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Hydrolytic embrittlement — a security breach in structural materials made of biodegradable polymers

Tristan Baumberger*

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Specifications regarding traditional *structural materials* include both strength *and* durability requirements. Accordingly, well designed stone and iron buildings have crossed the ages, bearing their load steadily. In the 21st century, the quest for a sustainable environment often challenge the material durability clause and substitute it for biodegradability (think of the “plastic” waste issue). In the more specific, biomedical applications such as drug delivery or organ repair, when materials are implanted in the body, ultimate biodegradability is vital. Biodegradable polymers such as the widely used, FDA-approved, poly(lactic acid) (PLA) studied by Shi et al. must preserve their integrity and strength in the very same aqueous environment which will eventually favor their degradation and disintegration. In such a planned obsolescence program — for the good cause — proper timing is crucial.

Two degradation processes compete: expected erosion and unwanted crack growth. Controlling the rate of hydrolytic erosion of a biodegradable polymer is usually achieved by tuning the physico-chemical properties of its backbone[5] — e.g. its hydrophobicity such as in the case of co-polyester poly(lactic-co-glycolic acid)[9]. Controlling the rate of *subcritical crack growth*, potentially leading to catastrophic rupture, in an aggressive environment is a challenging issue, not a new one, indeed.

Stress corrosion cracking is a long-standing concept in material science, referring to the widely documented fact (for metals[7], ceramic and glasses[4] or rubbers[6]) that even mildly aggressive vapors or liquids may induce damages outrunning erosion in load-bearing materials, due to environment-aided nucleation and growth of cracks from stress-concentrating surface flaws. It is remarkable that an issue first raised by structural integrity of stainless steel pipelines and rubber tires may remain relevant to the new generation of “soft” structural materials such as medical suture fibres, drug delivery patches[9] or hydrogel wound dressings[2]. Owing to the wealth of polymer structures encountered in the biomaterial world — from thermoplastic entangled polymers[10] to highly

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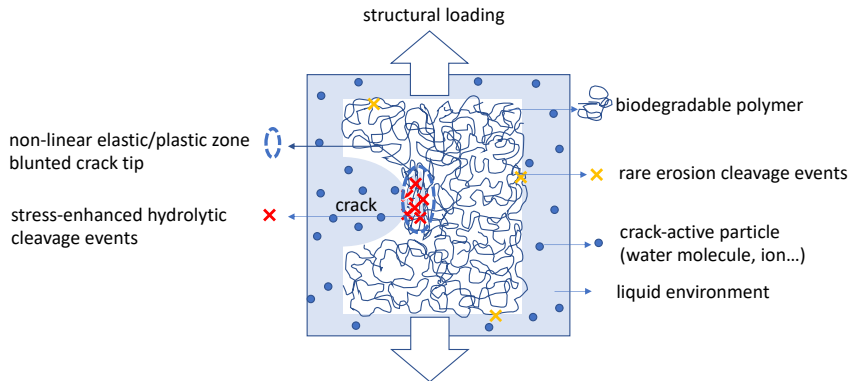


Figure 1: Schematic representation of an edge crack in a biodegradable polymer material immersed in an aqueous environment. Crack blunting makes the tip zone readily accessible to crack-active particles (water molecules themselves, ions...). The ultimate stress state may enhance hydrolytic bond cleavage through various mechanisms, overrating stress-free erosion.

hydrated networks (hydrogels), either chemically or physically cross-linked[3] — the environment-assisted fracture mechanics of bio- or bioinspired-polymer materials is an immense field which remains mostly unexplored.

Shi et al.[8] and the Suo group at Harvard University have identified and studied in great detail one of these basic environmental fracture phenomena — coined *hydrolytic embrittlement* — occurring in PLA, considered a model system for biodegradable polymers with hydrolysable bonds. They have conducted careful fracture tests on edge-notched, large molecular mass PLA films. In the air, crack growth proceeds via extensive plastic deformation ultimately limited by chain scission. The energy dissipation, dominated by plastic yield, amounts to a fracture energy of order 10^4 J.m^{-2} . When the edge-notched film is immersed in water, subcritical crack growth can be observed over a several decades of energy release rate \mathcal{G} (the driving “force” for the crack) and velocity V , indicating an underlying rate-dependent process. The role of pH on V at fixed \mathcal{G} parallels that of pH on the rate of hydrolysis of lactic acid oligomers, a strong hint that bond hydrolysis is at work. For steady state growth, \mathcal{G} equals the fracture energy dissipated by the advance of a unit crack area and falls to $1\text{--}10 \text{ J.m}^{-2}$ at low velocities. The authors interpret it convincingly as a consequence of the finite time required for hydrolysing enough bonds so as to knock-out plastic yield. A

final confirmation comes from the microscopic inspection of the fracture surfaces post-mortem: When substantial plastic deformation occurs, the surfaces are rough and porous in agreement with the free volume creation associated to plastic yield in amorphous solids. This is in contradistinction to the smooth surfaces exhibited by slow cracks, reminiscent of brittle fracture patterns observed when rupture proceeds via breaking bonds right at the crack tip. This reveals the existence of a hydrolysis-induced ductile \rightarrow brittle transition upon decreasing the crack velocity.

This stimulating work raises two questions: What is the nature of the transition and what fixes the corresponding critical velocity ? How is hydrolysis affected by the existence of the crack ? They found that during the time a cleavage would occur in vitro, the crack has time to grow by a macroscopic millimeter length. This intriguingly large value, suggesting that hydrolysis at the crack tip may be strongly exacerbated, certainly deserves further study.

Generally speaking, a surface crack adds up two reasons for being qualified a “breach” through which aggressive particles may pervade the polymer structure and jeopardize its integrity:

- (i) a crack opens an easy path for environmental fluids to invade the material
- (ii) the ultimate stress and strain state prevailing in the crack tip zone can exacerbate the cleaving reaction.

Point (i) is particularly true for cracks involving blunting, either plastic or elastic, resulting in a large crack-tip opening displacements and a process zone with free volume cavities ; among several candidates, point (ii) may be ascribed to the stress-induced lowering of the bond-breaking energy barrier. Non-covalently cross-linked (“physical”) hydrogels such as gelatin[1] and calcium-alginate[2] are highly prone to such effects. Investigating the role of solvent or ions on crack propagation has provided deep insight into the fracture mechanism itself. The work of Shi et al.[8] confirms that detailed studies of the environment-crack coupling in biodegradable or bio-derived materials is not only a matter of mapping risks of premature rupture but also a way to decipher the subcritical crack growth and degradation mechanisms so as to adopt a rational way of designing load-bearing structures in soft robotics, food science and healthcare.

Conflict of interest

The authors declare no conflict of interest or other disclosures.

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