



저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

A MASTER THESIS

**Tribological and Physico-Chemical
Properties of Electron Beam Irradiated
Polyoxymethylene Copolymer (POM-C)**

MD. SHAHINUR RAHMAN

DEPARTMENT OF NUCLEAR AND ENERGY ENGINEERING

GRADUATE SCHOOL



November, 2015

PREAMBLE

This thesis is submitted for the degree of Master of Engineering in the Department of Nuclear and Energy Engineering, Jeju National University, Korea under the supervision of Professor Heon-Ju Lee. No segment of this thesis has been submitted for any degree at any other research Institution or University. According to knowledge of the author, this thesis works is fully original unless reference is taken from others works. Parts of this thesis have been published in two international conferences as listed below:

Conference proceedings:

1. Md. Shahinur Rahman, Ulugbek Shaislamov , Jong- Keun Yang, Rai Suresh, Seung-Hyeon Kim, M. Waqar Ahmed, Heon -Ju Lee*, “Effect of Electron Beam Irradiation on Tribological and Physico-Chemical Properties of Polyoxymethylene (POM)”, CoMMET 2015- Conference on Material and Manufacturing Engineering and Technology, Korea (Seoul), July 29-30, 2015.
2. Md. Shahinur Rahman, Heon-Ju Lee*, “Tribological and Physico-Chemical Properties of Electron Beam Irradiated Polyoxymethylene Copolymer (POM-C)”, AEPSE 2015- The 10th Asian-European International Conference on Plasma Surface Engineering, Korea (Ramada Plaza Hotel, Jeju), September 20-24, 2015.

ABBREVIATIONS

POM-C	Polyoxymethylene copolymer.
COF	Coefficient of friction.
R _a	Average surface roughness.
EB	Electron beam irradiation.
KGy	1000 J/KG.
1 MeV	1.6×10^{-13} J
τ	Shear stress
A _r	Real area of contact
d	Sliding distance
F	Friction force
L	Normal load
H	Hardness
V	Wear volume
N	Normal load
K	Dimensionless coefficient of wear
μ	Coefficient of friction

Dedicated To My

Teachers And Beloved Family Members

ACKNOWLEDGEMENTS

This is the best opportunity to acknowledge and express my gratitude to nice people for their huge supports and encouragement throughout my masters at Jeju national University. First of all, I would like to give my heart-felt gratitude to my advisor Professor Heon-Ju Lee for providing me this great opportunity to pursue my masters at Jeju National University. This work was impossible without his invaluable guidance, astute supervisions, encouragement and supports. He was not only my advisor, but also he was my mentor in “Plasma and Electron beam irradiation technology”. It’s his full credit to give me the opportunity to work with him in a promising field by selecting me as his student.

I am highly grateful to Dr. Konstantin Lyakhov (Research Professor, Plasma Applications Lab., Nuclear and Energy Engineering Department, Jeju National University) for his invaluable supports and guidelines in radiation physics and chemistry, who was also my another mentor. I would like to express my special gratitude to Assistant Professor Soo-Seok Choi under whom I have taken one course learned about different aspects and applications of advanced plasma materials engineering. It was very helpful to think about my experimental methods and characterization results. The lessons he delivered with great care and blended theoretical knowledge with practical directions. I am thankful to Dr. Ulugbek Shaislamov for his assistance in many ways.

I am very grateful to Dr. Karthikeyan Krishnamoorthy, Kamran Ali, Siddiqui Ghayas Uddin, Memmon Sajid and Shaheed Aziz (Mechatronics Department, Jeju National University) for their huge supports in different surface characterizations, who also taught me Raman spectroscopy, 3D Nano Profiler, Water contact angle analyzer and Optical Microscopy analysis throughout my masters in Jeju National University.

In many ways, I am indebted to my lab mates M. Waqar Ahmed, Rai Suresh, Jong-Keun Yang and Seung –Hyeon Kim for their huge supports. I will always keep in mind their friendship and attitude. I would like to give my special thanks to my senior lab mate Jong –Keun Yang who helped me a lot in different aspects.

I am highly grateful to my parents who gave birth to me and also educated me with their highest supports. Lamia Sultana (my loving wife) supported me a lot with her optimum affection and suggestion to study in Jeju National University.

I greatly acknowledge the financial support provided by Korean Government under Brain of Korea 21+ (BK 21+) project. I would like to give thanks to Dr. B.H. Choi and Professor K.H. Chung for their huge efforts on electron beam irradiation in KAPRA (Korea Accelerator and Plasma Research Association, Gangwon-do, 269-843, South Korea). I am very much lucky, delighted and grateful to study in master of engineering in Jeju National University. I will always remember the spectacular surroundings & landscapes of the University and Jeju Island.

Overall I have to pay my earnest gratitude to almighty God who has given me the invaluable life, opportunity and ability to study and do research in plasma field for gathering knowledge.

Md. Shahinur Rahman

2015.11.30

TABLE OF CONTENTS

TABLE OF CONTENTS	I
LIST OF FIGURES	IV
LIST OF TABLES	VI
ABSTRACT	VII
CHAPTER I	1
INTRODUCTION.....	1
1.1 Brief introduction from literature review.....	1
1.2 Objective	3
CHAPTER II	4
TRIBOLOGY.....	4
2.1 Importance of tribology	4
2.2 A brief history of tribology	5
2.2.1 Friction	5
2.2.2 Adhesion in friction	7
2.2.3 Wear	8
2.2.4 Lubrication	10

2.2.5 Solid lubricants	10
2.3 Tribological applications	11
CHAPTER III	13
SURFACE MODIFICATION TECHNIQUE	13
3.1 Introduction	13
3.2 Electron beam irradiation process	14
3.3 Basic of electron and its interactions	19
3.4 Electron beam accelerator and its mechanism	20
3.4.1 Electron beam accelerator	20
3.4.2 Electron beam parameters	23
3.4.3 Advantages and limitations of electron beam irradiation Process	25
CHAPTER IV	27
Polyoxymethylene (POM-C)	27
4.1 Introduction	27
4.2 Properties of KEPITAL	28
4.3 Applications	29
4.4 Limitations	29
CHAPTER V	30
Experimental	30

CHAPTER VI	35
RESULTS AND DISCUSSION	35
6.1 Friction coefficient	35
6.2 Chemical structure	38
6.3 SEM-EDS analysis	41
6.4 Morphology of abraded surfaces	46
6.5 Surface roughness	48
6.6 Wettability	53
 CHAPTER VII	 55
7.1 Conclusions	55
7.2-7.3 Future works and references	56

LIST OF FIGURES

Fig. 1. A schematic diagram of friction.....	6
Fig. 2. Schematic representations of adhesion, deformation and wear.....	7
Fig. 3. Schematic diagram of three body mechanism	9
Fig. 4. Schematic representations of different wear mechanisms	9
Fig. 5. Schematic diagram of electron-matter interactions	15
Fig. 6. Schematic diagram of radicals formation	16
Fig. 7. Electron energy deposition vs thickness x density in POM-C at 0.8, 1.0, 1.5, 2.0, 3.0, 5.0 and 7.5 MeV incident electron energy.....	16
Fig. 8. Schematic diagram of electron acceleration	18
Fig. 9. EB irradiation effects on polymer chain structure	18
Fig. 10. Scattering of an electron inside the electron cloud in an atom	20
Fig. 11. General diagram of ELV-8 accelerator	22
Fig. 12. Molecular chain and 3 D structure of POM-C	30
Fig. 13. Schematic diagram of electron beam irradiation	34
Fig. 14. Contact schematic diagram of ball on disk method	34
Fig. 15. Friction coefficient of POM-C blocks against SUJ 52100 ball	37
Fig. 16. Raman spectra on POM-C blocks	40
Fig. 17. SEM-EDS analysis for morphological and elemental composition	43

Fig. 18. Optical microscopic images of the worn surfaces at sliding tracks	47
Fig. 19-25. 3D Nano images of Surface roughness.....	49
Fig. 26. Correlation among water contact angle, friction coefficient and irradiation dose	54
Fig. 25. Water contact angle on POM-C blocks	54

LIST OF TABLES

Table 1. Polymeric material properties modified by electron beam irradiation.....	15
Table 2. Beam parameters of ELB accelerator	21
Table 3. $\frac{\Delta E}{\Delta R}$ (Energy absorption ratio)	25
Table 4-6. Physical, thermal and mechanical properties of KEPITAL	28
Table 7. The vibrational band assignments of POM-C	34
Table 8. The vibrational band assignments of Polyoxymethylene copolymer (POM-C)	41

ABSTRACT

Polyoxymethylene copolymer (POM-C) is an attractive and widely used engineering thermoplastic across many industrial sectors owing to outstanding physical, mechanical, self-lubricating and chemical properties. In this research work, the POM-C samples were irradiated with 1 MeV electron beam energy in five doses (100, 200, 300, 500 and 700 KGy) in vacuum condition at room temperature. The tribological and physico-chemical properties of electron beam irradiated POM-C have been analyzed using Pin on disk tribometer (under dry friction condition), Raman spectroscopy, SEM-EDS, Optical microscopy, 3D Nano surface profiler system and Contact angle analyzer. Electron beam irradiation at a dose of 100 kGy resulted in a decrease of the friction coefficient of POM-C sample due to well suited cross-linking, carbonization, free radicals formation and energetic electrons- atoms collisions (physical interaction). The irradiation doses at 200, 300, 500 and 700 kGy resulted in increase of the friction coefficient as compared to unirradiated POM-C due to severe chain scission, chemical structural and physical degradation. 100 kGy electron beam irradiated POM-C sample also shows lowest surface roughness and highest water contact angle among unirradiated POM-C and all others irradiated POM-C, which gives the lowest friction coefficient and wear loss. The electron beam irradiation transferred the wear of unirradiated POM-C sample from the abrasive wear, adhesive wear and scraping to mild scraping for the 1 MeV, 100 kGy irradiated POM-C sample which can be concluded from SEM-EDS and Optical microscopic observations. The degree of improvement for tribological attribute relies on the electron beam irradiation condition (energy and dose rate).

Key words: Polyoxymethylene Copolymer; Electron Beam Irradiation; Friction Coefficient; Wear; Raman Spectroscopy; Water Contact Angle

CHAPTER I

INTRODUCTION

1.1 BRIEF INTRODUCTION FROM LITERATURE REVIEW

Polyoxymethylene copolymer (POM-C) is the most prominent engineering thermoplastic consisting of repeating carbon-oxygen bonds in the form of oxymethylene groups (OCH₂) [1]. It has been a focus of major attention in the field of polymer due to its promising properties i.e. low coefficient of friction, high abrasion resistance, high heat resistance and self-lubricating [4]. It is widely used to make small gear wheels, ball bearings, precision parts, automotive and consumer electronics [5, 6]. To expand POM-C applications in low and high tech areas with good processibilities into valuable products, it has been ever-rising interest in the surface modifications of the tribological and physico-chemical properties [7, 8]. Many reactions occur during desired surface modification of POM-C in the molecular structure level [12, 36-42].

Several methods have been used to get the best surface modifications, varying from usual flame treatments, “wet” chemical treatments, electrical treatments (corona discharge) and plasma treatments , to particle beam irradiation (electrons, ions, photons and neutrons) method [9-11].

The application of ionizing radiation on polymers introducing energy into materials to create useful changes will sustain to attract great attentions in polymers field due to flexibility, effectiveness and environmentally friendly nature compared to usual methods [13, 34-45]. The degradation reduction mechanism of POM-C polymer was observed in the 1960s [46].

Reduction of friction coefficient for polyether- ketone with a cardo group (PEK-C) in the process of electron beam bombardment was reported by few researchers [15], which resulted in the formation of carbonated solid thin film layer on PEK-C surface during irradiation process. Effects of low and medium energy electron beam irradiation on different polymers have been observed by several researchers [20-22, 40-45]. Electron beam (EB) irradiation system is becoming an optimistic process to improve the tribological and physico-chemical properties of polymers at a large scale [14, 26, 36-41]. Modified polymers are leading materials for a vast range of useful applications e.g. light- emitting diode, solid state battery, optical display and electronic devices [16-19].

Electron beam irradiation causes modification on polymer surfaces as a result of cross-linking (electronic stopping), chain scission (nuclear stopping) and evolution of gases (CO₂, CH₄, CO and H₂) leading to physical and chemical properties changes on a molecular scale e.g. carbonization, generation of highly reactive intermediates (free radicals), cyclization through the formation of intermolecular bonds and ionization [13, 20-26, 36-45]. Cross-linking creates three dimensional strong chemical networks, strengthens rigidity of the backbone structure, contributes to anchoring parts for the chain and refrains chain displacement, thus promoting dimensional durability with creep resistance [21, 36-45]. Chain scission reduces molecular weight and it breaks the chemical bonds of polymers, which subsequently degrades the polymers surface. The radiation not only modifies the desired tribological and physico-chemical properties of polymer, but it can create flaws with deformation on the polymer materials. The cross-linking becomes more dominant in vacuum condition, while the availability of oxygen increases the chain scission and gas formation during electron beam irradiation [36-38]. The controlled cross-linking and chemical free radicals layer formation

on polymer surface lead to better tribological, mechanical, morphological and chemical properties [25-26, 36]. However, the optimum improvement level relies on the electron beam bombardment parameters and polymeric structure [20-22, 36].

1.2 OBJECTIVE:

The principal objective of this work is to study the effects of electron beam irradiation parameters on the friction coefficient, abrasion wear, surface roughness, chemical structure and water contact angle of POM-C polymer with correlation among tribological, morphological and chemical properties.

CHAPTER II

TRIBOLOGY

2.1 IMPORTANCE OF TRIBOLOGY

Tribology is the discipline to study the science and technology of interacting surfaces in relative motion and of associated subjects and practices [David Tabor and Peter Jost, 1966]. It encompasses the study and application of the principles of friction, lubrication and wear, which is also the branch of materials science and mechanical engineering. Friction is the resistive force to resist relative motion between two sliding surfaces in contact. Friction and adhesion can change depending upon the attractive force between sliding surfaces and the chemical property of surface materials. Wear is described as the interaction mechanism between two sliding surfaces and particularly the removal and deformation phenomena of surface material due to mechanical action of attraction/repulsion force. Friction and wear mechanisms are very intricate phenomena in rolling and sliding surface contacts. By changing the shape of surface material during sliding and rolling, the friction can drop extensively according to the environment. In general, high friction and adhesion play a vital role to increase wear of surfaces by causing debris particles. There are many methods available to reduce friction and wear. Tribology plays a vital role in durability, processibility and reliability for valuable and precise products in industrial and engineering applications e.g. small gear wheels, ball bearings, precision parts, biomedical appliances, consumer electronics, aerospace, land transportation, power generations, vehicles and machining operations, where relative motion is experienced. A small reduction of bearings friction can save a noticeable amount of frictional power loss from automobiles and industrial applications (Bowden and Tabor 1973). Power wastage with maintenance and product failures with processibility problems closely related to tribology cost

billions of dollars per annum in highly industrialized country (Devine 1976 and Peterson 1979). As estimation, the annual loss is around 1-2 % of GDP in USA due to tribological interaction (Heinz, 1987). Any nation could be saved their GDP from 1.3 to 1.6% with proper attention on tribological interaction mechanism (Peter Jost, 1990).

Tribology is becoming an optimistic discipline for observing friction, wear and lubrication principles to save energy and environment tremendously.

2.2 A BRIEF HISTORY OF TRIBOLOGY

The word “Tribology” comes from the Greek word “Tribos” which denotes rubbing [Dowson 1979]. Ancient people had limited knowledge in tribology, but they knew to use lubricant to drag stones easily. Human civilization has been recognized the significance of tribology few years ago as an independent discipline regarding with friction and wear interaction phenomena. Egyptian used sledges with water lubrication in 1880 BC to transport big statues.

2.2.1 FRICTION

Leonardo da Vinci (1452-1519) stated two laws of friction first. Guillaume Amontons (1699) rediscovered the friction classic rules through experiments that friction force is proportional to applied normal load and is independent of the apparent real surface area of contact between two sliding surfaces (Fig. 1). Charles- Augustin de Coulomb (1785) developed further aforementioned rules of friction that sliding velocity does not influence kinetic friction directly. Aforementioned three laws of friction were stated depending on experimental analysis for dry friction. Famous mathematician Leonhard Euler described the real difference between kinetic and static friction (Dawson 1998).

Coulomb assumed that friction is generated from interlocking between two sliding surface asperities, which are rigid. In real world, all asperities are not rigid which is examined from many experiments. The shape and rigidity of asperities during sliding can be controlled by elastic or plastic deformation using applied load. As a matter of fact, adhesion is a crucial factor for friction. Friction (F_{friction}) can be calculated from the given formula:

$$F_{\text{friction}} = \mu N.$$

Here,

N = Normal load

μ = Friction coefficient

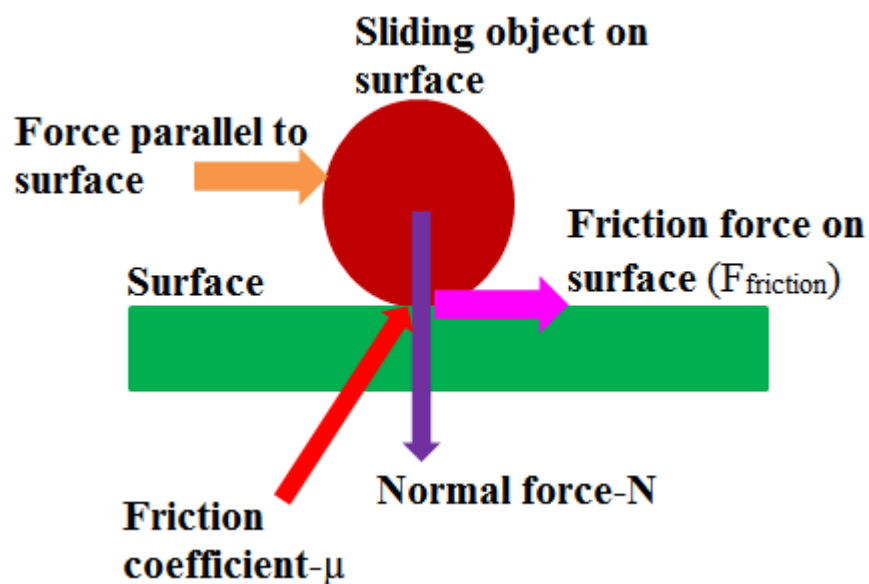


Fig. 1. A schematic diagram of friction

2.2.2 ADHESION IN FRICTION

When two surfaces are in contact, there is a tendency between two sliding surfaces to cling with each other and is called adhesion. Bowden and Tabor (1986) enunciated the fundamental model of adhesion influencing to friction. The fundamental model describes that when two surfaces are in sliding condition, the asperities at sliding contact points suffer elastic or plastic deformation (Fig. 2). The friction can be stated as $F = \tau A_r$ (τ = shear stress, A_r = real surface area of contact).

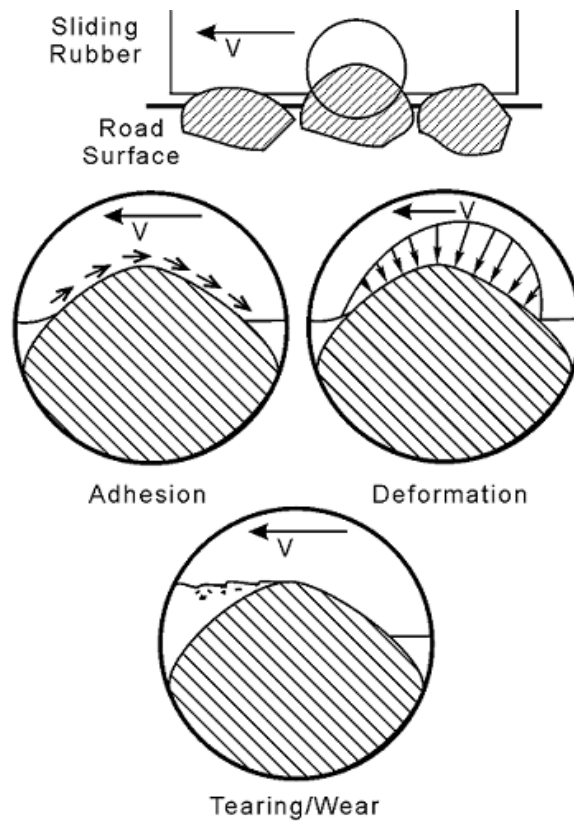


Fig. 2. Schematic representation of adhesion, deformation and wear (Maura Crobu, 2012).

2.2.3 WEAR

Wear is defined as the interaction between two sliding surfaces and particularly the deformation and removal of top layer material from a surface due to mechanical action of opposite surface (Fig. 2). Wear mechanism is also influenced by “three body mechanism” shown in Fig. 3 (Maura Corbu, 2012). Wear study is very important phenomena in friction discipline to reduce premature failure of precision parts related to economical loss in industrial sector. A systematic analysis of wear mechanism has initiated recently in rail-road, aerospace and transportation industry focusing on adhesive, abrasive and fatigue wear. The complex nature of wear mechanism can be divided in some specific names depending on several factors e.g. adhesive, abrasive, surface fatigue, fretting, erosive, delamination and oxidation wear shown in Fig. 4. A few standard test mechanisms exist for wear phenomena to specify the amount of surface material removal during a given time period under well defined surface conditions. Lim and Ashby (1987 and 1990) introduced first “wear maps” summarizing from several researchers research findings. Those maps are very helpful to determine the optimum operating regimes for a material surface in any given operating conditions. Many intricate problems are still existing regarding with wear mechanism, when the wear is influenced by many factors at a time. Moreover, Archard equation (classic wear prediction model) can predict the wear behavior of any specific material in an ideal condition. The Archard equation is: $k = VH/Ld$ (k = dimensionless wear coefficient, V = wear volume, d = sliding distance and L = normal load). This equation is very accurate to determine the wear resistances of any specific material, if the sliding conditions are fixed.

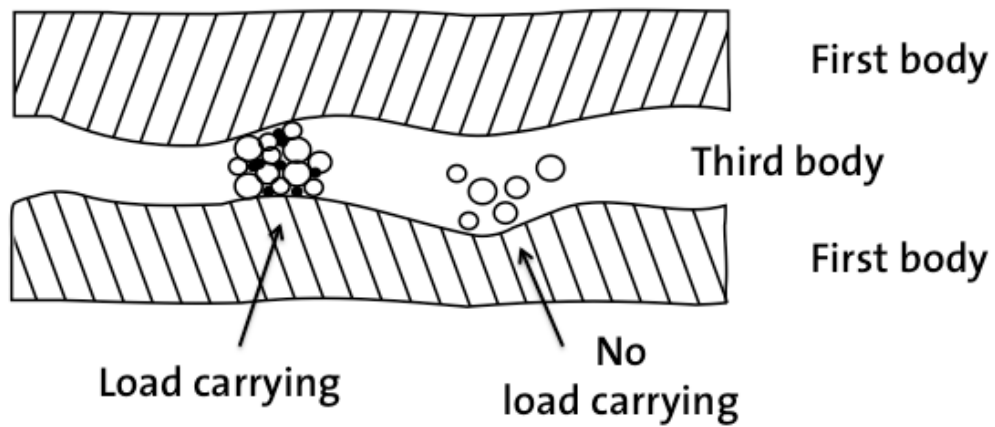


Fig. 3. Schematic diagram of three body mechanism

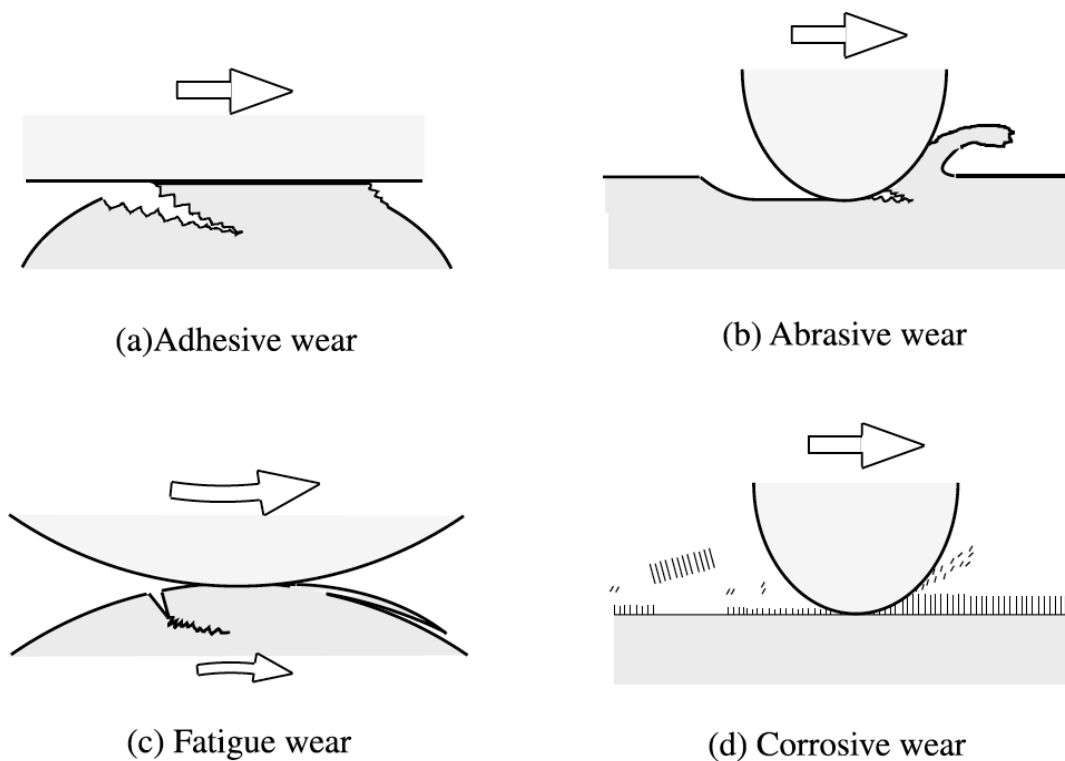


Fig. 4. Schematic representation of different wear mechanisms (Maura Corbu, 2012).

2.2.4. LUBRICATION

Lubrication is the most applied method to reduce friction and wear of contact material surfaces by interposing a substance called lubricant between two sliding surfaces. Lubricant's substances have many state e.g. solid, liquid, gas or a combination of them. Tower's experiment (1883) led to true realization of hydrodynamic lubricant (the contacting surfaces are in close proximity and moving relative to each other under ultra low coefficient regime e.g. viscosity, bearing pressure and relative motion). The lubrication could play a lot of roles depending on situation to allow smooth operation of equipments.

2.2.5 SOLID LUBRICANTS

The usage of grease and petroleum oil as a liquid lubricant was started in eighteen century at a large scale (Tower 1883). Reynolds (1886) developed a basic equation for hydrodynamic lubrication (viscous liquids) based on Tower's experimental results. These viscous liquids can control friction by reducing shear resistances and real surface area of direct contact between two sliding surfaces. These liquid lubricants can be squeezed out depending on operating conditions (load, temperature and sliding velocity) and, the two sliding surfaces could come into direct contact, which can increase the friction coefficient at extreme sliding conditions. Moreover, solid lubricants could play a pivotal role to reduce friction at extreme sliding conditions, where the liquid lubricants effectiveness are limited (Clauss 1972).

2.3 TRIBOLOGICAL APPLICATIONS

Tribology as a multidisciplinary discipline has taken place in most of the sectors of our civilized life.

The vast applications of tribology are divided into several areas e.g. industrial, MEMS, biomedical and ecological tribology.

2.3.1 INDUSTRIAL TRIBOLOGY

The industrial tribology is the mainstream of tribology discipline, which is directly related with economical system. Several recent studies show that 55-60 % of mechanical equipments are damaging due to tribology (poor lubrication and severe wear). Industrial tribology has occupied vital place in manufacturing, aviation, fabrication, automobile and production. The term tribology is closely related to mechanical products design and optimization with some objectives-

- Conservation of material resources by wear reduction.
- Conservation of useable energy by friction reduction.
- Increase the lifetime of mechanical products and equipments by proper engineering maintenance.
- Increase the feasibility and reliability of manufacturing products.

2.3.2 MEMS/NEMS TRIBOLOGY

With the commercialization and development of MEMS/NEMS products (disk drives, magnetic storage devices and precision parts for small gear, wheel, fan, chip, IC, detector and laser), it has been noticed that wear and friction at micro / nano scales are the main concern for efficiency, feasibility and reliability of products. In MEMS/NEMS products, surface forces play dominant role in operating conditions.

2.3.3 BIOMEDICAL TRIBOLOGY

With the development of biomedical applications, biotribologists are incorporating concepts of friction wear and lubrication tremendously for the better functioning of medical implants e.g. design of prosthetic devices, plate in bone fracture repair, contact lenses, denture and restorative materials. Tribology in biomedical sectors is involved extensively in increasing implants life and in decreasing patients' trauma.

CHAPTER III

SURFACE MODIFICATION TECHNIQUE

3.1 INTRODUCTION

Surface modification is the integration of physics and chemistry to modify materials surface to expand applications in low and high tech areas with good processibilities. Surface engineering is a branch of materials science which involves with the surface modification of solid matter. It interacts with solid phase surface in order to increase the reliability, feasibility and processibility. It reduces the degradation phenomena of surface over time related to wear, friction, corrosion, fatigue and creep. Surface engineering is highly applicable in electronics, power, textile, production, aerospace, automotive, biomedical and missile industries. It is also widely used at micro to nano scales to develop functional properties of materials leading to mechanical, wear resistant, physical, electrical, chemical, electronic and magnetic. Actually, surface engineering makes surface robust life from mechanical and tribological problems [1-3]. Latterly, Surface engineering has shifted intensively from traditional electroplating to CVD, PVD, PEVCD, VPD, thermal spray using plasma, electron, ion, laser, solar beam, microwave, RF and synchrotron radiation [3-7] to change in microstructure and composition selectively. Of the available techniques, electron beam irradiation is becoming promising technology in polymer surface modification because it combines versatility and low temperature processing with optimum reliability, feasibility, reproducibility and processibility. Electron beam irradiation has so many processing techniques for surface modification of different materials having their own specific advantage and disadvantage. Electron beam irradiation specifically has proven successful in polymer and biomaterial arena, because it offers optimum level surface property modifications selectively without changing the bulk properties of materials.

3.2 ELECTRON BEAM IRRADIATION PROCESS

Electron beam irradiation means the irradiation of electron to any material to induce a chemical chain reaction in the material. When it penetrates into material and distributes some portion of energy to the atom or molecules, the scattered electrons (secondary electrons) are generated. The secondary electrons continuously generate the scattered electron shower until the accelerating energy becomes low (Fig. 5). The generated secondary electrons generate free radicals or ions with high reactivity, which cause chemical chain reaction in material (Fig. 6). Electron beam irradiation is a convenient technique to modify the tribological and physico-chemical properties of the near surface region of materials selectively. It is different mechanism compared to surface coatings technology to modify surface. Electron beam irradiation is a sophisticated technology which actually penetrates the surfaces to alter the surface material composition for formation a stronger barrier and, this stronger barrier can prevent wear, delimitation, corrosion and friction. The penetration depth of electron beam irradiation in irradiated materials can increase linearly with the incident electron energy. The calculation of electron energy deposition versus thickness x density in POM-C at 0.8, 1.0, 1.5, 2.0, 3.0, 5.0 and 7.5 MeV incident electron energy is shown in Fig. 7, when the beam window thickness is 50 μm [48]. The air gap between beam window and the treated material is 25 cm at 0.0012 g/cu cm. By using low, medium and high energy electron beam irradiation of the species to be introduced, electron beam irradiation gives the controlled introduction of one or more free radicals into the near surface of materials. Electron beam irradiation can modify many types of surface material properties which are given in table 1.

Table 1. Polymeric material properties modified by electron beam irradiation.

Friction	Delamination	Physical
Wear	Adhesion	Color
Fatigue	Bonding	Hardening
Creep	Crystallinity	Lubrication
Corrosion	Electronic	Chemical structure

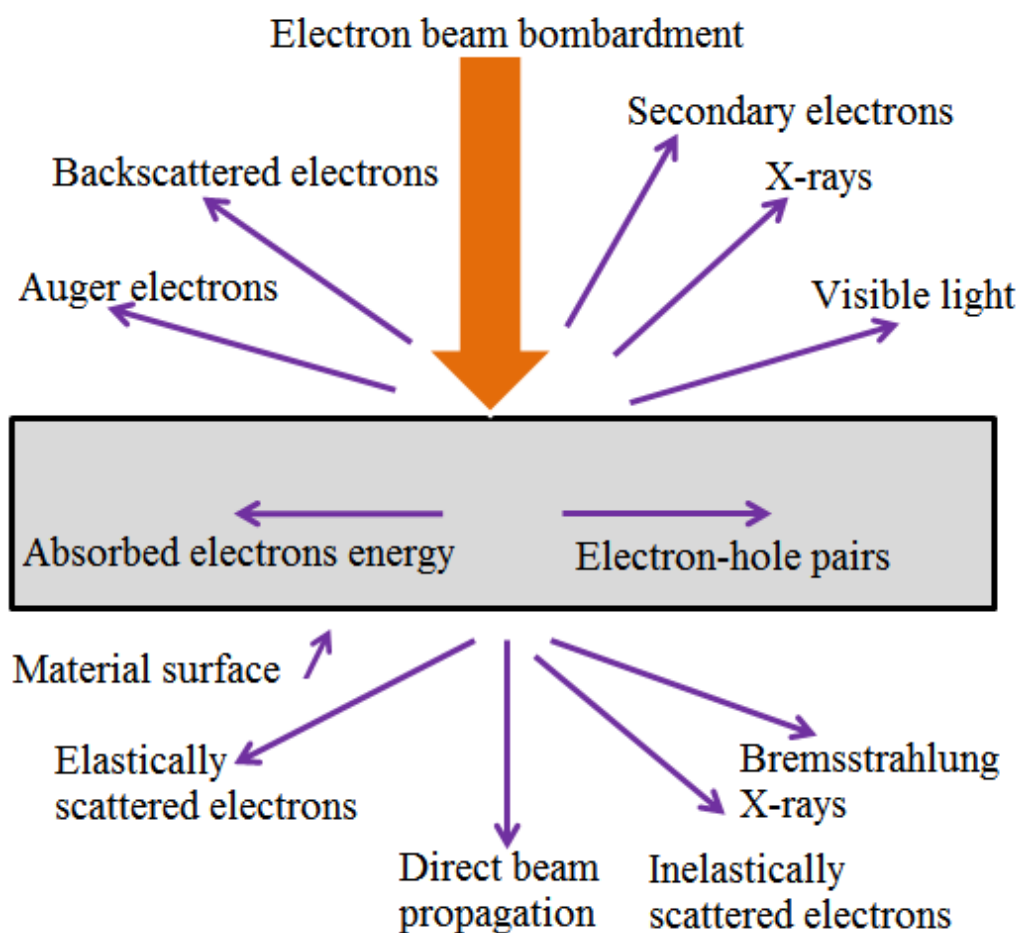


Fig. 5. Schematic diagram of electron-matter interaction

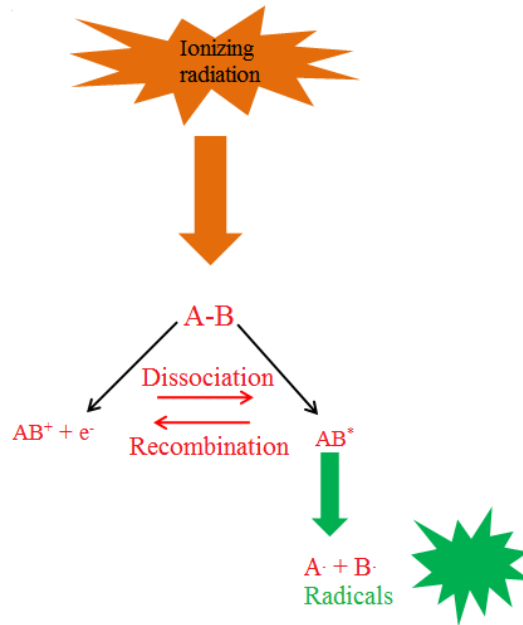


Fig.6. Schematic diagram of free radicals formation.

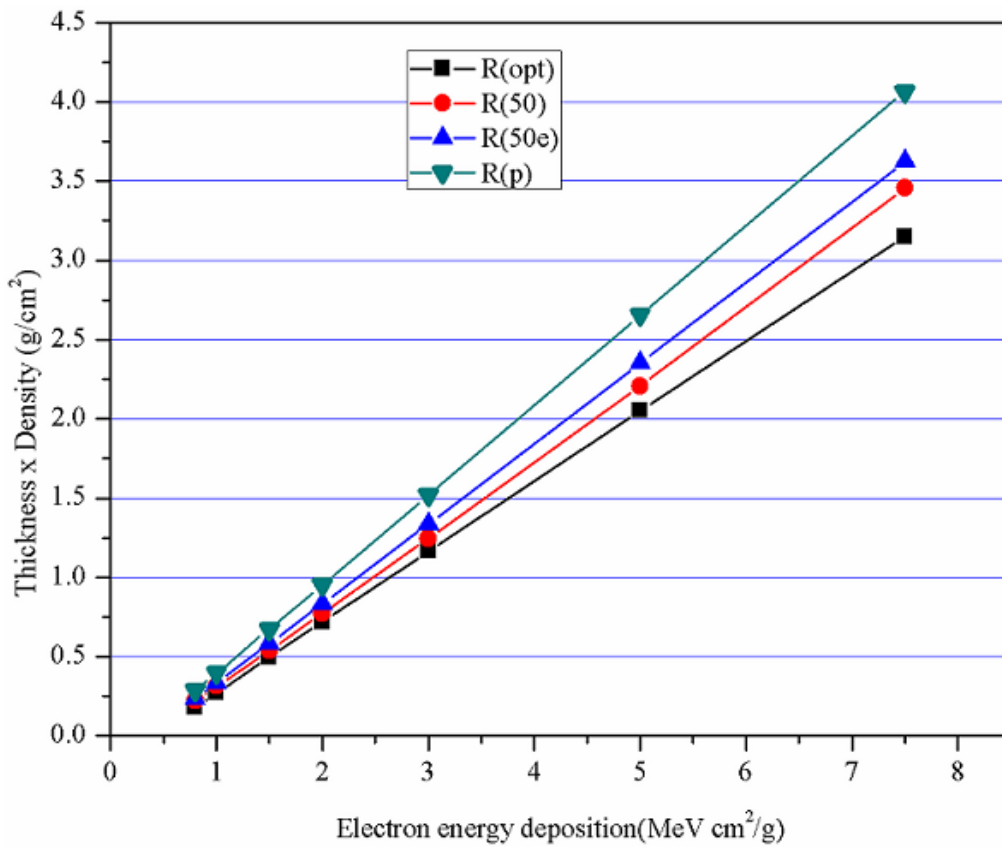


Fig. 7. Electron energy deposition vs thickness x density in POM-C at 0.8, 1.0, 1.5, 2.0, 3.0, 5.0 and 7.5 MeV incident electron energy.

The systematic process in which electron beam is bombarded to any material surface to induce chemical chain reaction and physical degradation, is called “electron beam processing system”. Electron beam denotes the flow of electrons with kinetic energy through a high electric field. The kinetic energy of electrons is also called as acceleration. The schematic diagram of electrons acceleration is shown in Fig. 8. Metal has abundant free electrons and the flow of these free electrons is called electric current. Free electrons are shaken roughly if the metals are heated enough. If the shaken energy is large enough compared to Fermi level of that material, then the free electrons are emitted from that material surface. The electrons can emit easily from cathode filament (negative terminal of power supply) due to repulsion force, if any additional negative voltage is applied to cathode terminal. Moreover, the free electrons can be accelerated rapidly from the cathode filament to anode electrode (positive potential terminal of power source) corresponding to applied electric field and electrode gap between anode and cathode filament.

The significant interactions between an accelerated electron beam and polymers, are “cross-linking (electronic stopping),” which is a polymerization chemical reaction for polymers; “graft polymerization,” which is a polymerization process with low molecules for polymers; “radical polymerization,” which is a chemical reaction in low molecules; and “chain scission,” which cuts the molecular chain of polymers (Fig. 9). These reactions occur in a complex manner at the same time, but the generation probability can be controlled by changing the electron beam irradiation parameters on a specific polymer.

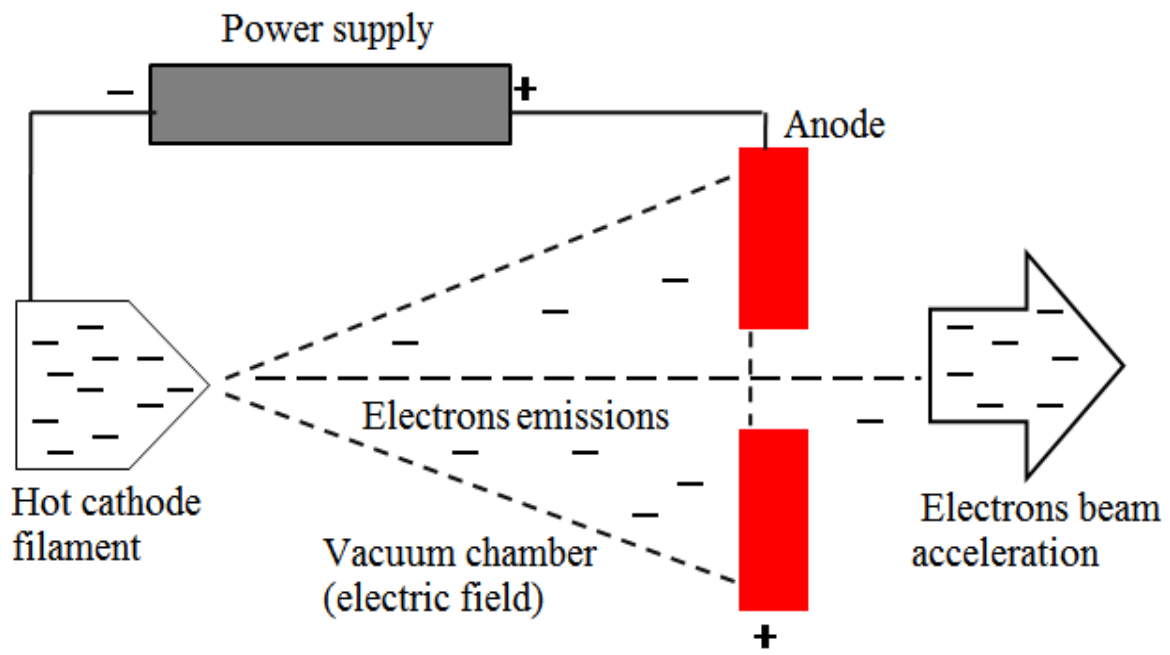


Fig. 8. Schematic diagram of electron acceleration.

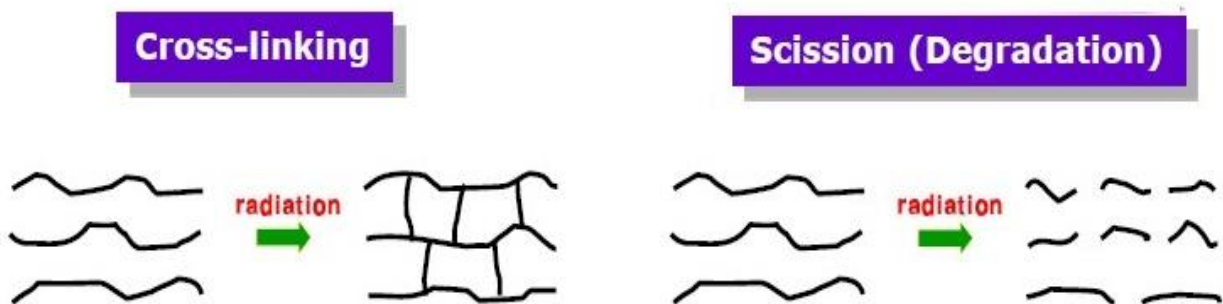


Fig 9. EB irradiation effects on polymer chain structure.

3.3 BASIC OF ELECTRON AND ITS INTERACTIONS

BASIC:

The electron is a subatomic particle which carries a negative elementary electric charge and, it is denoted as e^- . J.J Thompson (1897) discovered the electron while studying about cathode rays (negative charged particles). Electron mass is 1836 times lighter than proton mass. Electrons mainly interact with matter in two ways.

i) Elastic interaction:

In elastic interactions, electron does not lose any energy to incident material surface. So, the electron will leave with its original energy (E_0) from the material surface:

$$E_{ei} = E_0$$

Such electrons can contribute to direct beam propagation that passes the material surface along the incident beam. Elastic scattering can also happen when the electron is deflected from its track by Coulomb force for positive potential inside the electron cloud (Fig. 10).

ii) Inelastic interactions:

In inelastic interactions, energy is transferred from the electron to material surface. After interaction with material surface, the electron energy (E_{lei}) is less than original energy (E_0): $E_{lei} < E_0$

The transferred electron energy to the material surface can induce further interactions e.g. secondary electrons, Auger electrons, backscattered electrons, X-rays and phonons (Fig. 5). The generated second electrons contribute to modify the surface properties during electron beam irradiation, which can be controlled by different mechanisms

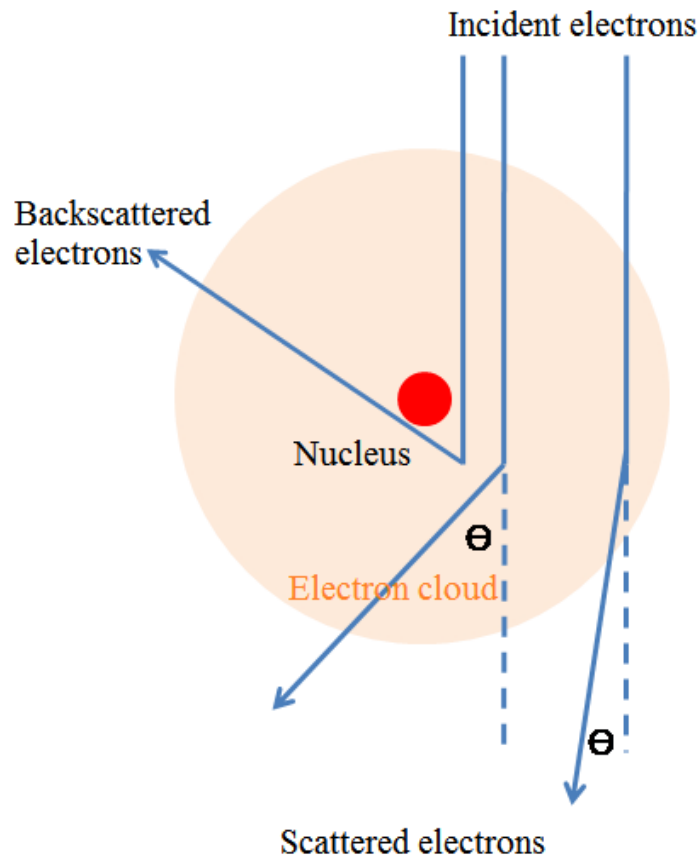


Fig. 10. Scattering of an electron inside the electron cloud in an atom.

3.4 ELECTRON BEAM ACCELERATOR AND ITS MECHANISM

3.4.1 ELECTRON BEAM ACCELERATOR

Electron accelerator generates thermal electrons from hot cathode filament, accelerates the velocity of thermal electrons, passes them into air through a thin titanium-foil window, irradiates material surface and induces chemical chain reaction into the irradiated material surface. The final attainable electron energy is determined by different parameters of electron accelerators e.g. acceleration voltage, electron current, working width, throughput, dosage distribution over working width and cooling mechanism. Many types of electron beam accelerators are available at the present market with different parameters and layouts:

- DC linear
- RF linear: pulsed and CW
- Linear induction
- Rhodotron
- Betatron
- Microtron
- Diode pulsed high current

DC linear type accelerators are very popular for surface property modifications in industry across the world. ELV (DC type, Russian) accelerator is very popular due to its simplicity, wide range of beam parameters with high stability, irradiation fields and easy controlling system. ELV accelerator has some model regarding with beam current, beam power and energy range. The general diagram of ELV-8 is shown in Fig. 11. The main beam parameters of ELV type accelerators are given in table 2.

Table 2: Beam parameters of ELV accelerator

Accelerator model	Energy range, MeV	Beam power, KW	Maximum beam current, mA
ELV-0.5	0.4 - 0.7	25	50
ELV-1	0.4 - 0.8	25	50
ELV-2	0.8 - 1.5	20	25
ELV-3	0.5 - 0.7	50	100
ELV-4	1.0 - 1.5	50	50
ELV-6	0.8 - 1.2	100	100
ELV-8	1.0 - 2.5	90	50
ELV-6M	0.75 - 0.95	160	200
ELV-12	0.6 - 0.9	400	500

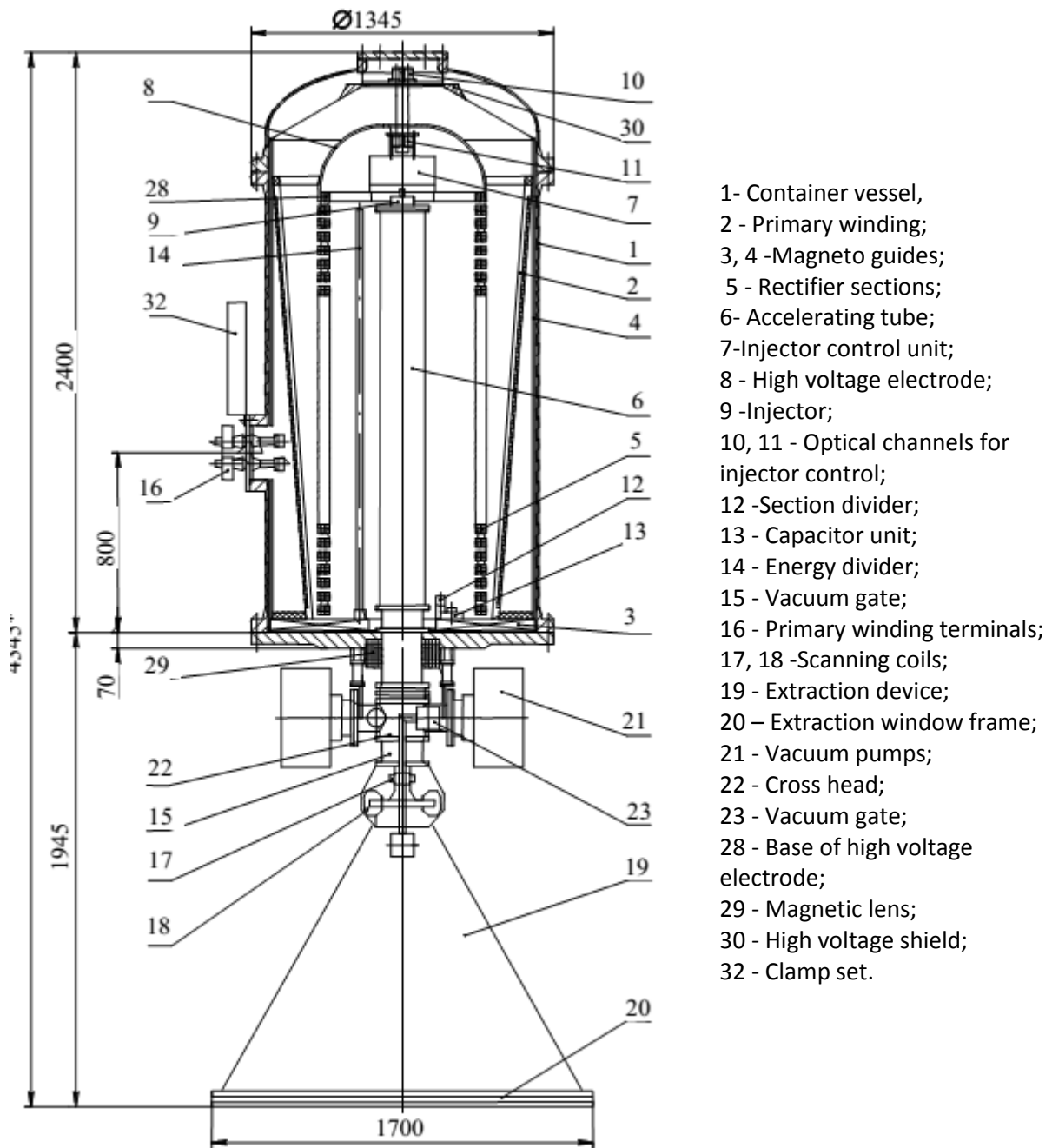


Fig. 11. General diagram of ELV-8 type accelerator (EB Tech Co., Ltd., Korea).

3.4.2 ELECTRON BEAM PARAMETERS

All electron beam accelerators have two fundamental parameters regarding with irradiation: electron beam current and energy. Electrons penetration depth into material surface is controlled by electrons kinetic energy, besides it is also dependent on the mass and density of the target material surface. The electron beam irradiation parameters can be calculated in the following ways:

I) ELECTRON BEAM ENERGY:

Electron beam energy is calculated by using these equations:

$$\text{Energy, } E = eV = m_0v^2 / 2 \dots \dots \dots \quad (\text{iv})$$

[m_0 = rest mass of electron; Kinetic energy, $E_{\text{kin}} = mv^2 / 2$].

The accelerated velocity of electron, $v = \sqrt{(2eV / m_0)}$. [V= electric field].

ii) ACCELERATING VOLTAGE:

It is defined from the electron penetration curve regarding with target material. The 60% penetration depth of relative dose is considered as effective thickness. The effective thickness is standardized by specific gravity of 1.0.

iii) **ELECTRON BEAM CURRENT:**

Beam current can be calculated in accordance with number of electrons, dose, electric field and irradiation width. The formula for beam current (I) is given as follows:

$$I = \frac{\Delta R}{\Delta E} \cdot \frac{W \cdot V}{\eta \cdot D} \times \frac{1}{1000} \dots\dots\dots (v)$$

Here,

D= dose (KGy)

W= irradiation width (cm)

V= Electric field/ handling speed (cm/s)

η = Electron accelerator efficiency (0.9 as standard)

(ΔR)/ ΔE = energy absorption ration

iv) **IRRADIATION DOSE:**

Electron beam irradiation dose is stated as the amount of electron energy deposited into the specific target material. The unit of dose is gray (Gy). The Gy can be expressed in J/Kg and rad (1Gy= 1J/Kg, 1Gy= 100 rad). The dose is also dependent on energy absorption ratio which is given in table 3. The calculation formula for dose is,

$$D = \frac{\Delta E}{\Delta R} \cdot \frac{\eta \cdot I}{W \cdot V} \times 1000 \dots\dots\dots (v)$$

Here,

D= dose (KGy)

W= irradiation width (cm)

V= Electric field/ handling speed (cm/s)

η = Electron accelerator efficiency (0.9 as standard)

$\frac{\Delta E}{\Delta R}$ = energy absorption ratio (MeV/g/cm²)

Table 3: $\Delta E/\Delta R$ (energy absorption ration)

	Energy Absorption Ratio (MeV/g/cm ²)
0.3	3.6
0.5	2.9
0.8	2.45
1.0 and above	2.0

3.4.3 ADVANTAGES AND LIMITATIONS OF ELECTRON BEAM IRRADIATION TECHNIQUE

Electron beam irradiation has many unique advantages over other existing surface engineering techniques e.g. surface coating, thermal spray, ion implantation, diffusion and vapor phase deposition. The electron beam irradiation process broadens the designers' selection criteria of engineering materials by modification of surface property, which can be less dependent on bulk material properties. Some existing advantages and limitations are given below:

Advantages:

- Selective surface material properties modification without affecting bulk material properties.
- Suitable productivity
- Good controlling system
- Low temperature process
- Clean vacuum/air process
- Good control for electron penetration depth
- Cost effective
- Simple layout of accelerator
- A fine distribution of electrons energy and chemical free radicals on target material during irradiation
- No waste products

Limitations:

- Shallow depth penetration of electrons
- Beam to line process system
- Very sensitive with temperature and irradiation atmosphere
- Need high experienced personnel to operate accelerator
- Facility is not available to all.
- Need further development of accelerator.

Chapter IV

Polyoxymethylene copolymer (POM-C)

4.1 Introduction

Polyoxymethylene copolymer (POM-C), also familiar as Delrin, acetal, polyacetal, Ultraform, Hostaform and Kepital is an engineering thermoplastic with good stability, rigidity, sliding properties, self lubrication, wear resistance and chemical resistance. It is widely used in precision sliding parts such as gears, wheels, shafts, bearings, guides and electronic parts due to its good dimension stability, low friction coefficient, excellent machining properties, high stiffness and good processibility.

Main properties:

- Excellent stability
- High rigidity
- High hardness
- Low wear rate
- Low absorption of moisture
- Good fatigue resistance
- High heat resistance
- Low coefficient of friction

4.2 PROPERTIES OF KEPITAL

The Kepital (POM-C) is very good engineering thermoplastic material for industrial applications due to its superior properties. The physical, thermal and mechanical properties are given in table (4-6):

Table 4. **Physical properties**

Physical properties	Test Standard	Unit	Value
Density	ISO 1183	g/cm ³	1.41
Melt flow rate	ISO 1133	g/10 min	3
Water absorption (23 °C, 50 % RH)	ISO	62 %	0.2

Table 5. **Thermal properties**

Thermal properties	Test Standard	Unit	Value
Heat deflection temperature(1.8 MPa)	ISO75	°C	100
Flammability	UL 94	°C	HB
Melting point(10 °C/min)	ISO 11357	°C	168
Coefficient of linear thermal expansion	ISO 11359	X 10 ⁻⁵ /°C	12

Table 6. **Mechanical properties**

Mechanical properties	Test Standard	Unit	Value
Tensile strength	ISO 527	MPa	68
Tensile strain at yield	ISO 527	%	12
Nominal strain at break	ISO 527	%	40
Flexural strength	ISO 178	MPa	90
Flexural modulus	ISO 178	MPa	2,650
Charpy impact strength (Notched) @ 23	ISO 179	179 kJ/m ²	7.0

4.3 Applications

- Sliding parts (gears, springs, guides, pump parts, chains, screws, fan wheels, bearings, bushes, counter parts).
- Electrical engineering parts (connectors, insulators, electronic devices parts).
- Automobile (demo of upcoming cars, power window, control unit, seat, door lock, cars body, fuel supply system, ventilation system, casing parts).
- Bio-medicals (hip joints, prosthesis, bolts, nuts, syringe, dental veneers, insulin pen, inhalers).

4.4 Limitations

- Sensitive to acid hydrolysis
- Sensitive to sliding distance and load
- Less stable for UV rays

Chapter V

Experimental methods:

Natural color POM-C round blocks of 10 mm thickness and 30 mm diameter were used for all the experiments. The blocks of POM-C used were supplied from DYNEX engineering plastic company (Korea), with a melt flow rate of 3 g/10 minute (ISO 1133) and density of 1.41 g/cm³ (ISO 1183). The molecular chain and 3D model structure of POM-C blocks are shown in Fig. 12. The POM-C blocks were polished by Grinder polisher (Twinprep5, ALLIED high tech. products Inc.) machine using 1200 (P4000) grit of SiC abrasive paper at 200 rpm speed with abundant water. All POM-C blocks surfaces were cleaned in ultrasonic bath in distilled water and 96% ethanol and, then placed in a dry desiccator, consecutively.

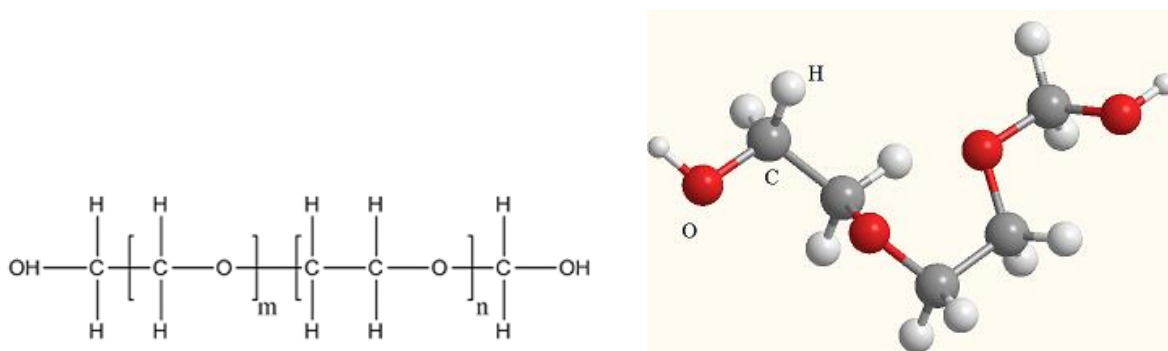


Fig.12. Molecular chain and 3D model structure of POM-C.

Electron beam (EB) irradiation was performed under vacuum condition at room temperature with an ELV-8 (electrostatic, coreless DC, induction coupling) electron accelerator at a voltage of 1 MeV in EB Tech Co., Ltd. (Daejeon, Korea). The full specifications of irradiation condition using ELV-8 accelerator is shown in table 7. The blocks of POM-C (numbered as a-f) were irradiated to doses of 0, 100, 200, 300, 500 and 700 kGy, respectively. The electron beam current was 40 mA and the dose rate was 25 kGy per pass. The schematic diagram of electron beam dose irradiation is shown in Fig. 13.

Friction coefficient was tested on a J&L Tech tribometer using a ball on disk method, in which the disk was fixed and the ball (SUJ 52100, bearing ball) was rotated at a sliding speed of 100mm/s unidirectionally. The contact schematic diagram of ball on disk method is shown in Fig. 14. Sliding was observed under a load of 10 N during 225 m sliding distance over a period of 38 min. The friction coefficient and sliding distance with time were filed automatically during measurement. The chemical structural modification of unirradiated and irradiated POM-C blocks was observed by micro Raman spectrometer system (LABRAM HR EV) with laser excitation source of 514 nm from laser diode.

The morphology and elemental composition analysis of EB dose irradiated POM-C blocks (a-f) were studied by Scanning electron microscopy (SEM) in 1000x magnification using a Hitachi model equipment coupled with Energy dispersive spectroscopy (EDS) facility (S-4300, Hitachi) in Korea Basic Science Institute at Seoul center. The worn surfaces morphology (abrasive and adhesive wear scars with crack formation) at sliding tracks of

unirradiated and irradiated POM-C blocks was observed with an Olympus BX51M computerized HR digital optical microscope. Changes in surface roughness of POM-C blocks surfaces were studied with 3D Nano profiling system (Non-contact white light scanning interferometer system, WT-250), and a 10x objective was used. The wettability of unirradiated and irradiated POM-C polymer blocks was observed using Contact angle analyzer (SEO Phoenix 300T). The average contact angle was measured according to 15 points for each POM-C sample and the standard deviation for measuring contact angles was around 1~2°.

Table 7. The full specifications of electron beam (EB) irradiation using ELV-8 accelerators:

EB irradiation energy	1.5 MeV
Maximum beam power	90 KW
Average beam current	40 mA
Pulse current range	5~40 mA
Beam size	5~8 mm
Beam window foil (Ti) thickness	50 μm
Distance between beam window and target material(POM-C)	25 cm
Beam scan width	5 m
Transport speed	5 m/min
Beam extraction widow dimension	1200 mm x 75 mm
Dose rate	25 kGy per pass

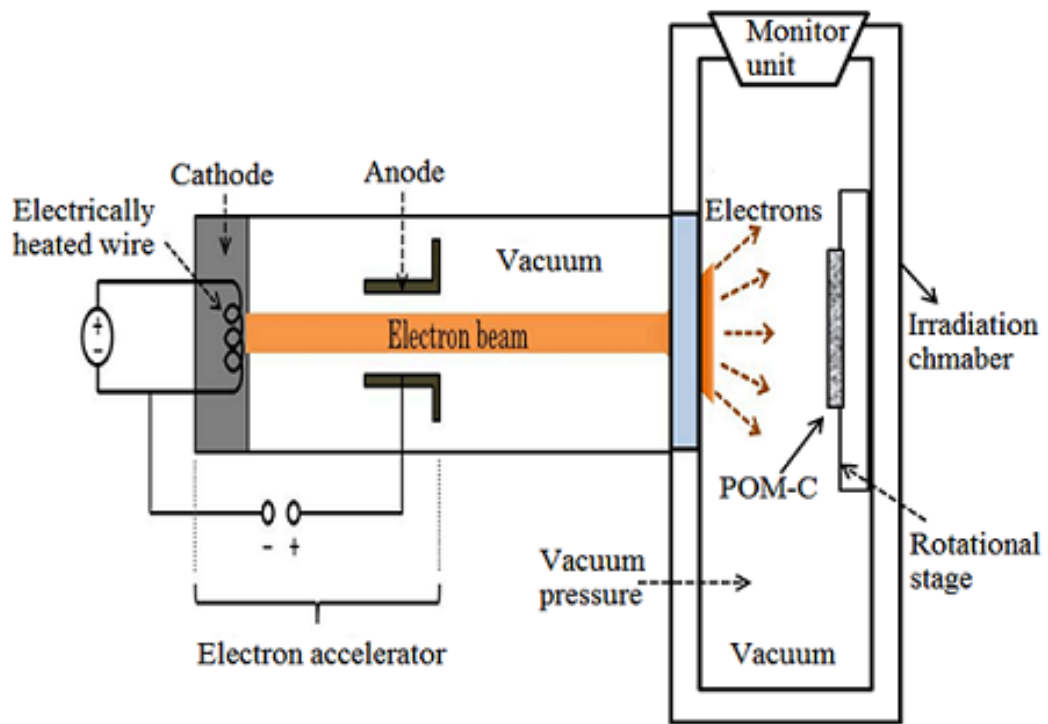


Fig. 13. Schematic diagram of electron beam irradiation.

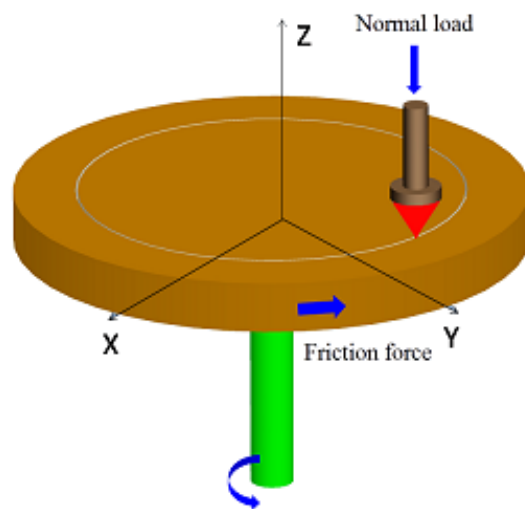


Fig.14. Contact schematic diagram of ball on disk method.

Chapter VI

RESULTS AND DISCUSSION:

6.1 FRICTION COEFFICIENT:

In this research work, reduction of friction coefficient in extreme operating environment was considered among all parameters. It is feasible to draw attention on such implementations which are connected to high tech operations where usual systems of lubrication cannot be applied. The variation of friction coefficient for both unirradiated and irradiated POM-C blocks as a function of sliding distance and irradiation dose is demonstrated in Fig. 15 (a-f). It is explicitly demonstrated that the curves of the friction coefficient had a shift from a lower value to higher value with sliding distance and irradiation dose. For the unirradiated POM-C block (Fig. 15-a), initial friction coefficient of 0.11 is noticed, after that, friction coefficient rises slightly with the increasing of sliding distance, and a friction coefficient of 0.21 is noticed at the sliding distance of 225 m. The 100 kGy EB dose irradiated POM-C block (Fig. 15-b) shows the lowest friction coefficient (0.20) compared to all irradiated and unirradiated POM-C polymer blocks, which might be referred as a result of the formation of carbonization (C free radical), occurrence of irradiation induced partial physical degradation (smoothness) and well suited cross-linking on POM-C surface during the irradiation process [21, 36-43]. The formation of a small molecular (chemical free radicals) substance and carbonization on POM-C surface during electron beam irradiation did may act as solid lubricant, which reduce the friction coefficient [15, 20-27, 35-45]. In Fig. 15-f, the 700 kGy EB dose irradiated POM-C block shows the highest friction coefficient (0.50). The 200, 300 and 500 kGy EB dose irradiation also increased the friction coefficient with the increasing of sliding distance

compared to 100 kGy EB dose irradiation, which might be the occurrence of severe chain scission and physical degradation shown in Fig 15 (c-e) [11, 20-24, 41-45]. Friction coefficient increased with increasing sliding distance, because the carbonization and a small molecular substance on POM-C surface might only sustain for certain sliding distance [24].

The tribological modification for specific polymer depends on optimum range of electron beam dose irradiation [21, 28-30] and molecular structure. Medium dose electron beam irradiation is the best suited for polymer surface modifications to get the damage free and even surface, where atomic displacement by energetic collisions are in controlled manner. More carbon-hydrogen atoms aggregated on the surface for higher dose irradiation, which were contiguously sputtered asperities formation on the top layer surface. The 100 kGy EB dose irradiation induced well suited carbonization and partial physical degradation on the top surface of POM-C polymer due to well suited cross linking and chemical chain reaction, which was helpful to reduce the friction coefficient [21, 29-30, 35-43]. So, it is very essential to select an optimum electron beam dose irradiation for any specific polymer to get the best tribological modification.

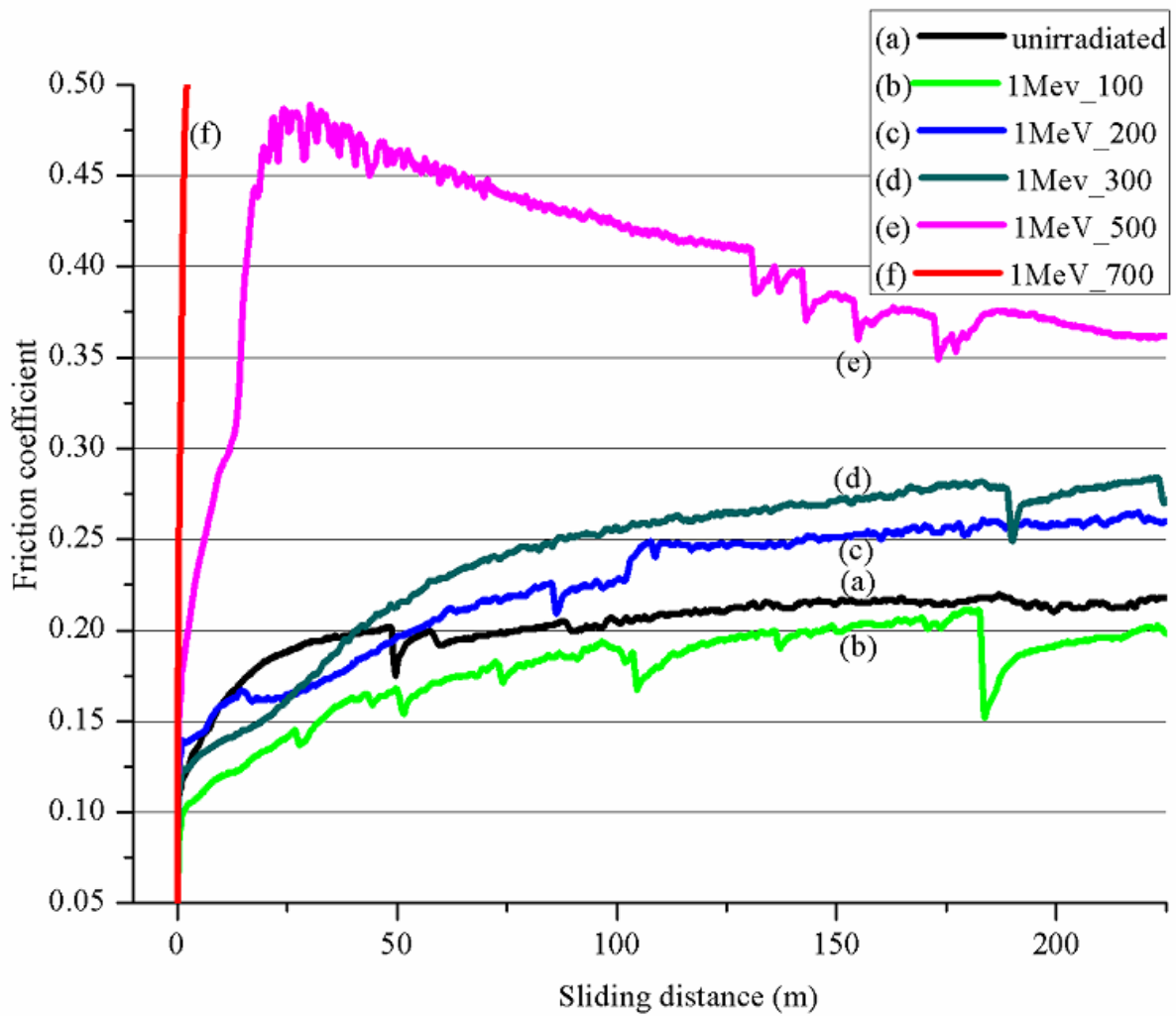


Fig. 15. Friction coefficient of POM-C blocks against SUJ 52100 ball for (a): unirradiated POM-C; (b): 100 KGy; (c): 200 KGy; (d): 300 KGy; (e): 500 KGy; (f): 700 KGy electron beam irradiated POM-C (load: 10 N, sliding speed: 100 mm/s, sliding distance: 225 m and time: 38 minutes).

6.2 CHEMICAL STRUCTURE:

The chemical structural modification induced by electron beam irradiation on POM-C blocks were observed using Raman spectroscopy shown in Fig. 16 (a-f). From Raman spectra it is very clear that the peak intensity and width at various band positions of POM-C blocks are changed significantly after electron beam irradiation. In Fig. 16-a, the C-O-C (aliphatic ethers) symmetrical stretching vibration (ν_g) observes at 917 cm^{-1} (ascribed to the POM-C backbone structure) in the unirradiated POM-C [33]. The unirradiated POM-C polymer block reveals the following peak vibrational assignments: 538 cm^{-1} (δ , C-O-C), 917 cm^{-1} (ν_g , COC), 1095 cm^{-1} (ν_a , C-O-C), 1333 cm^{-1} (t, CH₂) and 1489 cm^{-1} (δ , CH₂). The peak vibrational assignments of all the fundamental bands for unirradiated POM-C are given in Table 8 [31, 32]. In figure 16-b, the peak intensity and width of vibrational bands at wave numbers 917 cm^{-1} (ν_g , COC), 1095 cm^{-1} (ν_a , C-O-C), 1333 cm^{-1} (t, CH₂), 1387 cm^{-1} (w, CH₂) and 1489 cm^{-1} (δ , CH₂) are increased highly due to well suited cross-linking by 100 KGy EB irradiation [5,15,21]. The 200 KGy electron beam irradiation affects the above mentioned peaks slightly compared to 100 KGy electron beam irradiation shown in Fig. 16-c, which is the reason of less effective cross-linking. The 100 kGy EB irradiation significantly increased the peak intensity, width and vibrational band strength of C-O-C symmetrical and asymmetrical stretching at 921 and 1104 cm^{-1} , respectively. It also increased the peak intensity, width and vibrational band strength of CH₂ bending at 1486 cm^{-1} . These vibrational bands strength can prevent from any kinds of chemical structural degradation which might be the effects of well suited cross-linking shown in figure 5-b [1-2, 13, 20, 30].

The energetic ions are slowed down in materials due to nuclear stopping or electronic stopping process. The electronic stopping or removal of valence band electrons could result in the formation of chemical free radicals layer on surface that can easily cross-link the POM-C polymer chains, besides it is dominated over chain scission process during optimum 100 KGy electron beam irradiation [20, 29-30, 37].

The electron beam irradiation at dose of 300, 500 and 700 kGy reduced the peak intensity and width of vibrational bands with increasing surface dose delivered at wave numbers 917 cm^{-1} (ν_g , COC), 1095 cm^{-1} (ν_a , C-O-C), 1333 cm^{-1} (t, CH₂), 1387 cm^{-1} (w, CH₂) and 1489 cm^{-1} (δ , CH₂) due to severe chain scission and molecular degradation on POM-C blocks, which are shown in Fig. 16 (d-f). These doses break different kinds of bonds and create new kinds of bonds with gases products evolution due to severe chain scission (nuclear stopping) during irradiation. The chemical structural degradations are severe in the range of $900\text{--}1200\text{ cm}^{-1}$, where the asymmetrical stretching vibration of C-O-C is highly modified into CH₃ end groups as deformation of polymer bond [21, 29-34]. Moreover, the reduction in peak intensity and width at various band positions shows the breakage of polymeric bonds in the chemical structure during electron beam irradiation with high surface dose delivered due to severe chain scission. The severe chain scission easily degrades the structural and physical properties in polymer, which is also ascertained from SEM-EDS, 3D Nano profiler, Optical microscope and tribology testing observations. The 100 kGy EB dose irradiation improves the structural and physical properties in POM-C block due to well suited cross-linking depending on chemical factors.

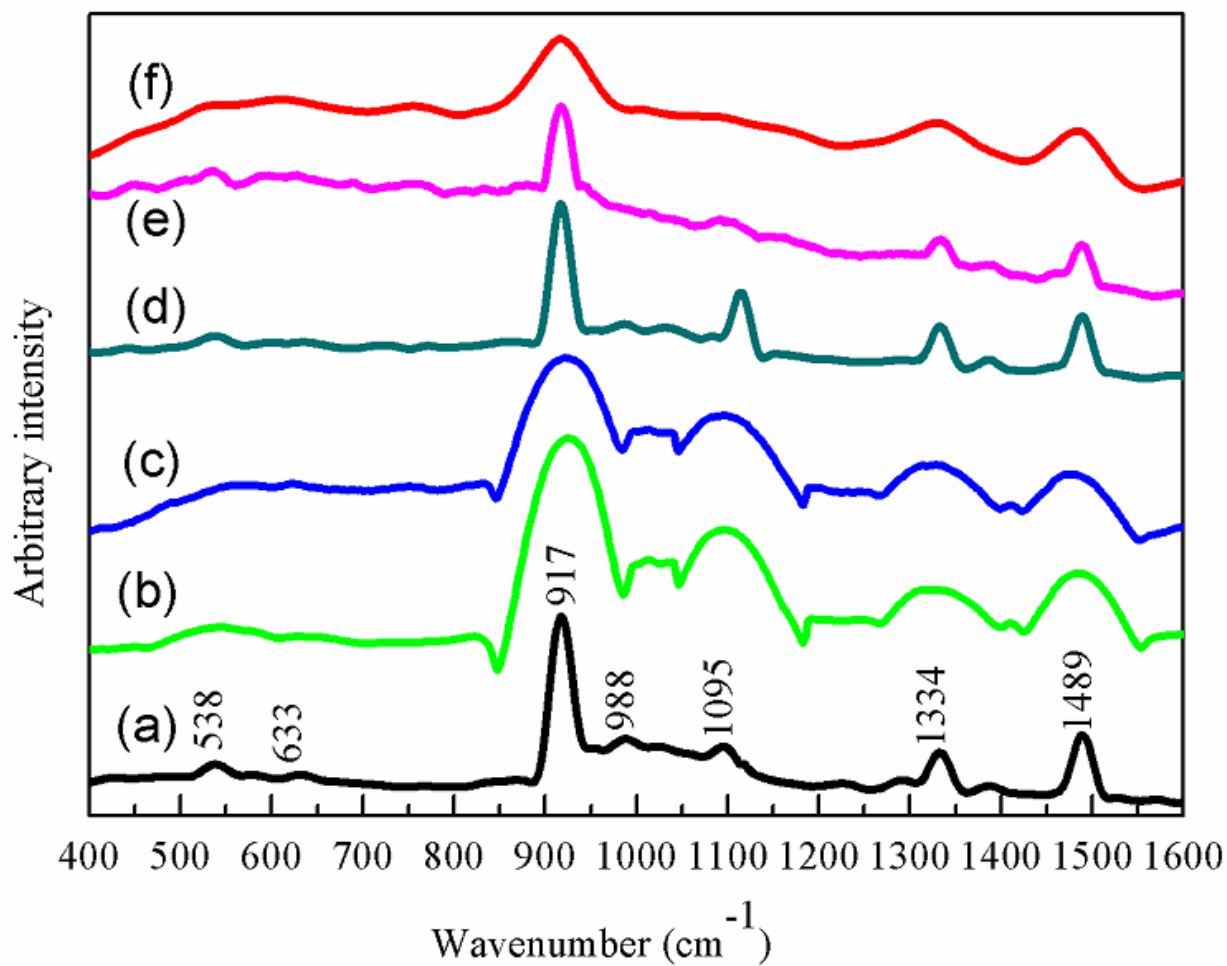


Fig.16. Raman spectra demonstrating the effects of electron beam irradiation on POM-C blocks: a- unirradiated; b- 100 KGy; c- 200 KGy; d- 300 KGy; e- 500 KGy; f- 700 KGy.

Table 8: The vibrational band assignments of Polyoxymethylene copolymer (POM-C)

Wave number/cm ⁻¹	Functional Group/ Vibration (Potential energy distribution %)	Reference
538	δ (COC) (59) – δ (OCO) (40)	[32,31]
631	δ (OCO) (90) + ν_a (COC) (8)	[32]
917	ν_g (COC) (85) – δ (OCO) (8)	[32,31]
988	r (CH ₂) (81) – ν_a (COC) (19)	[31,32]
1095	ν_a (COC) (81) – δ (OCO) (11)	[32]
1225	r (CH ₂) (50) – δ (COC) (25) + ν_g (COC) (24)	[32]
1292	t (CH ₂) (91) + ν_a (COC) (8)	[32,31]
1333	t (CH ₂) (95) – ν_g (COC) (4)	[32]
1387	w (CH ₂)	[31]
1489	δ (CH ₂)	[32,31]

δ , bending; ν_a , asymmetrical stretching; ν_g , symmetrical stretching; r, rocking; t, twisting; w, wagging.

6.3 SEM-EDS ANALYSIS:

The SEM-EDS is a conventional technique for local micro-chemical analysis in solid samples. Morphological and elemental composition analysis of different EB dose irradiated POM-C blocks were carried out by SEM-EDS technique at 20 KeV accelerating voltage and 1000x magnification. EDS analysis for individual POM-C block was performed on the area within the pink color box shown in Fig. 17 (a-f). Table 17 (a-f) present the weight % as well as atomic % of the elements C and

O for different EB dose irradiated POM-C blocks carried out by EDS technique. EDS cannot detect H element due to its lowest atomic number. The basic chemical elements of POM-C are C, O and H according to its chemical formula $(\text{CH}_2\text{O})_n$.

The weight percentages in unirradiated POM-C block were quantified as 11.67% C and 88.3% O from EDS analysis shown in Fig 17-a. The weight percentages of C and O elements in 100 kGy EB dose irradiated POM-C block are highest and lowest among all unirradiated and irradiated POM-C blocks shown in Fig. 17-b, respectively. The surface is also smoother compared to others and C free radical (carbonization) is also formed on the surface. This can be the increase in the carbon containing functional group (CH_2) due to well suited cross-linking and energetic electrons- atoms collisions by the absorption of high electron energy radiation [49-50]. A threshold value of cross-linking induces free radicals formation on polymeric surface by the absorption of high electron energy irradiation, which can often improve the structural and physical properties in specific polymer depending on chemical and physical factors [49-52]. The threshold value of cross-linking depends on the specific surface EB dose delivered. The weight percentages of O element are increased with the increasing surface dose delivered (200-300 kGy) shown in Fig. 17 (c-d). It means Carbon containing functional group is reduced and oxygen containing functional groups ($-\text{OH}$ and $-\text{C}-\text{O}-\text{C}$) are increased with the increasing surface dose delivered. Craze, cracking and rougher surface are also noticed from SEM observations in 200 and 300 kGy EB dose irradiated POM-C blocks. This may be the increase in surface dose delivered (absorption of high electron energy irradiation) which induces chain scission in polymer. This chain scission can degrade polymer surface by displacing atoms, evolution of gas products (CO_2) and breaking bonds from polymeric chains. The weight percentages of O element in 500 and 700 kGy EB dose irradiated POM-C blocks are very high and C element is totally absent, which might be the reason for severe chain scission. The severe chain scission can highly increase the oxygen containing functional groups and displace the target atoms with breaking polymeric chain bonds, and it can damage the polymeric surface permanently shown in Fig. 17 (e-f). Severe craze and cracking are also noticed in SEM observations with the increasing surface dose delivered due to

more accumulated local stresses of gaseous products (CO₂) resulting from severe chain scission [49,52] . 100 kGy EB dose irradiated POM-C block (Fig. 17-b) is best among all unirradiated and irradiated POM-C blocks due to well suited cross-linking and physical interactions between energetic electrons-atoms collisions, which are determined from SEM-EDS analysis.

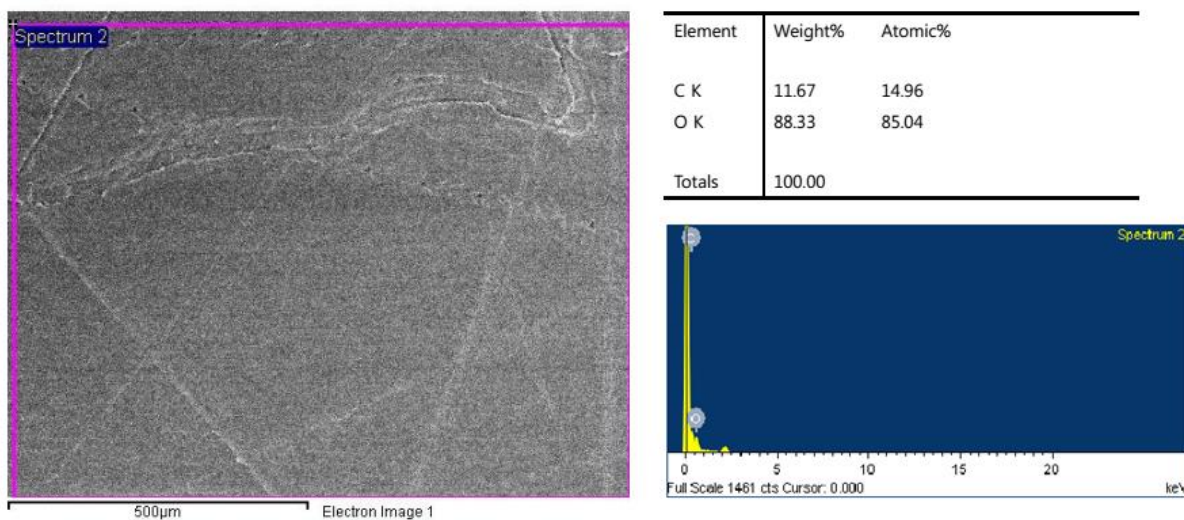


Fig. 17-a. SEM image of unirradiated POM-C block with characteristic EDS spectra at 20 KeV and 1000x magnification.

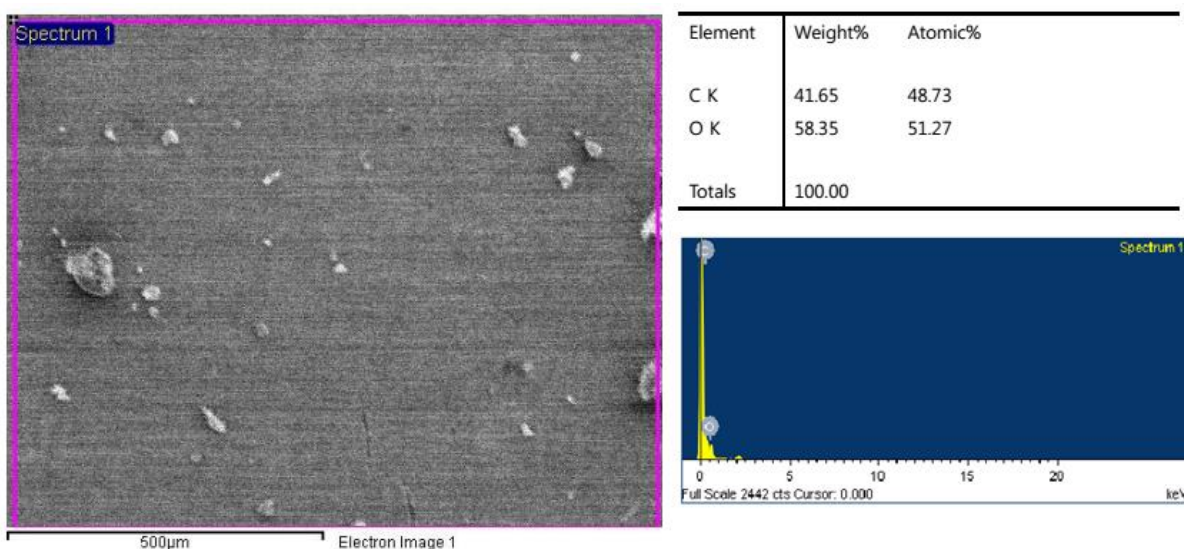


Fig. 17-b. SEM image of 100 kGy electron beam irradiated POM-C block with characteristic EDS spectra.

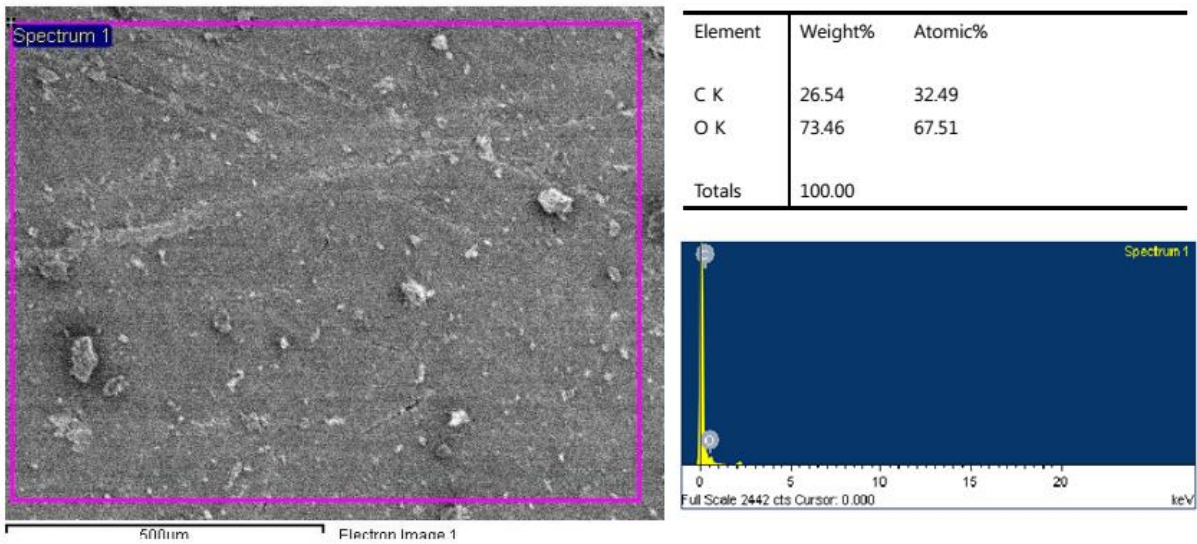


Fig. 17-c. SEM image of 200 kGy electron beam irradiated POM-C block with characteristic EDS spectra.

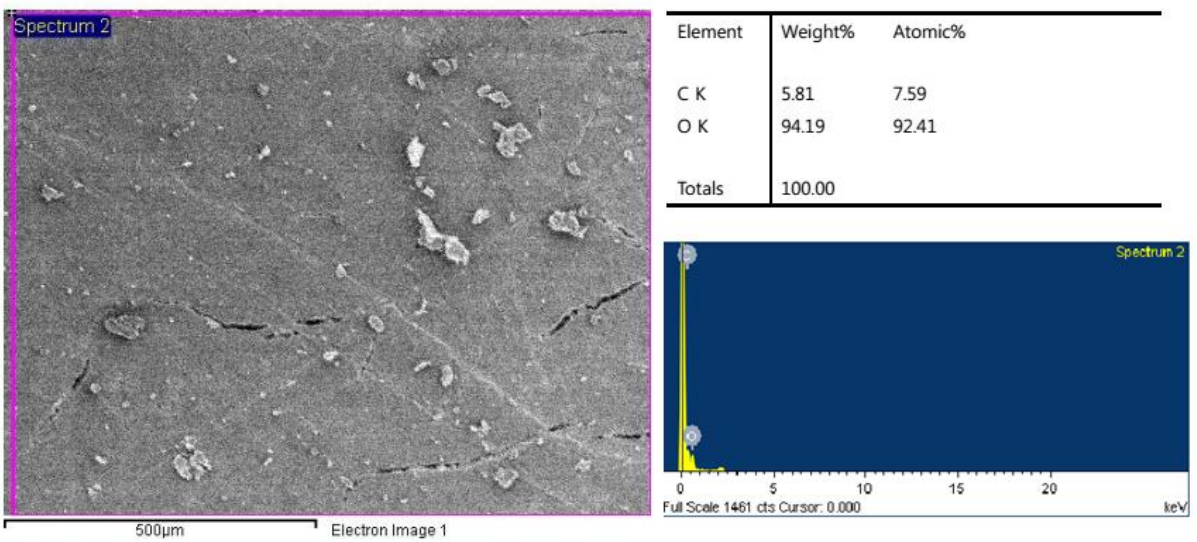


Fig. 17-d. SEM image of 300 kGy electron beam irradiated POM-C block with characteristic EDS spectra.

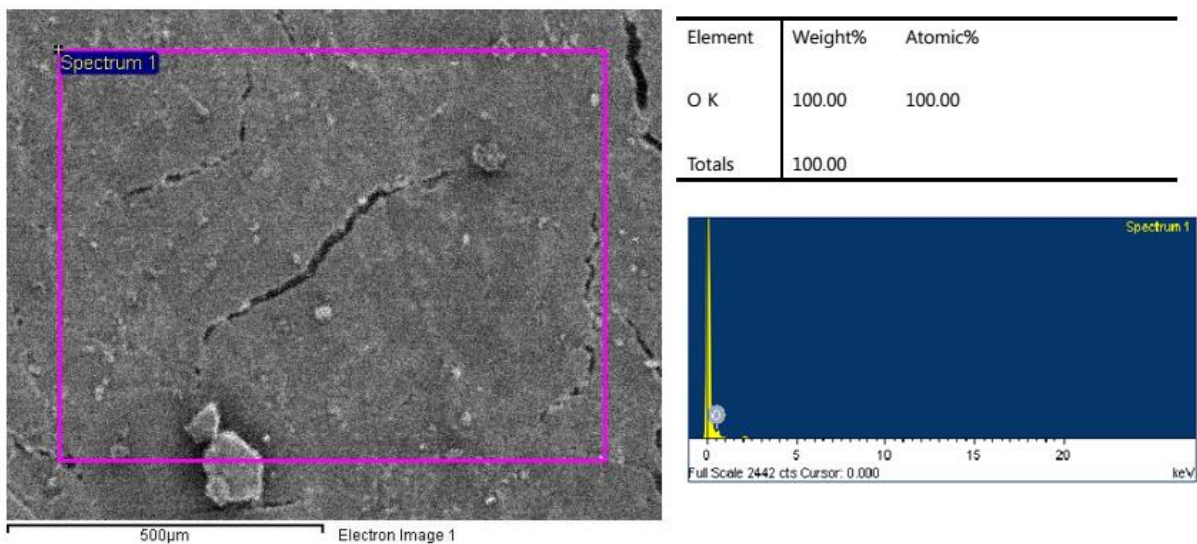


Fig. 17-e. SEM image of 500 kGy electron beam irradiated POM-C block with characteristic EDS spectra.

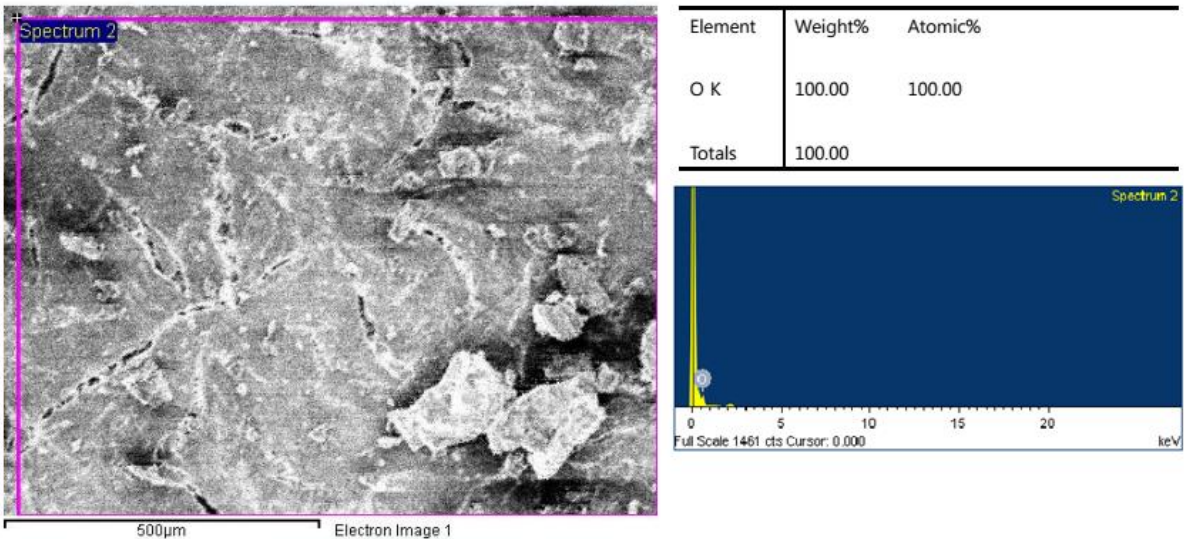


Fig. 17-f. SEM image of 700 kGy electron beam irradiated POM-C block with characteristic EDS spectra.

6.4 WORN SURFACES MORPHOLOGY:

The Optical microscopic images at x20 resolution in Fig. 18 (a-f) show the worn surfaces to analyze the friction and wear mechanism at sliding tracks on POM-C blocks with and without EB dose irradiation. The worn surface of unirradiated POM-C block experienced huge plastic ruffles and ripples flow with polymer deformation along the sliding track. Shrouded with grooving, scuffing, friction traces and crack formation perpendicular to sliding track are also noticed shown in Fig. 18-a. In Fig. 18-b, the worn surface of 100 kGy EB dose irradiated POM-C appears smooth with shallower and milder scuffing. The carbonization, free radicals formation and stack of polymer deformation debris along sliding track were observed, which were also ascertained from SEM-EDS and 3D Nano surface profiler. In Fig. 18 (c-f), abrasive wear (plough and surface crack), polymer deformation, grooving, scuffing, flaws, huge fatigue cracks and ribbon tracks were observed from 200-700 kGy EB dose irradiated POM-C worn surfaces.

From the Optical microscopic, SEM-EDS and 3D Nano surface profiler observations, it can be concluded that 1 MeV, 100 kGy EB dose irradiation transferred the wear behavior of POM-C block from the abrasive wear, adhesive wear and scraping for the unirradiated surface to shallow and mild scraping for the irradiated surface due to well suited cross-linking, partial physical degradation, carbonization and formation of a small molecular substance [15, 21-24, 35-44]. So, the 100 kGy EB dose irradiated POM-C block surface treated as self- lubricating surface during dry sliding condition.

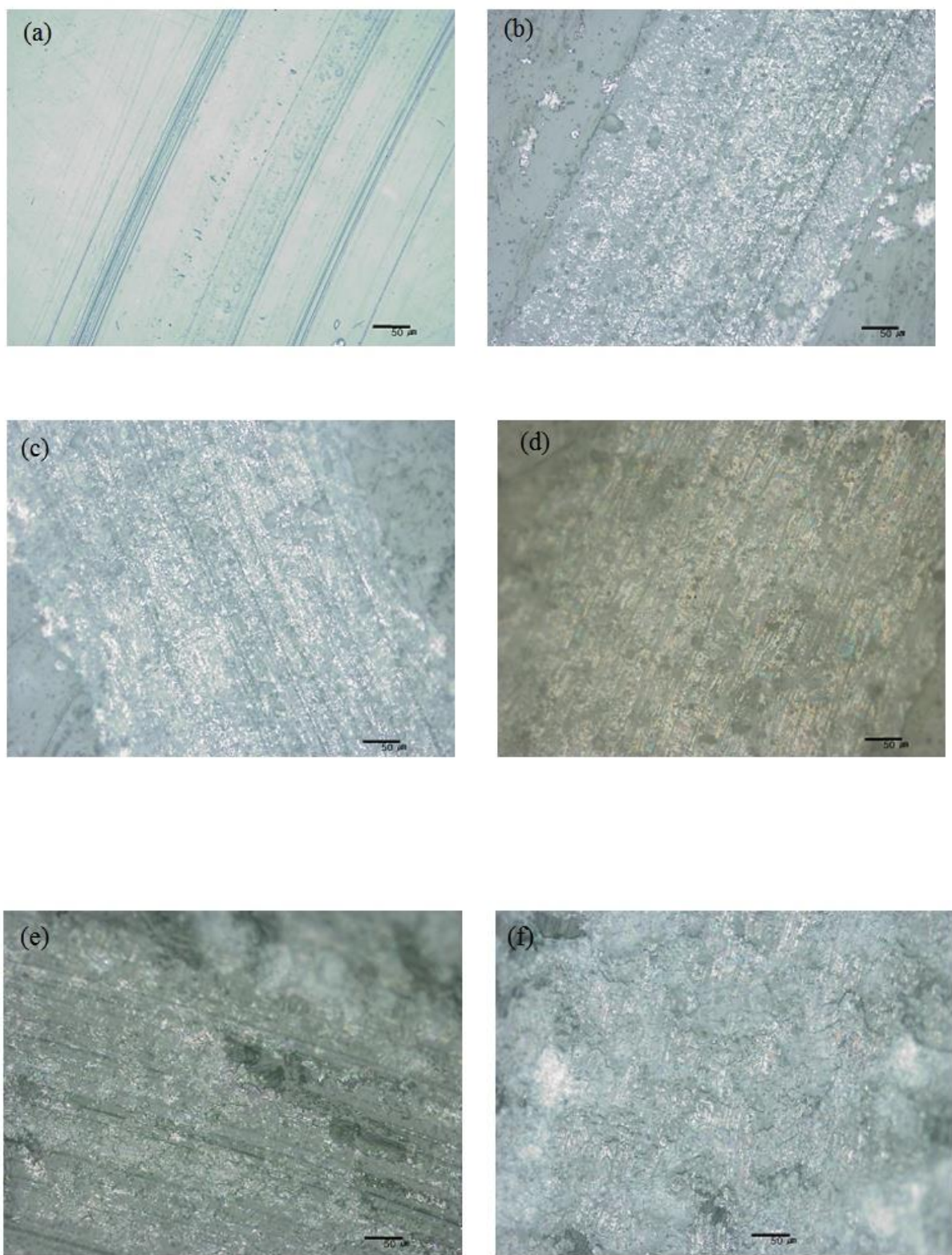


Fig. 18. Optical microscopic images of the worn surfaces at sliding tracks on POM-C surfaces with x20 resolution: (a) unirradiated POM-C; (b) 100 KGy; (c) 200 KGy; (d) 300 KGy; (e) 500 KGy and (f) 700 KGy electron beam irradiated surfaces. Scale bar 50 μm in each case.

6.5 SURFACE ROUGHNESS:

The effect of electron beam irradiation on the surface roughness of POM-C polymer blocks was examined by 3D Nano surface profiler system (10x Objective and high accuracy non-contact mode). Changes in surface roughness of POM-C blocks with different electron beam irradiations were shown in Fig. 19. In Fig. 19 and 21, significant surface roughness reduction are noticed on the POM-C surface by 100 kGy EB dose irradiation compared to all unirradiated and irradiated POM-C blocks. In Fig. 20-21, the average surface roughness (R_a) of unirradiated POM-C block was 170 nm and, the R_a of 100 kGy EB dose irradiated POM-C block was 130 nm. The reduction of R_a by 100 kGy electron beam irradiation might be the reason of well suited cross-linking, partial physical degradation (smoothness by energetic electrons-atoms collisions), carbonization and chemical structural modification, which is also well suited to friction coefficient reduction [49-52]. The threshold value of cross-linking can reduce surface roughness and it can give optimum macroscopic network when aggregation and atomic displacement are suppressed. The extent of changes in physical properties (morphology, mechanical strength and molecular weight) of specific polymer depends on the surface electron beam dose delivered [49, 52]. The threshold value of cross-linking for specific polymer mainly depends on the electron beam energy used to deliver the surface specific dose (absorption of high energy irradiation). In Fig. 22-25, the R_a of POM-C surfaces irradiated at electron beam dose of 200, 300, 500 and 700 kGy increased linearly to 334.27, 414.30, 475.18 and 610 nm, respectively. The increase of R_a also increased the friction coefficient linearly, which is ascertained by tribology test. The increase of surface roughness during 200, 300, 500 and 700 kGy electron beam dose irradiation might be the reason of severe chain scission, chemical and physical structural degradation. The degradation phenomena at EB dose of 200, 300, 500 and 700 kGy is noticed by Optical microscopic, SEM-EDS, 3D Nano profiler and Raman spectroscopic observations. In Fig. 22-25, the crazing and cracking are also noticed with the increase of EB dose (200-700 kGy), which might be the

reason of accumulated local stress. Accumulated local stress in polymer is experienced when gaseous products (CO₂) can be trapped in polymeric chain [49].

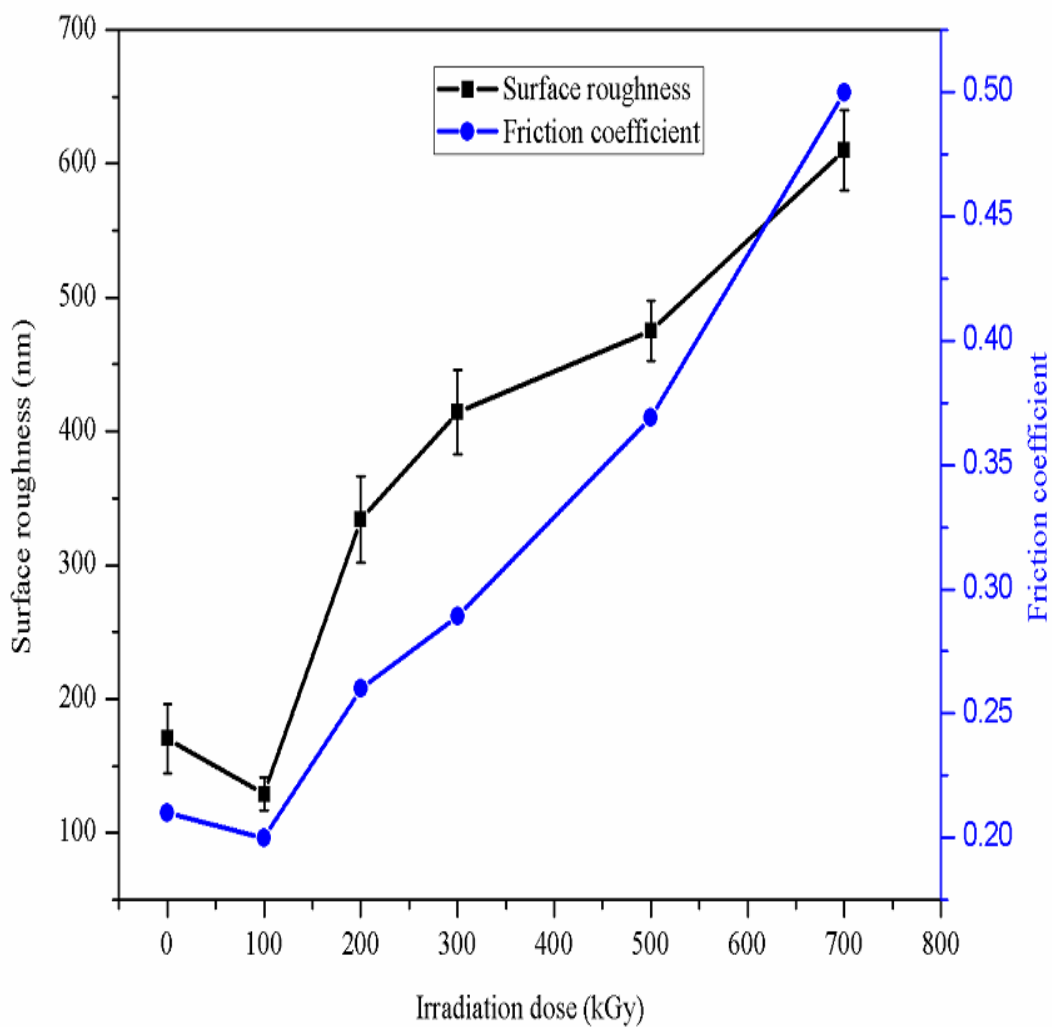


Fig. 19. Correlation among surface roughness, friction coefficient and irradiation dose.

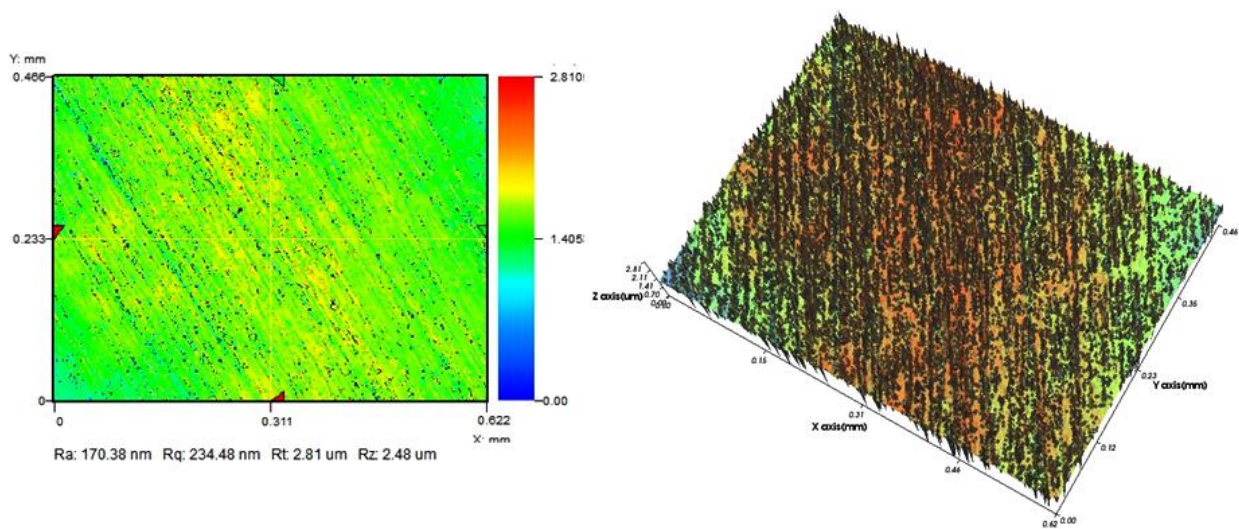


Fig. 20. Surface roughness of unirradiated POM-C (R_a -170.38 nm, R_t - 2.81 μ m).

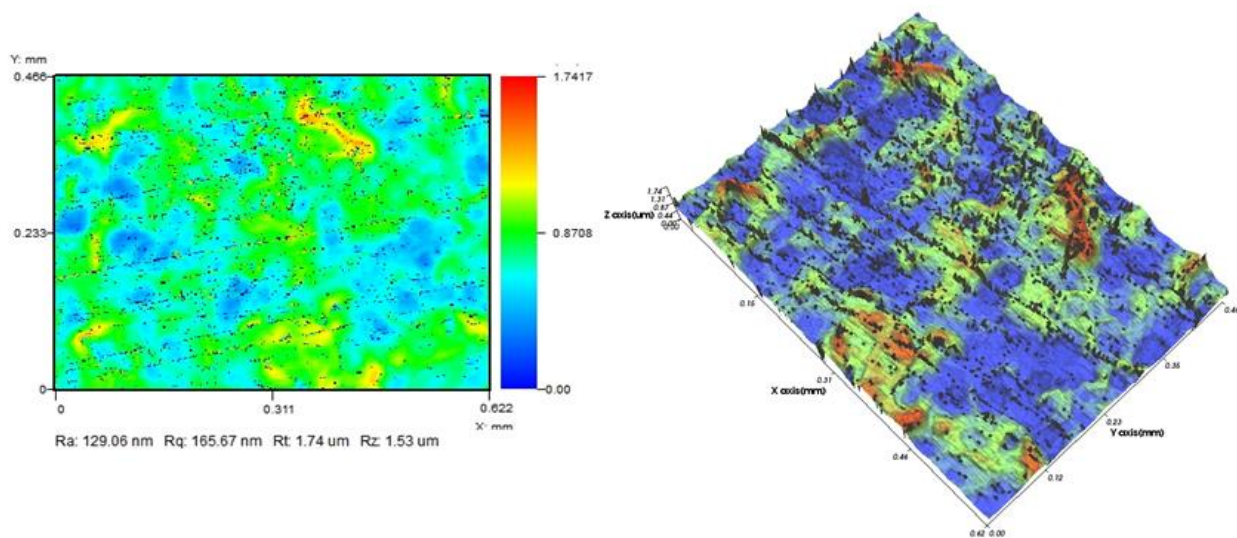


Fig. 21. Surface roughness of 1 MeV, 100 KGy electron beam irradiated POM-C surface (R_a -120.89 nm, R_t - 1.67 μ m).

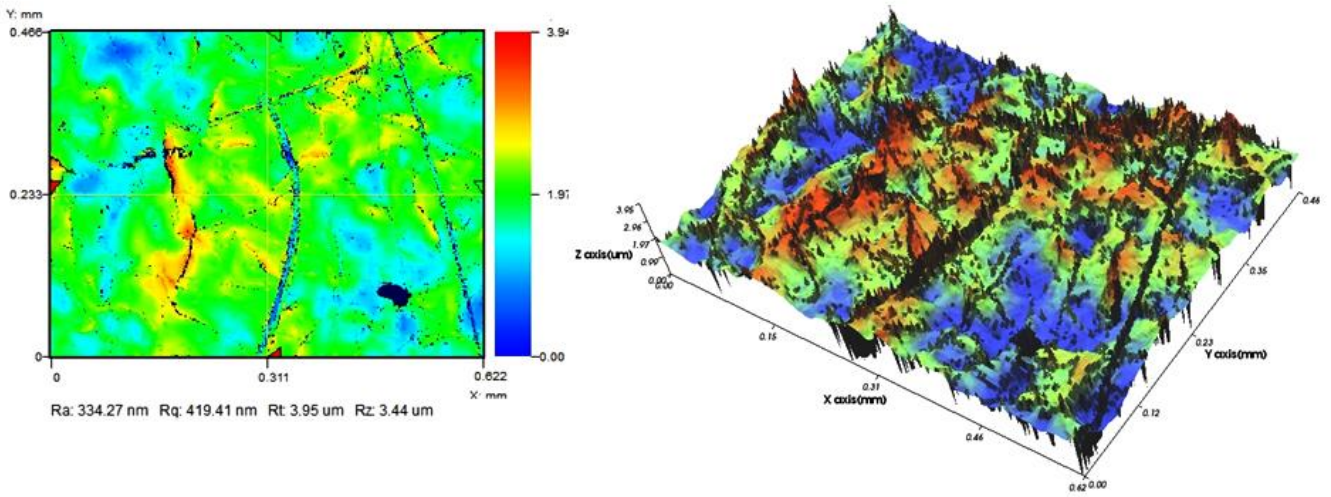


Fig. 22. Surface roughness of 1 MeV, 200 KGy electron beam irradiated POM-C surface (R_a -334.27 nm, R_t -3.95 μ m).

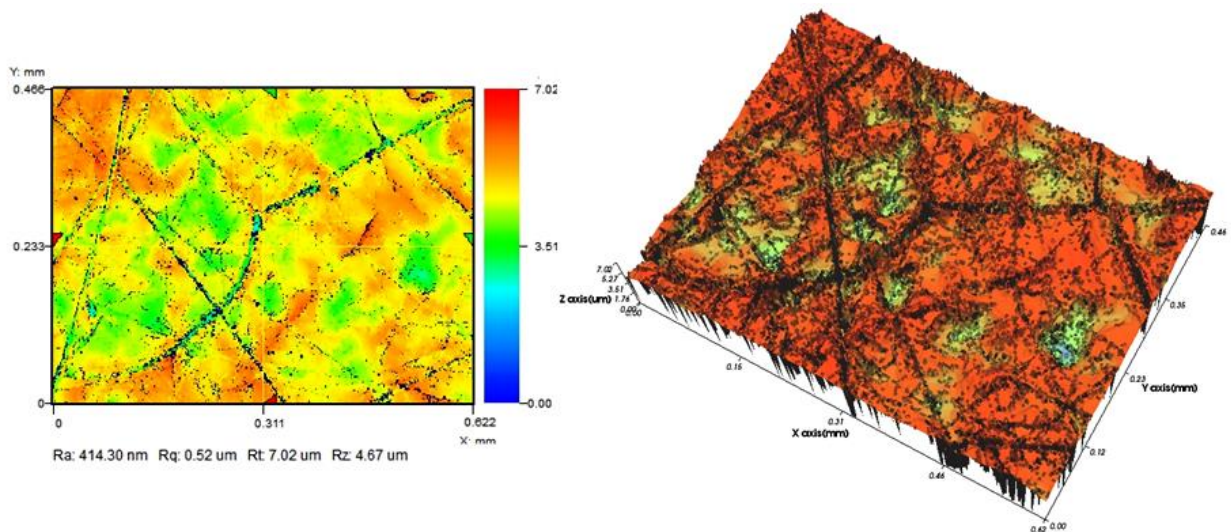


Fig. 23. Surface roughness of 1 MeV, 300 KGy electron beam irradiated POM-C surface (R_a -414.30 nm, R_t -7.02 μ m).

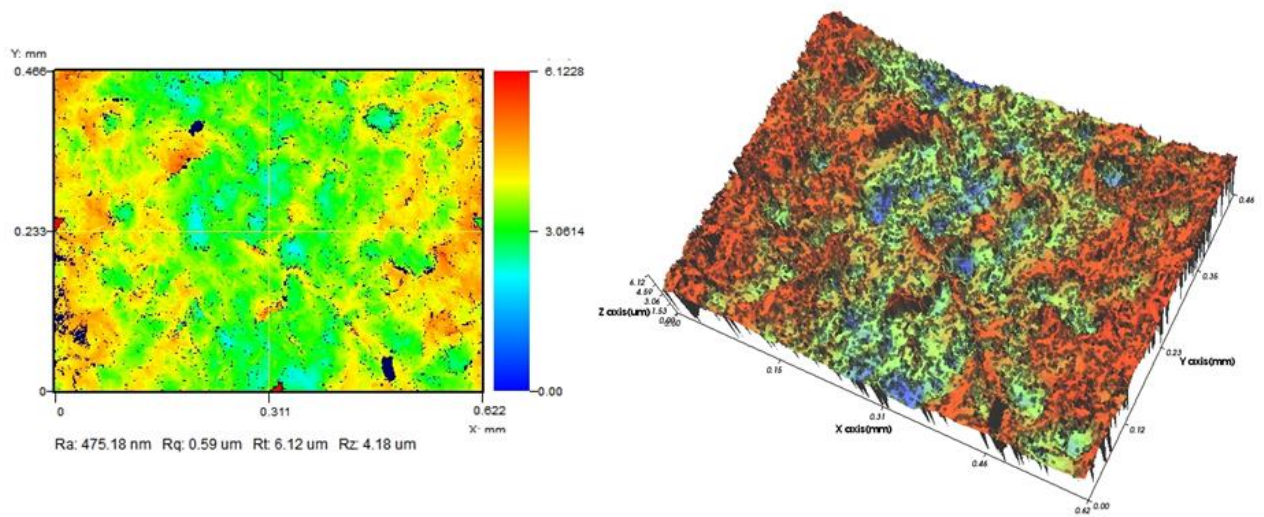


Fig. 24. Surface roughness of 1 MeV, 500 KGy electron beam irradiated POM-C surface (R_a -475.18 nm, R_t -6.12 μ m).

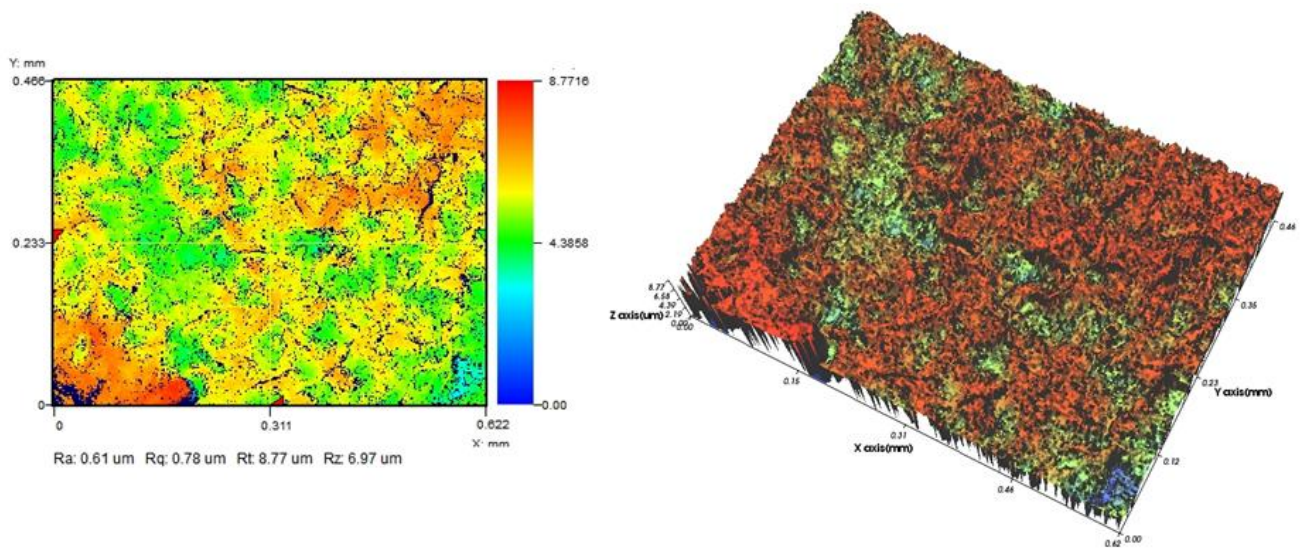


Fig. 25. Surface roughness of 1 MeV, 100 KGy electron beam irradiated POM-C surface (R_a -610 nm, R_t -8.77 μ m).

6.6 WATER CONTACT ANGLE:

Wettability of polymeric surface is mostly ignored in the study of mechanical properties. One matter should consider that “dry sliding in air” literally denotes “sliding in water vapor”. A sliding system should be considered as a three-body mechanism (substrate-water layer-counter substrate), which is also important issue for ecological reason. The friction is occurred due to cutting of adhesive bonds between material surface and water molecules in any environment. Reduction of the adhesion between water molecules and real surface of contact under dry sliding condition might be effective to reduce friction coefficient [47].

The aforementioned analysis is examined from Fig. 26, which reveals the correlation among friction coefficient, water contact angle and EB dose irradiation for POM-C blocks. The lowest friction coefficient (0.20) at highest water contact angle (84°) was observed for 100 kGy EB dose irradiated POM-C block. The 100 kGy EB dose irradiation induced carbonization, formation of a small molecular substance, hydrophobic functional groups (CH_2) and cross-linking on POM-C block surface, which reduce the adhesion between two sliding surfaces by increasing water contact angle [49-52]. The reduction of adhesion might play a vital role to reduce the friction coefficient [28, 47]. The highest friction coefficient (0.50) at lowest water contact angle (16°) was observed for 700 kGy EB dose irradiated POM-C block, which can be attributed to the formation of hydrophilic functional groups (-OH and -C-O-C-) due to severe chain scission and chemical chain reaction [21-23, 28, 49-52]. In general, oxygen enriched functional groups play vital role to increase polarity and ability to hydrogen bond, and it increases the wettability and adhesion. It has been noticed that the increase of water contact angle (decreasing wettability) using EB dose irradiation can contribute to friction coefficient reduction by decreasing the adhesion and real surface of contact for POM-C block in dry sliding condition [23, 28, 47].

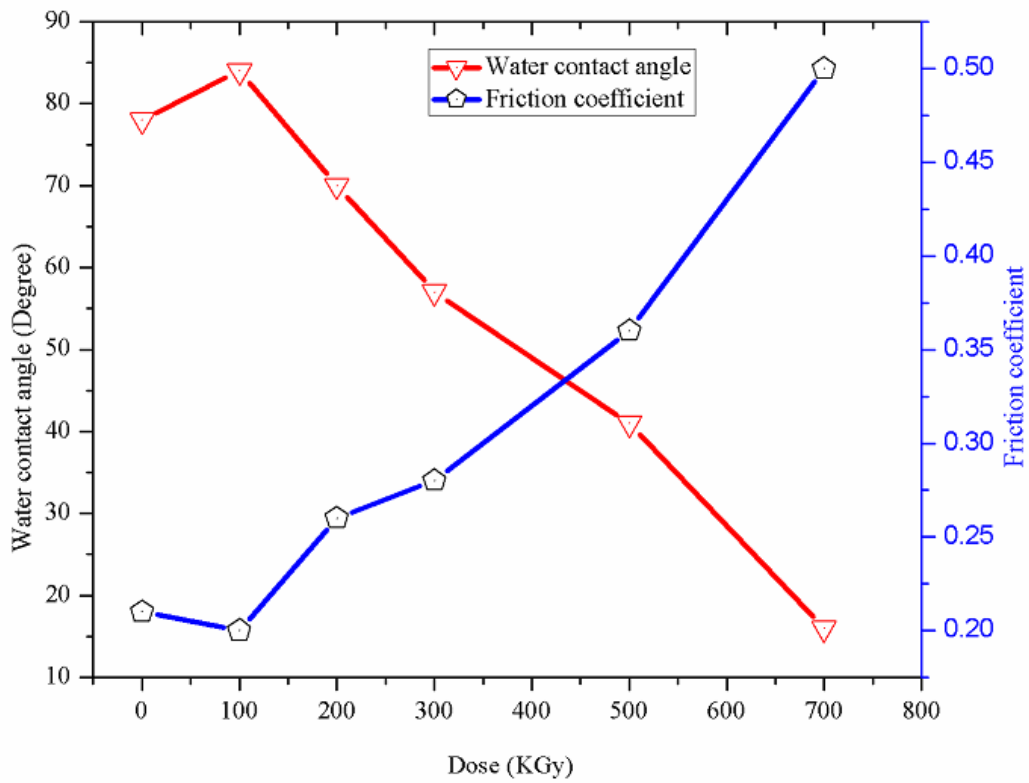


Fig. 26. Correlation among water contact angle, friction coefficient and irradiation dose on POM-C polymer: a- 0 (unirradiated); b- 100 KGy; c- 200 KGy; d- 300 KGy; e- 500 KGy; f- 700 KGy electron beam irradiated.

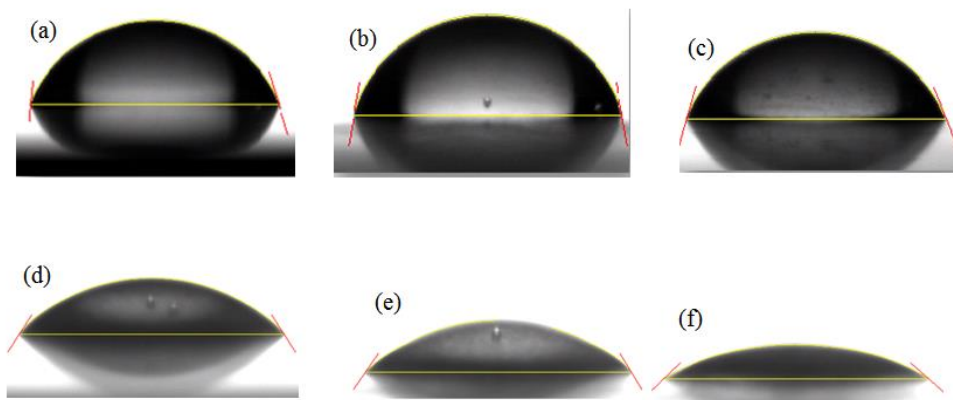


Fig. 27. Water contact angle on POM-C blocks: a-78⁰; b-84⁰; c-70⁰; d- 57⁰; e- 41⁰; f- 16⁰.

Chapter VII

7.1 CONCLUSIONS:

1. Electron beam irradiation induced carbonization, chemical structural modification, free radicals formation and partial physical degradation on POM-C surface. The 1 MeV, 100 KGy electron beam irradiation reduced friction coefficient, surface roughness and wear loss significantly, which is attributed to the well suited cross-linking, carbonization and partial physical degradation (smoothness). So, the wear system transferred from abrasive wear, adhesive wear and scraping to shallow and mild scraping due to the formation of carbonization and a small molecular substance on the top surface of POM-C, which are ascertained from SEM-EDS, 3D Nano surface profiler system and Optical microscopic observations.
2. The 1 MeV, 100 KGy electron beam irradiation also modified the chemical macromolecular structure of POM-C polymer surface as chemical structural modification, free radicals formation and strengthening the C-O-C and CH₂ vibrational bands strength.
3. The contact angle had a good contribution to reduce friction coefficient and wear loss, which can control the adhesion and real surface of contact between the two sliding surfaces. So, the highest water contact angle gives the lowest friction coefficient inducing carbonization and hydrophobic functional group formation on the top surface due to well suited cross-linking.
4. After all, the optimum electron beam energy and its dose are the main parameters to reduce friction coefficient and wear loss depending on chemical and physical factors of POM-C surface.

7.2 Future works:

The promising electron beam irradiation technology has huge possibilities and applications in semiconductors, nano-materials, bio-materials and medical field to discover. The works that could be explored are stated below:

- Find out the optimum electron beam energy and dose to modify materials parameters selectively with highest benefits.
- Analysis for the optimum carbonization and free radicals formation to reduce friction coefficient.
- Find out threshold surface roughness to reduce friction coefficient by optimum electron beam energy and dose.
- Analysis for the degree of cross-linking occurrence at optimum condition.
- Combining this process with another existing plasma technology to get best results.

7.3 References

- [1] Yifei Duan, Huilin Li, Lin Ye, Xiaolong Liu, J. App. Polym. Sci., Vol.-99, 3085-3092(2006)
- [2] Chang, F.C., Yang, M.Y. Polym Eng Sci 1990, 30, 543
- [3] Strong, A.B. Plastics Materials and Processing, 2nd ed., Prentice Hall, NJ, 2000
- [4] J Wang et al., Journal of Applied Polymer Science, Vol. 110, 91-96 (2008)
- [5] P. Samyn and P. De Baets, Tribology Letters, Vol. 19, No.3, July 2005
- [6] P. Samyn and P. De Baets, Mat Sci Forum, 475-479: 1077 (2005)
- [7] Xianguo Hu, Tribology Letters, 5(1998), 313-317
- [8] J. Horrión et al., Polymer Engineering Science , 36(1996), 2061
- [9] W.J. Feast, H.S. Munro, R.W. Richards (Eds), Polymer Surfaces and Interfaces II, Wiley, Chichester, UK, 1993

- [10] Chan, Chi Ming, polymer Surface Modification and Characterization, Carl Hanser, Munich, 1993
- [11] Andrzej Tuross et al., Vacuum, 70(2003), 201-206
- [12] V. –M. Archodoulaki et al., Polymer Degradation and Stability , 92(2007), 2181-2189
- [13] A. Adurafimihan Abiona et al., IJPS, Vol. 5(7), pp. 960-967, July, 2010
- [14] Cleland, M. R.; Parks, L. A.; Cheng, S. *Nuclear. Instruments and Methods in Physics Research B. 2003, 208, 66–73.*
- [15] N. Tian , T. Li, X. Liu, W. Liu, J. Appl. Polym. Sci., 82(2001), 962
- [16] Santos et al., J. Non-cryst . Solids, 338-340
- [17] Clough et al., Nucl. Instrum. Methods B 185, 8, 2001
- [18] Sevil et al., Radiation Physical Chemistry , 67, 575-580, 2003
- [19] Suzuki et al., Nucl. Instrum. Methods B 206, 501-506, 2003
- [20] S. Raghu et al., Radiation Physics and Chemistry, 98(2014), 124-131
- [21] Xianqiang Pei, Qihua Wang, Tribology Transactions, 50:2, 268-272, 2008
- [22] Zhongfeng Tang et al., Wear, 269 (2010), 485-490
- [23] Kieran A. Murray et al., IJMCSI, Volume-3, Issue-1, March 2013
- [24] X.Q. Pei, Q.H. Wang, H.J. Wang, B. Mu, J. Appl. Polym. Sci., 94 (2004), 1043
- [25] Razif Nordin, Hanafi Ismail, IJERA, 2013, Volume-3, Issue-6, pp-1820-1825
- [26] Khonakdar, H.A., Jafari, S.H. et al., Radiation Physics and Chemistry, 75 (2006), 78-86
- [27] Marletta , G. Iacona , F. and Toth, A. (1992), Macro-molecules, 25, 12, pp-3190-3198
- [28] Jacek Jagielski , Vacuum , 78(2005), 409-415
- [29] Calcagno, L.; Compagnini, G.; Foti, G., Nucl. Instrum. Meth.B, 65, 1-4, pp 413-422, 1992
- [30] Mazzoldi, P and Arnold, G.W (Eds), Ion Beam Modifications of Insulators, vol. 2 (Elsevier, Amsterdam), 1987
- [31] G. Zerbi et al., Journal of Molecular Spectroscopy, 27, 17-26 (1968)
- [32] Hiroyuki Tadokoro et al., The Journal of Chemical Physics, 35, 369 (1961)
- [33] Pieter Samyn, Isabel Van Driessche, Gustaaf Schoukens, J Polym Res (2007) 14:411-422

- [34] Singh, S., Prasher, Radiation Measurement, 40, 50-54, 2005
- [35] Ramola et al., Physica B404, 26-30, 2009
- [36] Vladimir N. Popok , Rev. Adv. Mater. Science, 30 (2012), 1-26
- [37] W. Liu, S. Yang, C. Li, Y. Sun , Wear 194 (1996), 103-106
- [38] Drobny JG, Ionizing Radiation and Polymers, Plastics Design Library/Elsevier, 2013, pp. 32-78.
- [39] K. Makuuchi, S. Cheng, Radiation Processing of Polymer Materials and Its Industrial Applications, Wiley 2012
- [40] A.V. Panin et al., Surface modification of structural materials by low-energy high-current pulsed electron beam treatment, AIP Conference Proceedings, 1623, 467 (2014)
- [41] Deepalaxmi R., Rajini V., Journal of Electrical Engineering and Technology, 2014, May, 9(3), 984-990
- [42] Nilay Kanti Pramanik et al., IJRSET, Vol-4, Issue-1, 2015
- [43] K V Aneesh Kumar et al., Journal of Physics: Conference series 618 (2015) 012032
- [44] Babak Jaleh et al., Membranes 2015, 5, 1-10
- [45] Joanna Maszybrocka et al., Journal of Applied Polymer Science Volume 132, Issue 31, August 15, 2015
- [46] Kern W, Cherdron H. Der Abbau von Polyoxymethylen. Makromol Chem 1960; 40:101-17
- [47] Bowden FP, Tabor D. Friction: An introduction to tribology. Garden city, New York: Anchor press, 1973
- [48] M.R. Clelend , Industrial applications of electron accelerators , Ion beam applications, Edgewood, NY 11717 , USA.
- [49] Elsa Reichmanis, Curtis W. Frank, James H. O'Donnell and David J. T. Hill, Irradiation of Polymeric Materials, Ch-1, pp 1-8, ACS Symposium Series, Vol. 527.
- [50] Clough, R.L., Gillen, K.T., and Dole, M. (1991), Ch- 3, Irradiation Effects on Polymers, ed. D.W. Clegg, A.A. Collyer (Elsevier Applied Science, New York).

[51] Dong, H. and Bell, T. (1999). Surface Coatings Technol, **111**(1), 29.

[52] Renuga Gopal, Ma Zuwei, Satinderpal Kaur, Seeram Ramakrishna, Surface Modification and Application of Functionalized Polymer Nanofibers, Vol-109, pp 72-91, 2007.