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Frequency-tunable toughening in a polymer-metal-ceramic stack using an interfacial molecular nanolayer

Matthew Kwan¹, Muriel Braccini^{1,2}, Michael W. Lane³ & Ganpati Ramanath¹

Interfacial toughening in composite materials is reasonably well understood for static loading, but little is known for cyclic loading. Here, we demonstrate that introducing an interfacial molecular nanolayer at the metal-ceramic interface of a layered polymer-metal-ceramic stack triples the fracture energy for ~75–300 Hz loading, yielding 40% higher values than the static-loading fracture energy. We show that this unexpected frequency-dependent toughening is underpinned by nanolayer-induced interface strengthening, which facilitates load transfer to, and plasticity in, the polymer layer. Above a threshold interfacial bond strength, the toughening magnitude and frequency range are primarily controlled by the frequency- and temperature-dependent rheological properties of the polymer. These results indicate the tunability of the toughening behavior through suitable choice of interfacial molecular layers and polymers. Our findings open up possibilities for realizing novel composites with inorganic-organic interfaces, e.g., arresting crack growth or stimulating controlled fracture triggered by loads with specific frequency characteristics.

¹Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180, USA. ²SIMaP, Grenoble INP, CNRS, Univ. Grenoble Alpes, F-38000 Grenoble, France. ³Chemistry Department, Emory and Henry College, Emory, VA 24327, USA. Correspondence and requests for materials should be addressed to G.R. (email: Ramanath@rpi.edu)

Tailoring the chemistry of heterointerfaces is crucial to controlling the fracture toughness of a variety of composite materials, such as, those used in load-bearing structures¹, nanoelectronics devices², energy systems³, and biomedicine⁴. Interfacial fracture can occur at significantly lower stresses than the static-loading fracture stresses^{5,6} of the materials comprising the interface, and can be exacerbated by chemical attack (stress corrosion) and cyclic loading (fatigue), thereby adversely impacting reliability and performance. Although fatigue has been widely investigated and well understood in bulk materials^{7,8}, much less is known about fatigue-induced interfacial fracture, especially in coatings and thin films. Recent works have examined the effects of chemical treatment^{9,10}, patterning¹¹, micrometer-thick adhesion layers^{4,10}, crack-tip blunting¹², and cyclic loading amplitude¹³ on interfacial fatigue, and described the results in terms of Paris law-based bulk-fatigue models^{14,15}. But, loading-frequency-dependence of interfacial fatigue, and related phenomena, remain largely unexplored. Our prior work has shown that introducing an interfacial molecular nanolayer (MNL) in model polymer-metal-ceramic structures can yield multifold increases in fracture energy under static loading^{16–19}, enhance thermal²⁰ and electronic^{21–25} transport, inhibit diffusion^{26–28}, and alter phase formation²⁹. However, the effects of cyclic loading on the fracture behavior of such molecularly modified model systems are not known. Understanding frequency-dependent effects in molecularly modified structures, such as, accelerated damage, crack growth mitigation, and interfacial healing, is not only of fundamental importance but also should enable the design of smart composites^{30–32} comprised of soft-hard and/or organic-inorganic interfaces for emerging applications in electronics, energy, and biomedicine.

Here we report loading-frequency-dependent multifold fracture toughening upon inserting a strongly binding MNL at the metal-ceramic interface of a layered polymer-metal-ceramic stack. The interfacial MNL results in up to threefold higher fracture energy in the ~75–300 Hz range than the invariant value at other frequencies. We demonstrate that this remarkable behavior is underpinned by MNL-induced interface strengthening that enables load transfer to, and plasticity in, the distal polymer layer. Furthermore, the magnitude and frequency range of fatigue toughening correlates with the rheological properties of the polymer, varied by altering the temperature relative to the polymer glass transition. Our findings suggest that fatigue fracture energy is tunable by appropriate choices of MNL(s) and polymer(s), opening up a completely new set of possibilities to tailor composite materials. For example, the interface can be tailored to shift from a crack growth mode to crack arrest mode, or controllably fracture in response to stimuli with specific loading-frequency characteristics.

Results

Experimental work. We prepared polymer-metal-MNL-ceramic structures sandwiched between two silica-capped Si(001) wafers for four-point-bend mechanical tests¹⁹ (Fig. 1a). We self-assembled a mercapto-propyl-tri-methoxysilane (MPTMS) MNL on a silica-capped Si wafer surface. We then sputter-deposited a 40-nm-thick Cu layer with a 7 mTorr Ar plasma in a 5×10^{-7} Torr base pressure CVC tool. Without breaking vacuum, we also deposited a 100-nm-thick Ta layer to facilitate metal-polymer bonding¹⁷. We glued the metal-MNL-silica structures to a dummy Si wafer with a System Three Resins® T88 epoxy polymer to obtain beams comprised of layered Si-polymer-Ta-Cu-MPTMS-SiO₂-Si structures for four-point-bend mechanical tests¹⁹ (Fig. 1a). We also created and tested beams without the MNL (see Methods).

Four-point bend tests were carried out under fatigue and static loading at temperatures ranging from $15 \leq T \leq 50$ °C and at preset water partial pressures between $0.6 \leq PH_{2O} \leq 2.8$ kPa. A Physik Instrumente P216-9S piezo actuator was used to produce load-cycling. Following crack initiation of the Cu-SiO₂ interface³³ at a critical strain energy release rate ($\Gamma_{Critical}$), we conducted displacement-controlled subcritical (i.e., $\Gamma < \Gamma_{Critical}$) load-shedding tests^{18,34}. Example stress-time curves from a load-shedding fatigue test, and a static-loading test, are schematically depicted in Fig. 1b. For the fatigue tests, we chose a displacement-amplitude between 5 and 30 μm to obtain an initial stress slightly higher than that corresponding to the fatigue fracture energy $\Gamma_{Fatigue}$ to be measured. We applied sinusoidal load oscillations in the $0.1 \leq \nu \leq 1000$ Hz range, with a maximum-to-minimum load ratio ~ 10 . We extracted the $\Gamma_{Fatigue}$ from strain energy release rate-crack velocity ($\Gamma-u_{crack}$) plots by recognizing that $\Gamma = \Gamma_{Fatigue}$ at $u_{crack} = 0$. We also determined the stress corrosion fracture energy Γ_{Static} from static load tests¹⁹, to explicitly separate the effects of chemical attack and load-cycling. The fracture surfaces were examined by X-ray photoelectron spectroscopy (XPS) and polarized-light microscopy.

Loading-frequency-dependent toughening. Our results show that introducing a MPTMS nanolayer at the Cu-SiO₂ interface of our polymer-metal-silica stacks significantly influences the fatigue fracture behavior. Stacks without the MPTMS nanolayer exhibit a $\Gamma_{Fatigue} \sim \Gamma_{Static} = 1.6 \text{ Jm}^{-2}$ at 25 °C and $PH_{2O} = 0.6$ kPa (Fig. 1c), irrespective of the loading frequency. Inserting an MPTMS

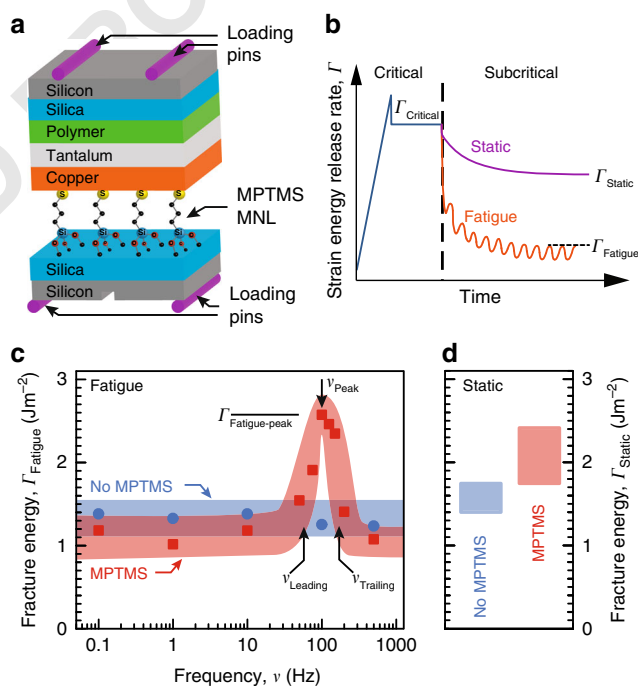


Fig. 1 Fracture energy of epoxy-Cu-MPTMS-SiO₂ structures under static and fatigue loading. **a** Schematic depicting the four-point bending test and **b** the strain energy release rate characteristics for load-shedding fatigue and static loading. **c** Fatigue fracture energy of polymer-metal-ceramic structures with Cu-MPTMS-SiO₂ interfaces (red squares) and Cu-SiO₂ interfaces (blue circles) determined at $PH_{2O} = 0.6$ kPa, shown together with **d** the corresponding static stress fracture energies. Each data point represents at least three tests. The width of the bands, drawn through the data points to guide the eye, connote the experimental uncertainty measured as standard deviation

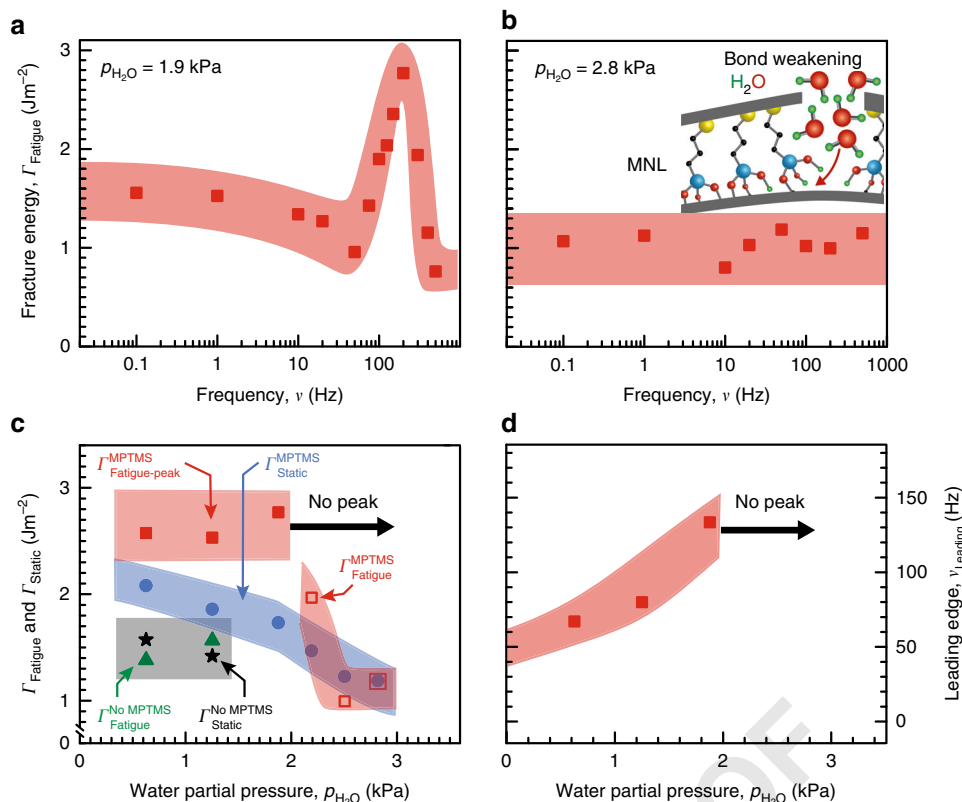


Fig. 2 Effect of moisture-dependent interfacial bond strength on fatigue toughening. Fatigue fracture energy Γ_{Fatigue} of polymer-metal-ceramic structures with Cu-MPTMS-SiO₂ interfaces shown for water partial pressures **a** $\rho_{\text{H}_2\text{O}} = 1.9 \text{ kPa}$ and **b** $\rho_{\text{H}_2\text{O}} = 2.8 \text{ kPa}$. **c** Γ_{Fatigue} peak value, i.e., $\Gamma_{\text{Fatigue-peak}}$ (red squares) and average Γ_{Static} (blue circles) plotted versus $\rho_{\text{H}_2\text{O}}$ for stacks with Cu-MPTMS-SiO₂ interfaces. Average Γ_{Fatigue} (green triangles) and Γ_{Static} (black stars) for stacks without MPTMS are also shown. There is no observable Γ_{Fatigue} peak for $\rho_{\text{H}_2\text{O}} > 2.2 \text{ kPa}$ (open red squares). **d** Leading edge frequency ν_{Leading} of the Γ_{Fatigue} peak for Cu-MPTMS-SiO₂ interfaces. No Γ_{Fatigue} peak is observed for $\rho_{\text{H}_2\text{O}} \geq 2.2 \text{ kPa}$. Each data point represents at least three tests. The width of the bands, drawn through the data points to guide the eye, connote the experimental uncertainty measured as standard deviation

nanolayer at the Cu-SiO₂ interface produces a 30% higher $\Gamma_{\text{Static}} = 2.1 \text{ Jm}^{-2}$, as expected³⁵ (Fig. 1d). But, MPTMS functionalization decreases the fatigue fracture energy to $\Gamma_{\text{Fatigue}} \sim 1.1 \text{ Jm}^{-2}$ (i.e., $\Gamma_{\text{Fatigue}} < \Gamma_{\text{Static}}$) at all frequencies, except $\nu \sim 75\text{--}125 \text{ Hz}$, where we observe $\Gamma_{\text{Fatigue}} > \Gamma_{\text{Static}}$ and a maximum of $\Gamma_{\text{Fatigue-peak}} \sim 2.6 \text{ Jm}^{-2}$. In particular, Γ_{Fatigue} increases above a threshold frequency ν_{Leading} , which we refer to as the leading edge (Fig. 1c). For $\nu > \nu_{\text{Leading}}$, Γ_{Fatigue} goes through a maximum at ν_{max} and decreases at higher ν . Fatigue toughening is not detectable $\nu > \nu_{\text{Trailing}}$, where ν_{Trailing} corresponds to the trailing edge of the Γ_{Fatigue} peak, i.e., where $\Gamma_{\text{Fatigue}} < \Gamma_{\text{Static}}$.

Our experiments revealing $\Gamma_{\text{Fatigue}} < \Gamma_{\text{Static}}$ at very low and very high load-cycling frequencies is not unexpected because sub-critical cyclic loading is known to hasten interfacial fracture¹¹. However, the observed loading-frequency-dependent toughening at intermediate frequencies (i.e., $\nu_{\text{Leading}} \leq \nu \leq \nu_{\text{Trailing}}$) indicated by the Γ_{Fatigue} peak in the MPTMS-modified structures, is unusual. This result indicates that molecular functionalization of the weakest interface can actually increase the fracture energy at certain loading frequencies, to values higher than the static-loading fracture energy.

In order to understand the MPTMS-induced fatigue toughening, we measured the fracture energy as a function of the water-sensitive siloxane bond strength³⁶ at the Cu-MPTMS-SiO₂ interface by adjusting the water partial pressure $\rho_{\text{H}_2\text{O}}$. For low $\rho_{\text{H}_2\text{O}} < 2.2 \text{ kPa}$ we obtain a Γ_{Fatigue} peak at $\nu \sim 75\text{--}300 \text{ Hz}$ in structures with Cu-MPTMS-SiO₂ interfaces (Fig. 2a). At higher $\rho_{\text{H}_2\text{O}} \geq 2.2 \text{ kPa}$ Γ_{Fatigue} is essentially invariant in the $0.1 \leq \nu \leq$

500 Hz range, with no observable fatigue toughening (Fig. 2b), reflecting a behavior similar to that in structures without MPTMS. Since moisture weakens siloxane bonds, our results indicate a minimum interface bonding strength, attainable below a threshold $\rho_{\text{H}_2\text{O}}$, is a prerequisite for fatigue toughening. This is reminiscent of static toughening at Cu-MPTMS-SiO₂ interfaces below a threshold $\rho_{\text{H}_2\text{O}}$ that provides adequate siloxane bonding strength to enable metal plasticity^{18,19}.

Unlike a monotonic increase in the magnitude of static toughening with desiccation, fatigue toughening increases with desiccation in the $1.9 \text{ kPa} \leq \rho_{\text{H}_2\text{O}} \leq 2.5 \text{ kPa}$ range, but saturates at $\Gamma_{\text{Fatigue}} = \Gamma_{\text{Fatigue-peak}}$ for $\rho_{\text{H}_2\text{O}} < 1.9 \text{ kPa}$ and is insensitive to further desiccation (Fig. 2c). We note that $\Gamma_{\text{Fatigue}} > \Gamma_{\text{Static}}$ at $\rho_{\text{H}_2\text{O}} = 2.2 \text{ kPa}$, despite the absence of a Γ_{Fatigue} peak. These observations suggest that the $\Gamma_{\text{Fatigue-peak}}$ is limited by a mechanism other than desiccation-induced interfacial siloxane bond strengthening. Fatigue toughening occurs only below a threshold $\rho_{\text{H}_2\text{O}}$ and only for $\nu \geq \nu_{\text{Leading}}$, indicating that ν_{Leading} corresponds to the threshold $\rho_{\text{H}_2\text{O}}$ at which the minimum required siloxane bond strength is attained at the crack tip. Toughening is precluded for $\nu < \nu_{\text{Leading}}$ because of facile water-induced siloxane bond-breaking due to a higher $\rho_{\text{H}_2\text{O}}$ at the crack tip than the threshold $\rho_{\text{H}_2\text{O}}$. Conversely, $\nu > \nu_{\text{Leading}}$ corresponds to a lower $\rho_{\text{H}_2\text{O}}$ at the crack tip than the threshold $\rho_{\text{H}_2\text{O}}$. Thus, increasing frequency for $\nu > \nu_{\text{Leading}}$ (or equivalently, downshifting ν_{Leading}) is tantamount to crack-tip desiccation. This is indeed corroborated by our results showing desiccation-induced downshifting of ν_{Leading} below $\rho_{\text{H}_2\text{O}} \leq 1.9 \text{ kPa}$ (Fig. 2d).

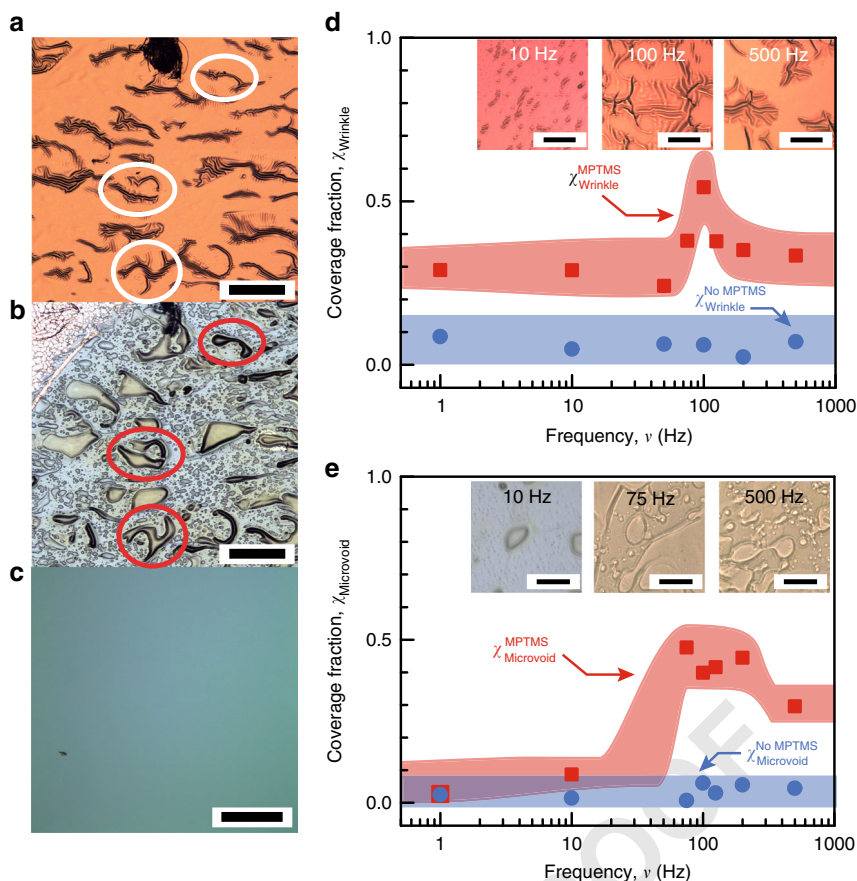


Fig. 3 Fracture surface analyses of epoxy-Cu-MPTMS-SiO₂ structures under fatigue loading. **a** Representative optical micrographs from an as-obtained Cu fracture surface (scale bar = 300 μ m), **b** the same with the metal film etched off to expose the polymer (scale bar = 300 μ m), and **c** the SiO₂ fracture surface (scale bar = 100 μ m). The sizes and shapes of the metal wrinkles and the polymer microvoids are correlated (circles regions). Average **d** metal wrinkle coverage χ_{Wrinkle} (scale bar = 100 μ m) and **e** microvoid coverage $\chi_{\text{Microvoid}}$ (scale bar = 200 μ m) from fracture surfaces of structures with (red squares), and without (blue circles) MPTMS. Representative optical micrographs inset in **d** and **e** capture metal wrinkling and polymer microvoiding at select frequencies. The data in this figure were from experiments at $P_{\text{H}_2\text{O}} = 1.3$ kPa. The width of the bands drawn through the data points connote the experimental uncertainties measured as standard deviation

The correlations between increasing ν and desiccation suggest that the water molecules are increasingly hindered from reaching the crack tip for $\nu > \nu_{\text{Leading}}$, similar to that reported for high loading rates^{37–39}. The build-up of elastic energy in the unbroken interfacial bonds increases the interfacial work of adhesion γ_a and becomes available for activating plastic energy dissipation γ_p in the adjacent layers. Thus, siloxane bond strength is the limiting determinant of the toughening magnitude with increasing frequency in the $\nu_{\text{Leading}} \leq \nu \leq \nu_{\text{Peak}}$ range and desiccation in the $1.9 \text{ kPa} \leq P_{\text{H}_2\text{O}} \leq 2.8 \text{ kPa}$ range. Decreasing Γ_{Fatigue} for $\nu > \nu_{\text{Peak}}$ and the invariance of $\Gamma_{\text{Fatigue-peak}}$ for $P_{\text{H}_2\text{O}} < 1.9 \text{ kPa}$ are contrary to desiccation-induced bond strengthening, confirming that Γ_{Fatigue} at high ν and low $P_{\text{H}_2\text{O}}$ is not limited by the interfacial strength.

Interfacial fracture and plastic energy dissipation. Fracture surface analyses suggests that MPTMS-functionalization leads to fatigue toughening by facilitating plasticity in the metal-polymer bilayer. Core-level XPS spectra from fracture surfaces confirm that fatigue fracture occurs via siloxane bond-breaking at the MPTMS-silica interface (Supplementary Fig. 1), as reported for static loading^{17,18}. Polarized-light micrographs of Cu fracture surfaces exhibit 5- to 20- μ m-scale wrinkles (Fig. 3a). Etching off the metal film reveals microvoids in the polymer that are similar

in shape and size of the metal wrinkles at the same location (Fig. 3b), suggesting that polymer voiding and metal wrinkling are correlated. In contrast, the silica fracture surfaces were featureless (Fig. 3c), consistent with our XPS analysis. Load-cycling results increases the average microvoid area $\zeta_{\text{Microvoid}}$ multifold, e.g., from 175 to 980 μm^2 (Supplementary Fig. 2). Radially oriented polarization fringes around the microvoids (Supplementary Fig. 3) indicate microvoid growth by shear banding involving the back-and-forth motion of polymer chains⁹. Fracture surfaces obtained by static loading show neither metal wrinkling nor polymer microvoid growth, confirming that these features arise from load-cycling-induced plasticity.

Both metal wrinkling and polymer microvoid coverages (χ_{Wrinkle} and $\chi_{\text{Microvoid}}$) are dependent on the loading frequency. We observe χ_{Wrinkle} peaks between ~ 75 and 125 Hz (Fig. 3d) with a 60% higher coverage than other frequencies, while $\chi_{\text{Microvoid}}$ increases eightfold and peaks over a wider frequency range of ~ 75 –200 Hz, and saturates at a slightly lower value above ~ 200 Hz (Fig. 3e). The frequency regimes of the coverage peaks correlate well with the 75–300 Hz regime of the Γ_{Fatigue} peak. In contrast, fatigue fracture surfaces of stacks without MPTMS exhibit ninefold lower $\chi_{\text{Microvoid}}$ and fourfold lower χ_{Wrinkle} , both of which are invariant with frequency. These results confirm that MPTMS-induced interfacial strengthening is key to activating

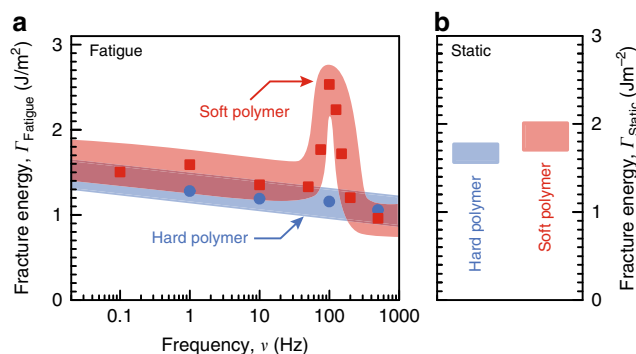


Fig. 4 Effect of polymer hardness on fatigue toughening. **a** Fatigue fracture energy Γ_{Fatigue} and **b** Γ_{Static} of polymer-metal-MPTMS-SiO₂ stacks with a soft System Three Resins® T88 polymer (red squares), and a harder EPO-TEK 375 polymer (blue circles) at $P_{\text{H}_2\text{O}} = 1.3$ kPa. Each data point represents at least three tests. The width of the bands, drawn through the data points to guide the eye, connote the experimental uncertainties measured as standard deviation

loading-frequency-dependent plasticity in the polymer-metal bilayer.

The greater overlap in the frequency regime of the $\chi_{\text{Microvoid}}$ peak and the Γ_{Fatigue} peak suggests a greater contribution of polymer plasticity to the observed fatigue toughening. Cu film strain, estimated from χ_{Wrinkle} and wrinkle amplitude⁴⁰ measurements (Supplementary Fig. 3), indicates a metal plastic energy $U_m \sim 0.02 \pm 0.01 \text{ Jm}^{-2}$, which accounts for <1% of the fracture energy at $\Gamma_{\text{Fatigue-peak}} \sim 2.5 \text{ Jm}^{-2}$ (Supplementary Methods). Such low metal plasticity is attributable to the high-yield stress Cu film that results in a highly confined plastic zone near the crack tip vicinity. This view is consistent with our estimates¹⁹ of <~2% plastic strain energy and a <1 nm plastic zone for a 40-nm-thick Cu film used in our experiments here. Thus, fatigue toughening observed in our experiments is underpinned primarily by polymer plasticity, while the metal film essentially serves as an elastic stress-transfer layer. We note that this mechanism is unlike MNL-induced metal-ceramic interface toughening due to metal plasticity under static loading¹⁹.

We propose that microvoid growth in the polymer leads to metal-polymer interface delamination at the voids. The consequent release of constraint leads to metal film wrinkling due to compressive stresses⁴¹. This hypothesis is supported by the disappearance of fatigue toughening and metal wrinkling when polymer plasticity is suppressed by replacing the T88 epoxy with the harder EPO-TEK 375 epoxy in our structures (Fig. 4 and Supplementary Fig. 3). The Γ_{Fatigue} peak frequency range is also consistent with the toughening of T88 epoxy composites^{42–45} at strain rates of $\sim 0.02\text{--}0.1 \text{ s}^{-1}$ (Supplementary Methods). If voiding were to initiate at the metal-polymer interface, we would expect significant metal wrinkling under static loading, and a fracture path change from the MNL-SiO₂ interface, neither of which we observe. These results indicate that MPTMS-induced polymer plasticity is the primary fatigue toughening mechanism.

Tuning the toughening magnitude and frequency range. In order to understand fatigue toughening magnitude and frequency characteristics in terms of polymer rheology, we examined the Γ_{Fatigue} peak at different temperatures below the polymer glass transition temperature T_g . Since T_g for our T88 epoxy is frequency-dependent (e.g., $52 \leq T_g \leq 75$ °C between $0.01 \leq \nu \leq 1000$ Hz (Supplementary Fig. 4)), we analyzed temperature-dependent toughening in terms of $\Delta T = T_g - T$ for data

acquired at a fixed $P_{\text{H}_2\text{O}} = 1.3$ kPa. Separate measurements of polymer film stress on SiO₂ indicate that water-induced polymer swelling is insignificant, e.g., <~3% of the compliance change seen during crack growth (Supplementary Fig. 5).

We find that lower ΔT (i.e., higher T , closer to T_g) correlates with a higher $\Gamma_{\text{Fatigue-peak}}$, and a larger peak width ($\Delta\nu = \nu_{\text{Trailing}} - \nu_{\text{Leading}}$), indicating that both the fatigue toughening magnitude and frequency range are sensitive to polymer plasticity (Fig. 5a). For instance, a 20 °C increase in temperature from 16 to 36 °C (i.e., decreasing ΔT from 59 to 39 °C) doubles the Γ_{Fatigue} peak magnitude to $\Gamma_{\text{Fatigue-peak}} = 2.9 \text{ Jm}^{-2}$ (Fig. 5b), which is 40% higher than the highest static-loading fracture energy Γ_{Static} measured at $P_{\text{H}_2\text{O}} = 0.6$ kPa (Fig. 2c). This $\Gamma_{\text{Fatigue-peak}}$ doubling correlates with the doubling of the loss-to-storage moduli ratio $\tan \delta$ of the epoxy for the same temperature increase (Supplementary Fig. 4), suggesting that polymer rheology determines the $\Gamma_{\text{Fatigue-peak}}$ magnitude. Since $\tan \delta$ increases with temperature for $T < T_g$, but decreases with frequency (Supplementary Fig. 4b-c), polymer plasticity is facilitated at higher temperatures but deterred at higher frequencies. Increasing $\Gamma_{\text{Fatigue-peak}}$ with temperature and decreasing Γ_{Fatigue} for $\nu > \nu_{\text{Peak}}$ mirror the $\tan \delta$ behavior, confirming that polymer plasticity is the predominant contributor to the observed fatigue toughening. Thus, decreasing polymer plasticity at $\nu > \nu_{\text{Peak}}$ counteracts increases in interfacial strength at $\nu > \nu_{\text{Leading}}$, leading to a fatigue toughening maximum.

Decreasing ΔT (i.e., increasing T , closer to T_g) also extends fatigue toughening to higher frequencies. Both ν_{Leading} and ν_{Trailing} shift to higher frequencies, but the ν_{Trailing} shift is ~120% greater (Fig. 5c). The temperature-induced ν_{Trailing} shifts can be understood by recognizing that plasticity is arrested above ν_{Trailing} due to the diminished responsiveness of polymer chains to high-frequency load-cycling, which is consistent with decreasing $\tan \delta$ with increasing frequency. Higher chain mobility at temperatures closer to T_g (i.e., high T and low ΔT) enables greater polymer plasticity, which is manifest as higher $\Gamma_{\text{Fatigue-peak}}$ and shifting of the plasticity arrest point ν_{Trailing} to higher frequencies as ΔT decreases. Since ν_{Leading} corresponds to a threshold strength of the water-sensitive siloxane bonds, and $P_{\text{H}_2\text{O}}$ is held constant here, the up-shifts in ν_{Leading} with decreasing ΔT indicates that increasing the temperature enhances the transport of water molecules to the crack tip.

Discussion

Based upon our results, the salient mechanistic aspects of the frequency-dependent toughening observed in polymer-metal-ceramic structures with an MNL-functionalized metal-ceramic interface can be understood as follows. Interfacial fracture energy has two main contributors: the metal-ceramic interface work of adhesion γ_a and plastic energy dissipation γ_p in the adjacent layers. Introducing the MPTMS MNL increases γ_a through siloxane bond formation at the MNL-SiO₂ interface. Water attack of siloxane bonds lowers γ_a . However, increasing load-cycling frequency curtails water transport to the crack tip, leading to an effective increase in γ_a . Thus, increasing frequency is tantamount to desiccation, which strengthens siloxane bonds. The consequent build-up in interfacial elastic energy becomes available for activating plasticity (i.e., $\gamma_p \neq 0$) in the adjacent layers. The minimum γ_a necessary for elastic energy build-up and plastic energy dissipation for detectable fatigue toughening is achieved at ν_{Leading} and increases for $\nu > \nu_{\text{Leading}}$.

In our experiments, plasticity γ_p occurs mainly in the polymer by microvoid growth via shear banding. The high-yield stress metal film serves as an elastic load transfer layer, and wrinkles due to compressive stresses generated through release of

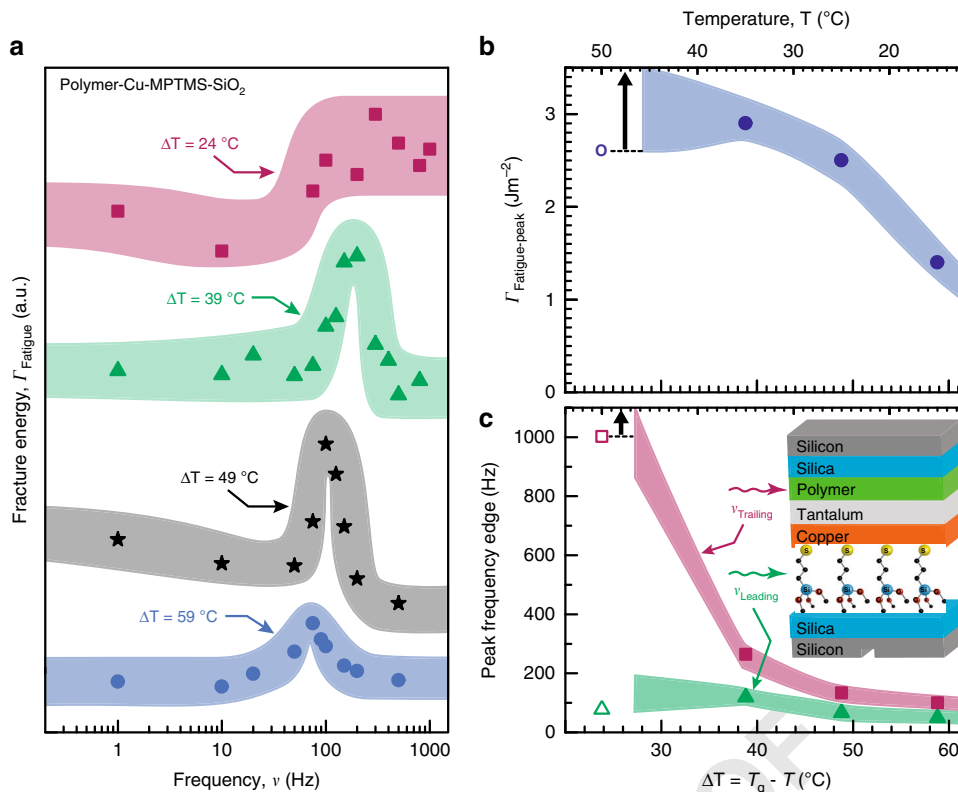


Fig. 5 Temperature-dependence of the fatigue toughening magnitude and frequency characteristics. **a** Fatigue fracture energy Γ_{Fatigue} of polymer-metal-MPTMS-silica interfaces for $24\text{ °C} \leq \Delta T \leq 59\text{ °C}$, at $P_{\text{H}_2\text{O}} = 1.3\text{ kPa}$. **b** The Γ_{Fatigue} trailing edge frequency ν_{Trailing} (magenta squares), leading edge frequency ν_{Leading} (green triangles), and **c** Γ_{Fatigue} peak height $\Gamma_{\text{Fatigue-peak}}$ (blue circles), plotted as a function of ΔT . The $\Gamma_{\text{Fatigue-peak}}$ and ν_{Trailing} values shown for $\Delta T = 24\text{ °C}$ represent the lower bounds (open symbols) because the ν_{Trailing} edge at this temperature extends beyond our instrument frequency range. Each data point in **b** and **c** is extracted from the corresponding curve in **a**. The width of the bands, drawn through the data points to guide the eye, connote the experimental uncertainties measured as standard deviation

constraint when microvoids reach the polymer-metal interface. Polymer plasticity itself, however, decreases with increasing frequency due to the increasing inability of polymer chain motion to keep up with load-cycling. Increasing γ_a and decreasing γ_p with frequency results in a fatigue toughening maximum, i.e., a Γ_{Fatigue} peak, at intermediate frequencies. The increase in Γ_{Fatigue} with frequency for $\nu_{\text{Leading}} \leq \nu \leq \nu_{\text{Peak}}$ indicates that fatigue toughening is limited by γ_a . At $\nu \geq \nu_{\text{Peak}}$, the decreasing contribution of γ_p due to inhibited chain motion begins to offset the frequency-induced increases in the elastic energy due to interfacial bond strengthening. Decreasing fatigue toughening for $\nu > \nu_{\text{Peak}}$ and saturation for $P_{\text{H}_2\text{O}} < 1.9\text{ kPa}$ are contrary to interfacial siloxane bond strengthening expected at high ν and low $P_{\text{H}_2\text{O}}$, confirming that fatigue toughening is limited by polymer plasticity at high frequencies.

Although bond strengthening γ_a through the use of the MNL is a necessary condition for fatigue toughening, polymer plasticity γ_p is the predominant contributor. This is clearly seen from the suppression of fatigue toughening in MNL-modified structures with a hard epoxy. Furthermore, the maximum toughening magnitude $\Gamma_{\text{Fatigue-peak}}$ and high-frequency limit of toughening ν_{Trailing} are determined by the rheological properties of the polymer. For example, both $\Gamma_{\text{Fatigue-peak}}$ and ν_{Trailing} increase with temperature (as T approaches T_g) due to facile chain motion, which is counteracted to some extent by the frequency-induced increase in T_g at higher frequencies. Therefore, choosing a polymer with the appropriate rheological properties is crucial for tailoring the toughening magnitude as well as the high-frequency limit.

Based upon the above, the overall mechanism of fatigue toughening of the epoxy-Cu-MPTMS-SiO₂ polymer-metal-MNL-ceramic stack enabled by the MPTMS MNL can be understood in terms of Fig. 6. At low loading frequencies, water-induced siloxane bond-breaking at the MNL-ceramic interface limits the interface fracture energy. At intermediate loading frequencies, the increased interface strength caused by the diminishing effect of water attack at the MNL-SiO₂ interface facilitates polymer plasticity resulting in fracture energies exceeding the static-loading fracture energy. Arrested polymer plasticity due to curtailed chain mobility at very high loading frequencies leads the disappearance of polymer plasticity, and hence, fatigue toughening. Although the metal serves as an elastic layer in our experiments, using metals of different yield stresses, moduli, and/or thicknesses, may alter the contributions of metal and polymer plasticity, which could amplify, suppress, and/or modify the fatigue toughening frequency range

Our findings are relevant to the design, monitoring, and controlling the stability of smart composites with tunable frequency-dependent toughening and/or weakening behaviors. For example, low-frequency fatigue toughening commencement ν_{Leading} in polymer-metal-MNL-ceramic structures can be controlled by suitable choice of MNLS with termini that enable strong interfacial bonding that supports sufficient interfacial elastic energy build-up for activating plasticity in the adjacent layers. Choosing polymers with appropriate viscoelastic properties should allow the tuning of the maximum toughening magnitude $\Gamma_{\text{Fatigue-peak}}$ and high-frequency toughening limit ν_{Trailing} . The use of multiple polymers with different rheological properties could result in

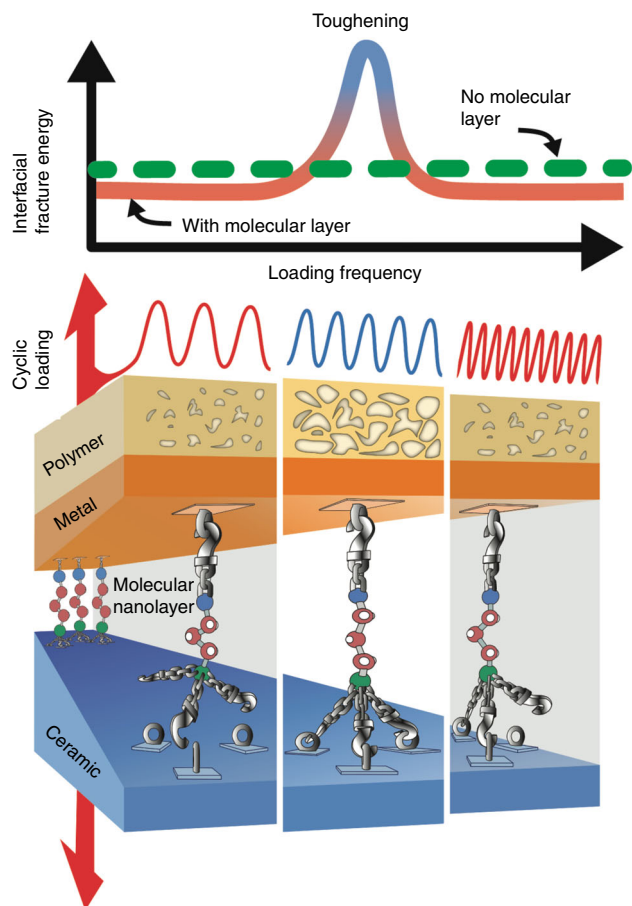


Fig. 6 Frequency-dependent toughening enabled by interfacial strengthening and polymer rheology. Schematic sketch of loading-frequency-dependent interfacial fracture energy increase in an epoxy-Cu-MPTMS-SiO₂ stack caused by plasticity in the polymer layer through voiding activated by MNL-induced interfacial strengthening. At low frequencies, water-induced siloxane bond-breaking at the MPTMS MNL-silica interface limits the interface fracture energy, and no polymer voiding is observed. At intermediate frequencies, the increased interface strength due to diminishing water attack at the crack tip facilitates load transfer to, and plasticity in, the polymer, yielding fatigue fracture energies exceeding the static-loading fracture energy; polymer voiding is observed. Arrested polymer plasticity (no voiding observed) due to curtailed chain mobility at very high loading frequencies leads to a low interfacial fracture energy despite high interfacial strength

novel $\Gamma_{\text{Fatigue}}-v$ characteristics with multiple peaks, plateaus, valleys, and combinations thereof. Such frequency-dependent phenomena could pave the way for realizing novel composites that respond to select loading magnitude/frequency stimuli by either controllably degrading^{46,47}, or self-healing⁴⁸ through polymer plasticity and crosslinking of healing agents released during microvoid growth in the polymers.

In summary, we have shown that functionalizing polymer-metal-ceramic structures with a MNL at the metal-ceramic interface can lead to multifold increases in fracture energy at certain loading frequencies, yielding values higher than that obtained during static loading. Nanolayer-induced interfacial strengthening allows load transfer to, and plasticity in, the polymer layer. While a threshold interfacial strength determines the minimum loading frequency for toughening, the magnitude and loading-frequency range of toughening are primarily dependent on polymer rheology. These facets of heterointerfacial mechanics

could be harnessed to design, monitor, and control the stability of composite materials for diverse applications including energy and electronics devices⁴⁶, biomedicine⁴⁷, and smart-degrading and self-healing systems⁴⁸.

Data availability

The data for the figures that support the findings of this study are available in figshare data repository with the identifier(s) 10.6084/m9.figshare.7154930 (fracture energy data), 10.6084/m9.figshare.7159529 (microscopy data), 10.6084/m9.figshare.7159541 (XPS data), and 10.6084/m9.figshare.7159553 (DMA data).

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Author contributions

M.K. and M.B. carried out the experimental work and data analyses. G.R. and M.W.L. conceived the project, designed the experiments, and supervised and contributed to, the execution of the experiments, data analyses, and paper writing.

Additional information

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