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Effects of metal-ion implantation on wear properties of polypropylene

G. R. RAO, E. H. LEE
Metals and Ceramics Division, P.O. Box 2008, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
X. YAO, I. G. BROWN
Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA

Polypropylene was implanted with 100 keV titanium and silver ions to fluences of 1, 10 and 50×10^{19} ions m^{-2} using a vacuum arc metal-ion source. The implanted specimens were tested for sliding reciprocating wear properties using a nylon counterface, 1 N normal load, 3 mm stroke length and 10 000 sliding cycles. The results of the wear tests showed that there was a dramatic improvement in wear properties for the 50×10^{19} ions m^{-2} titanium-implanted specimen, to the point that no wear damage was visibly evident after 10 000 cycles. A similar wear improvement was not obtained for the lower fluences for titanium implantation or for the silver-implanted specimens. The improvement in wear properties was related to the mechanisms of linear energy transfer from the incident ions to the polypropylene substrate, and consequent effects on cross-linking, which is responsible for changes in properties. The linear energy transfer was quantified using Monte Carlo calculations. In addition, friction coefficient values were also correlated with the wear test results. The significance of high fluences for wear improvements by ion implantation was demonstrated in this study. The investigation showed that metal-ion implantation can be effective in significantly improving wear properties of polymers with a judicious choice of ion type and ion fluence.

1. Introduction

Ion implantation has been shown significantly to alter surface-sensitive properties of polymers [1]. Recent work at Oak Ridge National Laboratory (ORNL) has shown that ion implantation can significantly improve surface-related mechanical properties such as hardness and wear properties, sometimes dramatically [2–4]. Improvements in wear properties are synergistically dependent on ion species, energy, fluence, as well as the type of polymer used. Significant improvements in wear properties have thus far been obtained for several polymers including polyethylene, polypropylene, polystyrene, polyethersulphone, poly(ether ether ketone), polyimide and polyethylene terephthalate using different ion species.

Polypropylene (PP) is a widely used, and one of the most important, thermoplastics available today. It is typically semicrystalline and has a melting temperature of 160 °C and a glass transition temperature of −20 °C. In a previous study [4, 5], 200 keV boron was implanted in polypropylene to three fluences of 1.7, 5 and 17×10^{18} ions m^{-2}. Reciprocating sliding wear tests using a nylon ball as the counterface for a 1 N normal load and 10 000 sliding cycles showed that wear properties were significantly improved after ion implantation. The best improvement was obtained for the intermediate fluence for which minimal wear damage was observed [4, 5].

In the present study, the effects of low-energy metal-ion implantation on wear properties of polypropylene have been investigated. Titanium and silver ions were implanted in PP using a vacuum arc metal-ion source. One previous study at ORNL examined the effects of metal-ion implantation using the vacuum arc ion source on near-surface hardness and electrical conductivity of polyethylene, polycarbonate and polyetherimide [6]. That study showed that the implantations significantly improved both surface hardness and electrical conductivity of the polymers. The present study shows that shallow depth metal-ion implantation of polymers using low energies and similar optimum implantation conditions can also significantly improve tribological properties.

2. Experimental procedure

Polypropylene in the form of 178 μm thick films was obtained from Dayton Plastics Company (Dayton, OH). The polymer was implanted with 100 keV titanium and silver ions separately, to fluences of 1, 10 and 50×10^{19} ions m^{-2}. Implantations were performed at Lawrence Berkeley Laboratory using a vacuum arc metal-ion source [7]. Ions are extracted from a pure metal-ion plasma formed using a vacuum arc process from a solid bar of the metal. A repetitively

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pulsed beam was used with maximum time averaged beam current around 1 mA.

A Monte Carlo simulation computer code TRIM (1992 version) [8] was used to calculate the depth ranges for titanium and silver in PP. The total implantation ranges for titanium and silver are approximately 250 and 150 nm, respectively. At the peak of the distribution, the metal species concentration was approximately 5%. The implantations resulted in a change in colour of the PP to dark brown from colourless. This colour change is typical for ion-implanted polymers and has been observed and noted earlier [1, 2]. It is basically attributed to changing optical properties due to increased carbonization and microstructural damage at the polymer surface caused by the ion implantation.

Wear tests were performed using a sliding-reciprocating tribometer developed at ORNL [2]. Nylon balls of 9.53 mm diameter were used as the counterface with a 1 N normal load. Tests were conducted under ambient conditions within a humidity range of 30–50%. A stroke length of 3 mm with a reciprocating frequency of 100 cycles $\min^{-1}$ was used for a period of 100 min corresponding to 10 000 sliding cycles. These conditions are identical to those used in previous tests at ORNL on ion-implanted polymers. The tangential force was measured periodically during a test for calculating friction coefficient values using a strain-gauge bridge interfaced with a desktop computer. The wear specimens were studied and photographed using a Leitz Metalloplan optical microscope.

3. Results

Fig. 1 shows wear test results for the titanium implanted polypropylene specimens as well as unimplanted PP. The figure shows wear damage on the polymer surface and corresponding wear of the nylon ball counterface. The wear of the unimplanted PP is mainly adhesive wear, characterized by material sheared from the surface and smeared back along the path. Several transverse cracks and ridges are also observed on the PP surface. For the lowest fluence of 1×10^{19} Ti ions m^{-2}, again wear similar to that on the unimplanted PP was observed. The thin implanted surface was removed and the underlying substrate was visible as is evident from the differing contrast in Fig. 1. The width of the wear tracks was more than that for the unimplanted PP specimen. This was also reflected in the larger diameter of wear scar on the nylon ball. It should be noted that the ball penetrated the PP surface as evinced by the minimal wear of the nylon ball as indicated by the preservation of the surface topography in the contact region.

Similar wear characteristics were also evident for the intermediate fluence (1×10^{20} ions m^{-2}) implanted specimen. However, in this case, the width of the wear tracks was less than that for the 1×10^{19} ions m^{-2} implanted specimen indicating some improvement over the lowest fluence case. Again the implanted layer was removed and the underlying substrate was exposed. In addition the removed implanted layer debris also caused abrasive wear of the substrate as seen from the nature of the wear tracks which are in the form of long grooves both on the PP and nylon surfaces. In the case of the highest fluence (5×10^{20} ions m^{-2}) implanted PP speci-

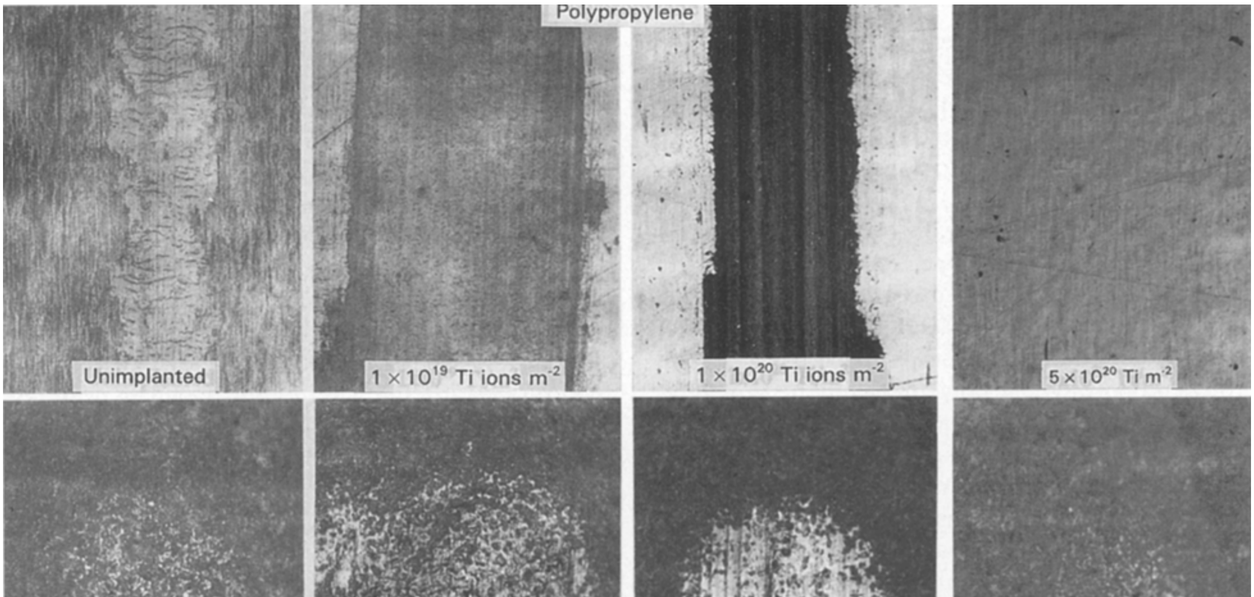

Figure 1 Wear test results for titanium-implanted polypropylene tested using a nylon counterface. The surface of the specimens as well as the corresponding nylon balls are shown for unimplanted and implanted PP for the three fluences used.

men, however, no wear damage was observed as can be seen in the micrograph at the extreme right in Fig. 1. Correspondingly, there was minimal damage on the nylon counterface.

Wear test results for the silver implanted specimens are shown in Fig. 2. In this case, wear damage was evident in all three specimens. With increasing fluence, the wear characteristics are similar to that of the titanium-implanted specimens. The wear damage on the lowest fluence silver-implanted specimen was very similar to that for the titanium-implanted specimen as seen from Figs 1 and 2. The wear tracks and wear track width for the highest fluence (5×10^{20} ions m^{-2}) implanted specimen was similar to the wear damage on the intermediate fluence (1×10^{20}) titanium-implanted specimen. The intermediate fluence (1×10^{20} ions m^{-2}) silver-implanted specimen showed wear damage that was intermediate to that observed for the lower and higher fluence-treated specimens. It is clear that even the highest fluence of 5×10^{20} ions m^{-2} was not sufficient for the Ag^+ implantation for improvement in wear properties as in the case of titanium-implanted PP.

Friction coefficient data for the wear tests on titanium- and silver-implanted PP specimens are shown in Figs 3 and 4, respectively, and compared with the unimplanted specimen test values. The friction coefficient values for the unimplanted specimen are in the 0.3–0.4 range. The implanted specimens, except for the 5×10^{20} ions m^{-2} titanium-implanted specimen (which showed the best wear properties), yielded friction coefficients in the 0.6–0.8 range for both the titanium- and silver-implanted specimens. The 5×10^{20} ions m^{-2} titanium-implanted specimen showed lower values than the other implanted specimens but higher than the unimplanted specimen friction values. The reported friction values were attained within the first few minutes for all tests, as seen from the figures.

4. Discussion

The results show that high fluences can be useful for significantly improving wear properties of polymers using relatively low-energy ion implantation. In particular, the 5×10^{20} ions m^{-2} titanium-implanted specimen showed no wear damage after 10 000 reciprocating cycles using a 1 N normal load and a nylon counterface. However, the wear improvement was dependent on the type of ion used because such a dramatic improvement was not observed for

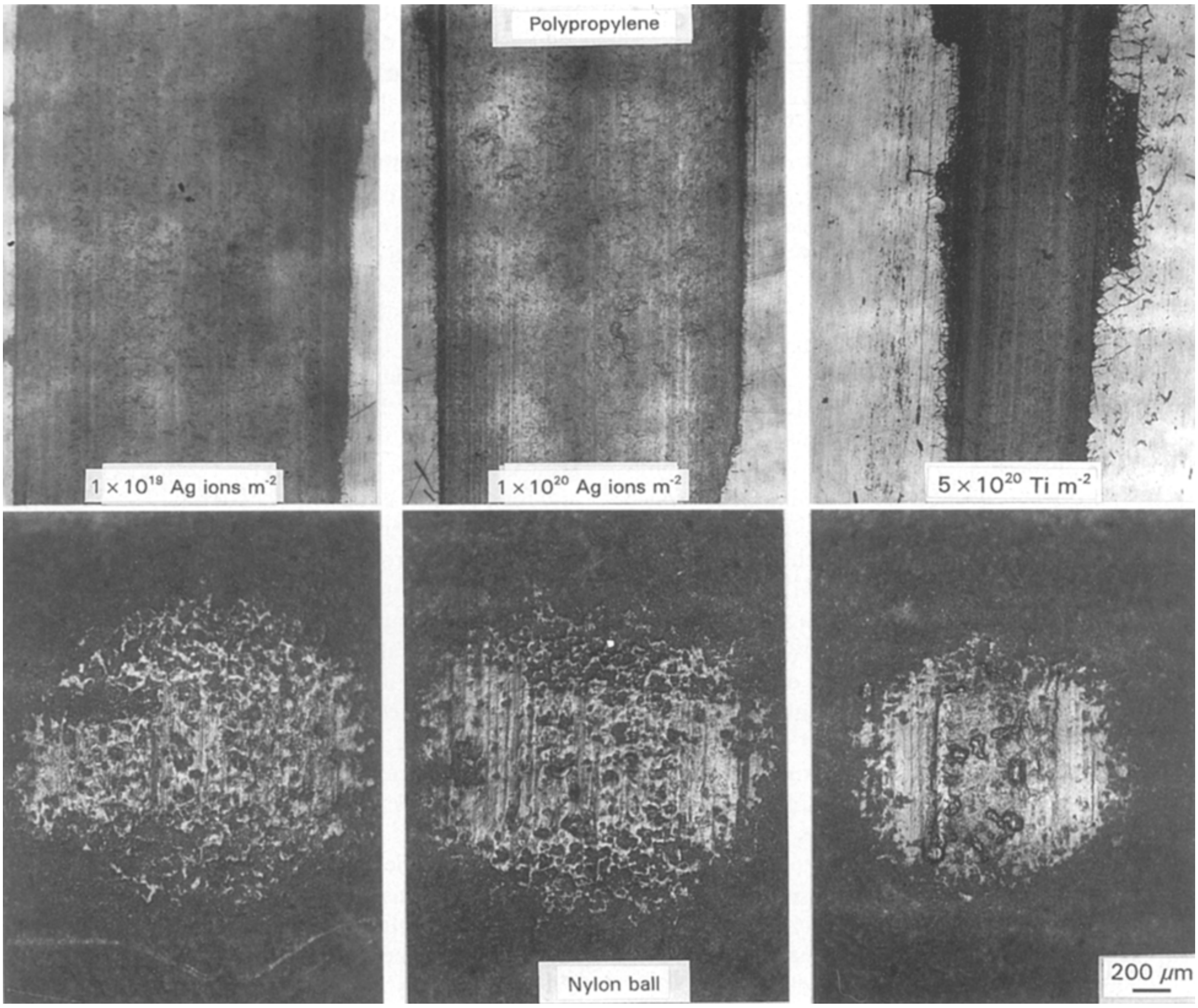

Figure 2 Wear test results for the silver-implanted PP specimens for the three fluences used in the study. The corresponding nylon ball surface is also shown.

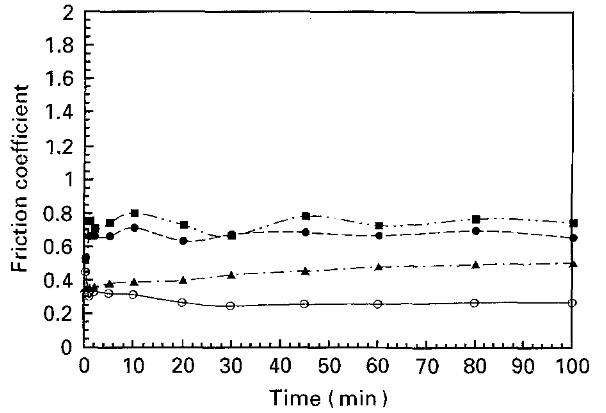

Figure 3 Friction coefficient data for the titanium-implanted specimen wear tests together with data (○) for the unimplanted polymer. (●) 1×10^{9} ions m^{-2}, (■) 1×10^{20} ions m^{-2}, (▲) 5×10^{20} ions m^{-2}.

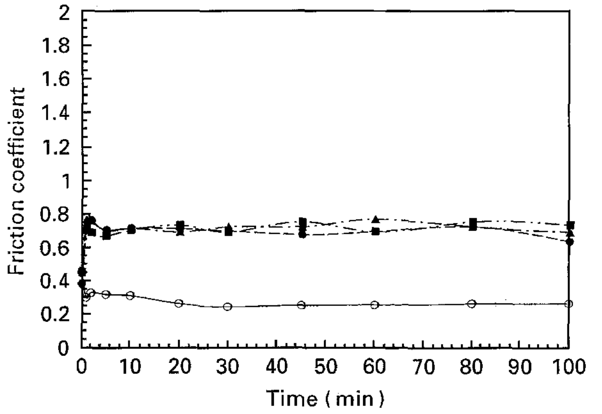

Figure 4 Friction coefficient data for the silver-implanted PP specimens together with data (○) for the unimplanted polymer. (●) 1×10^{19} ions m^{-2}, (■) 1×10^{20} ions m^{-2}, (▲) 5×10^{20} ions m^{-2}.

the silver implantation under similar implantation conditions.

It has been shown that implantation-induced cross-linking of polymers is the main cause of improved mechanical properties [2–5]. The cross-linking significantly improves hardness of the modified surface layer as well. In an earlier study on PP, for example, it has been shown that implantation with 200 keV boron ions increases hardness (as measured using a nano-indentation technique at 100 nm depth) from 0.144 GPa for the unimplanted polymer to 0.485, 0.96 and 2.63 GPa for fluences of 1.7, 5 and 17×10^{18} ions m^{-2} [5]. In the present study, similar nanohardness measurements yielded values of 0.39, 0.75 and 0.97 GPa for titanium implantation, and 0.3, 0.42 and 0.6 GPa for the silver implantation for a fluence of 1×10^{19}, 1×10^{20} and 5×10^{20} ions m^{-2}, respectively, for each ion. In addition, higher molecular weights, higher entanglement densities and a more rigid backbone structure have been shown to enhance wear properties [9]. Cross-linking effectively increases molecular weight and entanglement density, and also results in increased rigidity through three-dimensional interlinking of the material. The formation of a thin, hard, highly cross-linked surface on a polymer by ion implantation therefore is essentially responsible for the improved wear properties.

Adhesive wear was dominant for unimplanted PP, which has been shown to be true for polymer-on-polymer wear [10–13]. For the implanted specimens, with the exception of the 5×10^{20} ions m^{-2} titanium-implanted specimen test, wear was a combination of adhesive and abrasive wear. Briscoe [10] has suggested a classification of wear mechanisms into two major categories, (1) cohesive wear that involves dissipation of frictional work and its damage in large volumes adjacent to the interface, including abrasion and fatigue wear, and (2) interfacial wear involving dissipation of frictional work in a very thin region at the interface, including adhesive and transfer wear. He indicates that most wear is not monomechanistic, and there can be an overlap between the two broad classifications.

In all implanted PP tests in this study, except for the 5×10^{20} ions m^{-2} titanium-implanted specimen test, the implanted surface layer was removed, exposing the underlying unimplanted substrate. However, with increasing fluence, the width of wear damage on PP was reduced, indicating that wear resistance improved with increasing fluence. The wear damage in terms of wear track was greater for the lowest fluence-implanted specimens than for the unimplanted specimen. This can be attributed to the abrasive action of the relatively harder debris particles that are formed from the implanted surface, which in turn cause increased wear of the polymer specimen. The polymer surface becomes more brittle even at low fluences. This is evident from the higher friction coefficient values for tests of all the implanted specimens, except for the 5×10^{20} ions m^{-2} titanium-implanted specimen, which showed exceptionally good wear properties for which no debris was created.

The 5×10^{20} ions m^{-2} titanium-implanted case represents the best dose of those tested in this study, where no wear damage was observed on the surface. Previous studies have shown such a dependence of fluence on wear improvement. An optimum fluence typically exists for a given ion type for a specific energy and for a specific counterface material [3–5, 9]. Below this optimum fluence, wear improvement is not significant and wear properties may actually be worse than for the unimplanted polymer, as is the case with the lowest fluence-implanted specimens in this study. Increasing fluence above this optimum level makes the film very brittle and causes the formation of cracks during the wear tests. For the silver-implanted PP, it is evident from the decreasing wear track widths with increasing fluence that the optimum fluence was not reached and it is conceivable that this value is over 5×10^{20} ions m^{-2}.

Previous studies have shown that for a given energy, with increasing fluence, hardness tends to increase and eventually saturate at some value. The saturation hardness values increase with increasing energy. This was attributed to more complete cross-linking at higher fluences [3]. Higher energies and lower ion masses seem to cross-link the polymer more effectively, thereby shifting the optimum fluence to lower values. In the previous study using 200 keV boron-implanted PP [4, 5], the best fluence was in the 5×10^{18} ions m^{-2} range, which is two orders of magnitude lower than the fluence of 5×10^{20} ions m^{-2} showing the best results for the titanium implantation in this study. Apart from more efficient cross-linking, higher energies and ion species with lower atomic masses also cause deeper penetration of the ions in the substrate and correspondingly, a thicker surface-modified layer which would be beneficial for tribological properties. However, it is also clear that a completely cross-linked structure is not desirable due to its typical glassy, brittle nature. The optimum fluence appears to be in the range that yields a level of cross-linking less than a completely cross-linked structure.

While cross-linking has been shown to be the major factor for surface property improvements in ion-implanted polymers, recent work by our group suggests that the linear energy transfer (LET) mechanisms from the incident ions to the substrate affect the extent of cross-linking and thereby changes in surface properties [14]. Incident ions transfer their energy to host atoms mainly through electronic stopping (ionization/excitation) and nuclear stopping (or recoils). Other energy loss mechanisms, for example through phonons, do not significantly affect polymer microstructure or properties. It was shown that electronic stopping was the most important factor for cross-linking and associated improvements in hardness and wear properties, whereas recoils or displacements had a detrimental effect on cross-linking, possibly by promoting chain-scission [14].

The LET values for ionization and displacement processes, as well as the difference in LET (ΔLET = LET(ionization) − LET(displacements)) for 100 keV titanium and silver in polypropylene, as calculated using TRIM, are shown in Fig. 5. It can be observed that ionization caused by the silver ions is greater than that caused by titanium ions. However, energy lost to displacements is much greater for silver than titanium. ΔLET, which gives a good measure of the extent of cross-linking, is slightly higher for silver at the surface but quickly drops to zero. On the other hand, ΔLET for titanium remains higher to a greater depth indicating a thicker cross-linked region than for the silver implantation. Thus, there was probably a greater overall extent of cross-linking for titanium-implanted PP as compared to silver-implanted material. The titanium ions also modified the polymer to a greater depth, which is beneficial for wear properties. This interpretation is consistent with our previous studies which showed that cross-linking is enhanced not only with increasing ionization LET but also with decreasing LET for recoil. Thus the ΔLET values serve as a useful guideline to estimate qualitatively the extent of cross-linking.

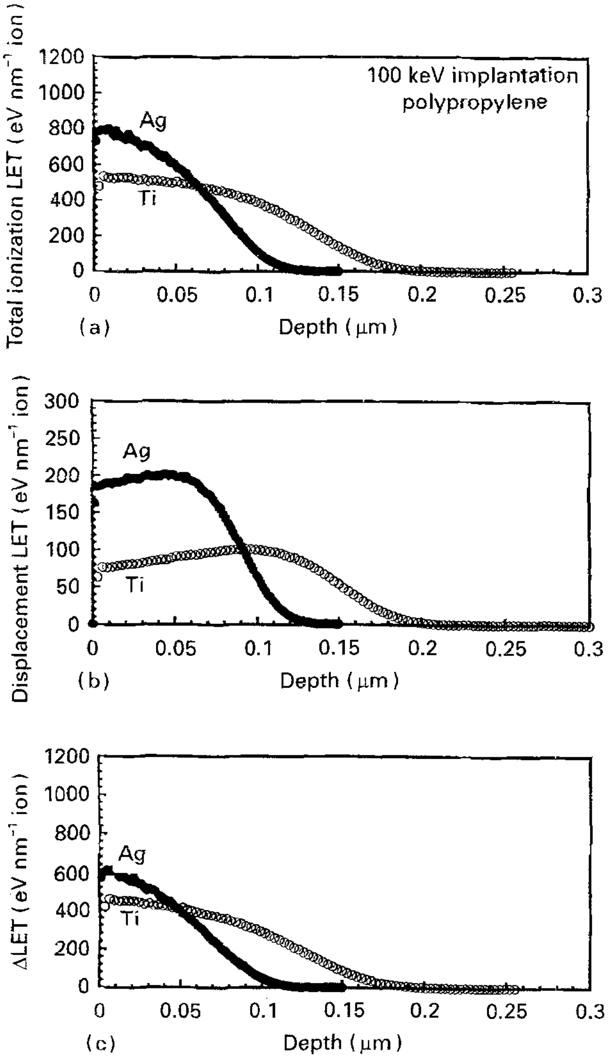

Figure 5 The linear energy transfer (LET) values for titanium and silver implantation showing calculated values for (a) ionization and (b) recoils, as well as (c) the difference between the two as a function of implantation depth.

This study shows that metal-ion implantation can be used to improve wear properties of polymers if a high fluence and metal ions with relatively lower atomic numbers are used. Based on the accumulated data in our recent studies [2–5, 14], chemical effects of the implanted species are not significant for ion implantation of polymers and most of the property changes realized are due to energy transfer effects. In addition, the present results are valid for PP and the effects may be different for other polymers. Changes in properties of polymers by ion implantation are highly structure dependent and the optimum condition regimes may be different. For example, it has been shown that when 200 keV boron is implanted in polyethylene, polypropylene, polystyrene and polyethersulphone, with increasing fluence the hardness tends to saturate at different levels [4, 5] whereas some polymers, such as polyacetal, disintegrate when subjected to ion bombardment due to the presence of weak –C–O– bonds [14].

5. Conclusion

Polypropylene (PP) was implanted with 100 keV titanium and silver ions to fluences of 1, 10 and 50×10^{19} ions m^{-2} and was subjected to wear tests using a nylon 66 counterface. Material implanted with 5×10^{20} Ti ions m^{-2} showed no wear damage over unimplanted material after 10 000 reciprocating cycles. The other two lower titanium fluences showed no improvement; none of the silver-implanted specimens showed any improvement. Monte Carlo calculations showed that the titanium-implantation had a greater overall difference between linear energy transfer for ionization and displacements, ΔLET, than the silver-implantation. This probably produced greater cross-linking for the titanium-implanted specimens for a given fluence. In addition, the highest titanium fluence caused a more complete cross-linking than the lower fluences, thereby significantly improving wear properties. Moreover, the lighter titanium ions penetrated deeper and resulted in a thicker cross-linked region leading to better wear properties. The present work showed that the vacuum arc metal-ion source has potential for implantation of polymers to improve tribological properties in spite of comparatively low energies, if ions with lower atomic numbers and higher fluences are used.

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