ACS Macro Letters

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# Fracture of Soft Foam Solids: Interplay of Visco- and Plasto-elasticity

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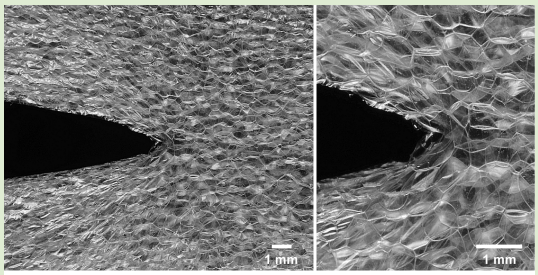
**ABSTRACT:** Fracture mechanical properties of a very soft solidified foam of polyethylene with Young's modulus about 1 MPa are studied by changing stretching velocity in a wide range, by using sheets of the material in order to suppress finite-size effects. Unexpectedly, we find that the fracture can be described well by linear elastic fracture mechanics for a given fracture rate in the wide range. This allows a direct determination of velocity-dependent fracture energy of the soft foam. As a result, we find that the fracture energy is composed of a static plastoelastic component and another dynamic viscoelastic component, elucidating a simple physical interpretation of each component and giving guiding principles useful for practical applications to reinforce industrial polymer materials. Furthermore, we introduce a finite stress criterion for fracture that is similar in spirit to the cohesive zone model and, using our data, demonstrate that this stress criterion is consistent with the Griffith's energy balance.



Crack tip in polymer foam inducing visco- & plasto-elastic failure

In nature and in daily life, there is a variety of cellular structures or foam solids, ranging from familiar ones, such as cork, balsa, bread, coral, and apples,[1] to exotic remarkable ones, such as the stereom of echinoderms,[2] the skeleton of a certain sponge,[3] and the frustules of diatoms.[4] Cellular solids are generally lightweight smart materials like spider webs[5,6] and support our life, for example, daily by their insulating or shock-absorbing features. Active studies on foam solids to date have revealed, e.g., (1) simple fracture mechanical properties that are well-understood as a function of the volume fraction of solid $\phi$[7−9] and (2) advantages of the porous structure for reinforcement.[10,11] However, experimental studies are limited to hard cellular solids with Young's modulus $E$ larger than 3000 MPa, such as poly(methyl acrylate) (PMA), rigid polyurethane (PU), and cellular glass. In addition, any velocity dependences of fracture properties of foam solids have never been discussed in a systematic way, while such an issue has received considerable attention for adhesive interface,[12−14] flexible laminates,[15] viscoelastic solids,[16,17] and weakly cross-linked gels.[18,19]

Recently, a very soft polyethylene foam with $E$ around 1 MPa has been studied, and scaling laws different from those for hard porous materials were established.[20] Here, we study the fracture energy of similar soft foams with changing fracture rate in a wide range to surprisingly find that linear elastic fracture mechanics[21,22] works well for a fixed velocity in the wide range. The velocity-dependent fracture energy is shown to be composed of a static plastoelastic component and another dynamic viscoelastic component, with the latter scaling linearly with the rate. The velocity dependence originates from that of a yield stress that is introduced through the opening distance at crack tips (Figure 1). Furthermore, we demonstrate that the Griffith criterion can be regarded as a stress criterion: we find with our data that the Griffith's energy-balance criterion[23] is equivalent to the criterion that failure occurs when a local critical stress matches a maximum force appearing at a crack tip.

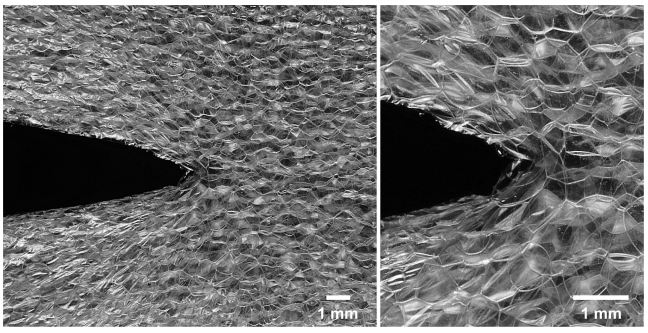


**Figure 1.** (a,b) Magnified images on a crack tip near the critical state for failure with different magnifications.

## ■ RESULTS

The foam sheet without any artificial cracks shows a quasilinear-elastic stress−strain relation for relatively small deformations for the pulling speeds of the wire in the range from $V$ = 0.1 to 1.6 mm/s, as demonstrated in Figure 2a. The relation for a given speed is well reproducible (although the breakage points slightly depend on samples): independent two representative measurements are shown to agree well with each other in Figure 2a. Young's modulus $E$ determined by the initial linear region is given as a function of the pulling velocity $V$ in Figure 2b. The velocity dependence is weak and can be expressed as $E = E_0 + \Delta E(V)$ with $E_0 \gg \Delta E(V)$ and $E_0 \simeq 1$ MPa.

The failure stress $\sigma_f$ are obtained as a function of the initial half length $a$ of a linear crack, introduced by a sharp knife, in the range from $a$ = 0.5 to 8 cm, as demonstrated in Figure 3a,b; here, each

**Received:** February 27, 2014
**Accepted:** March 27, 2014
**Published:** April 14, 2014

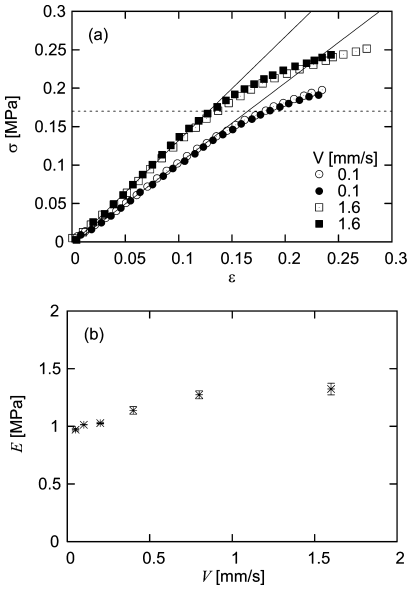



**Figure 2.** (a) Stress $\sigma$ vs strain $\varepsilon$ at velocity $V = 0.1$ and 1.6 m/s. At each velocity, two representative measurements agree well with each other, suggesting high reproducibility. Two solid lines and one horizontal line are guides for the eye, representing the initial linear regimes and the yield stress $\sigma_y$ discussed below, respectively. (b) Young's modulus $E$ vs $V$.

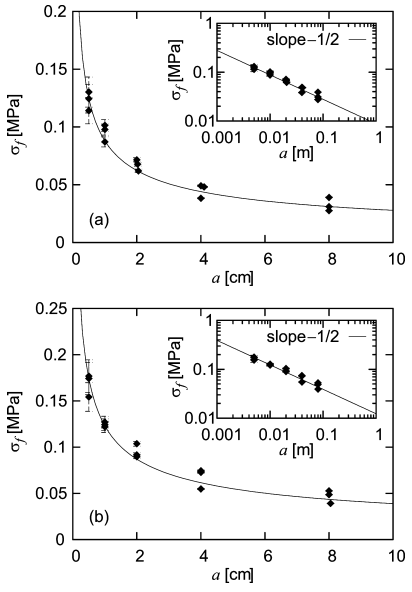



**Figure 3.** (a,b) Failure stress $\sigma_f$ vs half crack length $a$ at velocity $V = 0.1$ (a) and 1.6 mm/s (b). The insets show the same data in log scales.

data point is obtained from a single measurement, reflecting the margin for the judgment of the onset of failure as an error bar as discussed in Experimental Section; note that the error bars are rather small. The insets show remarkably that the data follow the formula of Griffith's failure stress for the plane stress condition (this condition is appropriate for thin sheets as in the present experiment), which is given by

$$\sigma_f = \left(\frac{2EG}{\pi a}\right)^{1/2} \tag{1}$$

where $G$ is the fracture energy per fracture area.

The fracture energy $G$ is determined from the measurements of $\sigma_f$ as a function of $a$ for a given $V$, as in Figure 3a,b. The results as a function of $V$ is given in Figure 4a, which shows relatively weak dependence and the dependence can be well described in the form

$$G = G_0 + \Delta G(V) \equiv G_0(1 + V/V_0) \tag{2}$$

with $G_0 \gg \Delta G(V)$, $G_0 = 128 \pm 5$ J/m$^2$, and $V_0 = 2.87 \pm 0.64$ mm/s.

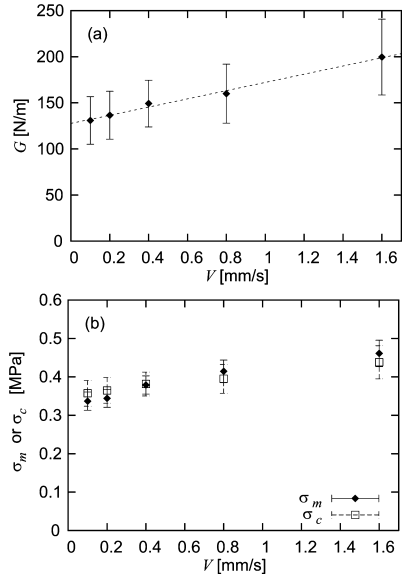



**Figure 4.** (a) Fracture energy $G$ vs $V$. (b) Agreement of local stress $\sigma_c$ and maximum stress $\sigma_m$ at the level of scaling laws in the experimental range of velocity.

## COMPARISON WITH PREVIOUS RESULTS

The Young's modulus and fracture energy obtained above are consistent with the ones obtained in ref 20, in which the same product is examined to give the values of $E$ and $G$ similar to above. In the previous work, unlike in the present experiment, the pulling velocity was not varied and limited only to one fixed value about 1 mm/s, while the $E$ and $G$ were obtained as a function of volume fraction $\phi$ for the fixed speed, establishing the simple linear relations, $E = \phi E_{LDP}$ and $G = \phi G_{LDP}$, with $E_{LDP}$ and $G_{LDP}$ Young's modulus and the fracture energy, respectively, if $\phi$ were one: $E_{LDP}$ and $G_{LDP}$ correspond to the ones for low-density polyethylene (LDP). In ref 20, the same product but with different thickness (0.5, 1, and 2 mm) was studied; the cell size, the volume fraction, and thus Young's modulus and the fracture energy were well-defined for samples in the same production lot for a given thickness but dependent on production lots.

In the present samples, an average diameter $d$ of the cells is $0.743 \pm 0.143$ mm and an average volume fraction $\phi$ is $0.0300 \pm 0.005$, which are both similar to the values obtained for the samples used in ref 20. This value of $\phi$ implies that $E_{LDP}$ and $G_{LDP}$ for the present samples ($E \simeq 1$ MPa and $G \simeq 130$ J/m$^2$) are of the order of 30 MPa and 3 kN/m$^2$; These values are reasonable for LDP.[7,24,25]

## VELOCITY DEPENDENT YOUNG'S MODULUS

The weak velocity dependence of $E$ (and the corresponding $E_{LDP}$), i.e., the slight increase of $E$ with velocity, might originate because effective cross-link points, such as entanglement points and small crystalline regions, possess different time scales for


dx.doi.org/10.1021/mz500122v | ACS Macro Lett. 2014, 3, 419−422

releasing their topological and/or geometrical constraints. When stretched slowly, many of the effective cross-links could be "unfolded", making Young's modulus smaller (see refs 18 and 26 for a similar idea). Note that the elastic modulus can be roughly estimated as the thermal energy $k_BT$ multiplied by the density of effective cross-links.

## VELOCITY DEPENDENT FRACTURE ENERGY

The static component of the fracture energy $G_0$ ($\simeq 128$ J/m$^2$) is much larger than a typical surface energy for braking chemical bonds ($\simeq 1$ J/m$^2$). In linear elastoplastic fracture mechanics, it is well established that the fracture energy is expressed as $\sigma_y\delta$, with $\sigma_y$ the yield stress and $\delta$ the crack opening distance.[21,22] As seen in Figure 1, $\delta$ in the present case seems comparable to a typical foam size $d$ ($\simeq 0.743$ mm), i.e., $\delta \simeq d$. This implies $\sigma_y \simeq 0.17$ MPa for the foams, giving a yield stress $\sigma_{y,LDP} = \sigma_y/\phi \simeq 5.7$ MPa for the corresponding LDP; this is a plausible value for LDP,[7,24,25] suggesting that the static competent $G_0$ has basically an elastoplastic origin: $G_0 \simeq \sigma_y\delta$. It is quite interesting that the stress−strain plots in Figure 2a deviate from the initial linear regime around at the above-introduced yield stress of foam $\sigma_y \simeq 0.17$ MPa.

On the contrary, the dynamic component $G_0V/V_0$, linearly dependent on the velocity $V$ can be interpreted as a viscous effect. If we introduce an effective viscosity $\eta$, corresponding to viscous flow in samples induced by a finite pulling speed, a characteristic viscous stress is estimated as $\eta V/d$. Here, we assume the region of the flow is limited to a dimension comparable to the cell size $d$ ($\simeq \delta$) near the tip where the stress is significantly concentrated. This assumption is plausible from the magnified views around the crack tip in Figure 1. It is natural that this extra viscous component is added to the static yield stress $\sigma_y$: $\Delta G \simeq \eta(V/d)\delta$, which results in $V_0 \simeq (G_0/\eta)d/\delta$. From this expression, the effective viscosity of the foam is estimated as $\eta \simeq 0.04$ MPa·s, which suggests a viscosity of the corresponding LDP: $\eta_{LDP} \simeq \eta/\phi \simeq 1.5$ MPa·s. Considering that typical glass transition temperatures $T_g$ of LDP are far below ambient temperatures ($T_g \simeq -20$ to $-120$ °C), viscosity of the foam can be very roughly estimated by the reptation model,[27] in which viscosity of entangled polymer is predicted as $\eta_{LDP} \simeq \eta_{mon}N^3/N_e^2$ with $N$ the number of monomers, $N_e$ ($\simeq$100) the entanglement distance, and $\eta_{mon}$ ($\simeq 1$ mPa·s) the viscosity of monomers. This crude estimation implies a plausible value $N \simeq 10^4$.

In summary, the fracture energy can be expressed as

$$G \simeq \tilde{\sigma}_y\delta \tag{3}$$

where $\tilde{\sigma}_y = \sigma_y + \eta V/d = \phi(\sigma_{y,LDP} + \eta_{LDP}V/d)$. Namely, the velocity-dependent yield stress $\tilde{\sigma}_y$ is given as the sum of the static (plastoelastic) and dynamic (viscoelastic) components.

Equation 3 leads to a number of simple guiding principles for toughening soft foams. For the reinforcement, it is advantageous to make (1) $N$ larger, which leads to the increase in $\eta$, thus the increase in $\Delta G$, (2) $d$ larger, which leads to increase in $\delta$, thus the increase in $G_0$, (3) $\phi$ larger, which leads to increase in $G$. Among them, (1) may be the most efficient because $\eta$ strongly depends on $N$ ($\eta \sim N^3$) and (1) is also effective for the reinforcement of the corresponding LDP, or other polymer solids, in general: polymer materials can efficiently be reinforced for fracture at finite rates by increasing $N$. In addition, (2) and (3) could be applicable for other soft solidified foams.

## STRESS CRITERION FOR FAILURE AND GRIFFITH'S ENERGY BALANCE

Following the idea of Griffith's flaws, materials without any macroscopic cracks start to fail at certain defects that play the role of small cracks. On the basis of this idea, a critical failure stress $\sigma_c$ for the present foams can be defined as

$$\sigma_c \simeq (EG/d)^{1/2} \tag{4}$$

by regarding the crack size $a$ in eq 1 with the cell size $d$.

On the other hand, the maximum stress $\sigma_m$ appearing at a crack tip can be estimated as follows. In linear elastic fracture mechanics, the stress $\sigma(r)$ near a tip of a crack of size $a$ is concentrated compared with a remotely applied stress $\sigma_0$ as $\sigma(r) \simeq \sigma_0(a/r)^{1/2}$, with $r$ the distance from the crack tip. This stress mathematically diverges at the tip, i.e., $r = 0$. However, this divergence is fictitious and the valid range of $r$ should actually be cutoff at a certain small length scale $r_c$, below which the continuum description breaks down. The cutoff stress $\sigma(r_c)$ has been shown to scale as the maximum stress appearing at a crack tip.[10,11,28−30] In the present case, the cutoff scale $r_c$ should be the cell size $d$, which gives

$$\sigma_m \simeq \sigma_0(a/d)^{1/2} \tag{5}$$

A plausible stress criterion for failure defined from the two stresses is $\sigma_c \simeq \sigma_m$: failure occurs when the maximum stress at a crack tip reaches the critical stress. When this stress criterion is solved for $\sigma_0$, which should be here identified with a failure stress $\sigma_f^*$ defined via the stress criterion, we obtain $\sigma_f^* \simeq (EG/a)^{1/2}$, which is nothing but the Griffith's failure formula in eq 1, conventionally obtained as a result of energy balance. The present arguments suggest that Griffith's energy balance can be viewed as a stress criterion if critical failure stress and the maximum crack-tip stress are properly introduced, while the energy-balance criterion and a stress criterion for failure are often considered as different and independent concepts. We stress here that the finite stress model introduced here is largely consistent with a well-accepted cohesive zone or strip yield model that has been widely used to describe a broad range of similar problems.[21,22,31,32]

In fact, we can check with our data, for a given velocity, that the above stress criterion actually holds, while our data are consistent with the Griffith criterion (i.e., the data can be described by eq 1). To show this, we determine $\sigma_c$ and the critical value of $\sigma_m$ on the basis of eqs 4 and 5 with assuming the numerical coefficients 1 and 0.705, respectively, by using experimental values of $E$, $G$, $d$, and $\sigma_f$ (the critical value of $\sigma_m$ is estimated as an average over $a$ by setting $\sigma_0$ to $\sigma_f$). As a result, the two stresses $\sigma_c$ and $\sigma_m$ thus obtained agree well with each other over the full range of $V$ examined in the present study, as shown in Figure 4b. This establishes that the stress criterion holds for the data at the level of scaling laws.

## CONCLUSION

We have shown that the velocity-dependent fracture energy for a soft solidified foam is composed of plastoelastic and viscoelastic components. We thereby provide a simple scenario for fundamental understanding of velocity-dependent fractures of polymer foams. In principle, the scenario may be applicable to other polymer foams and polymer solids. The idea of effective viscosity could be useful in understanding the physics of polymer dynamics in various contexts, such as viscoelastic and/or plastoelastic phenomena, which include crazing,[26] adhe-


dx.doi.org/10.1021/mz500122v | ACS Macro Lett. 2014, 3, 419−422

sion,[12−17] and fracture.[18,19] In addition, we demonstrated that the Griffith's energy-balance can be viewed as a stress criterion, introducing a finite stress model similar in spirit to the cohesive zone model. This criterion is actually a generalized version of the one employed in ref 33. Furthermore, our results are useful for applications: we provided a number of simple guiding principles for toughening soft foams. Some of the principles are universal and can be applied to the reinforcement of other soft solidified foams, LDP, and other polymer solids, in general. We thereby envision that the present results would contribute significantly to our understanding of physics of polymers and fracture of materials, providing simple and practical principles for the reinforcement of industrial polymer materials.

## EXPERIMENTAL SECTION

We examined a commercially available shock-absorbing sheet for packing, Lightron S no. 52 (Sekisuiplastics), of thickness 1 mm. The milk-white soft sheets suitable for wrapping fragile things such as porcelain are a closed-cell foam of solidified non-cross-linked polyethylene (see Figure 1). Unlike usual foams,[7] volume collected at the edges of cells is less than or comparable to the volume of the wall of cells. The foam sheets are anisotropic: they are slightly wavy when not stretched as a result of the manufacturing process. In the present experiment, the tensile force is always applied in the direction perpendicular to the wavy texture.

To minimize finite-size corrections, we developed a fracture measurement system that can hold a sheet of width and height both about 50 cm, which are much larger than the thickness (1 mm). A sample sheet that is clamped by two aluminum plates of 1 m long is homogeneously stretched in the direction perpendicular to the long plates through a wire connected to a digital force gauge (FCC-50B, NIDEC-Shimpo) that is mounted on an automatic slider system (EZSM 6D040 K, Oriental Motor). The stretching speed $V$ is changed well over 1 order of magnitude, from 0.1 to 1.6 mm/s. The stretched length is monitored by a laser distance censor (ZX0-LD300A61, OMRON) synchronized with the force measurement by the force gauge. The critical state of failure is judged by the eye with a margin ($\simeq$ 1 mm) that is reflected as error bars in the data; see Figure 1 for magnified views of a crack tip near the critical state. The measurements were performed at ambient temperatures in the duration from February to April, 2013, at our university.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was partly supported by Grant-in-Aid for Scientific Research (A) (no. 24244066) of JSPS, Japan, and by Grant-in-Aid for Scientific Research on Innovative Areas, "Fusion Materials (area no. 2206)," of MEXT, Japan.

## REFERENCES

(1) Khan, A.; Vincent, J. *J. Texture Stud.* **1996**, *27*, 143−157.
(2) Emlet, R. *Biol. Bull.* **1982**, *163*, 264−275.
(3) Aizenberg, J.; Weaver, J.; Thanawala, M.; Sundar, V.; Morse, D.; Fratzl, P. *Science* **2005**, *309*, 275−278.
(4) Hamm, C. E.; Merkel, R.; Springer, O.; Jurkojc, P.; Maier, C.; Prechtel, K.; Smetacek, V. *Nature* **2003**, *421*, 841−843.
(5) Aoyanagi, Y.; Okumura, K. *Phys. Rev. Lett.* **2010**, *104*, 038102.
(6) Cranford, S.; Tarakanova, A.; Pugno, N.; Buehler, M. *Nature* **2012**, *482*, 72−76.
(7) Gibson, L. J.; Ashby, M. F. *Cellular Solids: Structure and Properties*; Cambridge University Press: Cambridge, U.K.1999.
(8) Ashby, M. *Philos. Trans. R. Soc., A* **2006**, *364*, 15−30.
(9) Gibson, L. J. *J. R. Soc. Interface* **2012**, *9*, 2749−2766.
(10) Murano, M.; Okumura, K. *J. Phys. Soc. Jpn.* **2014**, *83*, 035001:1−2.
(11) OkumuraK. Simple models of tough and strong biocomposites: from nacre to spider webs. 2014; *Soft Matter*, under revision (invited review).
(12) Gent, A.; Schultz, J. *J. Adhes.* **1972**, *3*, 281−294.
(13) Chaudhury, M. K. *J. Phys. Chem., B* **1999**, *103*, 6562−6566.
(14) Morishita, Y.; Morita, H.; Kaneko, D.; Doi, M. *Langmuir* **2008**, *24*, 14059−14065.
(15) Kinloch, A.; Lau, C.; Williams, J. *Int. J. Fract.* **1994**, *66*, 45−70.
(16) Greenwood, J.; Johnson, K. *Philos. Mag., A* **1981**, *43*, 697−711.
(17) Schapery, R. *Int. J. Fract.* **1975**, *11*, 141−159.
(18) de Gennes, P. *C. R. Acad. Sci. Paris* **1988**, *307*, 1949.
(19) Saulnier, F.; Ondarcuhu, T.; Aradian, A.; Raphaël, E. *Macromolecules* **2004**, *37*, 1067−1075.
(20) Shiina, Y.; Hamamoto, Y.; Okumura, K. *Europhys. Lett.* **2006**, *76*, 588−594.
(21) Anderson, T. *Fracture Mechanics*, 2nd ed.; CRC Press: Boca Raton, FL, 1995.
(22) Lawn, B. *Fracture of Brittle Solids*, 2nd ed.; Cambridge University Press: Cambridge, 1998.
(23) Griffith, A. A. *Philos. Trans. R. Soc. London, Ser. A* **1920**, *221*, 163.
(24) Williams, J. G. *Fracture mechanics of polymers*; E. Horwood: 1984.
(25) Tonyali, K.; Rogers, C. E.; Brown, H. R. *Polymer* **1987**, *28*, 1472−1477.
(26) de Gennes, P. G. *Soft Interfaces: The 1994 Dirac Memorial Lecture*; Cambridge University Press: Cambridge, U.K., 2005.
(27) De Gennes, P. G. *Scaling concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(28) Nakagawa, S.; Okumura, K. *J. Phys. Soc. Jpn.* **2007**, *76*, 4801.
(29) Aoyanagi, Y.; Okumura, K. *J. Phys. Soc. Jpn.* **2009**, *78*, 034402.
(30) Hamamoto, Y.; Okumura, K. *Adv. Eng. Mater.* **2013**, *15*, 522−528.
(31) Barenblatt, G. I. *Advances in Applied Mechanics* **1962**, *7*, 55−129.
(32) Dugdale, D. *J. Mech. Phys. Solids* **1960**, *8*, 100−104.
(33) Okumura, K.; DeGennes, P. G. *Eur. J. Phys. E* **2001**, *4*, 121−127.