA and (iii) PDAN doped PVA films are described in Figure 4. The results show that the entire ion images are best in contrast. It is also observed that as PVA film (Cts 1429772) doped with higher mass species i.e. first with diaminonaphthalene (Cts 1039767) and than poly(diamino naphthalene) (Cts 541900), the total ions count (secondary ion intensities) decrease which concluded that low mass hydrocarbon fragments related film are much less affected by surface density whereas higher mass fragments related films can be highly affected. The whole measurements were carried out using positive secondary ions.



(a) **(b)** **(c)**

Fig.4 Total ion image of (a) PVA sample (b) DAN doped PVA sample (c) PDAN doped PVA sample. Scale: 100 µm, Resolution 256 X 256 pixels

PVA sample

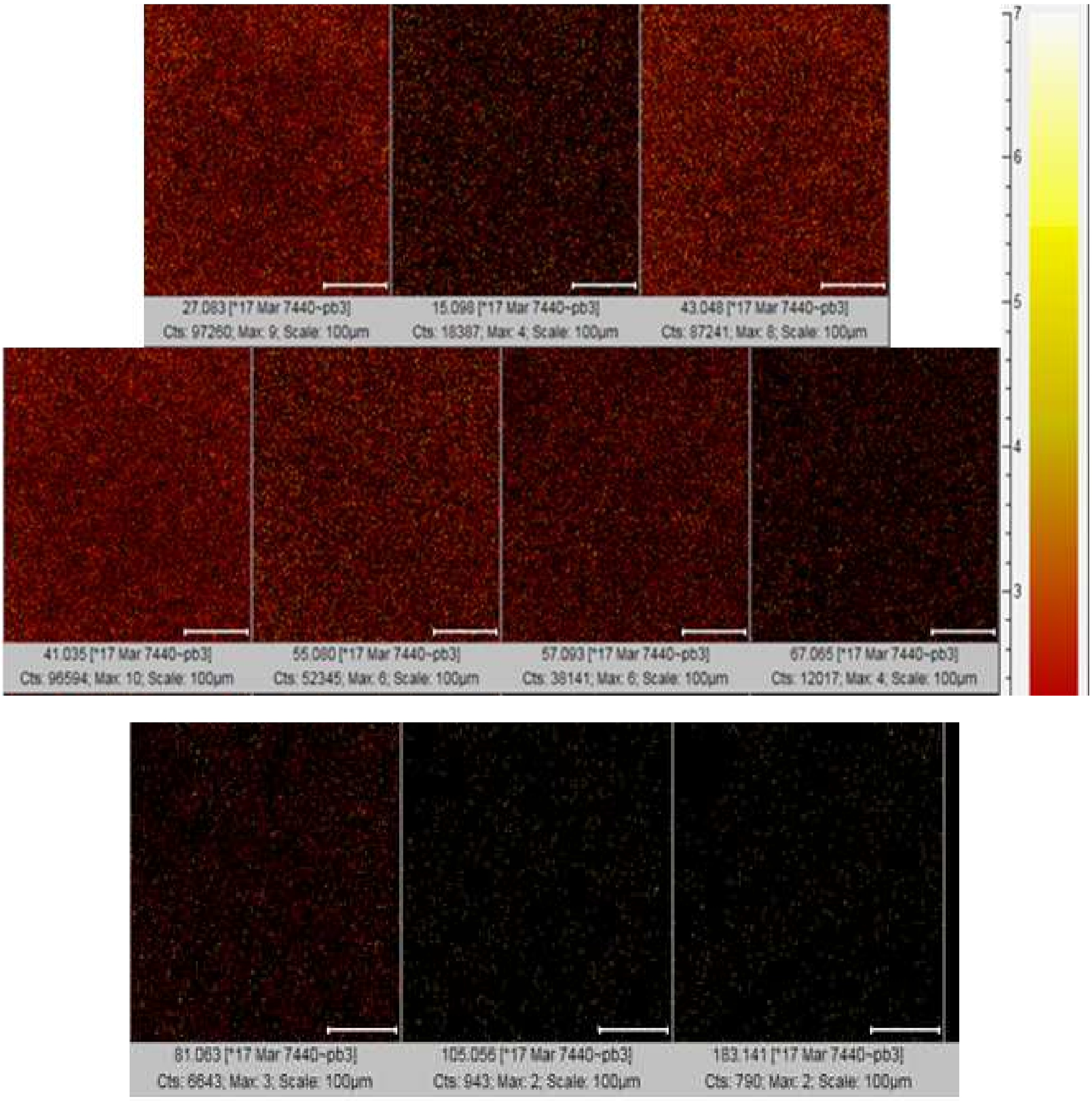


Fig.5 Imaging ToF-SIMS positive ion images 200 X 200 μm^2 acquired at a resolution of 256 X 256 pixels showing the charge distribution of the poly(vinyl alcohol) upper surface

PDAN doped PVA

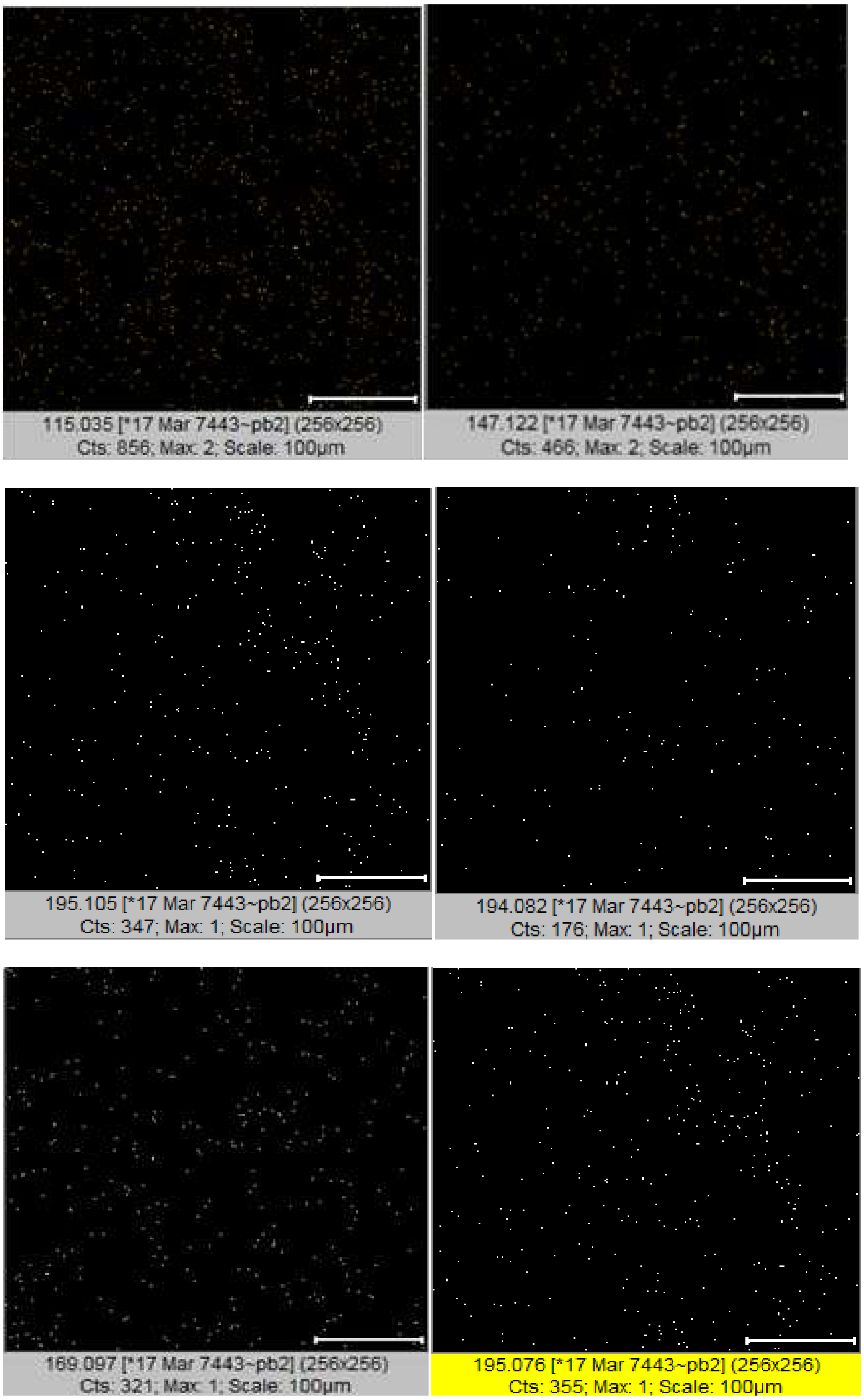


Fig.6 Imaging ToF-SIMS positive ion images 200 X 200 µm^2 acquired at a resolution of 256 X 256 pixels showing the charge distribution of poly(diamino naphthalene) doped poly(vinyl alcohol) upper surface

DAN doped PVA

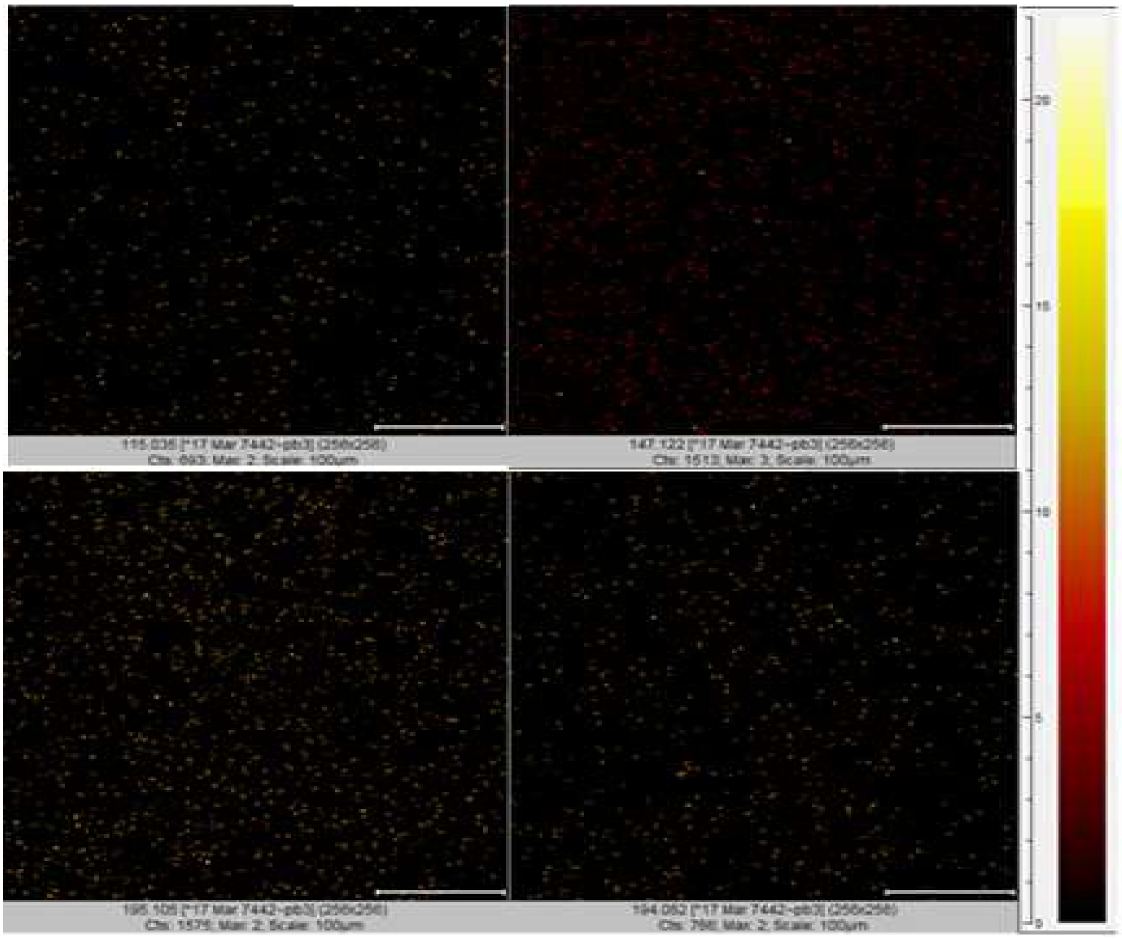


Fig.7 Imaging ToF-SIMS positive ion images 200 X 200 µm^2 acquired at a resolution of 256 X 256 pixels showing the charge distribution of the diamino-naphthalene doped poly(vinyl alcohol) upper surface

For PVA film, positive species ion images are obtained for 15 m/z, 27 m/z, 41 m/z, 43 m/z, 55 m/z, 57 m/z, 67 m/z, 81 m/z, 105 m/z and 183 m/z segments depicted in Figure 5. It is clearly observed that as the mass of the species increases, secondary ions intensity decreases. Although for masses 15 m/z, 41 m/z and 43 m/z which are the main fragments of the PVA film, the above mentioned concept will not be applied. The contrast of the ions images decrease as the ion masses increases. It indicates that, for higher ions masses the static limit will not remains constant. It is obvious because the primary ions flux decreases due to binding energy of the combination of the monomers segments and, therefore, fewer secondary ions are liberated of higher molecular masses.

For PDAN doped PVA film, positive species ion images are obtained for 115 m/z, 147 m/z, 169 m/z , 194 m/z , 195 m/z, and 195 m/z segments as depicted in Figure 6. At the same time for DAN doped PVA film, positive species ion images are obtained for 115 m/z, 147 m/z, 195m/z and 194 m/z segments depicted in Figure 7. Unusual variation in the secondary ions count in image profile of DAN doped PVA are obtained, though image profile of PDAN doped PVA provides secondary ions count in prescribed manner. Even when compare the ions flux of ion masses 147 m/z, 194 m/z and 195 m/z of DAN doped PVA and PDAN doped PVA, shows that the secondary ions intensity decreases as the ions molecular mass increases. The unusual secondary ions counts of DAN doped PVA and against the concept of the counts behavior of ion mass 115 m/z species, are the matter of concern.

CONCLUSION

The image profiling of PVA sample, DAN doped PVA sample and PDAN doped PVA sample provide usual behavior of secondary ions emission by ToF-SIMS technique. The normal image profile can explain the resolution and contrast of the different images of species without much concern with the parameter “static limit”. The less ions flux of PDAN doped PVA sample are due to binding energy between the monomer segments and polymer-polymer complex matrix. Topographical and ion yield effect can be obtained with the help of ToF-SIMS applications.

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REFERENCES

[1] R.G.Wilson, F.A.Stevie, C.W.Magee, Secondary Ion Mass Spectrometry, Wiley, New York, **1989**

[2] J.C.Vickerman, I.S.Gilmore (Ed.) , Surface Analysis: The Principal Techniques, 2nd edition, John Wiley and Sons, Chichester, UK, **2009**, 47–203

[3] J.C.Vickerman, D.Briggs (Ed.), ToF-SIMS: Surface Analysis by Mass Spectrometry, IM Publications, Chichester and Surface Spectra Limited, Manchester, **2001**, 75–161

[4] P.Fardim, J.Gustafsson, S.Schoultz, J.Peltonen, B.Holmbom, *Coll. and Surf. A: Physicochem. Engg. Aspt.*, **2005**, 255, 91–103

[5] N.E.Zafeiropoulos, P.E.Vickers, C.A.Baillie, J.F.Watts, *J. Materl. Sci*., **2003**, 38, 3903–3914

[6] B.Hagenhoff, D.Rading, Handbook of surface and interface Analysis, New York, **1998**, 209-253

[7] N.Bourdos, F.Kollimer, A.Benninghoven, M.Sieber, H.J.Galla, *Langmuir*, **2000**, 16, 1481-1484

[8] M.C.Biesinger, P.Y.Paepegaey, N.S.Mclntyre, R.R.Harbottle, N.O.Prtersen, *Anal. Chem.*, **2002**, 74, 5711-5716

[9] J.C.Vickerman, Surface Analysis, Wiley, Chichester , **1997**