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

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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.
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 structures, nanoelectronics devices, energy systems, and biomedicine. Interfacial fracture can occur at significantly lower stresses than the static-loading fracture stresses 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, much less is known about fatigue-induced interfacial fracture, especially in coatings and thin films. Recent works have examined the effects of chemical treatment, patterning, microthickness adhesion layers, crack-tip blunting, and cyclic loading amplitude on interfacial fatigue, and described the results in terms of Paris law-based bulk-fatigue models. 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, enhance thermal and electronic transport, inhibit diffusion, and alter phase formation. 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 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 tests (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 bonding. 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 tests (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 ≤ T ≤ 50 °C and at preset water partial pressures between 0.6 ≤ P_{H₂O} ≤ 2.8 kPa. A Physik Instrumente P216-9S piezo actuator was used to produce load-cycling. Following crack initiation of the Cu-SiO₂ interface at a critical strain energy release rate (Γ_critical), we conducted displacement-controlled subcritical (i.e., Γ < Γ_critical) load-shedding tests. 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 Γ_{Fatigue} to be measured. We applied sinusoidal load oscillations in the 0.1 ≤ ν ≤ 1000 Hz range, with a maximum-to-minimum load ratio ~ 10. We extracted the Γ_{Fatigue} from strain energy release rate-crack velocity (Γ – u_{crack}) plots by recognizing that Γ = Γ_{Fatigue} at u_{crack} = 0. We also determined the stress corrosion fracture energy Γ_{Static} from static load tests 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 Γ_{Fatigue} ~ Γ_{Static} = 1.6 Jm⁻² at 25 °C and P_{H₂O} = 0.6 kPa (Fig. 1c), irrespective of the loading frequency. Inserting an MPTMS...
Effect of moisture-dependent interfacial bond strength on fatigue toughening. Fatigue fracture energy $\Gamma_{\text{Fatigue}}$ of polymer-metal-ceramic structures with Cu-MPTMS-SiO$_2$ interfaces shown for water partial pressures $p_{\text{H}_2\text{O}}$ = 1.9 kPa and $p_{\text{H}_2\text{O}}$ = 2.8 kPa. $\Gamma_{\text{Fatigue}}$ peak value, i.e., $\Gamma_{\text{Fatigue}}$-peak (red squares) and average $\Gamma_{\text{Static}}$ (blue circles) plotted versus $p_{\text{H}_2\text{O}}$ for stacks with Cu-MPTMS-SiO$_2$ interfaces. Average $\Gamma_{\text{Fatigue}}$ (green triangles) and $\Gamma_{\text{Static}}$ (black stars) for stacks without MPTMS are also shown. There is no observable $\Gamma_{\text{Fatigue}}$ peak for $p_{\text{H}_2\text{O}}$ ≥ 2.2 kPa (open red squares). d Leading edge frequency $\nu_{\text{Leading}}$ of the $\Gamma_{\text{Fatigue}}$ peak for Cu-MPTMS-SiO$_2$ interfaces. No $\Gamma_{\text{Fatigue}}$ peak is observed for $p_{\text{H}_2\text{O}}$ ≥ 2.2 kPa. Each data point represents at least three tests. The width of the bands, drawn through the data points to guide the eye, connotes the experimental uncertainty measured as standard deviation.

nanolayer at the Cu-SiO$_2$ interface produces a 30% higher $\Gamma_{\text{Static}}$ = 2.1 Jm$^{-2}$, as expected$^{15}$ (Fig. 1d). But, MPTMS functionalization decreases the fatigue fracture energy to $\Gamma_{\text{Fatigue}}$ ~ 1.1 Jm$^{-2}$ (i.e., $\Gamma_{\text{Fatigue}}$ < $\Gamma_{\text{Static}}$) at all frequencies, except $\nu$ ~ 75–125 Hz, where we observe $\Gamma_{\text{Fatigue}}$ > $\Gamma_{\text{Static}}$ and a maximum of $\Gamma_{\text{Fatigue}}$-peak ~ 2.6 Jm$^{-2}$. In particular, $\Gamma_{\text{Fatigue}}$ increases above a threshold frequency $\nu_{\text{Leading}}$ which we refer to as the leading edge (Fig. 1c). For $\nu > \nu_{\text{Leading}}$, $\Gamma_{\text{Fatigue}}$ goes through a maximum at $\nu_{\text{max}}$ and decreases at higher $\nu$. Fatigue toughening is not detectable for $\nu > \nu_{\text{Trailing}}$, where $\nu_{\text{Trailing}}$ corresponds to the trailing edge of the $\Gamma_{\text{Fatigue}}$ 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 subcritical cyclic loading is known to hasten interfacial fracture$^{11}$. However, the observed loading-frequency-dependent toughening at intermediate frequencies (i.e., $\nu_{\text{Leading}}$ ≤ $\nu$ ≤ $\nu_{\text{Trailing}}$) indicated by the $\Gamma_{\text{Fatigue}}$ 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 strength$^{18}$ at the Cu-MPTMS-SiO$_2$ interface by adjusting the water partial pressure $p_{\text{H}_2\text{O}}$. For low $p_{\text{H}_2\text{O}}$ < 2.2 kPa we obtain a $\Gamma_{\text{Fatigue}}$ peak at $\nu$ ~ 75–300 Hz in structures with Cu-MPTMS-SiO$_2$ interfaces (Fig. 2a). At higher $p_{\text{H}_2\text{O}}$ ≥ 2.2 kPa $\Gamma_{\text{Fatigue}}$ is essentially invariant in the 0.1 ≤ $\nu$ ≤ 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 $p_{\text{H}_2\text{O}}$, is a prerequisite for fatigue toughening. This is reminiscent of static toughening at Cu-MPTMS-SiO$_2$ interfaces below a threshold $p_{\text{H}_2\text{O}}$ 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 kPa ≤ $p_{\text{H}_2\text{O}}$ ≤ 2.5 kPa range, but saturates at $\Gamma_{\text{Fatigue}}$ = $\Gamma_{\text{Fatigue}}$-peak for $p_{\text{H}_2\text{O}}$ < 1.9 kPa and is insensitive to further desiccation (Fig. 2c). We note that $\Gamma_{\text{Fatigue}}$ > $\Gamma_{\text{Static}}$ at $p_{\text{H}_2\text{O}}$ = 2.2 kPa, despite the absence of a $\Gamma_{\text{Fatigue}}$ peak. These observations suggest that the $\Gamma_{\text{Fatigue}}$-peak magnitude is limited by a mechanism other than desiccation-induced interfacial siloxane bond strengthening. Fatigue toughening occurs only below a threshold $p_{\text{H}_2\text{O}}$ and only for $\nu$ ≥ $\nu_{\text{Leading}}$, indicating that $\nu_{\text{Leading}}$ corresponds to the threshold $p_{\text{H}_2\text{O}}$ 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 $p_{\text{H}_2\text{O}}$ at the crack tip than the threshold $p_{\text{H}_2\text{O}}$. Conversely, $\nu > \nu_{\text{Leading}}$ corresponds to a lower $p_{\text{H}_2\text{O}}$ at the crack tip than the threshold $p_{\text{H}_2\text{O}}$. Thus, increasing frequency for $\nu > \nu_{\text{Leading}}$ (or equivalently, downshifting $\nu_{\text{Leading}}$) is tantamount to crack-tip desiccation. This is indeed corroborated by our results showing desiccation-induced downshifting of $\nu_{\text{Leading}}$ below $p_{\text{H}_2\text{O}}$ ≤ 1.9 kPa (Fig. 2d).
The correlations between increasing \( \nu \) 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 \( \gamma_a \) and becomes available for activating plastic energy dissipation \( \gamma_p \) 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 kPa \( \leq p_{\text{H}_2\text{O}} \leq 2.8 \text{ kPa} \) range. Decreasing \( T_{\text{fatigue}} \) for \( \nu > \nu_{\text{peak}} \) and the invariance of \( T_{\text{fatigue}} \)-peak magnitude for \( p_{\text{H}_2\text{O}} < 1.9 \text{ kPa} \) are contrary to desiccation-induced bond strengthening, confirming that \( T_{\text{fatigue}} \) at high \( \nu \) 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-\( \mu \text{m} \)-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 \( \chi_{\text{Microvoid}} \) multifold, e.g., from 175 to 980 \( \mu \text{m}^2 \) (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 chains \(^9\). 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 (\( \chi_{\text{Wrinkle}} \) and \( \chi_{\text{Microvoid}} \)) are dependent on the loading frequency. We observe \( \chi_{\text{Wrinkle}} \) 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 \( T_{\text{fatigue}} \) peak. In contrast, fatigue fracture surfaces of stacks without MPTMS exhibit ninefold lower \( \chi_{\text{Microvoid}} \) and fourfold lower \( \chi_{\text{Wrinkle}} \), both of which are invariant with frequency. These results confirm that
MPTMS-induced interfacial strengthening is key to activating loading-frequency-dependent plasticity in the polymer-metal bilayer. The greater overlap in the frequency regime of the $\chi$microvoid peak and the $I^{\text{Fatigue}}$ peak suggests a greater contribution of polymer plasticity to the observed fatigue toughening. Cu film strain, estimated from $\chi^{\text{Wrinkle}}$ and wrinkle amplitude measurements (Supplementary Fig. 3), indicates a metal plastic energy $U_{\text{plastic}} \sim 0.02 \pm 0.01$ J m$^{-2}$, which accounts for $<1\%$ of the fracture energy at $I^{\text{Fatigue-peak}} \sim 2.5$ J m$^{-2}$ (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 estimates$^{19}$ 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 loading$^{19}$. 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 stresses$^{41}$. 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 $I^{\text{Fatigue}}$ peak frequency range is also consistent with the toughening of T88 epoxy composites$^{2,42}$ at strain rates of $<0.02-0.1$ 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-SiO$_2$ 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 $I^{\text{Fatigue}}$ 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 SiO$_2$ 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 $\Delta T$ (i.e., higher $T$ closer to $T_g$) correlates with a higher $I^{\text{Fatigue-peak}}$ and a larger peak width ($\Delta \nu = \nu^{\text{Leading}} - \nu^{\text{Trailing}}$), indicating 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 $\Delta T$ from 59 to 39 °C) doubles the $I^{\text{Fatigue-peak}}$ magnitude to $I^{\text{Fatigue-peak}} = 2.9$ J m$^{-2}$ (Fig. 5b), which is 40% higher than the highest static-loading fracture energy $I^{\text{Static}}$ measured at $P_{\text{H}_2\text{O}} = 0.6$ kPa (Fig. 2c). This $I^{\text{Fatigue-peak}}$ 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 $I^{\text{Fatigue-peak}}$ 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 $I^{\text{Fatigue-peak}}$ magnitude with temperature and decreasing $I^{\text{Fatigue-peak}}$ 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 $\Delta T$ (i.e., increasing $T$ closer to $T_g$) also extends fatigue toughening to higher frequencies. Both $\nu^{\text{Leading}}$ and $\nu^{\text{Trailing}}$ shift to higher frequencies, but the $\nu^{\text{Trailing}}$ shift is ~120% greater (Fig. 5c). The temperature-induced $\nu^{\text{Trailing}}$ shifts can be understood by recognizing that plasticity is arrested above $\nu^{\text{Leading}}$ 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 $\Delta T$) enables greater polymer plasticity, which is manifest as a higher $I^{\text{Fatigue-peak}}$ magnitude and shifting of the plasticity arrest point $\nu^{\text{Trailing}}$ to higher frequencies as $\Delta T$ decreases. Since $\nu^{\text{Leading}}$ 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 $\nu^{\text{Leading}}$ with decreasing $\Delta T$ 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 $\gamma_a$ and plastic energy dissipation $\gamma_p$ in the adjacent layers. Introducing the MPTMS MNL increases $\gamma_a$ through siloxane bond formation at the MNL-SiO$_2$ interface. Water attack of siloxane bonds lowers $\gamma_a$. However, increasing load-cycling frequency curtails water transport to the crack tip, leading to an effective increase in $\gamma_a$. 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 $\gamma_a$ necessary for elastic energy build-up and plastic energy dissipation for detectable fatigue toughening is achieved at $\nu^{\text{Leading}}$ and increases for $\nu > \nu^{\text{Leading}}$.

In our experiments, plasticity $\gamma_p$ 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 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 $\gamma_a$ and decreasing $\gamma_p$ with frequency results in a fatigue toughening maximum, i.e., a $\Gamma_{\text{fatigue peak}}$, at intermediate frequencies. The increase in $\Gamma_{\text{fatigue}}$ with frequency for $\nu_{\text{loading}} < \nu < \nu_{\text{peak}}$ indicates that fatigue toughening is limited by $\gamma_a$. At $\nu > \nu_{\text{peak}}$, the decreasing contribution of $\gamma_p$ 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 $p_{\text{H}_{2}O} < 1.9$ kPa are contrary to interfacial siloxane bond strengthening expected at high $\nu$ and low $p_{\text{H}_{2}O}$, confirming that fatigue toughening is limited by polymer plasticity at high frequencies.

Although bond strengthening $\gamma_a$ through the use of the MNL is a necessary condition for fatigue toughening, polymer plasticity $\gamma_p$ 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 $\nu_{\text{Trailing}}^*$ are determined by the rheological properties of the polymer. For example, both $\Gamma_{\text{fatigue peak}}$ and $\nu_{\text{Trailing}}^*$ 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-SiO$_2$ 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-SiO$_2$ 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 to 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 $\nu_{\text{Loading}}$ 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...
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 devices\textsuperscript{16,17}, biomedicine\textsuperscript{18}, and smart-degrading and self-healing systems\textsuperscript{16,18}.

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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the tuning of the maximum toughening magnitude $T_{\text{Fatigue-peak}}$ and high-frequency toughening limit $\nu_{\text{Tailing}}$. The use of multiple polymers with different rheological properties could result in novel $T_{\text{Fatigue-\nu}}$ 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\textsuperscript{16,17}, or self-healing\textsuperscript{18} 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 interfacial fracture energy. Frequency-dependent loading, polymer plasticity (no voiding observed) due to curtailed chain mobility at the static-loading fracture energy; polymer voiding is observed. Arrested plasticity in, the polymer, yielding fatigue fracture energies exceeding 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.
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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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