Hot cracks in rubber: origin of the giant toughness of rubber-like materials

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We study crack-propagation in rubber-like materials and show that the non-uniform temperature distribution which occurs in the vicinity of the crack tip, has a profound influence on the crack propagation, and may strongly enhance the crack propagation energy $G(v)$ for high crack velocities v. At very low crack-tip velocities, the heat produced at the crack tip can diffuse away, but already at moderate crack tip velocities a very large temperature increase occurs close to the crack tip resulting in a "hot-crack" propagation regime. The transition between the low-speed regime and the hot-crack regime is very abrupt and may result in unstable crack motion, e.g. stick-slip motion or catastrophic failure.

The invention of vulcanization by Charles Goodyear in 1839 represents one of the most important discoveries in materials science. Natural rubber is, at room temperature, a sticky substance (high-viscosity liquid) of limited technological importance. After cross-linking of the long hydrocarbon chains it forms a soft elastic solid with remarkable elastic, frictional and toughness properties, which forms the basis for most practical applications involving rubber, e.g., for tires, wiper blades, sealings and conveyor belts[1].

Rubber has one of the highest toughness of all known materials. The toughness of rubber-like materials reflects the high energy G necessary to propagate cracks[2–4]. Thus, the crack propagation energy G at crack velocities of order ~ 1 cm/s may be a million times higher than the surface energy of rubber. This shows that the classical Griffith theory[5], where G is identified with the surface energy, 2γ, of the created surfaces, is not directly valid for rubber-like materials. The strong enhancement of G is mainly due to the viscoelastic energy dissipation in front of the crack tip, which occur even at very low crack tip velocities, e.g., 1 μm/s. In this letter we will show that the heating of the rubber close to the crack tip enhances this viscoelastic energy dissipation, and may result in crack propagation instabilities.

The strength of adhesion and cohesion of elastomers can be characterized by the amount of energy G required to advance the crack tip by one unit area. Experiments have shown that G depends on the crack tip velocity v and on the temperature T and that [2–4] $G(v,T) = G_0\left[1 + f(v,T)\right]$, where $f \to 0$ as $v \to 0$. Here $f(v,T)$ describes the bulk viscoelastic energy dissipation in front of the crack tip. This term is determined by the viscoelastic modulus $E(\omega,T)$ of the rubber. The factor $G_0 = 2\gamma_0$ is due to the bond breaking at the crack tip (in the so called *crack-tip process zone*), which involves highly non-linear processes [e.g., cavity formation, stringing, chain pull-out (for polymers), and bond breaking]. This factor cannot be calculated theoretically at present, and is taken as an experimental input in the theory presented below. The strongest velocity and temperature

dependence of $G(v,T)$ is derived from the factor $f(v,T)$, which at high crack tip velocities may enhance G by a factor 10^3 or more. This contribution to G arises from bulk viscoelastic energy dissipation well ahead of the crack tip, where the stress and strain are so small that linear viscoelasticity theory should be a good approximation.

Consider a crack loaded in tension (mode I) in a viscoelastic solid. We calculate the crack propagation energy $G(v)$, which is an intrinsic material quantity that does not depend on the geometry of the sample, or how the system is loaded – in the following we focus on the simplest case of plane stress[7]. For plain stress, the crack propagation energy G is given by[8] $G = K^2/E$, where E is the elastic modulus. The stress intensity factor K is proportional to the applied stress. Let us first calculate the bulk energy dissipation per unit time and unit length of the crack line, P, for the general case of a crack propagating with velocity $\mathbf{v}$ in a linear viscoelastic solid. We have

$$P = \int d^2x \; \dot{\epsilon}_{ij}\sigma_{ij} \tag{1}$$

where σ_{ij} is the stress tensor and $\dot{\epsilon}_{ij}$ the strain rate tensor. In continuum mechanics, for a homogeneous material, the general form of the stress in the vicinity of a crack tip is independent of the detailed relation between the stress and strain (i.e., also valid for a viscoelastic material), and takes the universal form[8]

$$\sigma_{ij}(\mathbf{x},t) \approx \frac{K}{(2\pi|\mathbf{x} - \mathbf{v}t|)^{1/2}} f_{ij}(\phi). \tag{2}$$

The tensorial aspect of the stress tensor enters via the universal function $f_{ij}(\phi)$ that depends on the polar angle ϕ in the xy-plane.

Now, let us consider the energy conservation condition relevant to the crack propagation. In the present case, the elastic energy stored in the solid in front of the crack tip is dissipated at the crack tip. The flow of elastic energy into the crack is given by Gv, which must equal the fracture energy G_0v plus the bulk viscoelastic dissipation P given by (1): $Gv = G_0v + P$. Substituting (2) into (1)

and using $K^2 = GE_0$ where $E_0 = E(0, T_0)$ (where T_0 is the background temperature) gives[7]

$$\left(\frac{G}{G_0}\right)^{-1} = 1 - \frac{2}{\pi} \int_0^1 dx\, x \int_x^1 dy\, y^{-2}$$
$$\times \left(y^2 - x^2\right)^{-1/2} \operatorname{Im} \frac{E_0}{E\left(x\omega_c, T_y\right)} \qquad (3)$$

In (3) we have introduced the large cut-off wavevector $q_c = 2\pi/a$, and the corresponding large cut-off frequency $\omega_c = 2\pi v/a$, where a is taken equal to the radius of the crack tip. T_q is the temperature in the spatial region in front of the crack tip probed by the q-wavenumber contribution to the integral (3), and defined as $T_q = \int d^2x\, \Phi_q(\mathbf{x}) T(\mathbf{x})$ with $\Phi_q(\mathbf{x}) = (q/2\pi)\delta(r - 1/q)$. We have defined $q = yq_c$ and $\omega = x\omega_c$, and T_y stands for T_q with $q = yq_c$.

The radius of curvature of the crack tip a can be calculated by considering that, in order for the crack to propagate, the stress at the crack tip must be equal to some characteristic (material dependent) yield stress σ_c. Using (2), with σ replaced by σ_c and $|\mathbf{x} - \mathbf{v}t|$ by a, leads to the relation $2\pi\sigma_c^2 a = K^2$. Substituting $K^2 = GE_0 = 2\gamma_{\text{eff}} E_0$ this equation gives $\sigma_c^2 a = E_0 \gamma_{\text{eff}}/\pi$ which shows that the crack tip radius is proportional to the effective energy $G = 2\gamma_{\text{eff}}$ necessary to propagate the crack. We define a reference radius $a_0 = E_0 \gamma_0/\left(\pi\sigma_c^2\right)$, and obtain $a/a_0 = G/G_0$.

We determine T_q from the temperature field $T(\mathbf{x}, t)$ which satisfies the diffusion equation

$$\frac{\partial T}{\partial t} - D\nabla^2 T = \frac{\dot{Q}(\mathbf{x}, t)}{\rho C_V} \qquad (4)$$

where $\dot{Q} = \dot{\epsilon}_{ij}\sigma_{ij}$ is the energy production per unit volume and unit time as a result of the internal friction of the rubber. The heat diffusivity $D = \lambda/\rho C_V$, ρ is the mass density, λ the heat conductivity, and C_V the heat capacity per unit mass. For a crack moving with constant velocity $\mathbf{v}$ we have $\dot{Q}(\mathbf{x}, t) = f(\mathbf{x} - \mathbf{v}t)$, so Eq. (4) can be easily solved to get $T(\mathbf{x}, t) = T_0 + (\rho C_V)^{-1} \int d^2q\, \left(-i\mathbf{q}\cdot\mathbf{v} + Dq^2\right)^{-1} f(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{x} - \mathbf{v}t)}$, where $f(\mathbf{q})$ is the Fourier transform of $f(\mathbf{x})$. In our study we have neglected the angular dependence of the viscoelastic energy dissipation $\dot{Q}$ so that $f(\mathbf{x})$ depends only on $r = |\mathbf{x}|$. This gives[9]

$$\frac{T_y}{T_0} = 1 + \Lambda \frac{4}{\pi} \int_0^1 dx\, x \int_x^1 dz\, z^{-1/2} \operatorname{Im}\left[\frac{E_0}{E\left(\omega_c x, T_z\right)}\right]$$
$$\times \left(z^2 - x^2\right)^{-1/2} \int_0^1 dw \frac{J_0\left(w/y\right) H\left(w, z\right)}{\left(1 + \xi^2 w^2\right)^{1/2}} \qquad (5)$$

where J_0 is the zero order Bessel function and

$$H(p, q) = \begin{cases} p^{-3/2}\left[{}_2F_1\left(3/4, 3/4; 1; q^2/p^2\right)\right] & q < p \\ q^{-3/2}\left[{}_2F_1\left(3/4, 3/4; 1; p^2/q^2\right)\right] & p < q \end{cases}$$
$$\qquad (6)$$

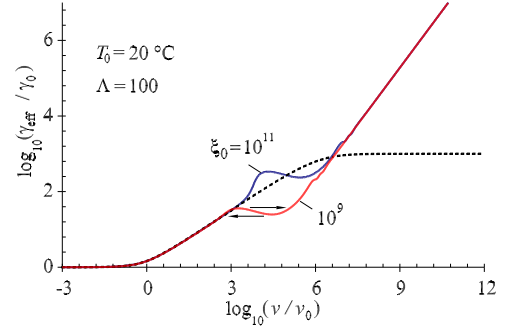
FIG. 1: The effective energy γ_{eff} to propagate the crack as a function of the crack velocity v for two different values of the dimensionless diffusivity ξ_0. The dashed line is obtained by neglecting the flash temperature effect.

where ${}_2F_1$ is the Gauss's hypergeometric function. In (5), $\xi = (a_0 v_0/av)\xi_0$ and $\Lambda = \gamma_0/(\rho a_0 C_V T_0)$ where the dimensionless diffusivity $\xi_0 = 2\pi D/(a_0 v_0)$, and where v_0 is a reference velocity. We will assume that the WLF transform[6] is valid so that $E(\omega, T) = E(\omega a_T)$, where $a_T = \exp[-8.86(T - T_g - 50)/(51.5 + T - T_g)]$, where T_g is the glass transition temperature. The WLF relationship is based on the thermally activated (free volume) theory of viscosity[10].

We assume that the rubber obeys the very simple Kelvin rheological model characterized by a single relaxation time τ. Thus, the complex elastic modulus of the rubber is $1/E(\omega, T) = 1/E_\infty + (1/E_0 - 1/E_\infty)(1 - i\omega a_T \tau)^{-1}$. In this case the reference velocity $v_0 = a_0/(2\pi\tau)$. Within the Kelvin model, $\gamma_{\text{eff}}/\gamma_0$ as a function of v/v_0 depends only on the parameters Λ, E_∞/E_0, $T_0 - T_g$ and ξ_0. Since typically $\gamma_0 \approx 30$ J/m^2, $a_0 \approx 3$ nm, $\rho \approx 10^3$ kg/m^3, $C_V \approx 10^3$ J/(kgK) and $T_0 = 20$ °C we get $\Lambda \approx 30$. In all numerical calculations presented in this paper we have used $E_\infty/E_0 = 1000$, $T_0 - T_g = 50$ K, $\Lambda = 10$ or 100, and several values for ξ_0.

Figure 1 shows the effective energy γ_{eff} to propagate the crack as a function of the crack propagation speed for $\Lambda = 100$ and for two different values of $\xi_0 = 2\pi D\tau/a_0^2$[11]. Also shown is the isothermal solution ($T \equiv T_0$; dashed line). At low crack-tip velocities the influence of the flash temperature is negligible and all three curves overlap. At higher crack velocities the effective energy γ_{eff} required to propagate the crack is non-monotonic, exhibiting a local maximum and a local minimum, which may give rise to crack propagation instabilities. As the velocity is increased further, γ_{eff} finally increases proportional to the crack speed. Note also that for the isothermal case the quantity $\gamma_{\text{eff}}/\gamma_0$ goes asymptotically to E_∞/E_0 for very high crack-tip velocities[12–17].

Figure 2 shows the effective energy γ_{eff} to propagate the crack as a function of the crack propagation speed for $\Lambda = 10$ and for different values of ξ_0. Three different regimes are shown: (i) the *low-speed* regime where
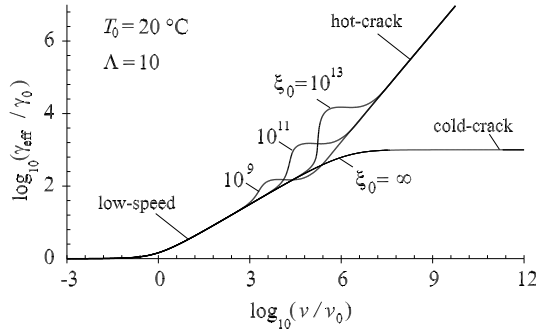
FIG. 2: The effective energy γ_{eff} to propagate the crack as a function of the crack velocity v for different values of the dimensionless diffusivity ξ_0.
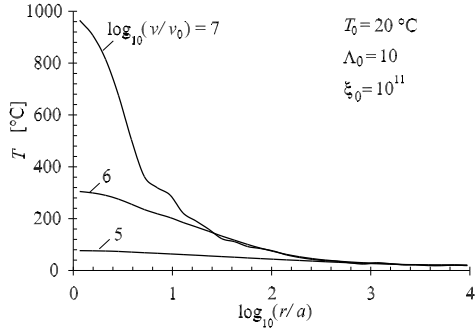

FIG. 3: The temperature profile in front of the crack tip for $\xi_0 = 10^{11}$ and for three different value of crack tip velocity. The temperature increase is significant for $r \lesssim 100a$.

FIG. 4: A qualitative picture of what happens when the flash-temperature is included in the theory. See text for details.

the increase of temperature in the rubber is negligible, (ii) the *hot-crack* regime, and (iii) the *cold-crack* regime corresponding to isothermal condition.

In Fig. 3 we show the temperature profile in the rubber, as a function of the distance from the crack tip in units of a, for different crack velocities. Notice that for large crack-tip velocities, the distance region in front of the crack tip where $T \gg T_0$ is quite large, of order $\sim 10a$.

The reason the crack propagation energy increases (for large crack tip velocities) when the crack-tip flash temperature effect is taken into account can be understood as follows. Consider a propagating crack and let us first neglect the flash temperature effect, i.e., we assume that the temperature everywhere equals the background temperature T_0 [Fig. 4(a)]. At high crack-tip velocity v, the region close to the crack tip is effectively in the glassy state, and contributes very little to the total viscoelastic energy dissipation. Similarly, the region very far away from the crack tip is effectively in the rubbery region of the viscoelastic spectra, and contributes also very little to the total energy dissipation. Most of the viscoelastic energy dissipation occurs in the transition region between the rubbery and glassy region (dark gray area in Fig. 4). Now, let us include the flash-temperature effect. Be-
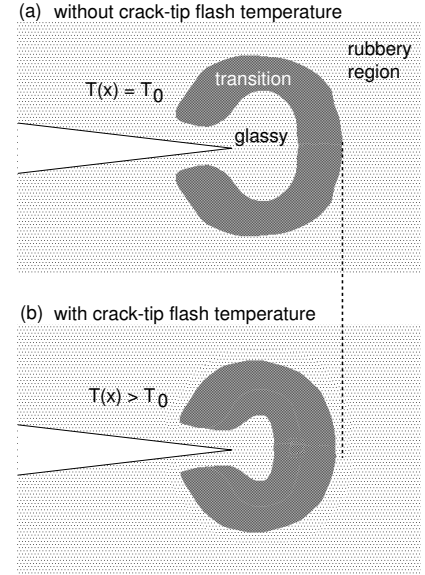
cause the crack tip moves toward the region where the viscoelastic energy dissipation occur, the temperature increase is highest close to the crack tip. Thus, part of what was the glassy region when the temperature effect was neglected, will now correspond to the transition region and will contribute strongly to the total viscoelastic energy dissipation. On the other hand, what was the outer rim of the transition region when the flash-temperature effect was neglected, will now be converted into the rubbery region, and will contribute very little to the total energy dissipation. However, since the temperature decreases monotonically with the distance from the crack tip, the reduction in the energy dissipation in the outer region is overcompensated by the increases in the energy dissipation in the inner region closer to the crack tip. The net effect is that the total energy dissipation *increases* when the flash-temperature effect is taken into account. By increasing the crack speed the dark gray region will become larger and larger until it reaches the crack tip: when this happens the crack is in the asymptotic *hot-crack* regime.

The reason for the non-monotonic behavior of the $G(v)$ relation can be understood as follows. In all cases $G(v)$ first increases and becomes larger than for the isothermal case before reaching the "flat" region. When this happens the crack tip velocity is already high enough that the rubber at the crack edge is in the glassy region, or at least on the glassy side of the transition region. Thus, the initial increase in the temperature will shift the region close to the crack tip into the middle of the transition region of the viscoelastic spectra, and $G(v)$ increases beyond the isothermal curve. However, a further increase in the velocity increases the temperature even more and shifts the region close to the crack tip toward

the rubbery side of the transition region in such a way that $G(v)$ is now nearly constant (or even decreasing). However, at very high velocities the region close to the crack tip get shifted back towards the middle of the transition region, and then it stays there for arbitrary high crack tip velocity; this is the so called hot crack regime.

The theory presented above explains why unstable crack propagation is observed [18–20]. In the transition region between the low speed regime and the hot-crack regime, a very rapid increase of crack propagation energy is first observed (see Fig. 1), followed by an almost flat region which is smoothly connected to the hot-crack regime. The overall transition region covers a velocity range of about two order of magnitude. Thus, in a displacement controlled test, as the system is loaded the crack initially moves very slowly, and when it reaches the transition region its velocity is still very small ($v < 10^{-4}$ m/s) so that its propagation cannot be easily detected. By increasing the displacement further a big amount of energy is stored in the solid, and when the flat area is reached the crack starts to propagate quite fast $v > 10^{-2}$ m/s, giving rise to the observed instability. However, the present theory cannot be used to study the detailed dynamics of the stick-slip as this involves non-uniform crack-tip motion.

The most detailed experimental study of stick-slip crack propagation in rubber was presented in Ref. [20]. They observed that when the (average) crack tip velocity is in the range $\sim 0.1 - 10$ cm/s unstable crack propagation occur. In this velocity region cracks grow at a slow or fast rate. Furthermore, the slope of the $\log G - \log v$ curve is much higher for the high-velocity branch. Both these facts are in good qualitative agreement with our analytical results (see Figs. 1 and 2). In Ref. [20] it was also found that the crack surfaces during slow crack propagation (left branch in Fig. 2) was very rough, while very smooth crack surfaces resulted when the crack propagated fast (right branch in Fig. 2). However, this change in surface morphology is not the primary reason for the two $G(v)$ crack-propagation branches, but rather a consequence of it. Thus, we believe that at high crack-tip velocities, the high temperature at the crack tip will result in a "liquid-like" region at the crack tip. This in turn will results in the formation of thin uniform layers of modified (degraded) rubber on the crack surfaces [21]. We note that it should be possible to study the temperature rise in the vicinity of the crack tip using an infrared camera with high spatial and temporal resolution.

Recent experiments[23] have detected fast crack propagation in rubber, where the crack tip velocity ~ 60 m/s is of order the rubber sound velocity. We believe that this motion is on the continuation of the cold-crack branch to higher velocities than considered in our study. When the crack velocity becomes of order the sound velocity, inertia effects can no longer be neglected, and the analysis presented above is no longer valid. Nevertheless, from
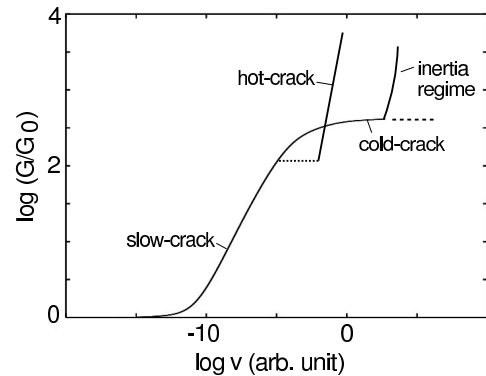

FIG. 5: Qualitative form of the relation $G(v)$

earlier theory work, one expect the crack propagation energy to rapidly increase as the crack tip velocity approach the sound velocity, and we therefore expect the complete relation between the crack propagation energy and the crack tip velocity to take the schematic form indicated in Fig. 5.

An important problem is to determine under what circumstances crack propagation will follow the hot-crack branch and the cold-crack branch. If the crack tip velocity is increased very slowly so that the temperature field around the crack tip can be fully developed, our calculations[9] show that for all physically reasonable rubber parameters, the crack will always follow the hot-crack branch. However, if the crack tip is initially accelerating very fast, there is not enough time for the full temperature distribution to develop, and in this case the system may follow the cold-crack branch. Thus, we believe that the path the system takes depends on how the crack is generated initially.

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the distance between two entanglements) $a_0 = 3$ nm gives $\xi_0 = 10^{11}$. However, the rubber relaxation time τ (and hence ξ_0) varies by many orders of magnitude between different types of rubber.

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