On the simultaneous etching of two neighboring swift heavy ion irradiated polymer foils

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Abstract

We found during our research that two polymer foils, irradiated under the same conditions, and thereafter facing each other in the same vessel while simultaneously being exposed to the same etchant solution, always behave different under the etchant attack, in spite of equal etching conditions. We showed that by making use of a well-known chemical recipe, this problem can be overcome. The equations derived here can be applied to the mentioned problem.

Let us introduce the following notations:
$m_a\,(t)$ is the polymer mass removed by etching at the time t in the foil *a*.
$m_b\,(t)$ is the polymer mass removed by etching at the time t in the foil *b*.
c_a is the local concentration of etchant at the time t at the foil *a*.
c_b is the local concentration of etchant at the time t at the foil *b*.
t is the total etching time, with t = 0 corresponding to the onset of etching.

With proceeding etching time, some difference will emerge between the amounts of removed polymeric material m_a and m_b in both foils due to statistical slightly different track numbers and track shapes, and similarly some difference will emerge between the concentrations c_a and c_b of the etchant in front of the polymer foils a and b, due to statistical slightly different etchant consumptions. To arrive at a consistent description, we have to consider on the one hand the dependence of the speed of removal of the irradiated polymer regions dm_i/dt, and on the other hand the dependence of the speed of etchant loss dc_i/dt, on both the amount of already removed material m_i and the remaining etchant concentration c_i, for both foils i = a and b. This leads to the kinetic equations (1-4):

$$\frac{dm_a}{dt} = \alpha_a c_a - \beta_a m_a \,, \tag{1}$$

$$\frac{dm_b}{dt} = \alpha_b c_b - \beta_b m_b \,, \tag{2}$$

$$\frac{dc_a}{dt} = \alpha_a' c_a - \beta_a' m_a \,, \tag{3}$$

$$\frac{dc_b}{dt} = \alpha_b' c_b - \beta_b' m_b \,, \tag{4}$$

where the rate coefficients α, α', β and β' are thought to be constant. Subtraction of Eq. (2) from Eq., (1) and of Eq. (4) from Eq. (3) yields:

$$\frac{d\left(m_a - m_b\right)}{dt} = \alpha\left(C_a - C_b\right) + \beta\left(m_b - m_a\right), \tag{5}$$

$$\frac{d\left(C_a - C_b\right)}{dt} = \alpha'\left(C_a - C_b\right) + \beta'\left(m_b - m_a\right). \tag{6}$$

Let us assume for simplicity that the rate coefficients are the same for both foils: $\alpha_a = \alpha_b = \alpha$, $\beta_a = \beta_b = \beta$, $\alpha_a' = \alpha_b' = \alpha'$ and $\beta_a' = \beta_b' = \beta'$ and let us simplify the concentration and mass differences: $|c_a - c_b| = c$, $|m_a - m_b| = m$. Then Eqs. (5) and (6) give:

$$\frac{dm}{dt} = \alpha c - \beta m \,, \tag{7}$$

$$\frac{dc}{dt} = \alpha' c - \beta' m \,. \tag{8}$$

This set of equations can be reduced to equations of second order for *m* and *c*, respectively:

$$\frac{d^2 m}{dt^2} = \left(\alpha'\beta - \alpha\beta'\right)m + \left(\beta - \alpha'\right)\frac{dm}{dt}, \tag{9}$$

$$\frac{d^2 c}{dt^2} = \left(\alpha'\beta - \alpha\beta'\right)c + \left(\beta - \alpha'\right)\frac{dc}{dt}, \tag{10}$$

which can be simplified to:

$$\frac{d^2m}{dt^2} = A\frac{dm}{dt} + Bm\,, \tag{11}$$

$$\frac{d^2c}{dt^2} = A'\frac{dc}{dt} + B'c \tag{12}$$

by introducing the coefficients A and B in (9) and A´, B´ in (10). Due to the identity of the rate coefficient terms in both Eqs. (9) and (10), A = A´ and B = B´. Eqs. (11) and (12) have simple solutions:

$$m \sim e^{\gamma t}\,, \tag{13}$$

$$c \sim e^{\gamma' t} \tag{14}$$

with the same exponent γ.

It depends on the sign of the exponent γ whether the etching speeds of both foils a and b converge or diverge. Whereas for $\gamma < 0$ eventual differences in etching speed would smooth out, $\gamma > 0$ would signify that both foils will be etched at increasingly different rates. This latter case was found to occur in our experiments.

By inserting Eq. (13) into Eq. (11) (or Eq. (14) into Eq. (12)), one obtains:

$$\gamma = \frac{A \pm \sqrt{A^2 + 4B}}{2} \tag{15}$$

or:

$$\gamma = \frac{(\alpha' - \beta) \pm \sqrt{(\alpha' + \beta^2) - 4\alpha\beta}}{2}\,. \tag{16}$$

A basic precondition in order to arrive at realistic non-fluctuating solutions is that the radicand $A^2 + 4B$ must be positive or at least zero, hence that: $A^2 \geq -4B$ or $(\alpha` + \beta)^2 \geq 4\alpha\beta`$.

From the criterion for convergence of etching speeds: $\gamma<0$ one can derive the condition: $\frac{\alpha'}{\alpha} > \frac{\beta'}{\beta}$, whereas the experimentally found case: $\gamma>0$ implies that $\frac{\alpha'}{\alpha} < \frac{\beta'}{\beta}$ should hold. This latter condition means that in this case the ratio of the correlation of {etchant concentration change to the actual etchant concentration} to the correlation of {speed of polymer mass loss to etchant concentration} is smaller than the ratio of the correlation of {etchant concentration change to dissolved polymer mass} to the correlation of {speed of polymer mass loss to dissolved polymer mass}.

In other words, the technologically preferred case of identical track etching speeds in both foils can be achieved only if track etching would be performed in a highly inefficient way, i.e. by using a huge amount of etchant to remove only very small amounts of polymeric matter. For contrast, when striving for efficient track etching (i.e. by removing much polymeric material with only little etchant consumption – as it usually done), one inevitably arrives at the technologically undesired result of strongly diverging etchant speeds for the two foils.

The competition of two neighboring foils for sufficient etchant solution can also be interpreted as some type of (here: undesired) communication between these foils via the mediating common electrolyte. This effect resembles somewhat the earlier observations of multiple track etching in a single polymer foil, where some tracks are etched much more pronouncedly and rapidly at the expense of others in their neighborhood, Eq. (6).