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Surface stress can initiate environment-assisted fracture in metals

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Abstract

Controlling environmental effects in surface plasticity/fracture of metals is of interest for areas as diverse as manufacturing processes, product performance and structural safety. The key to controlling these effects is understanding the effect of adsorbates on surface energy (γ) and surface stress (f). While γ has been well studied, the role of surface stress has received much less attention. We characterize surface stress induced in metals by adsorption of organic monolayers. Linear alkanoic acids of varying chain length (3 to 18) are deposited by molecular self-assembly onto one side of an aluminum cantilever, several centimeters in length. The surface stress is estimated from *in situ* measurement of the cantilever deflection. We find that the organic adsorbates induce large surface stress of -4 to $+30$ N/m. Furthermore, we show that f may be tuned by varying adsorbate-molecule chain length. The stress data explain beneficial embrittlement of metal surfaces by organic adsorbates in cutting and comminution processes; and point to a critical role, hitherto ignored, for f in environment assisted cracking (EAC) phenomena. Our results suggest opportunities for utilizing controlled environment-assisted fracture as an aid – fracture as a friend – to enhance material removal processes, apart from using surface stress itself as an experimental probe to explore various manifestations of EAC.

Introduction

Understanding chemical effects on surface plasticity and fracture in metals is of vital importance for ensuring the safety of engineering systems exposed to ambient environments [1, 2]. Less well-recognized is that this understanding can also be valuable for utilizing chemical effects in a controlled positive way: to improve the efficiency of machining and comminution processes [3], or to develop altogether new surface generation routes by increasing the propensity of a metal to fracture. In the latter category, are examples such as the Rehbinder effect in material removal processes [3, 4]; and the recently reported organic monolayer embrittlement (OME) in cutting of metals (see [5]) [6]. It is the "fracture as a friend" concept [4, 7] that motivated the present study.

While the phenomenology of environment effects in metal plasticity and fracture has been extensively studied, the underlying mechanisms are still far from clear. A somewhat common theme in the proposed mechanisms is that molecules from the ambient medium "weaken" the atomic bonds at crack tips making it easier for surface cracks to propagate [1]. In the language of continuum fracture mechanics, this involves lowering of the surface energy (γ) of the material in the vicinity of the crack by molecule adsorption, making it easier to create new surfaces. A change in dislocation activity at the surface is another consequence, promoting plasticity in some instances and fracture in other cases [2, 8].

Several outstanding questions pertaining to these effects are, however, difficult to answer within this framework of adsorbate-induced changes in γ. For example, it is nearly impossible to justify how lowering of γ by adsorbates can be drastic enough to render a ductile metal completely brittle, as in environment assisted cracking (EAC) phenomena [6, 9–12]. Explaining the well-known specificity of the damaging environment in EAC is also a challenge [1, 4, 9]. Then there is the general observation that metallic materials, among the most resistant to uniform corrosion, are particularly susceptible to stress corrosion cracking, contrary to expectation.

Given these open questions, it becomes important to consider the role of the other key surface thermodynamic parameter, viz. surface stress (f), in influencing surface plasticity and fracture. As was pointed out by Gibbs nearly 150 years ago [13, 14], the solid surface is characterized by two distinct thermodynamic parameters – γ and f (see [5]) [15–18]. While γ has figured prominently in

analysis of fracture, dating back to Griffith [1], the role of f has been less visible. This is surprising given that surface residual stress (though different from f) is known to strongly influence fracture, dating back even to early observations with Prince Rupert's drops [19].

With regard to EAC, Oriani [20] made the important suggestion that a change in f, rather than γ, due to adsorption of chemical species could cause embrittlement. Following this, there have been some inconclusive theoretical speculations on the role of surface stress in fracture [21–23]. Compelling evidence for the role of surface stress in disrupting surface plasticity and triggering fracture has emerged from recent experimental work with self-assembled organic monolayers (SAMs) in simple shear deformation (cutting) of ductile metals such as Al, Cu, Ta - an example of organic monolayer embrittlement (OME) (see [5]) [6, 12]. In the experiments, organic monolayers with different chain lengths (l_c), but similar in all other respects (e.g., same molecule groups at either ends of the chain), were deposited onto the metal surface before imposing the shear deformation. This ensured that the bonding between the various SAMs and the metal substrate, which is determined by the head group, remained the same. As a result, the surface energy/interface energy remained a constant across the various SAMs, a fact confirmed by measurements [6] and calculations [12]. Thus l_c was the only parameter that was varied in these experiments. The bare (uncoated) Al substrate showed significant plasticity under the imposed simple shear, with large deformation forces. Similar observations were also recorded with the Al substrates containing short chain SAMs. The intriguing aspect of the phenomenon was that Al substrates containing molecules with (carbon) chain length (l_c) > 7 were embrittled. Specifically, deformation of the workpiece with the long chain adsorbates caused repeated crack formation and propagation from the metal surface and much less plastic straining (see [5]) despite the surface/interface energy of the film-substrate system not being dependent on l_c in any way [6,12] (Note surface energy changes often play a major role in fracture *á la* Griffith). Furthermore, the deformation force decreased by as much as 80% compared to the bare and short-chain cases. This phenomenon is referred to as the OME, and the deformation transition from plasticity to quasi-periodic fracture as a ductile to brittle transition. Having thus eliminated surface energy as the driver for the embrittlement, surface stress is left as the only remaining surface thermodynamic parameter that might be influ-

enced by the chain length. Hence we hypothesize that it is the surface stress that is responsible for the fracture/embrittlement.

To explore this surface-stress based fracture hypothesis, it is necessary to obtain accurate measurements of f induced in the metal by the SAM adsorbates, and to characterize the effect of l_c on f. This would also help understand whether f can play a significant role in influencing the broader class of EAC phenomena, especially since most metal systems used in service are typically exposed to adsorbate films.

The scarcity of surface stress data from large metal samples may explain why f has received less than adequate attention in environmental effects on plasticity. Absolute values of f can be obtained via measurements of (surface) lattice spacing [24, 25], or via the elastocapillary effect for soft materials [26, 27] or through atomistic calculations [28]. However, for environment-induced effects, the change in f caused by species adsorption onto the substrate is the relevant parameter. With organic adsorbates, this stress change (also denoted f) has usually been estimated by coating one side of an AFM microcantilever with the species of interest and measuring the deflection induced [29, 30]. However, the reported stress values, and molecule chain length effects if any, are at complete variance with each other [29, 31, 32]. Perhaps, because of this large variability, f as a physical quantity has been insufficiently explored. This is especially true with materials distinct from Si/Au/SiN typically used with AFM tips.

In this study, we present accurate measurements of adsorbate-induced surface stress in commercially pure Al – a system of practical interest [6, 12] – using large-area cantilever samples. Alkanoic acid SAMs of different chain lengths (l_c) are used as the adsorbates. This system also provides a framework for exploring l_c effects on f, since γ as a variable is largely eliminated by keeping the SAM end groups unaltered. The organic monolayers are shown to induce large f, both tensile and compressive. A strong dependence of f on l_c is noted, providing a direct means for controlling (tuning) f. This opens opportunities for studying both EAC, and new chemically assisted manufacturing processes that utilize controlled fracture.

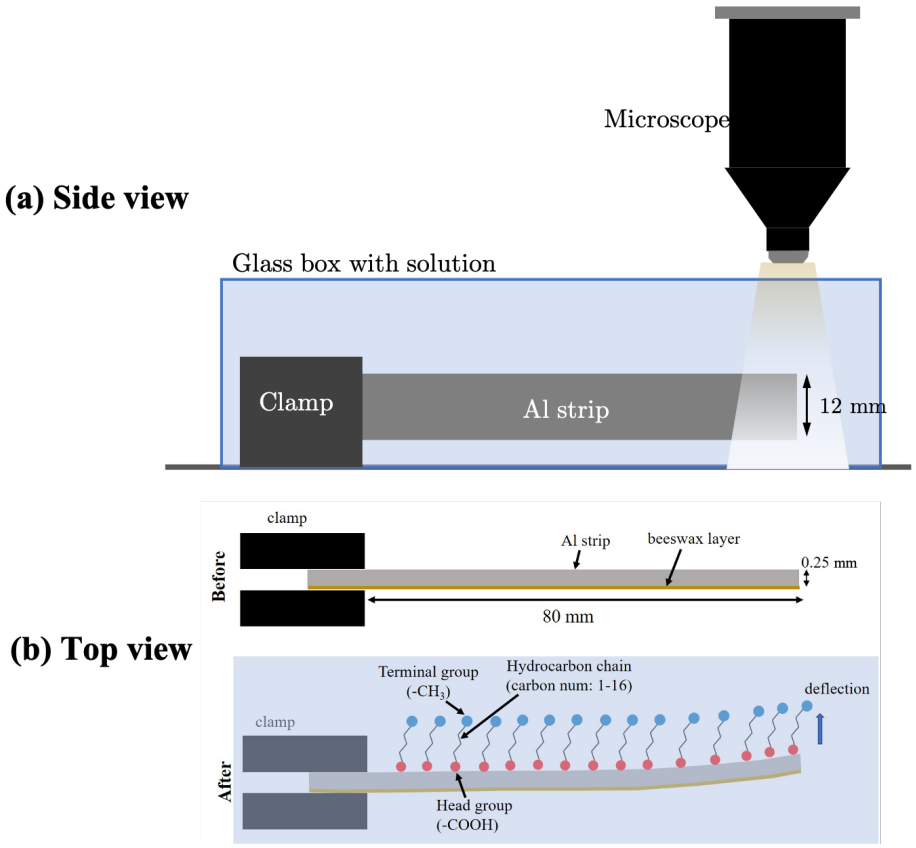


Figure 1: Schematic of macroscale cantilever setup used for surface stress measurement (a) side and (b) top view, before and after adsorbed layer forms. The Al strip is 80 mm (cantilever length) $\times$ 12 mm width $\times$ 0.25 mm thickness. One of the 80 $\times$ 12 mm surfaces is coated with wax (mask) before immersion into the solution containing the SAM molecules. Upon immersion, a monolayer adsorbs on to the second 80 $\times$ 12 mm (uncoated) surface. The resultant unbalanced f causes the strip to deflect. The adsorbate molecules are shown with head group (red), terminal group (blue) and intermediate hydrocarbon chain. Note that only the tip ($\sim$1.5 mm) of the 80 mm long cantilever is imaged by the microscope to measure the deflection.

Results

Figure 1 and **Fig. S1** show the experimental setup for surface-stress measurement. The cantilever system consists of an Al 1100 strip (0.25 mm $\times$ 12 mm $\times$ length 80 mm) clamped at one end in a vise. One surface of the cantilever, 80 mm $\times$ 12mm, is coated with a thin ($\sim$25 μm) layer of beeswax to prevent adsorption of any media (the wax coating has negligible effect on cantilever stiffness because of its very low Young's modulus, see [5]). The wax-coated strip and vise are then placed in a transparent glass box containing 1 mM solution of the desired organic molecule (adsorbate) in ethanol. The molecules adsorb onto the opposite wax-free (80 mm $\times$ 12 mm) surface forming SAMs [33, 34]. Due to chemical interactions between the molecules and the Al, and the molecules themselves, a surface stress is induced on the adsorbing surface, causing the cantilever

to deflect. This deflection (Δh) of the cantilever-tip is measured continuously using an optical microscope, with images recorded every 30 s. The time-history of the deflection is obtained from the image sequences, with spatial resolution of 1.5 μm per pixel. f is estimated from the measured Δh using Stoney's equation (eq. (1)) [35] as:

$$f = \frac{Et^2}{4(1-\nu)} \cdot \frac{\Delta h}{L^2} \tag{1}$$

where E and ν are Young's modulus and Poisson's ratio of Al, respectively (see [5]); and t is the beam thickness. If the cantilever deflects such that the adsorbate is on the concave side, then f is tensile (positive); else, it is compressive (negative).

The stress measurement was done for straight-chain alkanoic acids with different l_c of 2, 3, 6, 12 and 18, see **Fig. 2**. The molecules in this family adsorb such that the –COOH head group dissociates, resulting in a carboxylate group that forms an ionic bond with the native oxide layer on the Al surface [33,36]. The free dangling (terminal) end of the molecules in all cases is $–CH_3$. The molecule itself stands at a tilt angle (θ) to the surface, characteristic of the adsorbate-adsorbent system. l_c is the only attribute that is different among the SAMs studied: 2 for acetic acid, 3 for propionic acid, 6 for hexanoic acid, 12 for dodecanoic acid and 18 for stearic acid.

SAM adsorption onto the Al surface was verified by Fourier Transform Infrared Spectroscopy (FTIR) and ellipsometry of the molecular film at select locations along the cantilever length. **Figure 2(a)** shows FTIR analysis of the Al strip surface exposed to the alkanoic acids for 6 h, and for the bare surface, see [5]. With the SAMs, there are distinct peaks in the 2800-3000 cm^{-1} range indicative of C–C bonds and the C–O bonds, confirming uniform adsorption. To ensure that the adsorbed film is a monolayer, we measured SAM thickness at several locations along the cantilever length using spectroscopic reflectometry (see [5]). **Figure 2(b)** (right axis, red curve) shows the film thickness, increasing nearly linearly with l_c, from $\sim$ 5 Å for $l_c = 3$, to $\sim$ 25 Å for $l_c = 18$. This thickness in each case correlated well with the molecule size indicating that the film is indeed a monolayer. Further confirmation of the adsorbed layer was obtained from contact angle measurements for a water droplet on the Al surface (with/without adsorbate), see **Fig. 2(b)** (left axis, black curve). The contact angle is determined primarily by the SAM terminal group ($–CH_3$in

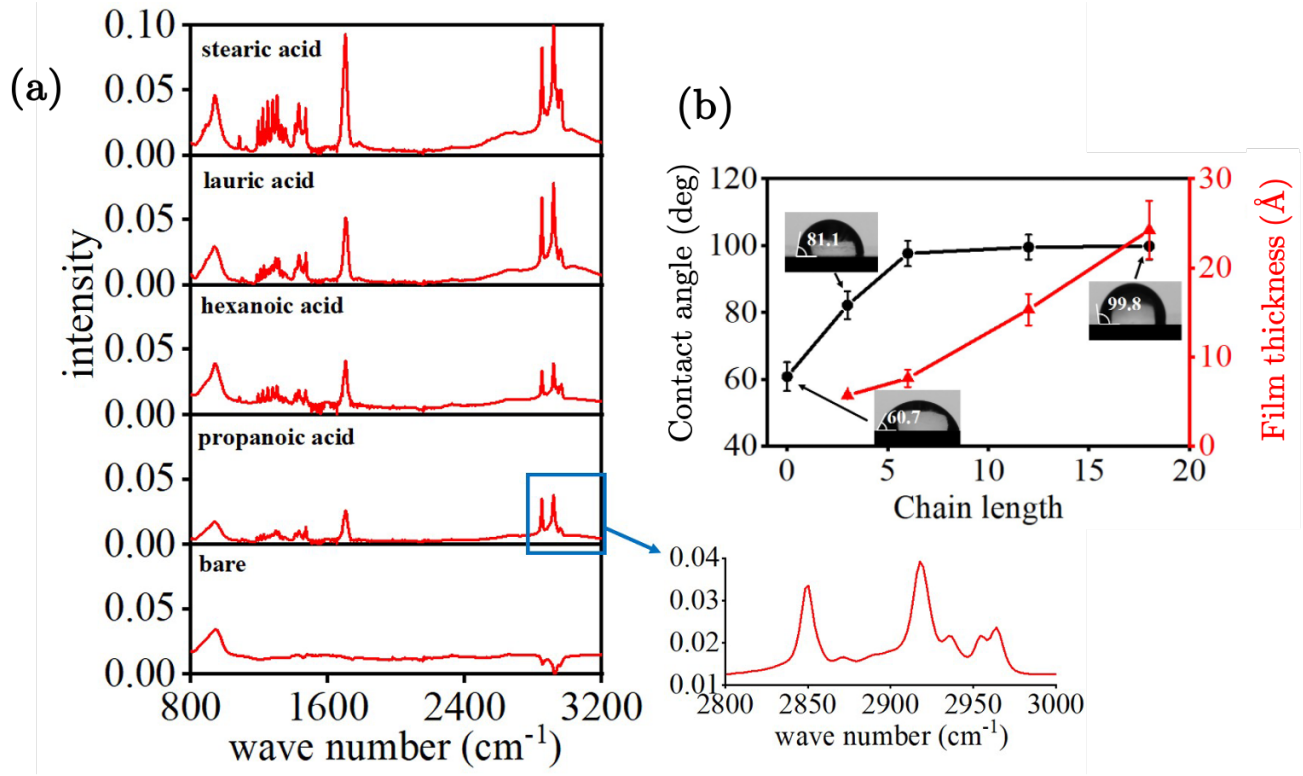


Figure 2: Adsorbed monolayer characterized by (a) FTIR analysis and (b) contact angle/film-thickness measurements.

our case). It is seen to change from $\sim 68°$, for the bare Al, to $\sim$100°once a SAM is fully adsorbed. The contact angle is relatively independent of l_c.

Having established that a monolayer is adsorbing, we analyzed the tip-displacement in the image sequences. See [5] for discussion of control experiments. **Figure 3** shows two image sequences, with stearic acid ($l_c = 18$), over a 360-minute adsorption duration. The top row is for a 0.25 mm thickness beam, while the bottom row is for a 0.125 mm beam. Δh was obtained by tracking the position of a specific point on the beam. The Δh is seen to be quite large; for example, after 360 minutes of adsorption, it is $\sim$150 μm for the 0.25 mm strip, and upward indicative of a tensile f. Also, as expected, the Δh for the thinner beam is much larger. Because of certain experimental difficulties associated with consistent preparation of the 0.125 mm samples, the stress measurements were pursued only with the thicker 0.25 mm strips.

Figure 4 shows the variation of Δh with time for the SAMs. The points represent measured Δh, while the curves are fits representing Langmuir adsorption (see eq. (2) in ensuing). A monotonic increase in Δh with time to a steady-state (equilibrium) value is seen in all cases. The

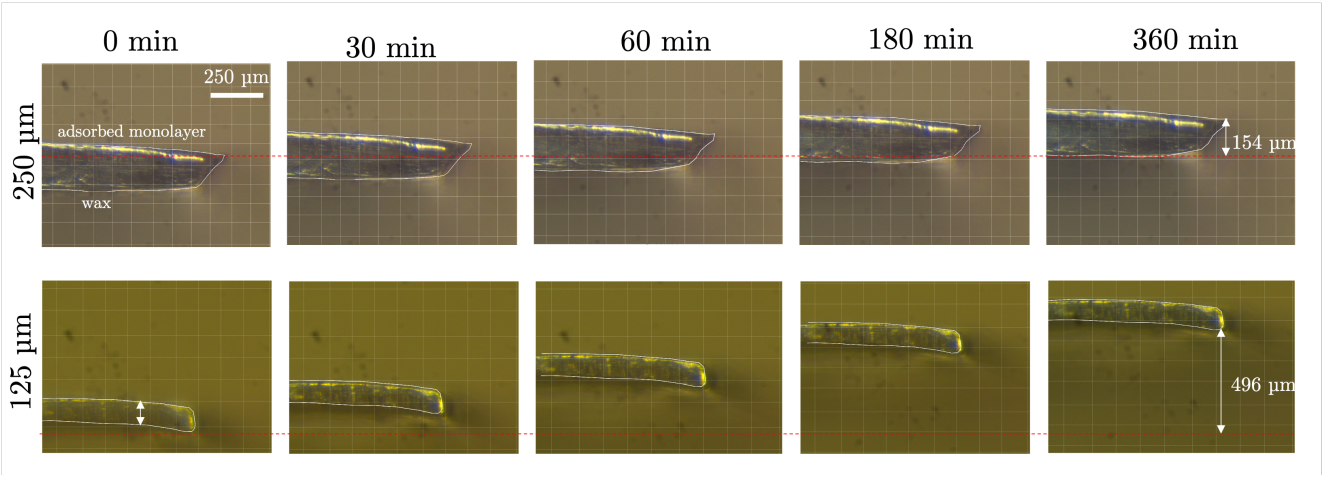


Figure 3: *In situ* images of deflection (Δh) of tip region of Al cantilever at various times during the adsorption (stearic acid, $l_c = 18$). Top sequence is for strip with $t = 0.25$ mm, and bottom sequence is for $t = 0.125$ mm.

equilibrium Δh is -16 μm for $l_c = 2$, $+10$ μm for $l_c = 3$ and ~ 145 μm for $l_c = 18$. The negative (downward) Δh for $l_c = 2$ indicates a compressive f. For all the other SAMs, the tip deflection is upward, indicating tensile f. To our knowledge, this is the first demonstration of a macroscopic deflection, tens of micrometers in extent, induced merely by organic monolayer adsorption on a metal surface – a truly nanoscale deformation phenomenon. The large Δh imply that although monolayer adsorption occurs at the nanometer length scale, its effects are certainly manifest at the macroscale.

The experiments were repeated 5 times with each SAM molecule to quantify the fidelity of the measurements (see [5]). While the variance in Δh shows some increase with l_c, it is within 15% of the equilibrium value in all cases (**Fig. 4**). Possible sources of errors are uncertainities in the various quantities in eq. (1). Particularly, uncertainties in thickness of the cantilever will double the uncertainty in the stress measurements. Measurements indicate that the uncertainty in the thickness is within 1%. Hence, it contributes at most to $\sim$ 2% of the uncertainty in the stress measurements.

Using the measured Δh and eq. (1), the surface stress induced by the SAMs was estimated (**Figure 5**). The f is compressive for $l_c = 2$, and tensile with the other adsorbates. It increases monotonically with chain length, from a value of -4 N/m for $l_c = 2$ to $+38$ N/m for $l_c = 18$. Various other measurements, including with multilayer films, suggest that the latter f is a saturation limit. For $l_c \geq 6$, the f is > 15 N/m. These are the largest f due to organic monolayer adsorbates

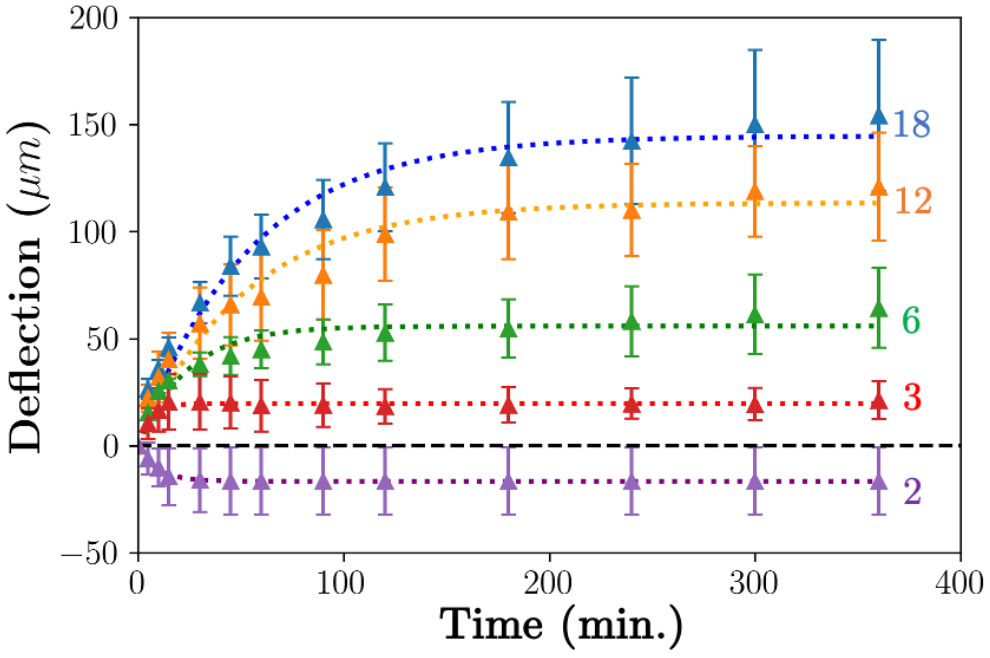


Figure 4: Variation of Δh with time (min) and chain length (l_c). The curve fits correspond to adsorption growth curves (eq. (2)).

reported to date. Both continuum and atomistic analyses suggest that when metal surfaces are subject to surface stresses akin to those measured here, the emission of dislocations from a crack tip (with crack blunting) is less preferred than brittle crack propagation á la Griffith – a local embrittlement [6, 21, 37].

The time-history of Δh in **Figure 4** contains information about the adsorption kinetics, and evolution of f (via a scaling constant eq. (2)). The kinetics in the case of non-interacting adsorbates is usually proportional to the number of available sites, following a Langmuir growth curve [38]:

$$\frac{d\Theta}{dt} = \frac{1}{\tau}(1 - \Theta) \tag{2}$$

where Θ is the fraction of (adsorbate) occupied sites, and τ is an adsorption time constant. Solution of eq. (2) gives $\Theta = A(1-\exp(-t/\tau))$, the evolution of sites occupied by the adsorbate. The curves in **Fig. 4** are least-squares fits of the deflection data for this solution, from which an estimate of τ is obtained for each molecule. The fitting gives τ as 5.6 mins for l_c= 3, 24.1 mins for l_c = 6, 51.9 mins for l_c = 15, and 53.9 mins for l_c = 18, indicating that molecules with longer l_c take progressively

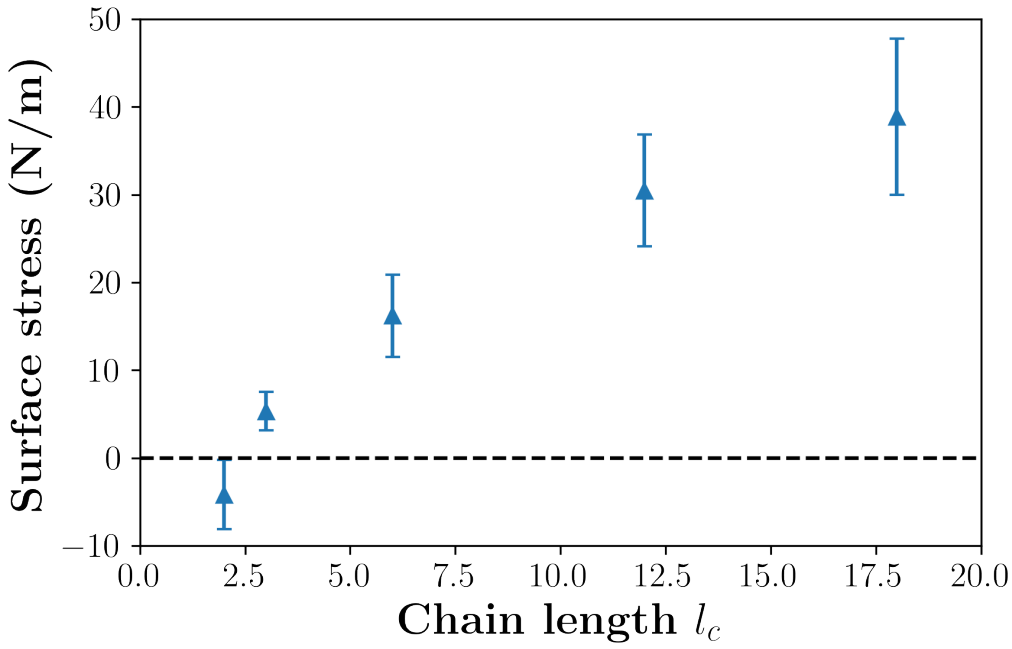


Figure 5: Surface stress induced by the SAMs with different l_c.

longer times to form the monolayer. The evolution of Δh is controlled by the adsorption kinetics. Prior studies have found that that in the initial adsorption stage, when the surface concentration of species is low, the adsorbed molecules are oriented parallel to the surface [39]. As the concentration increases and the monolayer approaches complete coverage of the surface, the molecule orientation changes to a tilt angle of $\sim$ 28 to 40 degrees with respect to the surface normal. Longer molecules must negotiate various steric hindrances before they find the optimal location and orientation, leading to longer adsorption times.

Two other series of experiments were done to demonstrate the relevance of f for manufacturing applications. In the first series, Al strips were exposed to naphthenic oil (carrier) containing alkanoic acid SAM molecules (10 wt%), with $l_c = 6$ and 8, for 1 hour. Monolayer formation caused the cantilever to deflect as before. The f value was 12.85 $\pm$ 0.6 N/m for $l_c = 6$, very similar to $f = 11.3 \pm 2.2$ N/m ($t = 1$ hour) measured earlier with this molecule (ethanol carrier). With the $l_c = 8$ molecule, the f value was 15.5 $\pm$ 4.5 N/m, which is intermediate between f for $l_c = 6$ ($f = 11.3 \pm 2.2$ N/m) and $l_c = 12$ ($f = 20.7 \pm 5.6$ N/m), measured with the ethanol carrier. The second series of experiments was done with a Cu 110 cantilever, and hexanoic acid ($l_c = 6$)

adsorbate introduced via naphthenic oil. The measured f in this case was 15.6 ± 2.3 N/m (t = 1 h), somewhat larger than $f = 12.85 \pm 0.6$ N/m obtained for the Al. These results show that the adsorbate molecules can be easily introduced over macroscopic sample areas using carrier fluids other than ethanol, and that monolayer formation can impose large f in substrates other than Al. The results suggest a pathway, via organic molecules in cutting oils or comminution media, for imposing f to effect local embrittlement, and using fracture as an aid to enhance material removal and comminution processes for metals.

Discussion

In summary, our measurements have shown that surface stress in Al and Cu induced by SAMs can be compressive or tensile depending on l_c; and that f can be varied over a wide range using molecule chain length. The measurements can explain various experimental observations pertaining to adsorbate influences on surface plasticity and fracture.

Firstly, it is known that certain organic media enhance comminution rates by embrittlement in ball milling of ductile metals like Al, Cu, and Fe [40, 41]. A chain-length effect on comminution effectiveness was also noted. Powder production by milling is otherwise difficult to achieve with these metals.

Secondly, surface stress effects on plasticity are revealed in cutting of highly strain-hardening metals such as Al, Cu, Ta and Ni. These metals are difficult to cut, despite being soft, with large forces and poor surface finish [37, 42]. The metals could, however, be machined readily, with up to 75% reduction in deformation force and order of magnitude improvement in surface finish, if the surface being cut was coated with organic (sub-200 nm) films, including common inks and adhesive substances, prior to the cutting. In such instances, the chip formation, which typically occurs by large-strain plasticity, was disrupted by recurring surface fracture [37, 42] (see [5]). Analysis of the films showed that while there was little commonality in their constituents, all of them contained long-chain molecules [37]. This disruption of plasticity by fracture was also observed with the alkanoic acid SAMs studied herein [6], the OME effect. Interestingly, the OME occurred only for $l_c > 7$ (tensile f). In contrast, the force increased for $l_c = 2$ (compressive f) without any

fracture occurring - an apparent increase in the surface plasticity (see [5]). Since l_c was the only variable across the SAMs used, *the observations point to a critical tensile surface stress as the fracture-controlling (embrittling) variable.*

The measured f values are quite large, in that they correspond roughly to bulk stresses of a few GPa, on the order of the theoretical strength for metals (assuming f is distributed over a surface layer of a few nm). Such bulk stresses, albeit over a nanometer scale surface layer, can strongly influence crack nucleation and propagation, as in the cutting and comminution. Other implications of the large f remain to be explored.

Thirdly, molecular dynamics simulations of adsorbate-metal interactions, have also shown f to increase monotonically with l_c, as in our measurements [6, 12]. And, when the tensile f exceeds a critical value, there can be suppression of dislocation emission at crack tips, with fracture ensuing [6,12]. This f dependence on l_c arises because of a corresponding increase in intermolecular van-der Waals forces with l_c.

Beyond material removal processes, the measurements strongly support the inclusion of f in analysis of EAC phenomena [2] since a monolayer or multilayer adsorbate film may be expected to form on the substrate. The resulting change in f can increase the propensity for fracture in various ways, such as by suppressing crack-tip dislocation emission at surfaces, enabling crack nucleation etc. Similarly, the measurements support the hypothesis that adsorbate-induced swelling of nanoporous materials (Bangham effect) [43] and phase transformation in nanowires [44] is a consequence of deformations arising from surface stress .

The surface stress measurements have several implications. A relatively macroscale simple cantilever configuration can be used for measurement of f over large sample areas, with applicability to nearly all adsorbate-adsorbent systems. The chain-length dependence of f suggests opportunities for studying EAC phenomena by controlling (tuning) f via SAM selection. In the context of "fracture as a friend", the f can be varied to initiate controlled fracture (tensile f) or enhance "plasticity" (compressive f), beneficial for improving machining and comminution processes with metals. Our f control approach could also be combined with other techniques of f modification, such as by changing the charge density at material surfaces electrochemically [45]. While chem-

ically assisted material removal processes are used in commercial practice with non-metals, e.g., planarization of Si, rock drilling [4], they have found very limited application to date in manufacturing processes with metals. The present results portend a transformative change on this front.

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[5] See Supplemental Material at **URL** for details of the experimental procedures, a list of the control experiments and background information on surface stress and organic monolayer embrittlement, which includes Refs. [46-48].

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