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Surface Modification Of Polyvinylchloride Using High Accelerated Lead Ions

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Abstract

This research work presents a comparative study for morphological effects of accelerated and non-accelerated lead ions on polymers. The ions are produced using lead target by high powered pulsed Nd: YAG laser (wavelength 1.064 µm, energy 10 mJ, pulse duration 12 ns, and power 1.1 MW) at low pressure of ~10^{-3} torr. The acceleration voltage of 500 V is used to accelerate lead ions on polyvinylchloride (PVC). The PVC samples are also irradiated without applying any potential, just to have a comparison of both types of irradiation. The samples were irradiated for 300 shots for each sample. The morphological changes were observed using Transmission optical microscope (Motic DMB series). The results showed the morphological changes in polymeric samples for accelerating potential of 500 V and 0 V. Long chain formation of laser accelerated lead ions is observed at 500 V as compared to the 0 V. The ion induced dragging effects are shown for 0 V which depend upon the energy of lead ions and also on the properties of the polymeric sample.

Keywords: *Thin Films, Ion Induced Effects, Chain Formation, Cross Linking, Laser Irradiation, Thermoplastics.*

1. Introduction:

Ion implantation is a special technique of plasma processing in the applications where surfaces of solid materials are to be treated. The implantation process requires a source of ions and a means to accelerate them towards the target surface [1-2]. The ablation of a solid target produces a plasma plume which acts as an ion source. The emitted ions are accelerated towards the biased (either negative or positive) substrate. Use of lasers for plasma implantation has made the technique comparatively simpler as compared to the traditional ones [3]. There are many advantages of ablation plasma ion implantation (APII) over the conventional plasma immersion ion implantation i.e., there is no toxic gaseous produced by this technique [4-5]. It is required to have a low pressure inside the chamber used for the process of implantation to minimize the collisions between charged particles during ablation. Metal nanoparticles formation of polymers [6], low energy negative ion implantation [7-8] and introduction of metal atoms into polymers to enhance cohesive nature of polymers [9-11] are some ongoing research lines.

Synthetic organic polymers have developed a diverse class of materials with tunable properties for desired applications. Modifications of polymers can be divided in two main categories based on ion energy. High energy ions (100 keV to 10 MeV) and the low energy ions range in several tens keV. High energy ions impinge deeply in polymers but can

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damage the polymers inducing some chemical reactions [12]. The low energy ions are used in impurity doping. Ions can impinge in polymers' surface without damaging on main chains of chemical bonding in polymers [13-14]. Low energy ions are preferable mode for surface modification.

Laser processing of polymers was first reported in 1982 since then, it is an attractive field both for fundamental and applied material science. Laser irradiations lead to irreversible changes on polymers' surfaces . Many polymers lose their mechanical properties and they form molecules of lower weights suffering chain degradation [15]. Irradiation of polymers induce small chemical changes in them but physical modifications are larger [16]. The surface morphology of polymers change forming cone like features and spikes [17]. Moreover, optical [18], and electrical properties [19-20] of polymers are also changed under the effects of ions.

Specifically talking about PVC, the processing requires stabilizers to prevent their decomposition into its constituents; oxygen and chlorine by thermal or chemical radiations and mechanical stresses. The stabilizers improve influence on the physical properties of the PVC formulation by improving the resistance, weathering and heat ageing and extends the life of PVC products. Lead compounds are widely used elements as stabilizers in polymers, include the applications in PVC pipes and cables [21]. It has been found with some controversy that lead may cause extensive changes in physical and chemical properties of PVC and raises questions on PVC recycling. In a recycled material, lead and tin stabilizers may react to form some residues of lead sulphide [22].

This work presents the morphological effects of laser produced lead ions on polyvinyl chloride (PVC). In a previous study, the laser induced ions on PVC are addressed at voltages of 100 V and 300 V [23]. The effects produced by accelerated and non-accelerated lead ions change the PVC surface topography. These morphological changes on PVC help to understand the strong radiation effects of lead ions on PVC. The observed changes include chain scission, chain degradation, cross-linking, collisional sputtering, cone formation, cluster formation, fractures, cracking, burning, sputtering and ion dragging.

2. Experimental:

A pulsed Nd: YAG laser (1.064 μm, 10-14 ns, 1.1 MW) was employed to irradiate the lead target. The tight focusing of laser requires the use of Plano convex lens on the target and setting the angle of laser with respect to target to be 45^0 to avoid the aberration defects and laser plasma interaction. PVC was used as a substrate. A high voltage power supply was used, positive potential was connected to lead target and negative terminal of battery was connected to a common ground. Samples of polyvinyl chloride were exposed at accelerating potentials of 500 Volts and non-accelerating mode (at 0 Volts). The four samples of the PVC were irradiated by laser generated lead ions at 0 V and 500 V. To get maximum ion flux, the optimized distance between the target and the sample was taken to be 3 cm. Equal numbers of shots were taken for each sample. A small pause was taken after each 50 shots with total shots of 300. In this way, ions from laser may have nearly uniform energy distribution. A rotary pump was connected to the port of chamber fixed for creation of vacuum $\sim10^{-3}$ Torr. After irradiating samples at accelerating voltage of 500 V and non-accelerating potential of 0 V, the samples were analyzed by transmission optical microscope (Motic DMB series). The details of experimentation using laser system effects are published somewhere else [24].

Figure 1 shows a schematic diagram of the experimental setup.

3. Results and Discussion:

Figure 2 shows an un-irradiated piece of polyvinylchloride (PVC) sample. The sample looks very clean and there are no defects and damages on the sample. Figure 3 (a - c) shows the morphological changes on PVC materials after irradiation with lasers at 0 V at different magnifications. Damages event in the form of ionization and recoil displacement that can modify the structure of polymers. In these images the induced effects by lead ions in the PVC are chain scission and chain degradation [25-26]. The breaking of a molecular bond by energetic ions cause the chain scission at the surface of PVC. The overall chain is also shortening due to the loss of side groups. All these changes cause the PVC as low weight molecules by losing of their mechanical properties [27].

Figure 4 (a) shows the formation of the stabilizing ligands cluster induced by ions in PVC sample due to lead ions at magnification 40 at 0 V. In Figure 4 (b), micrograph shows the same effect on the structure of PVC at higher magnifications 400. The clusters are formed in the polymers due to high degradation of polymers by ions. Laser radiation may produce non-uniform energy distribution which produces defects. These defects in the molecular structure lose some HCl. Removal of HCl forms polyene, a different polymer but longer in length. The elimination of HCl is called dehydrochlorination which lowers the resistance of original polymers and they become thermally unstable. The successive removal of hydrogen and chlorine atoms increases the concentration of carbon atoms in the structure of PVC. This forms the carbon networks in the form of clusters as shown in micrographs [25].

Table 1: The table shows the effects of laser irradiation on PVC by lead ions. The reasons for these effects are described relatively referring specific figures

	Effects	**Reason**	Relative Figures show these effects
Non-irradiated Sample At 0 V	chain scission and chain degradation	Breaking of a molecular bond by energetic ions	Figure 3
	Cluster formation	Non-uniform energy distribution/high degradation of energetic ions	Figure 4
	Cone formation	Angular distribution of sputtering yield	Figure 5
	Collisional effects	Energetic incident ions	Figure 5
	Ion dragging	Low energy ion effect	Figure 6
Irradiated Samples At 500 V	Parallel chains/ Cross linking	Deep penetration of high energetic ions	Figure 7
	Fractures	Transfer of stress through and the breaking of secondary bonds	Figure 8
	burning	Accumulation of energetic ions at certain level	Figure 9
	Sputtering	Blow off due to high energetic ions	Figure 9
	cracking	A stress along the depth of sample	Figure 9

Figures 5 (a) and 5 (b) show the collisional effects in two different samples of PVC at magnification 1000 at 0 V. The collisional affects and cones formation are very clear in these micrographs. Cone formation occurs due to the fact that the ions escape from the plasma plume in the form of cones when they are accelerated to fall on other material surface [28]. Ion-implanted surface will go through a cone formation due to either the angular variation of the sputtering yield, cracking of PVC, during ion bombardment from impurities or from scattering. The ions with very high energy scattered at larger angles whereas the ions with appropriate low energy moved in a straight line, resulting in a forward peaked angular distribution of laser-generated flux [29-30].

It is obvious from figure 5 that the displacement of the atoms of the sample has resulted due to the collisional sputtering of sample surface caused by the energetic incident ions. The high-energy particles produce knock-on atoms and vacancies. This gives rise to a cascade defect and cracking. The high-energy particles cause large variations in nearby atoms. Some of the incoming energetic ions might have gone in ionization and excitation of the electrons, the rest into kinetic energy of the atoms. This disturbance continues till the energy becomes less than the minimum energy required to displace a surface atom, termed as displacement energy threshold for that particular material. In figure 5 (a) and (b), there are circular regions that are more damaged as compared to its surrounded area, represent the cones. Hence the process of fracturing and cone formation is produced in PVC sample due to its low melting point [26-31].

Figure 6 (a) and (b) show the ion induced effects on the surface of PVC at zero potential. This shows that ions moves through the surface of the polymer without producing damages in the structure of the PVC i.e. ions drag on the surface instead of impinging into the structure of polymer. The energy of these impacting ions is not high enough so that they can burry below the polymer's surface and interact with its atoms to produce the structural changes [27].

Figure 7 (a - b) shows the morphological changes after the irradiation of laser generated accelerated lead ions at +500 volts. Figure 7 (a) shows the long parallel chains induced by the ions at potential 500 V at magnification 100. Micrographs in figure 7 (b) shows the same long parallel chains at higher magnifications 400. It is clear from the micrographs that these long parallel chains cover almost the whole sample which shows that ions are very energetic that's why they produce the long chains. Ions cover a long distance inside the polymer structure. They penetrate deeply in PVC instead of stopping after transfer their energy to the target atoms [27]. At lower potentials (Figure 3 at 0 V), ion irradiation has induced the chains in PVC but they are not long enough like the chains formed at 500V. Figure 7 (b) also shows the formation of a short chain while dragging of ions is induced by the ions between these two parallel chains [25-31].

In Figure 8, micrograph shows the fracture produced by the energetic ions. There is chain formation along with this fracture induced by ions. In fracture through crack propagation of a solid polymer, chains must be disengaged from each other across the fracture plane. In thermoplastic solids, where chains cohere through van der Waals forces, this involves several terms, which all depend on the stress transfer through and the breaking of secondary bonds. The relative contributions of the different mechanisms are well reflected by the fracture energy plot as a function of chain length (molecular weight). In a solid, where cohesion occurs more or less exclusively through the lateral van der Waals interaction between chain segments, the fracture energy levels off for very long chains. Most of the fracture energy is loss of elastic energy when the highly loaded chains are discharged; the chemical surface energy of breaking primary bonds (chain scission) is compared with the elastic term. Weak dependence of chain length is also obtained for the elastic and an elastic property of glassy polymers, which are cohesive in nature [30,32].

In Figure 9, micrograph shows the different effects at higher potential there is cross linking, burning effects and also sputtering are clear in the micrograph. The effects are shown at magnification 400. These surface changes may also induce some microstructural changes. As cross-linking and chain scission is proportional to ion dose so it is observed that at higher potentials cross-linked chains are induced by ions instead of chains scission. This shows that at higher potential ions are more energetic than at lower potential that's why cross linking and other effects like fracturing and craze are also observed. These high-energy ions produce a stress on the outside of the sample and initially a craze is produced along the depth of the sample and then crack is produced [33,34].

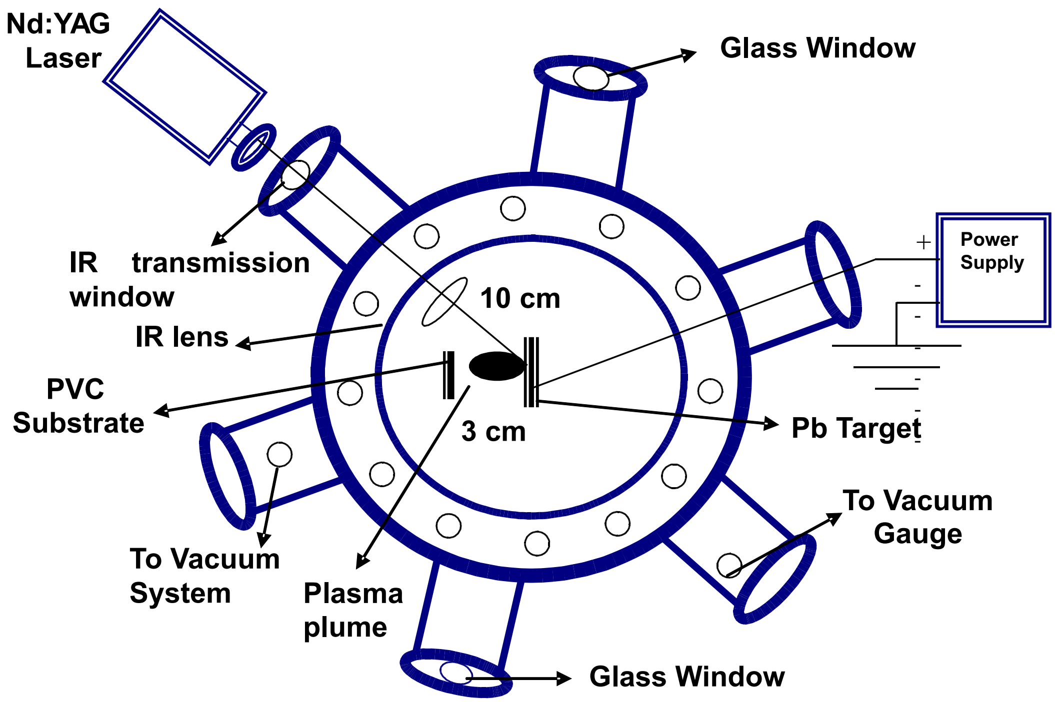

Figure 1: A schematic diagram of experimental setup

Figure 2: Micrograph of non-radiated piece of PVC sample at magnification of 50.

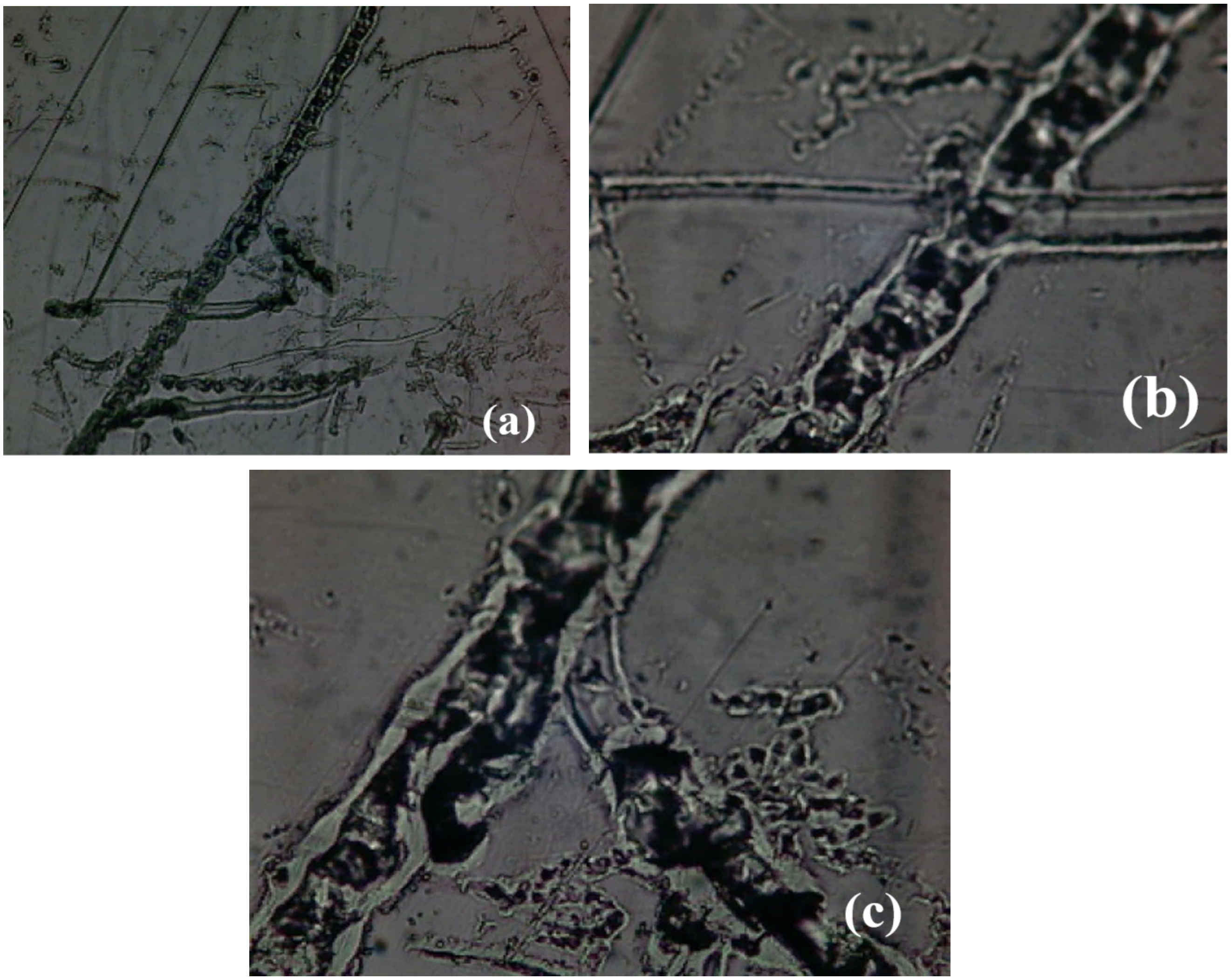

Figure 3: Micrographs of PVC irradiated by laser produced lead ions show chain scission at 0 V (a) at magnification 100, (b) at magnification 400, and (c) at magnification 400.

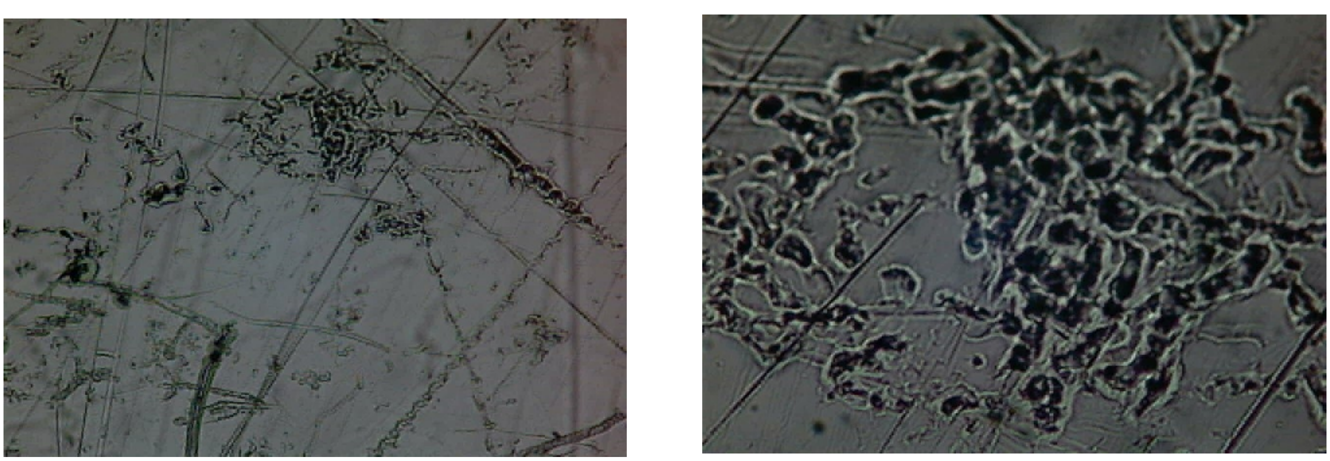

Figure 4: Micrographs of PVC irradiated by laser produced lead ions at 0 V show cluster formation (a) at magnification 40 and (b) at magnification 400.

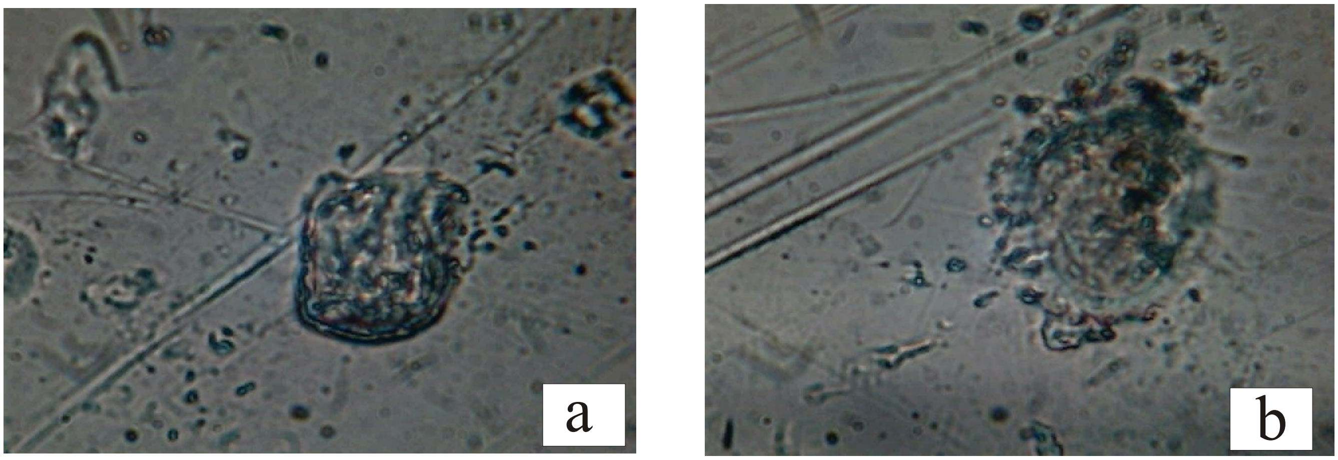

Figure 5: Micrographs of PVC irradiated by laser produced lead ions at 0 V show collisional effects at two different samples of PVC at magnification of 1000.

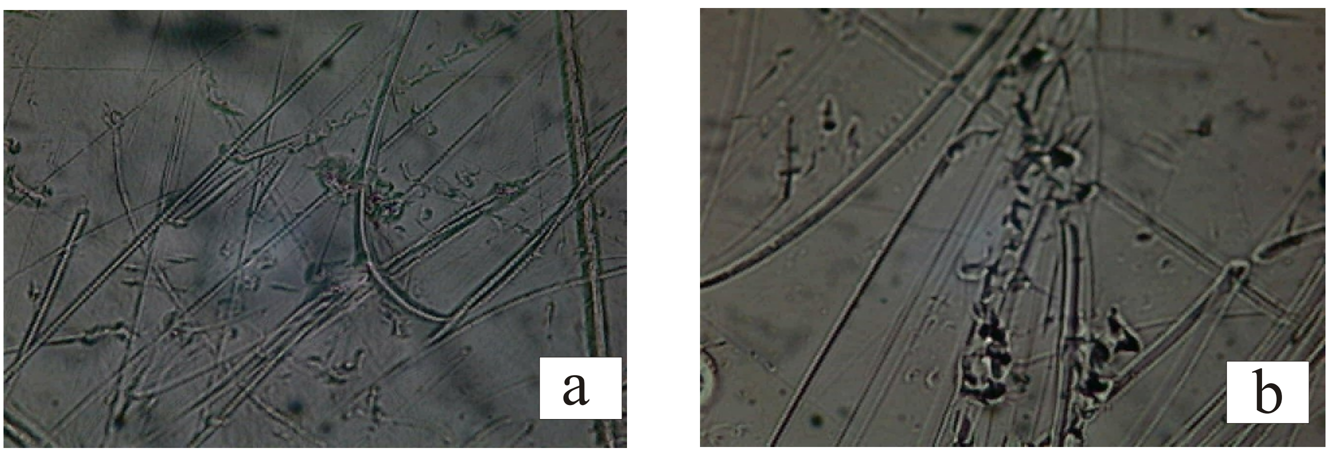

Figure 6: Micrographs of PVC irradiated by laser produced lead ions at 0 V show ion dragging at two different samples of PVC at magnification 400.

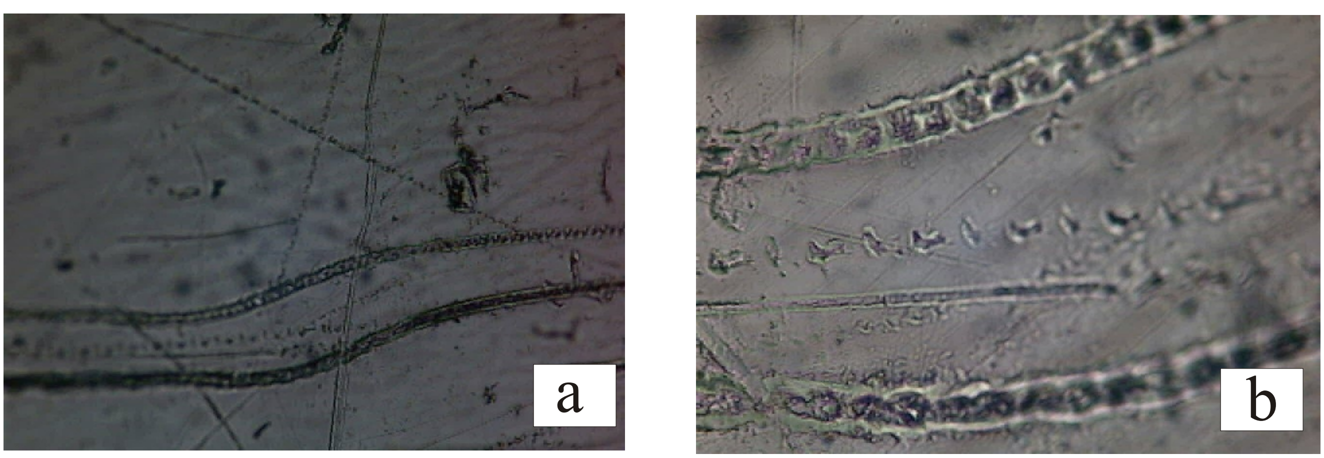

Figure 7: Micrographs of PVC irradiated by laser produced lead ions at 500 V show the chain formation at different magnifications (a) at magnification 100 and (b) at magnification 400.

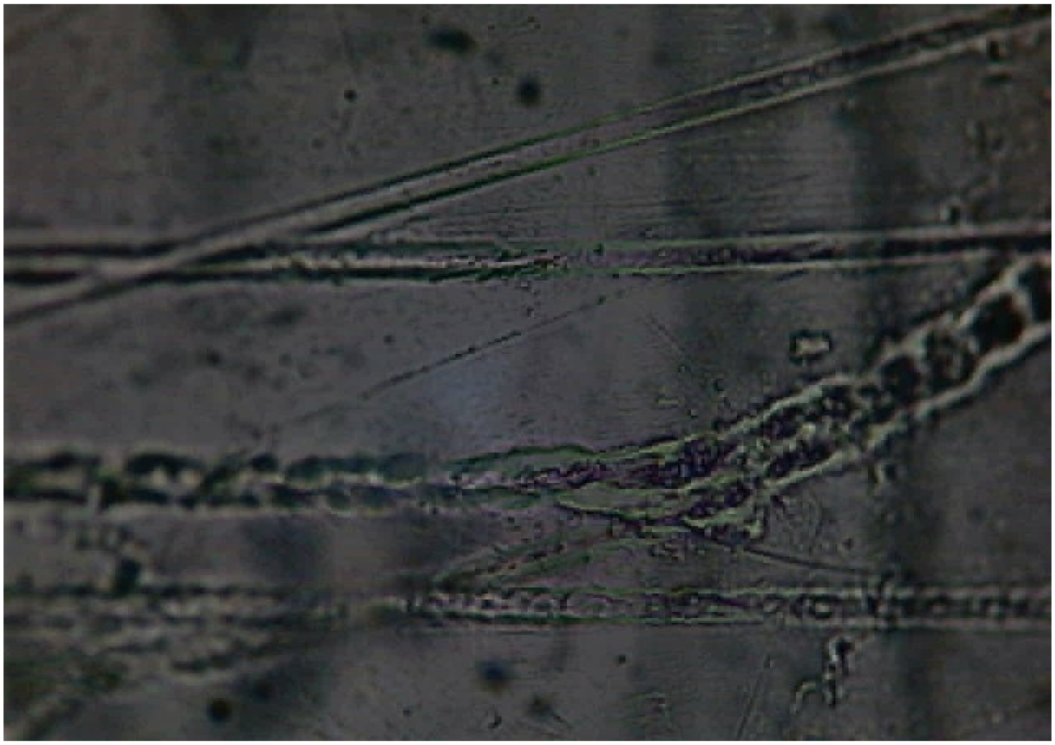

Figure 8: Micrograph of PVC irradiated at 500 V by lead ions at magnification of 400 show fracture and cracks

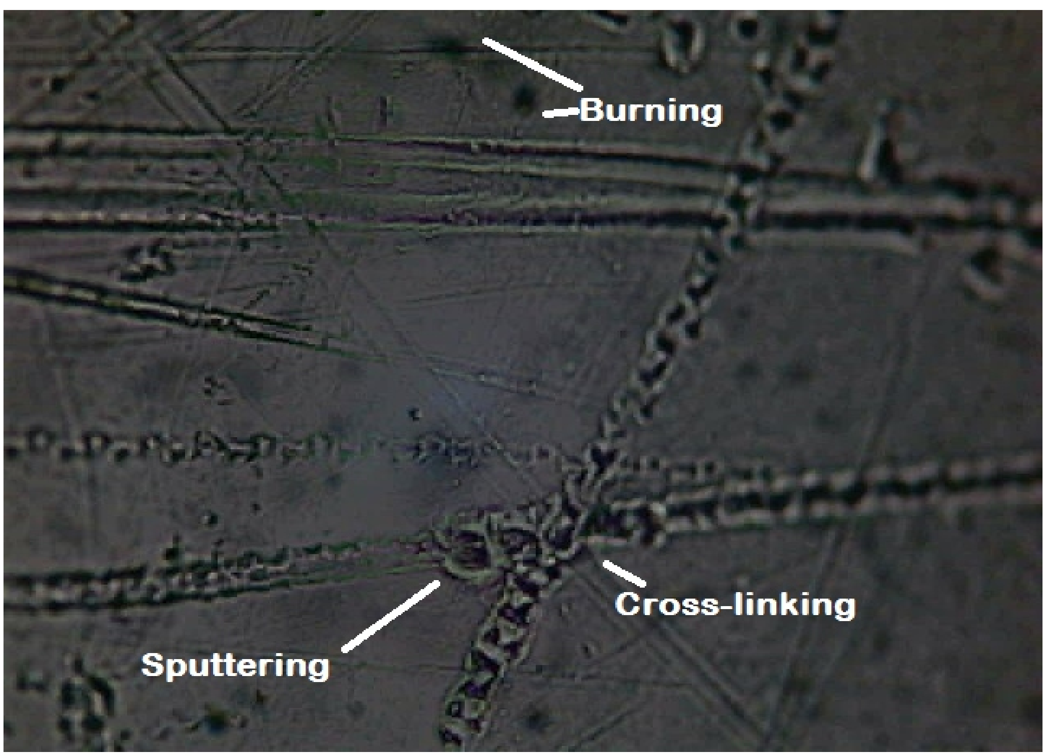

Figure 9: Micrographs of PVC irradiated by laser produced lead ions at 500 V, cross-linking, burning and sputtering at magnifications of 400.

4. Conclusions:

When polymers are exposed to radiation, they suffer main-chain scission, cross-linking and many other morphological changes. The chains formed at zero potential are straight chains induced by lead ions in PVC sample. However no cross-linking is observed at this potential. Thus incident ions have no sufficient energy so that they enhance the process of cross-linking after the chain scission. At 500 V, same long parallel chains are formed. These long parallel chains cover almost the whole sample which shows that ions are very energetic that's why they produce the long chains. They cover a long distance inside the polymer structure and penetrate deeply instead of coming at rest after transfer their energy to the target atoms. At high potential, fracture and cracks are also observed showing the non-uniform distribution of energetic ions. The dragging effect are observed only at 0 V because low energy ions are unable to penetrate deeper into the structure so they produce only drags on the substrates surface.

References:

1. Lee, E. H.; "Ion beam modification of polymeric materials fundamental principles and applications" J. Nucl. Instr. and Meth, B 151, 29-41 (1999).
2. A. Anders, Handbook of Plasma Immersion Ion Implantation (New York, Wiley, 2000).
3. Cutroneo, M.; "High-intensity laser for Ta and Ag implantation into different substrates for plasma diagnostics" J. Nucl. Instr. Meth. Phys. Res., B 354, 56-59 (2015).
4. Matsuyama, N., Yukimura, K., and T. Maruyama; "Amorphous diamond like carbon film prepared by pulsed laser deposition with application of pulsed negative bias voltage" J. Appl. Phys., 89, 1938-1941 (2001).
5. Tian, X. B.; "Plasma immersion ion implantation of insulating materials" J. Surf. & Coat. Tech., 196, 162-166 (2005).
6. Ishikawaet, J.; "Negative-ion implantation technique" J. Nucl. Instr. and Meth. 96 (1-2), 7-12 (1995).
7. Ueda, M.; "Aluminum plasma immersion ion implantation in polymers" J. Nucl. Instr. Meth. Phys. Res., B 206, 760-766 (2003).
8. Boldyryeva, H.; "Surface modification and nanoparticle formation by negative ion implantation of polymers" J. Nucl. Instr. Meth. Phys. Res., B 219-220, 953-958 (2004).
9. Faupel, F., Willecke, R., and A. Thran; "Diffusion of metals in polymers" J. Mater. Sci. Eng., R 22, 1-55 (1998).
10. Foitzik, A., and F. Faupel; "Structural Investigation of the SilverPolyimide Interface by CrossSectional Ten and IonBeam Sputtering" J. Mater. Res. Soc. Symp. Proc., 203, 59 (1991).
11. Awaja, F.; "Autohesion of Polymers" Polymers, 97, 387-407 (2016).
12. Ruck, D. M.; "Ion induced modi?cation of polymers at energies between 100 keV and 1 GeV applied for optical waveguides and improved metal adhesion" J. Nucl. Instr. and Meth., B 166-167, 602 (2000).
13. Koshida, N., and Y. Wachi; "Application of ion implantation for doping of polyacetylene films" J. Appl. Phys. Lett., 45, 436-439 (1984).
14. Flitsch, R., and D. Y. Shih; "A study of modified polyimide surfaces as related to adhesion" *J. Vac. Sci. Tech., A* 8(3), 2376-2381 (1990).
15. Carlson, J. D.; "Surface property changes induced in poly(1-hexene) elastomer by high energy ion irradiation" J. *Nucl. Instrum. Meth. Phys. Res., B 7-8*, 507-12 *(*1985).
16. Aziz, F., and M. A. J. Rodgers; "Radiation Chemistry Principles and Applications" (VSH, New York & Germany, 1987).
17. Michael, R., and D. Stulick; "Surface topography development on Teflon under KeV Xe atom bombardment" *J. Vac. Sci. Tech., A 4*, 1861 *(*1986).
18. Elman, B. S.; "Ion implantation studies of polydiacetylene crystals" J. *Appl. Phys., 57, 4996 (*1983).
19. Mazzoldi, P., and P. G. Arnold; "Ion-beam Modification of Insulators" (Elsevier, Amsterdam 1987).

20. Wang, Y. Q., Giedd, R. E., and L. B. Bridwell; "Ion induced structures and electrical conduction in implanted polymer films" J. *Nucl. Instrum. Meth. Phys. Res., B 79*, 659-663 (1987).

21. Wypych, G.; 'PVC degradation and stabilization" 2nd ed., Chem. Tec., Toronto, 2008).

22. Braun, D.; "Recycling of PVC" J. Prog. Poly. Sci., 27, 2171-2195 (2002).

23. Dildar, I. M.; "Morphological effects of accelerated Lead ions on Polyvinylchloride" Pakistan Journal of Science, 67 (3), 252-258 (2015).

24. Rahman, M. K.; "Investigation of Silver Plasma and Surface Morphology from a nanosecond laser ablation" J. Mat. Phys. Chem., 114, 978-982 (2009).

25. Feld, H.; "Carbon cluster emission from polymers under keV and MeV-ion bombardment" J. Phys. Chem. 94, 4595-4599 (1990).

26. Yanling, C.; "Non-thermal plasma assisted polymer surface modification and synthesis" A rev. Int. J. Agric. & Biol. Eng., 7 (2), 1-9 (2014).

27. Horie, K.; "Definitions of terms relating to reactions of polymers and to functional polymeric materials" J. Pure Appl. Chem., 76 (4), 889-906 (2004).

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

29. Han, S.; "Polymer surface modification by plasma source ion implantation" J. Surf. Coat. Tech., 93, 261-264 (1997).

30. Meckenzie, D. R.; "Modification of polymers by plasma-based ion implantation for biomedical applications" J. Surf. Coat. Tech., 186, 239-244 (2004).

31. Lu, W.; "Plasma-Assisted Synthesis of Chlorinated Polyvinyl Chloride (CPVC) Characterized by Online UV-Vis Analysis" J. Chem. Eng., 207-208, 923-930 (2012).

32. Qi, B., Lau, Y. Y., and R. M. Gilgenbach; "Extraction of ions from the matrix sheath in ablation-plasma ion implantation" J. Appl. Phys. Lett., 78, 706 (2001).

33. http://pac.iupac.org (visited on)

34. Http://www.cigrjournal.org/index.php/ Ejounral / article/download/3317/2240 (visited on)