Energy loss for heavy ions in polymers: A possible correlation with the induced changes in optical and electrical properties

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Abstract. Polymers are being widely used as versatile materials in many scientific and technological applications because of their excellent inherent characteristics along with the possibility to further improve their properties through various treatments like chemical doping, gamma irradiation, ion beam irradiation etc. There are many reports in the literature where the optical, mechanical and electrical properties of the polymers are improved after irradiation to ion beams. Such changes are as a result of the energy transferred by the incident ion leading to the structural changes in the polymers. For the quantitative data interpretation in such experiments it is highly essential to know the exact values of energy deposited by the incident ion in the polymeric material. In the present work, a new approach without any empirical parameterizations for the correct evaluation of energy transfer by the incident ion beam within the polymeric material has been developed. Finally, the observed changes in the optical and electrical properties of PET polymer, as quoted in the literature, have been tried to be explained in terms of the energy transferred by the incident ions.

1. Introduction
In recent days, MeV ion beams are widely being used to tailor the properties of polymers as per requirements for their applications as versatile materials in various fields [1-5]. In this regard, the basic process involved is the linear energy transfer (LET) by the incident ions within the polymeric material leading to the structural changes which are, finally, responsible for the modification in their optical, electrical, mechanical properties etc.[6-11]. To understand these changes in terms of LET, it is highly essential to know the exact values of energy loss by the incident ion while traversing through the polymeric material. Although various formulations [12-21] for energy loss rate calculations are available in the literature but most of these employ empirical/ semi empirical means for effective charge parameterization which is one of the most crucial input parameter. In the present work, we have developed an approach without resorting to any empirical parameterization for correct evaluation of LET for MeV heavy ions. Finally, observed changes in the properties like optical energy gap and conductivity of PET polymer after irradiation to C and Si ions have been tried to be understood in the light of these calculations.

2. Theoretical Calculations
The present calculations are based on the Bohr’s equation [22], which is applicable in classical as well as quantum mechanical regime. According to this equation, the energy loss rate (-dE/dx) is given by
\[
\frac{dE}{dx} = \frac{2\pi Z^* e^4 n}{m v^2} \left[ \sum_i \ln \left( \frac{\eta_i^2 \chi}{2} \right) + \sum_i \ln \left( \frac{Z^*}{\eta_i} \right) \right] 
\]

(1)

where \( \chi = 2Z^* v_0 / \nu \) with \( Z^*, v_0 \) and \( \nu \) as the effective charge, Bohr’s velocity and ion velocity respectively and \( \eta_i = \left[ \frac{2\nu}{u_i} \right] \) with \( u_i \) being the orbital speed of the \( i^{th} \) electron of the target atom; \( n \) is the number of target atoms per unit volume. The quantities in the square brackets i.e. \( \chi \) and \( \frac{Z^*}{\eta_i} \), if less than unity, are to be replaced by unity. In the above equation, the two input parameters involved, i.e. \( u_i \) and \( Z^* \), are calculated in the following manner.

2.1. Calculation of \( u_i \)

The orbital velocity \( u_i \) of the \( i^{th} \) electron of the target atom is related to \( I_i \) (the successive ionization energies) through the relation \( I_i = \frac{m u_i^2}{2} \) where \( m \) is the mass of the electron. The values of \( u_i \) are calculated after modifying the values of \( I_i \), which were initially taken to be x-ray critical absorption energies[23], following the Sternheimer’s [24, 25] approach, so as to be consistent with the most accepted values of mean ionization potential \( I \) of the target atom.

2.2. Effective Charge Calculations

When a projectile ion at high velocities enters in a material medium, it loses all its electrons. Under this situation the charge on the incident ion is same as that of the nuclear charge. However, during the passage of the ion, its velocity continuously reduces and when it becomes comparable with the velocity of the orbital electrons, it starts picking up of the electrons in a gradual manner. Under this situation, the effective charge \( Z^* \) is related to the total nuclear charge through the relation

\[
Z^* = Z - S
\]

(2)

where \( S \) is the combined shielding effect of all inner electrons which is the sum of individual shielding contribution by various electrons. During the passage of an ion, the velocity of the orbital electrons is the resultant of its instantaneous orbital velocity \( (v_e) \) and its velocity by virtue of motion of the ion \( (\nu) \). For the electron to escape from the atom, its resultant speed needs to be \( \geq \left( \frac{2}{\eta_i} \right)^{1/2} v_e \). The values of \( v_e \) can be obtained from the successive ionization energy values quoted in the literature [27, 28]. The shielding effect can be determined using Slater or Clementi and Raimondi rules [27] taking in to account the extent of capture. The total shielding effect \( S \) can now be determined from the sum of the individual shielding effects and finally the effective charge \( Z^* \) can be determined using equation (2). On substituting the values of effective charge \( Z^* \) and orbital velocities of electron \( u_i \) in equation (1), the energy loss rate values of the incident ion can be determined. For the calculations in the composite materials, like polymers, the Bragg’s additive rule has been used.

3. Results and discussion

In order to understand the role of energy loss rate by impinging ions resulting in the observed changes in the optical and electrical properties of polymers: the experimental data related to optical band gap and conductivity due to C (90 MeV) and Si(120 MeV) ion irradiation in PET as available in the literature [29, 30, 31] have been considered. For the evaluation of energy loss per unit path length (-dE/dx) for C and Si ions, the presently developed approach as already discussed in the previous section has been followed and the results are presented in figure 1.
Figure 2 presents the values of optical band gap as already quoted in the literature [29] for PET polymer after irradiation to C (90 MeV) and Si (120 MeV) ions as a function of ion fluence. The figure clearly indicates that the reduction in optical band gap as a function of ion fluence is more pronounced in case of Si ions than for C ions. Such a behavior in the reduction of optical band gap as a result ion irradiation is due to induced structural changes within the host polymeric material and is directly correlated to energy loss rate of impinging ions, being higher for Si ions than for C ions throughout the trajectory of these ions. These results are also supported by the increased conductivity of the polymers [30, 31] due to formation of defects and carbon clusters arising as a result of scissoring of polymer chains caused by energy loss after ion irradiation.

Figure 1. Variation of energy loss rate as a function of energy for C and Si ions in PET polymer.

Figure 2. Variation of optical band gap as a function of ion influence for C and Si ions in PET polymer (the experimental data taken from reference 29)

4. Conclusion
A new approach to evaluate energy loss rate without resorting to any major empirical parameterization has been developed. The energy loss along the trajectory of impinging ions seems to be directly correlated with the induced changes in optical and electrical properties of the polymers.

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