MORPHOLOGICAL EFFECTS OF ACCELERATED LEAD IONS ON POLYVINYLCHLORIDE

I. M. Dildar, A. Saleem, M. K. Rahman, K. A. Bhatti and A. Shuaib

Department of Physics, University of Engineering and Technology, Lahore - 54890, Pakistan
Corresponding Author: ishratmubeen@gmail.com

ABSTRACT: The present study was aimed to correlate the surface differences on the PVC samples for their stability. The morphological changes on the surface of polyvinylchloride (PVC) were studied by increasing the applied potential of the lead ions. The lead target was exposed by a pulsed Nd: YAG laser under low vacuum ~10^{-3} Torr. Samples of PVC were irradiated with accelerated Lead ions at 0 Volts, 100 Volts and 300 Volts. After irradiation, the results were investigated using Transmission optical microscope (Motic DMB series) for morphological changes in polymeric samples. The morphology showed the dominant and enhancing features of chain formation and cross linking with increase of potential. At lower potential i.e., 100V, the thermal sputtering, crater formation and cracking of surface was observed while at higher potential of 300V, energetic ions burnt the surface and ions were dragged far away on the surface. Cluster formation was also observed at this potential.

Keywords: Ion induced effects, Cross linking, Laser induced plasma, Ion implantation (APII), Thermoplastics, Clusters, Sputtering.

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INTRODUCTION

Ion implantation is a technique to accelerate the ions to a target surface with high enough energies, from a few K eV to M eV. It is used to treat the surfaces of materials in plasma processing applications and modify the surface properties of materials without changing their bulk properties. Some of the surface properties that can be modified by this process are hardness, fatigue, toughness, adhesion, wear, friction, corrosion oxidation, dielectric properties, magnetic properties, superconductivity, resistivity, and catalysis, has reported by Lee, (1999) Dong and Bell, (1999) and Elipe *et al.*, (2003).

Ion implantation of electrically insulating materials, such as polymers, can drastically change the structure of polymers. The implanted ions can impinge into the target surface and are advantageous in improving optical, mechanical and biocompatible properties (Oates *et al*., 2005). It includes tri-bological improvements, optical and electrical changes, and increase in wettability (Ueda *et al.*, 2003). High kinetic-energy ions striking the surface of polymer target are slowed down by electronic stopping mechanisms, resulting in chain scission, cross-linking, bond disruption, formation of free radicals and so on (Bouffard *et al.*, 1995).

A lot of research has been reported in the field of ion implantation, both positive and negative. Negative ion implantation has been applied to fabricate metal nanocomposites and polymers (Boldyryeva *et al.*, 2004), (Fu *et al.*, 2005). To enhance the antibacterial properties, medical grade PVC is modified by coating with triclosan and bronopol (Zhang *et al.*, 2006). The ordered state of some ion implanted polymeric materials like polyvinyl alcohol [PVA] and polyethylene oxide [PEO] is investigated using surface micro morphology and surface conductivity (Murthy and Rao, 2002). Polyvinylchloride (PVC) sheets are treated using plasma immersion ion implantation (PIII) technique and effects of the exposure time on the PVC wettability have been investigated (Bento *et al.*, 2003).

In this study, polyvinylchloride (PVC) will be used as a substrate, being the member of thermoplastic family as it is thermally low stable and responds to any kind of thermal stress or energy application. The PVC samples will be used for ion implantation and irradiated with the accelerated lead ions at potentials 0 Volts, 100 volts and 300 volts. After the ion implantation, the surface morphological changes in PVC will be studied by the Transmission optical microscope.

MATERIALS AND METHODS

A pulsed Nd: YAG laser (1.064 µm, 1.1 MW) was used to irradiate the lead target. For ion acceleration, positive potential was applied to lead target and negative terminal of battery was connected to ground. Four samples of polyvinyl chloride (PVC) were exposed at different accelerating potentials i.e. at zero, 100 and 300 Volts. A plano convex lens with focal length - 10 cm was used for the tight focusing of laser on the target and also to avoid the aberration defects. The target was irradiated by laser at 45^o to avoid the laser plasma interaction (La`ska *et al.*, 2002). The target was adjusted so that the middle point of the polymeric sample was along the normal to the plasma plume. The optimized distance between the target and the sample was 3 cm. A total of 300 shots were taken for each sample and for each potential. After each 50 shots the laser was given a rest, so that the ions falling on the sample had nearly uniform energy distribution. The vacuum port was connected to the double stage rotary pump. After about one hour the vacuum, up to 10^{-3} Torr, was established. The accelerated ions from the laser-produced plasma were used to irradiate the polymeric samples. The high potential terminal of the power supply was connected to the PVC sample while low potential end was connected to the common ground of the chamber and other electronic equipment. The rotary pump was kept working during the conduct of the experiment to maintain the vacuum inside the chamber. After that the samples were analyzed by transmission optical microscope. The experimental arrangement of the setup is shown in Figure 1.

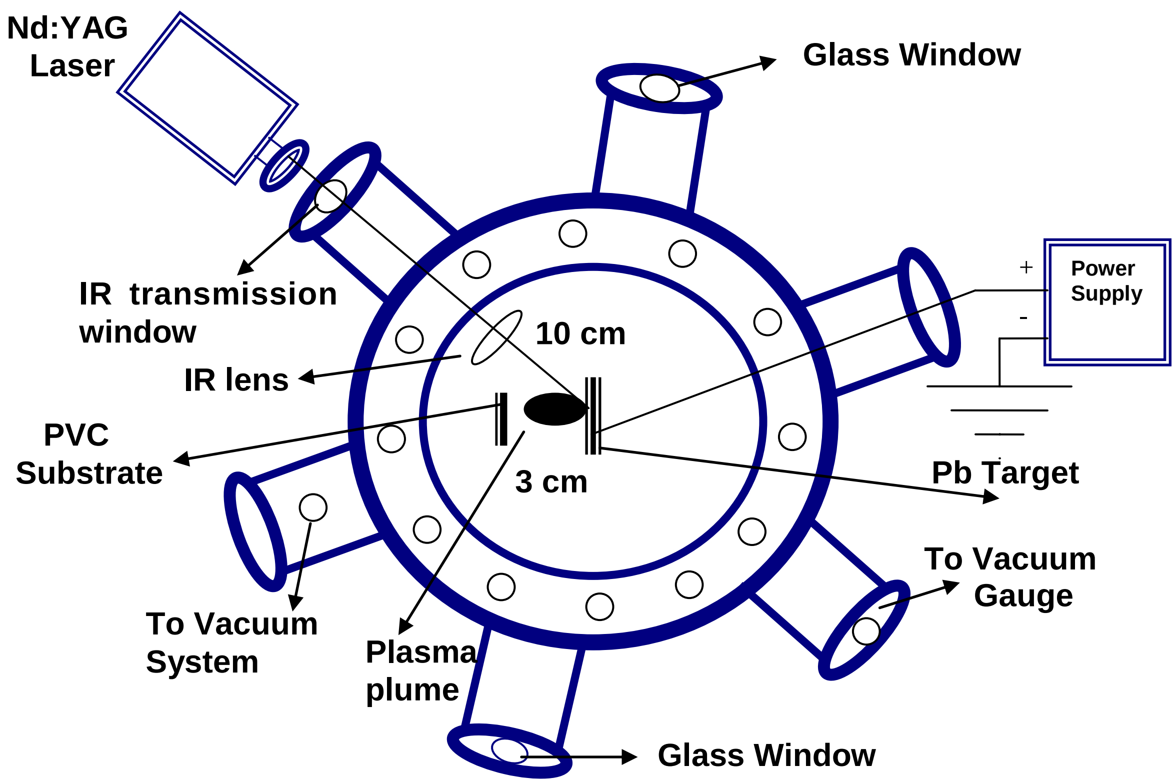

Fig-1: Schematic diagram of experimental setup

RESULTS AND DISCUSSION

The samples of polyvinylchloride (PVC) were irradiated with laser produced lead ions for three different potentials i.e., 0 Volts, 100 Volts and 300 Volts. The surface morphological effects were analyzed by transmission optical microscope. The following section presented the results obtained using three different applied potentials on PVC by accelerated Lead ions.

The first sample of PVC was irradiated by laser generated lead ions at 0 V. Figure 2 (a, b and c) which showed the chain formation at magnification of 100, 400 and 1000 respectively. Ion irradiation lead to irreversible changes in the sample of polyvinylchloride (PVC). They suffered main-chain scission leading to the formation of low weight molecules and loss of their mechanical properties. This resulted in the production of chain degradation and plasticization through monomer formation through cross linking reactions and chain weakening (Horie *et al.*, 2004).

Fig-2: Micrographs of PVC irradiated by laser lead at 0 V showed Chain scission at magnification of (a) 100, (b) 400 abd (c) 1000.

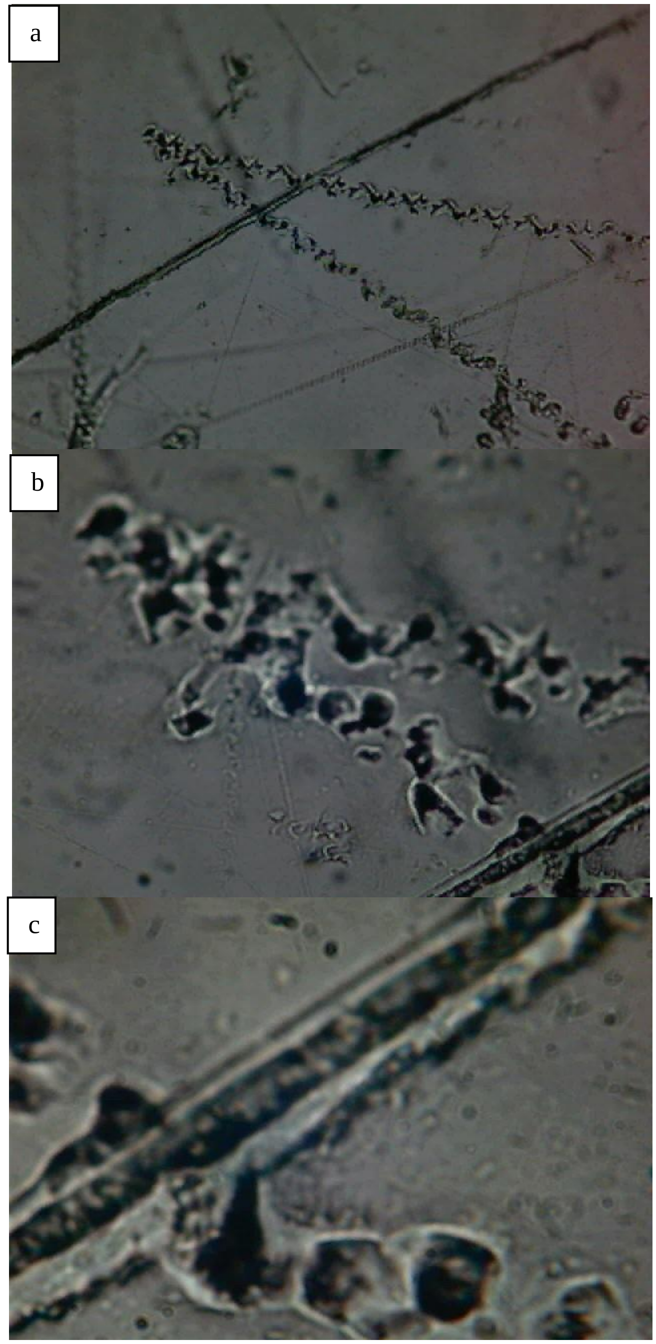

Fig- 3: Micrographs of PVC irradiated by laser produced lead ions at 100 V showed cross linking at magnification, (a) 100, (b) 400 and (c) 1000.

Figure 3 show the cross-linking induced by accelerated lead ions at a magnification of 100, 400 and 1000 at 100 volts. This cross-linking was not observed at zero potential where straight chains were induced by Lead ions. The effect of ions was simply chain scission and no cross-linking. While applying the retarding potential to the target, impact of ions appeared in the form of cross-links and craters.

Figure 3 also showed the burned surface inside the chain and re-solidification of material around it. This burning made the material blackish. Due to various imperfections in material, surface becomes darker, has also been reported by Wilding *et al.*, (1996) Murthy and Rao, (2002) Horie *et al.*, (2004) Kausch and Schmeling,(2005) and Itagaki *et al.*, (2006).

In Figure 4 (a), ion induced chains and crater formation were shown irradiated at 100 V, at magnification of 100. Other effects were also clear at the higher magnifications i.e. in Figure 4 (b) and (c). Figure 4 (c) showed the large depth of the crater with dark colors, indicating that there was a large material removal, which lowered its temperatures. The ejected material was re-solidified on the crater boundaries with light color indicating a high temperature region. This crater was not in circular shape because of the phenomenon of splashing. The melt flew in one direction, so changing the crater shape. Figure 4 (c) also showed the cracking of the material. The energetic ions at 100 V comparatively at 0 V, which produced a stress on the outside of the sample. Initially a craze was produced along the depth of the sample and then crack was produced. These cracks depend on the melting, boiling point of the polymeric samples and intensity of the ions. The results reported by Murthy and Rao, (2002) and Horie *et al.*, (2004).

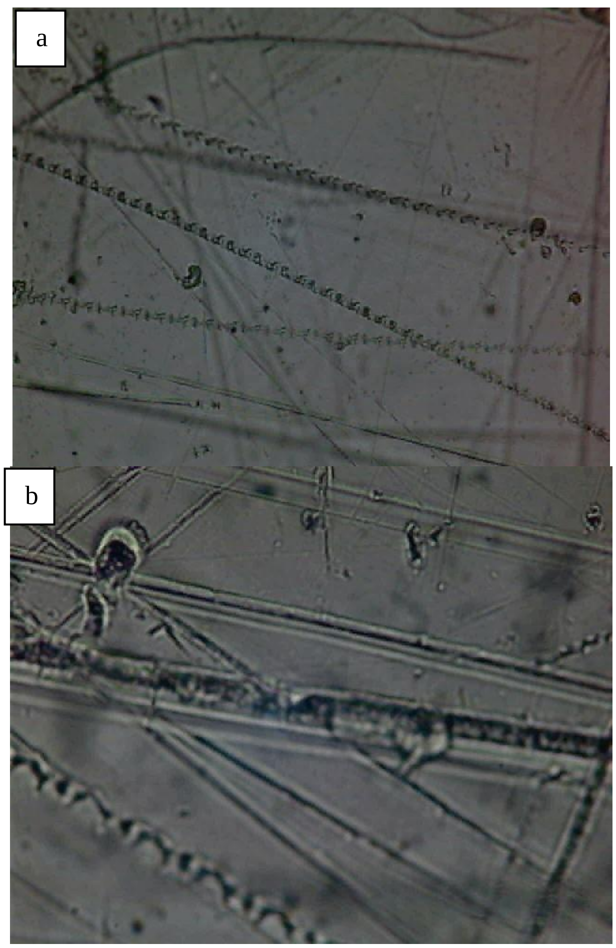

Fig- 4: Micrographs of PVC irradiated by laser produced lead ions at 100 V show craters and cracking, at magnification of (a) 100, (b) 400 and (c) 100.

Figure 5 (a) and 5 (b) showed the ion induced dragging at 100 V. It also showed sputtering of the material in PVC sample. The ions with low energies moved through the surface of the polymer without producing damages in the structure of the PVC. The energy of these impacting ions was not high enough so that they could bury below the polymer's surface and interact with its atoms to produce the structural changes. So, the ions were dragged on the surface instead of impinging into the structure of PVC as found by (Wu *et al*., 1995). Some parts of micrograph also showed ejection of molten material in the form of thermal sputtering. The ejected material might include the atomic species, ions, electrons, and the molten globules as reported by (Lee *et al*., 2001).

In Figure 6 (a) - 6 (d), micrographs showed the ion induced effects in the form of chain formation at magnification 40 and 100 and 1000 at applied potential of 300 V. There was clear difference in the chains induced by ions at l00 V (Figure 3).

These micrographs clearly differentiated that ions at 300 V potential were more accelerated than previous applied potentials. The ions were energetic so that they could not come at rest soon in the structure of the substrate instead of that they moved deeper inside the polymer surface and produced long and twisted chains. Formation of these twisted chains showed that ions were more energetic so that they impart their energy to the target atoms after covering long distance in the polymer structure. The similar results were found and discussed by Wilding *et al.*, (1996), Murthy and Rao, (2002), Horie *et al.*, (2004), Kausch and Schmeling, (2005) and Itagaki *et al.*,(2006). the efficiency of our program.

Figure 7 showed the circular spots showing burning and swelling effects at magnification of 1000 at two different parts of sample. The white portion of spots represented the swelling produced in the material and black portion around it was burnt. At this point, ion flux may not be appreciable and ions only impart energy to the substrate atoms as a heat and due to continuous thermal energy provided by the ion results in surface burning. Due to this burning material became blackish. It also indicated that the energy of the incident lead ions was only sufficient to burn the surface of polymeric samples and was insufficient to cause sputtering. Various imperfections in surface may occur in material due to which surface becomes darker, as reported by Han *et al.*, (1997), Mckenzie *et al.*, (2004), Pelletier and Anders, (2005), Lu *et al.*, (2012), and Yanling *et al.*, (2014).

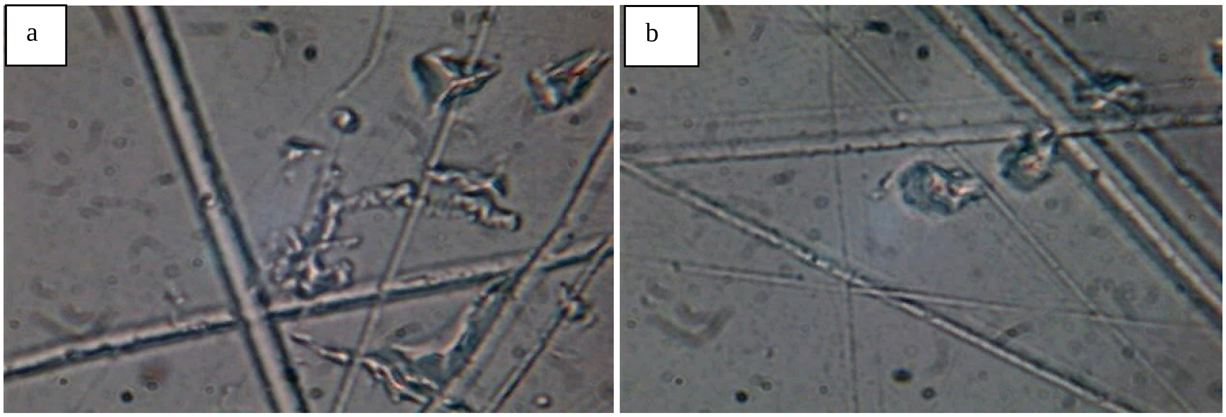

Fig- 5: Micrographs of PVC irradiated by laser produced lead ions at 100 V show thermal sputtering (a & b) at magnification 1000.

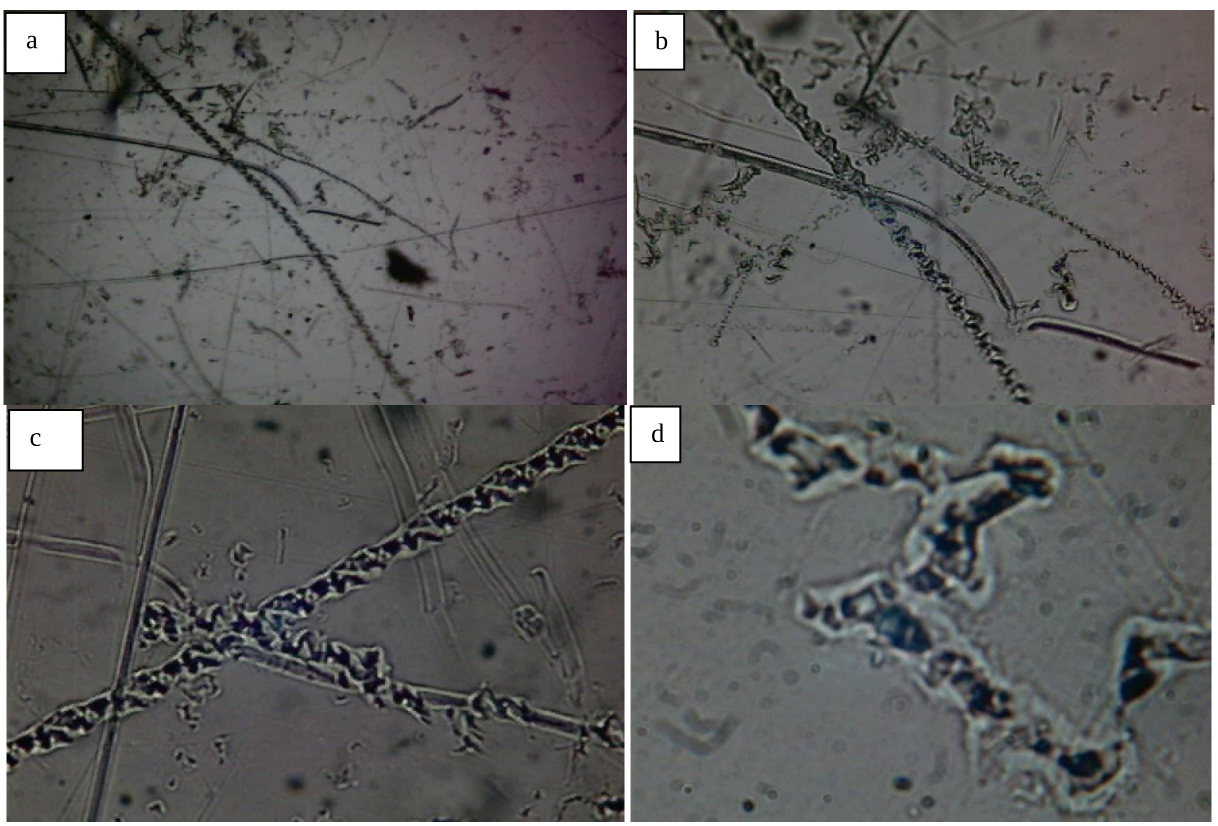

Fig- 6: Micrographs of PVC irradiated by laser produced lead ions at 300 V show chain scission and linking at magnification. (a) 40, (b) 100, (c) 100 (d) 1000.

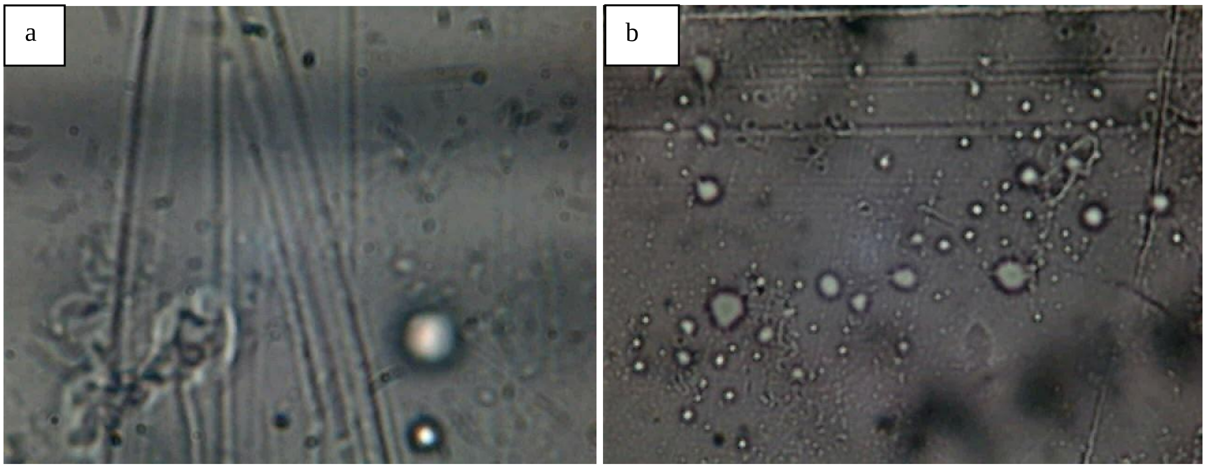

Fig- 7: Micrographs of PVC irradiated by laser produced lead ions at 300 V showing surface burning at magnification, (a) 400, (b) 1000.

Figure 8 (a-b) showed clusters formation at 300 V at magnification of 100 and 400 respectively. Clusters were formed in the polymers due to high degradation of polymers by ions. PVC had low thermal stability caused by the presence of defects in the molecular structure formed during the polymerization. This resulted in the formation of polyene structures in the chain due to elimination of HCL, if exposed to high temperature or high mechanical stress. Due to successive elimination of hydrogen and chlorine atoms there was a concentration of carbon atoms in the structure of PVC which formed the carbon networks in the form of clusters as found by (Feld *et al.*, 1990).

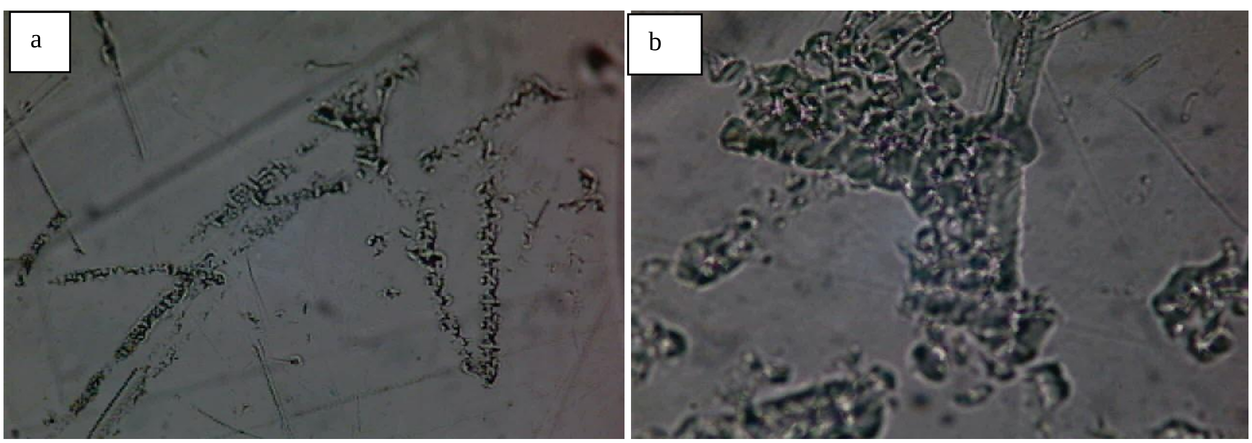

Fig- 8: Micrographs of PVC irradiated by laser produced lead ions at 300 V show cluster formation at magnification of (a) 100 and (b) 400.

Conclusion: The results showed the morphological changes on PVC samples at three different accelerating potentials for the lead ions. At zero potential, PVC samples are fractured forming cones, chains are formed and irregular distribution of ions form clusters. By increasing the retarding potential to 100 V to the lead target, craters are formed as a result of the explosive outflow of material from the hot molten core of the spike. By increasing the potential upto 300 V the changes induced by the accelerated lead ions in PVC are chain scission, cross-linking, swelling. The results show that highly energetic ions imping into the surface produce significant changes as compared to the low energetic ions.

REFERENCES

Bento, W.C.A., R. Y. Honda, M. E. Kayama, W. H. Schreiner, N. C. Cruz and E. C. Rangel (2003) Hydrophilization of PVC surfaces by argon plasma immersion ion implantation. Plasmas and Polymers, 8 (1): 1-11.

Bouffard, S., B. Gervais and C. Leroy (1995) Basic phenomenon induced by swift heavy ions in polymers. Nucl. Instr. Meth. Phys. Res. B, 105: 1.

Boldyryeva, H., N. Kishimoto, N. Umeda, K. Kono, O. A. Plaksin and Y. Takeda (2004) Surface modification and nanoparticle formation by negative ion implantation of polymers. Nucl. Instr. Meth. Phys. Res. B**,** 219-220: 953-958.

Dong, H. and T. Bell (1999) State-of-the-art overview: ion beam surface modification of polymers towards improving tribological properties. Surf. Coat. Technol., 111: 29-40.

Elipe, A.R.G., F. Yubero, and J. M. Sanz (2003) Low Energy Ion Assisted Film Growth. Imperial College Press, London.

Feld H., R. Zurmiihlen, A. Leute and A. Benninghoven (1990) Carbon cluster emission from polymers under keV and MeV ion bombardment. J. Phys. Chem.**,** 94: 4595-4599.

Fu, R.K.Y., I.T.L. Cheung, Y. F. Mei, C. H. Shek, G. G. Siu, P. K. Chu, W. M. Yang, Y. X. Leng, Y. X. Huang, X. B. Tian and S. Q. Yang (2005) Surface modification of polymeric materials by plasma immersion ion implantation. Nucl. Instrum. Meth. Phys. Res. B**,** 237: 417-421.

Han S., Y. Lee, H. Kim, J. Lee, J. -H. Yoon, and G. Kim (1997) Plasma surface modification by plasma source ion implantation. Surf. Coat. Technol**.,** 93: 261-264.

Horie, K., M. Baron, R. B. Fox, J. He, M. Hess, J. Kahovec, T. Kitayama, P. Kubisa, E. Marchal, W. Mormann, R. F. T. Stepto, D. Tabak, J. Vohlidal, E. S. Wilks and W. J. Work (2004) Definitions of terms relating to reactions of plymers and to functional polymeric materials. Pure Appl. Chem*.*, 76 (4), 889-906.

Itagaki, H., Y. Nishimura, and E. Sagisaka (2006) Entanglement of polymer chains in ultra thin films. Langmuir, 22: 742-748.

Kausch H. H., B. von Schmeling (2005) The role of chain length and conformation in stress-transmission and fracture of thermoplastic polymers. Physics of Solid State, 47: 934-941.

La´ska, L., J. Kra´sa, M. Pfeifer, K. Rohlena, S. Gammino, L. Torrisi, L. Ando`, and G. Ciavola (2002) Angular distribution of ions emitted from Nd:YAG laser produced plasma. Rev. Sci. Instr. , 73 (2): 654.

Lee, E.H. (1999) Ion beam modification of polymeric materials-fundamental principles and applications. Nucl. Instrum. Methods Phys. Res. B**,** 151: 29-41.

Lee Y., S. Han, H. Lim, H. Jung, J. Cho and Y. Kim (2001) Surface characterization of polymers modified by keV and M eV ion beams. J. Adhesion Sci. Technol.**,** 15: 1079-1090.

Lu W., Q. L. Yang, B. H. Yan and Y. Cheng (2012) Plasma-assisted synthesis of Chlorinated polyvinyle chloride (CPVC). Chem. Engg. J., 207-208: 923-930.

Meckenzie D. R., K.N. McGee, P. Ruch, M. M. Bilek, and B. K. Gan (2004) Modification of polymers by plasma based ion implantation for bio-medical applications. Surf. Coat. Technol., 186: 239-244.

Murthy, M. R. and E.V. Rao (2002) Ion beam modification of the surface morphology and conductivity in some polymer thin films. Bull. Mater. Sci.**,** 25 (5): 403-406.

Oates, T.W.H., D. R. McKenzie, and M.M.M. Bilek (2002) Plasma immersion ion implantation using polymeric substrates with a sacrificial conductive surface layer. Surf. Coat. Technolo.**,**156: 332-337.

Pelletier J., and A. Anders (2005) Plasma based ion implantation and deposition: a review of physics, technology and applications. Plasma Science IEEE Transaction**,** 33 (6): 1944-1959.

Ueda, M., I. H. Tan, R. S. Dallaqua, J. O. Rossi, J. J. Barroso and M. H. Tabacniks (2003) Aluminimum plasma ion immersion implantation in polymers. Nucl. Instr. Meth. Phys. Res. B**,** 206: 760-766.

Wilding N. B., M. Muller and K. Binder (1996) Chain length dependence of the polymer-solvent critical point parameters. J. Chem. Phys., 105 (2): 802.

Wu Z., Y. Shi, H. Xie, Y. Chen, J. Zhang, J. Xu, and H. Chen (1995) Surface modification of polymers by low temperature plasma techniques. Surf. Engg.**,** 11: 53-56.

Yanling C., W. Yingkuan, P. Chen, S. Deng and R. Ruan (2014) Non-thermal plasma assisted polymer surface modification and synthesis, a review. Int. J. Agric. & Biol. Eng., 7 (2): 1-9.

Zhang, W., P. K. Chu, J. Ji,Y. Zhang, X. Liu, P. K. Fu, P. C. Ha, Q. Yan (2006) Plasma surface modification of polyvinyle chloride: improvement of antibacterial properties. Biomaterials**,** 27 (1): 44-51.