Crack propagation in viscoelastic solids

The propagation of cracks in rubber is of fundamental importance, e.g., in rubber wear and for pressure sensitive adhesives. The strength of adhesion and cohesion of elastomers can be characterized by the energy G required to advance a fracture plane by one unit area. Experiments have shown that G depend on the crack tip velocity v and on the temperature T and that

$$G(v,T) = G_0 \left[1 + f(v,T)\right] \tag{1}$$

where $f \to 0$ as $v \to 0$. G_0 is then a threshold below which no fracture occurs. The measured value of G at extremely low crack velocities and high temperatures, when viscous effects in the rubber are minimized, is of order 1 eV/Å^2 and is denoted G_0. At high crack velocities G may be up to 10000 times higher. For simple hydrocarbon elastomers, the effect of temperature can be accounted for by applying a factor a_T to the crack velocity v, i.e., $f(v,T) = f(a_T v)$. Moreover, values of a_T determined experimentally are equal to the Williams–Landel– Ferry function determined from the T-dependence of the bulk viscoelastic modulus. This proves that the large effects of crack velocity and T on crack propagation in rubber materials are due to bulk viscoelastic processes.

The energy dissipation at a crack in a viscoelastic solid has two contributions, one associated with the innermost region at the crack tip (the so-called crack tip process zone) and involving highly non-linear processes [e.g., cavity formation, stringing, chain pull-out (for polymers), and bond breaking] and is described phenomenologically via G_0. This contribution to $G(v)$ cannot be calculated accurately and is taken as (experimentally determined) input to the theory. The second contribution comes from the viscoelastic dissipation in the polymer in the linear viscoelastic region in front of the tip. This contribution can be calculated, and we have shown that the exact form of the crack tip process zone is not important for calculating the viscoelastic contribution to G.

Classical fracture mechanics is based on continuum mechanics and predicts a stress singularity at a crack tip, $\sigma \sim r^{-1/2}$, where r is the distance from the tip. However, real materials will yield when the stress becomes sufficiently high. In an ideal brittle material such as mica, $\sigma \sim r^{-1/2}$ may hold until $r \sim a$ is of order a lattice constant a, but $\sigma \sim r^{-1/2}$ will break down at much larger distances r in most materials. The region in the vicinity of a crack tip where $\sigma \sim r^{-1/2}$ is no longer valid is called the *crack tip process zone.*

The crack propagation energy G will generally depend on the nature of the processes occurring in this zone. Since these bond-breaking processes may be highly complex, e.g., involving cavity formation and stringing, G cannot be calculated in general, but must be deduced from experimental data. Only in the limiting case of ideal brittle solids (e.g., mica) will the crack propagation energy $G \approx 2\gamma$ be nearly equal to the energy per unit area to break the bonds at the (atomically sharp) crack tip, which is known for many solids (γ is the surface energy), e.g., it can sometimes can be calculated using electronic structure methods.

The standard model used to describe the crack tip process zone is due to Barenblatt, who assumed that bond breaking at the crack tip occurs by stretching the bonds orthogonal to the crack surfaces until they break at some characteristic stress level σ_c. The process zone extends a distance a in front of the crack tip as indicated by the horizontal white line in Fig. 1(b). We introduce the cut-off in a more *ad hoc* manner, which may be roughly interpreted as a blunting of the crack tip as in Fig. 1(a). However, we have shown the details of the cut-off are unimportant, and the process zone is much more complex than assumed in the theory, see Fig. 2. The cut-off should be introduced to simplify the analytical calculations as much as possible, and for crack propagation in viscoelastic solids our cut-off procedure leads to a simple formalism.

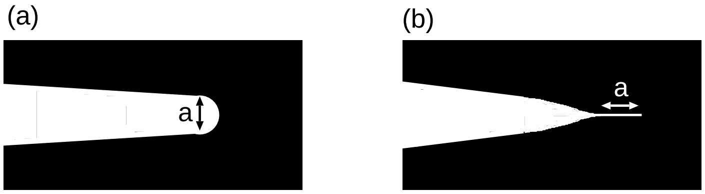

Figure 1: The singular stress region at a crack tip in continuum mechanics can be removed by (a) tip blunting (tip diameter a), or (b) by introducing a lateral region (linear size a) over which bond breaking occurs. The latter is the so-called Barenblatt process zone.

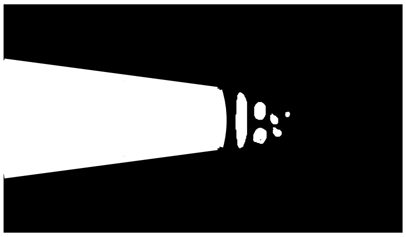

Figure 2: The crack tip process zone in most materials is very complex, involving cavity formation, stringing, chain pull-out (for polymers), and bond breaking.

In reality, G_0 will also depend on the crack tip velocity (and the temperature), albeit weaker than the factor $f(v,T)$. Thermal effects, cavity formation, stringing, chain pull-out, and bond breaking all depend on the speed with which the surfaces are separated at the crack tip and on the temperature.

Our theory shows that G has indeed the form given by (1), and it determines the function $f(v,T)$. The prefactor G_0 correspond to the energy per unit area to pull-out and break the polymer chains at the crack tip, and this energy is much larger than the surface energy of normal rubber (a few meV/$\AA^2$). In general, G_0 increases with increasing chain length, and it appears to be directly proportional to the density of interfacial bonds in measurements of the adhesive strength of partly crosslinked rubber sheets. These results are supported by simple model calculations.

Our treatment of crack propagation in viscoelastic solids can be extended to include the crack tip flash temperature, which - because of the low heat conductivity of rubber materials - is likely to be of extreme importance already at relative low crack tip velocities.