SURFACE ENGINEERING OF POLYMERS BY PARTICLE BEAM TREATMENTS FOR FUNCTIONAL APPLICATIONS

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Ion beam-induced modifications of physical and chemical properties of polymers have been widely studied in recent years providing a large body of experimental data [1-3].

In particular, it has been shown that beam-induced modifications may dramatically change important properties of the polymers, by modifying some of the different levels of organization of the polymer structure. Thus, modifying the chemical structure and composition of the monomers (i.e., the "primary structure") the optical properties [4, 5], the electrical properties [6, 7] and the chemical properties, including the modification of biocompatibility [8], can be dramatically changed. Similarly, the modification of chain configuration (i.e., the "secondary structure") and macromolecule shape (i.e., the "tertiary structure") involves the dramatic modification of the rheological [3], thermomechanical properties [9, 10] as well as the local microstructure and in turn the microhardness and the wear resistance [11, 12].

The suitable choice of the relevant beam parameters (in particular the primary ion mass and energy and the total ion current) in connection with the composition of the polymeric target allows the control of the total amount of deposited energy, the relative importance of energy deposition mechanisms (i.e. collisional impulse transfer and electronic interactions), the penetration depth and the track area [13].

For an ion of given energy and mass, an useful parameter has been shown to be the total ion dose, as it is a measure of the total deposited energy per ion. It is clear that changing the primary ion energy and mass also the associated deposited energy will be different. However, for projectiles having energy in the keV range (due to the relatively small range of energy deposition rate for heavy projectiles) a schematic picture of the evolution of the chemical and physical modifications can be elaborated just in terms of the total ion dose [14].

Figure 1 summarizes the relationship between ion fluence, type of predominant chemical modification and related physical properties. A relatively ordered succession of the modification events is apparent, going from very low up to high ion fluences.

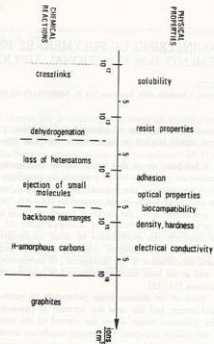In particular, on the basis of general considerations about the mean ion

Fig. 1 - Qualitative trends of ion fluence vs. typical chemical reactions and related physical properties [adapted from ref. 14].

track radius (roughly 1-2 nm for keV ions) we may identify *three main dose regimes* in terms of the progressive covering of the surface with the primary physical tracks.

The *first fluence regime* includes the single track events, in which there is no overlap among the distinct modified regions and a very low density of chemical modifications is being produced. The related fluence range between 10^{13} and 5×10^{13} ions/cm². Within this fluence range the chemical events which involve the most of modifications are dehydrogenation and chain rupture, which in turn induce cross-linking and chain scissions. These beam-induced modifica-

tions directly affect the Molecular Weight Distribution (M.W.D.) as well as the thermomechanical properties, including the enthalpy of melting and the related melting temperature, Tm, as well as the glass transition temperature, Tg [9, 10].

Figure 2 shows a characteristic example of modification of the M.W.D. induced by He⁺ 100 keV in a monodisperse polystyrene (M.W. = 3.5×10^4) [15]. In particular, figure 2a reports the Gel Permeation Chromatograms (GPC) for the sample before irradiation and after 5×10^{12} ions/cm². She shows the two main effects on the M.W. induced by the irradiation, i.e., the formation of higher and lower mass chains respectively due to cross-linking and chain scission events. It is an important part of the cross-links produces an insoluble gel fraction which is not detected by the GPC technique and needs to be detected with solubilization. Figure 2b reports the evolution of the different fractions of the polymer with increasing fluence (between 5×10^{12} to 1×10^{14} ions/cm²). It is interesting to note that the two processes of chain scissions and cross-links proceed parallel in the fluence range between 5×10^{12} and 5×10^{13} cm², the cross-linking process becoming predominant after 5×10^{13} cm², producing the technologically important insoluble gel phase. Evidence has been obtained that the rate of production of cross-links depends essentially upon the deposited energy density [3].

At higher fluence (*second regime*, roughly between 1×10^{14} and 10^{15} ions/cm²) other characteristic events become detectable. In particular, the chemical structure of the monomer units is heavily modified. Hence, the basic patterns of modification include the depletion of small stable molecules (often including heteroatoms present in the polymer structure), reduction or oxidation reactions, destruction of the aromatic rings, etc [1, 16-25]. As an example of the process, the beam-induced modifications of N 1s chemical state in PMDA-ODA polyimide is reported in figure 3. The figure reports the evolution of the XPS signal for N 1s band with 5 keV Ar⁺ irradiation. The initial imidic moiety is depleted, as it is figured out from the decrease of related N 1s component, while other nitrogen species (including pyridine-like structures, iminic groups and tertiary amines) are formed with a peculiar evolution in time. The transformation of the nitrogen species is accompanied by the depletion of nitrogen (probably by loss of simple N-containing fragments). The absolute loss of nitrogen starts only *after* a threshold fluence, suggesting that there is an "*incubation*" fluence for the depletion processes. The existence of such an "*incubation*" fluence is a quite general feature of the beam-induced processes for several types of polymers, confirming that the evolution of a polymeric system in the considered fluence regime is characterized by relatively simple and well-defined primary reactions prompting the following catastrophic degradation, what we can define a "*mild chemistry*" [1].

Within the same fluence regime, one can obtain the modification of properties related to the local local electronic structure of the monomer unit like
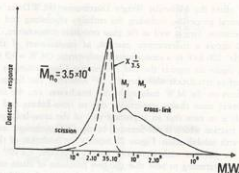
Fig. 2a - MWD for a nearly monodisperse PS film ($\overline{M}_n$ = 35 000) before (—) and after bombardment (—) with 100 keV, 5 x 10^{12} He$^+$ cm^2. For drawing clarity the curves have been height normalized [adapted from ref. 15].

for instance optical properties, and properties related to the chemical reactivity of the moiety, like for instance biocompatibility and adhesion. In particular, figure 4 reports the modification of the optical properties of polyethersulfone (PES) films irradiated with 150 keV Ar$^+$ at fluence ranging between 1 x 10^{14} and 1 x 10^{16} ions/cm^2. The analytical technique employed in this case is Reflection Electron Energy Loss Spectroscopy (REELS), a technique able to extract the
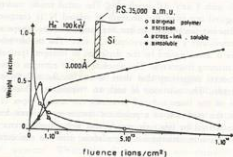

Fig. 2b - Weight fraction of the various components as a function of ion fluence [adapted from ref. 15].
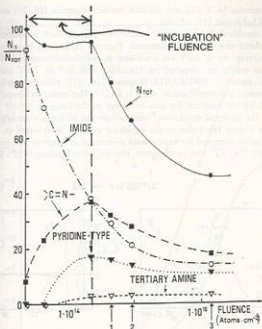
Fig. 3 - Modification of the relative concentration of N-containing groups in ion-irradiated PMDA-ODA. The data are derived by the peak analysis of the N 1s bands in XPS spectra.

optical functions of the sampled layers from the Inelastic Loss Function [14, 26]. It is important to point out that the optical properties are substantially modified before the electrical conductivity is changed in a substantial way. This depends upon the fact that electrical properties are dependent both on the local electronic structure and the structure and distribution of the conducting domains, which are severely affected only at higher fluence.

The *third fluence regime* may be defined as a regime of reimplantation. At fluence higher than 1015 ions/cm² each point on the surface has been struck several times, so that the initial "mild" chemistry products have been further modified several times. Characteristic examples of modification involve the elec-

trical properties [6, 7, 27], the diffusion barrier properties [28, 29] and the tribological behaviour [11, 12, 30].

The modification of electrical conductivity is particularly interesting in view of the related technological applications. Figure 5 reports the characteristic rise in conductivity due to MeV ion irradiation in polyphenylenesulphide (PPS) [7]. Analogous results are obtained by irradiating with keV or MeV ions various polymers, including PMDA-ODA (Kapton) [16, 17], polyvinylpyridine, polyvinylcarbazole, polyvinylchloride, etc. [1, 2, 23]. The resistivity drops suddenly around 2-3 x 10^{15} ions/cm^2 for ions of energy in the range of 10^2-10^3 keV. The onset of the electrical conductivity being a function of the ion energy for MeV ions. The doping effect due to the implanted ions has been found to be relatively negligible, excepted for experiments performed at relatively low energy with 30-50 keV Na$^+$, Cl$^-$ ions in polymers like polyparaphenilene (PPP) and PPS,
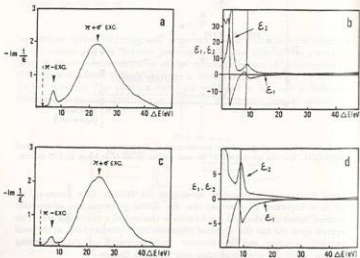
Ar$^+$ 150 keV — PES

Fig. 4 - a) Energy loss function (− Im $1/\varepsilon$) and b) complex dielectric constants obtained from REELS spectra of PES before bombardment and c) after bombardment with Ar$^+$ 150 keV at a fluence of 1 x 10^{15} ions/cm^2. The energy of the primary electron beam (E$_p$) was 1200 eV, with a FWHM of the elastic peak of 0.9 eV [adapted from ref. 14].
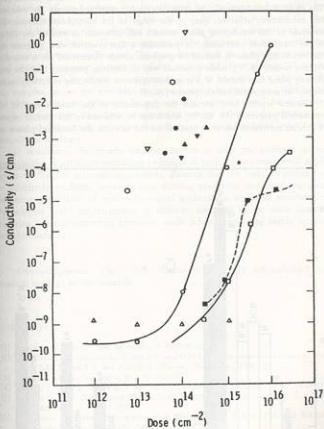
Fig. 5 - Results of conductivity measurements on poly (phenylene sulfide) irradiated with 5.6 MeV F (○), 0.32 MeV Li (△), 50 MeV I (□), 57.5 MeV I (▽), 25 MeV I (●), 28 MeV Si (▼), and 40 MeV Ca (▲). Also plotted for comparison are 0.20 MeV Br (◇) and 0.10 MeV as (■) measurements [adapted from ref. 7].

which show different electrical behaviour (i.e., p versus n doping effect) [31]. The effect is quite general, the main limitation remaining however the relatively low conductivity achieved, lying in the range of the amorphous carbons. The structure of the conducting phase remains still uncertain as well as the nature of the conduction mechanism. In particular, a first point of view propose that the conducting phase is formed of graphitic islands "immersed" in a non-conducting moiety [4, 7], while a second way of thinking proposes that the conducting phase may consist of a quasi-homogeneous conducting materials, mainly formed of amorphous carbon phases [16, 17, 21].

Recent reports have stressed the importance of the modification of the mechanical properties [11, 12, 30] which can be achieved in this fluence regime. A general agreement has been reached on the fact that the hardened phases are

Fig. 6 - Modification of the hardness for three polymers, irradiated with single ion beams and with multiple beams. The total dose per single ion is 1×10^{15} ions/cm^2 [adapted from ref. 30].

mainly formed by amorphous carbon moieties. Recent results show that important increase of the hardness can be achieved by irradiating polymers at characteristic fluence around 3-4 x 10^{15} ions/cm² [11, 30]. Figure 6 reports the characteristic hardening effect obtained by irradiating various polymers with multiple or single ion beams. The measurement of the hardness has been performed with nanoindentation techniques. The comparison with the hardness of stainless steel is quite intriguing, showing a relative increase of about 2 times. However, the problem of fully reliable measurements is still to be solved for such a difficult samples, as are the irradiated surficial layers in polymers, i.e., thin hardened skin on a plastic substrate! In any case, the occurrence and the qualitative trends of the effect have been confirmed in several different experiments and the main problem seems to involve the adherence of such hardened layers to the unmodified substrate.

In conclusion, the present summary intends to draw the attention on the potentialities of ion beam irradiation technique in such a non-conventional application to "brittle" materials as polymers, showing that the basic properties can be effectively modified, inducing new exciting properties and involving some intriguing possibilities of new technological applications, especially promising in technologies based on integration of different functions in the same material requiring effective patterning processes, easily achieved by using highly focused particle beams.

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