Peer Review File

Manuscript Title: Multiscale stress deconcentration amplifies fatigue resistance of rubber

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

Suo et al demonstrate particle reinforced elastomers with both high modulus and high fatigue threshold. Dense entanglements scale the modulus of the composite, with the scaling factor increasing steeply when the particles percolate. The entangled polymer network greatly enhances the strength at a crack tip. This high stress is deconcentrated first through long polymer chains, and then through the percolated particle network. Upon fracture, stress in a large volume of the composite is released, leading to a high fatigue threshold. This composite achieves a fatigue threshold of ~1,000 J m-2. They mold an elastomeric gripper that bears high loads and resists crack growth over repeated operation, as excellenty illustrated in the videos that I watched multiple times since they were so convincing.

The originality and significance are high. It will without any doubt attract a lot of attention from experts in the field of elastomers, but also from people working in soft robotics etc.
I really enjoyed reading this work after realizing what a major breakthrough it is. However, at first, I thought that this study sounded a bit incremental after reading first page only. Then I watched the videos which were amazing and really showed that this by no means could be regarded as incremental. I wonder if the title could be rephrased to really make it clear that this is a major leap for elastomers. Also I would suggest that the 10 fold increase of the fatigue threshold should be stressed clearer in the abstract (at least be mentioned in words, as opposed to now where one has to go back and compare numbers).
The data & methodology is sound. The approach is really nice. There is high quality of data, and the article reads very nicely. With respect to the presentation, as a suggestion, I think that there should really be a picture of the tearing process of the elastomers. It is so visual in the videos, and it is really a shame that there is no real figure of it in the main text. One could maybe take out after x seconds where normal material tears and the new material does not (does not even show that it is in its way to it).
There is an appropriate use of statistics and treatment of uncertainties
The conclusions are scientifically sound. The manuscript stands out a manuscript that in my opinion is ready to publish, maybe with a few of the changes suggested above. As such they are not necessary but I think that they will improve the understanding of the importance of this article.
With respect to citations, I find a single reference missing, namely that it has previously been shown that a silicone polymer network where entanglements greatly outnumber crosslinks that superior stretchability is achieved (Hu et al, Nature Communications volume 13, Article number: 370 (2022)). I think this should be mentioned as background knowledge.
The references have a few missing details, see e.g. ref 5 that misses an issue/vol number. Likewise,

with reference 18 – it spreads over four volumes? Ref 35 has no issue number.
Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions.

I therefore recommend that the publication is accepted after a few minor corrections, as suggested above.

Referee #2 (Remarks to the Author):

To address the challenge of low fatigue threshold in rubber (~ 100 J m-2), the authors have proposed utilizing entangled polymer network and percolated particle network in silica-nanoparticle reinforced PEA elastomers for achieving simultaneous high modulus and high fatigue threshold (~ 1,000 J m-2). Through systematic experimental studies, the authors explored the effects of two governing parameters volume fraction of silica particles F and crosslinker-to-monomer molar ratio C on stress-strain curves, modulus, cyclical mechanical responses, and fatigue thresholds etc. The mechanism for both high modulus and high fatigue threshold is proposed from the multiscale synergistic effects of both polymer network and nanoparticle percolation networks. Lastly, the authors demonstrated the application of high modulus and high fatigue resistant composite elastomers in a compliant kirigami gripper for high cyclic life.

The manuscript is well written. This reviewer enjoyed reading through the flow of the story. The mechanisms governing the high fatigue threshold are well explained from the proposed synergy of two networks and examined by parametric mechanical testing. It is an excellent work.

However, the reviewer has several major comments on this work:

First, there is a recent closely related work by Li et al., that reported the achievement of both high modulus and high fatigue resistant in a different composite elastomer, see Li et al., Superstretchable, yet stiff, fatigue-resistant ligament-like elastomers, Nature Communications, 13, 2279 (2022).

Li et al. reported a ligament-like composite elastomer (rigid PMMA nanodomains and soft PEGA) that achieves a high Young's modulus of 18 MPa and high fatigue threshold of 2682 J m-2 via a hierarchal crosslinking design to deconcentrate the stress. Despite the different mechanisms, the performances of both Young's modulus and fatigue threshold in Li et al.'s work are superior to the reported values of 14 MPa and 1020 Jm-2 in this work, especially for the fatigue threshold value, which is over 2.6 times higher than the current work. In addition, Li et al.'s work can also simultaneously achieve a high stretchability of 3,000% and high self-healing efficiency (98%).

The authors may consider justifying their performances by comparing their work with Li et al.'s work.

Second, the proposed key mechanism of two synergistic networks for both high modulus and fatigue

threshold are indirectly examined by the experimental mechanical testing on the macroscopic level.

Direct evidence from the microstrutured level may be needed to validate the proposed mechanisms as schematically illustrated in Fig. 1. For the percolation networks, several basic questions arise including how the silica nanoparticles percolate, how the percolate nanoparticle network look like and how they are correlated to the stiffness and enhance the fatigue resistance with the entangled polymer network, etc.

Third, theoretically, how to understand the synergistic effects considering the development of percolation network theory?

Fourth, regarding the application in kirigami grippers, it is true that high fatigue resistance and high stiffness are beneficial for the elastomer kirigami gripper. However, a kirigami gripper (e.g., Ref. 24) normally employs a rigid, thin, less-stretchable sheet like PET to favor the out-of-plane buckling deformation to release the stress concentration at the cut tip. The benefit of an elastomer kirigami gripper compared to less-stretchable rigid elastic sheets may need to be justified. Minor comment: the thickness of kirigami gripper is not specified in the manuscript.

The authors showed the comparison between two sample grippers: one is C= 10^-4, F=0.45 and C = 10^-2, and F = 0.45. What are the displacement applied to stretch both samples for the reported cyclic fatigue life? The magnitude of stretching displacement is highly related to the fatigue life since the gripper samples have largely different tensile strength as shown in Fig. 4d.

There is a compromise for design the kirigami elastomer gripper: on one hand, an applied large stretching displacement/strain is preferred to even potentially close the two “arms” for accommodating different sizes of grasped objects. On the other hand, the materials may failure under large stretching as shown in Fig. 4d. How to synergistically integrate stiffness, fatigue, materials stretchability, and deformed gripper shapes for grasping may be considered for its potential applications as a kirigami gripper.

Another comparison on the fatigue life between two cases may also be needed to justify the high fatigue life, i.e., gripper with C= 10^-4, F = 0.45, and C= 10^-4, F = 0 despite its lower modulus. As mentioned above, the lower modulus and higher stretchabilty in C=10^-4 and F = 0 could have other applications in grasping lightweight objects.

Referee #3 (Remarks to the Author):

A. Steck et al propose to study model elastomers obtained by coreacting acrylate monomers (chain extender and crosslinker) with functionalized filler. The idea is to systematically vary the content of fillers and crosslinks, at high entanglement ratio, to study the fatigue of the materials.
B. Even if the paper is very didactic and the work perfectly executed and discussed, the proposed materials are not new. In fact, rubber industry working on NR, silicones or EPDM systems, has long introduced in their materials functionalized silica or carbin black for both reinforcement and fatigue resistance. The figure 3i does not acknowledge some works that actually show materials that outperform the presented performances (see e.g. two reviews that the authors know because they actually cited it in other works: Rep. Prog. Phys. 79 046601, 2016 and J. Phys.: Condens. Matter 17 (2005) R1071–R1142). In particular, prestretched NR filled with carbon black show G threshold of more than 3000J/m2 at dc/dn of few nanometers. This is ascribed to strain-induced crystallization. I advise the authors to really go deep into the literature of reinforced fillers so that not to rediscover already existing knowledge. By the way, the materials presented here have a high level of viscoelasticity that woud not be accepted by industry (very bad elastic return, large deformation with low level of strain, what would it give at 300% deformation?)
C. Data are good and very well presented, presentation is good and methodology is good as well. I have however some reserves on the description of the chemistry applied here that, IMHO, is totally eluded. We don't know the conversion in monomers after polymerization, the level of functionalization of fillers, their specific surface and their reactivity, the experimental crosslink density. All explanation are based on theoretical values: this is not acceptable for a paper in Nature.
D. Not appropriate here.
E. Conclusions are going to far on tire pollution and claiming of totally new materials, this is not true. Introduction about skin and cartilage mimicking is overstretched as well.
F. I advise the authors to submit their work in a specialized journal, after they improved the literature survey and chemistry description. I also suggest to correct the quotes to supporting information, the numbers were not correct. I have also minor comments that again show the paper is not at the level of Nature: DSC is differential scanning calorimetry, not dynamic! and deltaH are better comparison than Tgs. Most likely, some chains break with strain, and this is not evoked at all in the paper.
G. see above.
H. This didactic study is nice for comprehension of model systems, but cannot shade other materials that have been optimized for more than 70 years now.

Author Rebuttals to Initial Comments:

Response to all reviewers

In response to the comments from the reviewers, we have revised the title, **Fig. 1**, and the first four paragraphs of the manuscript.

Previous title: Fatigue resistant rubbers by multiscale stress deconcentration

New title: Multiscale stress deconcentration amplifies fatigue resistance of rubber

We revise **Fig. 1b** to highlight the role of particle clusters in deconcentrating stress and amplifying fatigue threshold. To help the general reader, we move the SEM images from the Supplementary Information to **Fig. 1c**.

The main finding of our paper is that fatigue threshold is amplified through not only long polymers, but also clustered particles. These requirements for high fatigue threshold are distinct from those commonly identified for high modulus. The revised introduction makes our finding explicit.

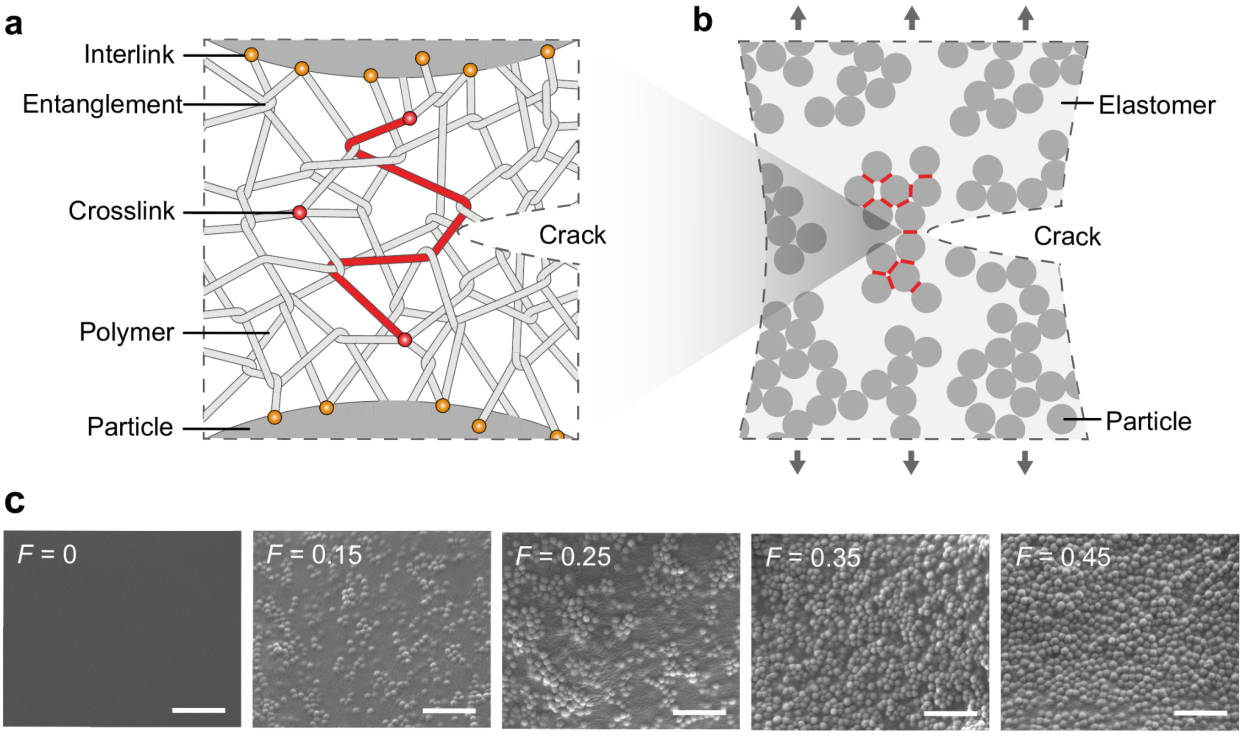


Figure 1. Fatigue threshold is amplified by synergy of long polymer chains and clustered particles. (**a**) When a crack impinges on a polymer chain, the rupture of a single bond on the chain dissipates the energy stored in all the bonds along the chain. (**b**) When a crack impinges on a cluster of particles, the rupture of a single particle-particle gap dissipates the energy stored in many particle-particle gaps in the cluster. **(c)** Scanning electron microscope images of cross-sections of PEA elastomers reinforced with various volume fractions of silica nanoparticles, F, and a fixed crosslinker-to-monomer molar ratio, $C = 10^{-4}$. The scale bars are 1 μm.

Before we get to the individual comments of the reviewers, we summarize the novelty and significance of our work.

Novelty. We identify for the first time multiscale stress deconcentration in particle filled rubbers, and demonstrate that this principle improves fatigue threshold by an order of magnitude. No works have reported particle filled rubbers with comparably high fatigue thresholds. We use filled rubbers in which polymer chains are ~100 times longer than those in typical rubbers. We show that the high fatigue threshold requires stress deconcentration not only along long polymers, but also through clustered particles. The latter has never been suggested in the literature. Furthermore, in this revision, a model of how particles deconcentrate stress has been added to Supplementary Note 1, and its predictions align with our experimental data.

Significance. Fatigue threshold is a measure of load below which cracks will not grow in a material under cyclic stretch. Below fatigue threshold, the material can operate without wear and tear. Particle filled rubbers have high-volume applications, including tires, belts, and seals. Wear and tear not only costs consumers, but also causes polymer pollution. Despite their significance, fatigue thresholds of particle filled rubbers have shown no significant enhancement ever since fatigue crack growth was first studied by Thomas (1958). Our discovery increases fatigue threshold by an order of magnitude, greatly expanding the window in which a material can operate without wear and tear. The principle of multiscale stress deconcentration applies to filled rubbers of different polymers and particles. Any load-bearing application that uses particle filled rubbers can benefit from our principle.

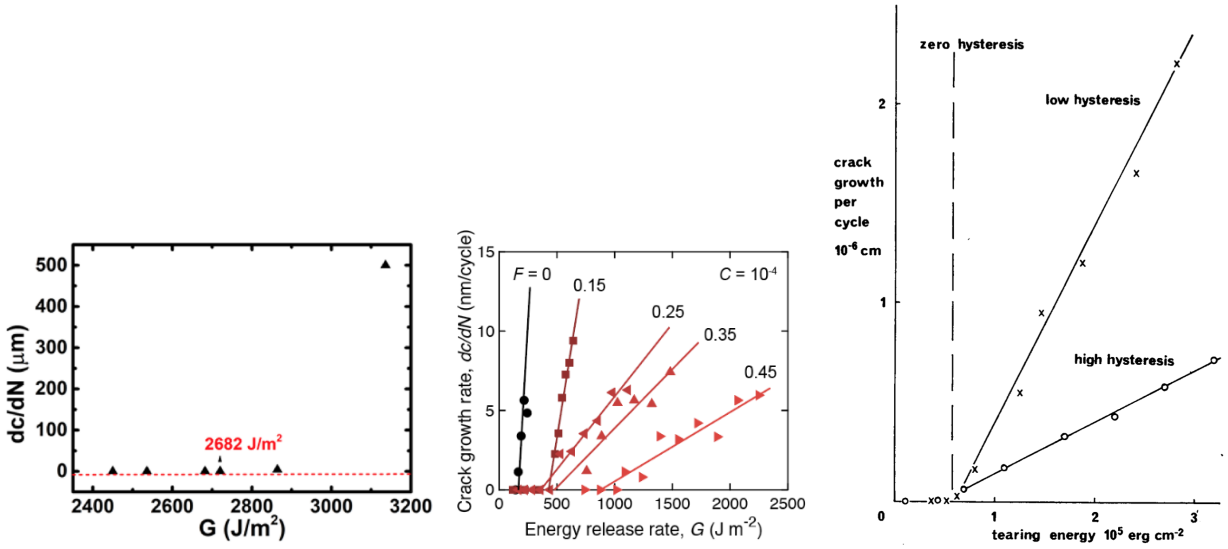
We next summarize the main issues raised by the reviewers and our responses.

Responses to the reviewers' concerns on novelty. The reviewers mentioned several papers that report high fatigue thresholds. On close reading of these papers, we respectfully disagree that these papers challenge the novelty and significance of our work. We next comment on these papers one by one.

1) Mengxue Li, Lili Chen, Yiran Li, Xiaobin Dai, Zhekai Jin, Yucheng Zhang, Wenwen Feng, Li-Tang Yan, Yi Cao, Chao Wang. Superstretchable, yet stiff, fatigue-resistant ligament-like elastomers. *Nat. Commun.* **13**, 2279 (2022).

We note several issues in this paper.

First, this paper greatly overestimated the fatigue threshold of their material. The reported fatigue threshold of 2,682 J/m^2 was measured with a low resolution of crack growth per cycle. The paper reports crack growth in units of 100 μm/cycle (left figure). Judging from this figure, the resolution of their measured crack growth per cycle is about 10 μm/cycle. By contrast, we measure crack growth with a resolution of 1 nm/cycle (middle figure), following the established literature in this field (Lake, Thomas, 1967; right figure), which is 10,000 times below their resolution. If we were to measure the fatigue threshold with a low resolution of crack growth of 10 μm/cycle, the fatigue threshold of our material would be much higher than we reported.



Second, they compute energy release rate G using healed samples, not those in the steady-state loading condition. Since the material is self-healing, the steady-state G will certainly be lower. Their procedure further overestimates fatigue threshold.

Third, the material used in this paper is not a particle filled rubber.

2) Creton, C., Ciccotti, M. Fracture and adhesion of soft materials: a review. *Rep. Prog. Phys.* **79**, 046601 (2016).

3) Persson, B. N. J., Albohr, O., Heinrich, G., Ueba, H. Crack propagation in rubber-like materials. *J. Phys. Condens. Matter* **17**, R1071 (2005).

Reviewer 3 pointed to the above two reviews and mentioned strain-induced crystallization of natural rubber. Strain-induced crystallization near a crack tip resists crack growth, making natural rubber tough. Under fatigue loading, strain-induced crystals melt when the load is removed each cycle. Both filled and unfilled natural rubbers have fatigue thresholds of ~100 J/m^2. By contrast, when the load is not fully removed each cycle, strain-induced crystal domains do not melt, and the fatigue threshold can be high (~3,000 J/m^2). In our work, following the majority of the literature in this field, we measure the fatigue threshold under full relaxation of load. Under these conditions, we have improved the fatigue threshold by ten times.

Furthermore, we have already discussed other classes of promising materials, including interpenetrating polymer networks, fiber-reinforced composites, fabrics, and thermoplastic elastomers. We have expanded this discussion to include semi-crystalline and phase separated polymers. We discuss natural rubber under partial unloading as a semi-crystalline polymer.

We next address the comments of reviewers point by point.

Referee #1

Comment: Suo et al demonstrate particle reinforced elastomers with both high modulus and high fatigue threshold. Dense entanglements scale the modulus of the composite, with the scaling factor increasing steeply when the particles percolate. The entangled polymer network greatly enhances the strength at a crack tip. This high stress is deconcentrated first through long polymer chains, and then through the percolated particle network. Upon fracture, stress in a large volume of the composite is released, leading to a high fatigue threshold. This composite achieves a fatigue threshold of ~1,000 J m^{-2}. They mold an elastomeric gripper that bears high loads and resists crack growth over repeated operation, as excellently illustrated in the videos that I watched multiple times since they were so convincing.

The originality and significance are high. It will without any doubt attract a lot of attention from experts in the field of elastomers, but also from people working in soft robotics etc.

I really enjoyed reading this work after realizing what a major breakthrough it is.

Response: Thank you for these kind remarks.

Comment: However, at first, I thought that this study sounded a bit incremental after reading the first page only. Then I watched the videos which were amazing and really showed that this by no means could be regarded as incremental. I wonder if the title could be rephrased to really make it clear that this is a major leap for elastomers.

Response: Thank you for appreciating our work. Our paper proposes a principle to increase fatigue resistance by deconcentrating stress over multiple length scales. We agree that our original title perhaps does not convey the novelty of the principle. To highlight this new principle, we modify the title as follows.

Previous title: Fatigue resistant rubbers by multiscale stress deconcentration

New title: Multiscale stress deconcentration amplifies fatigue resistance of rubber

Comment: Also I would suggest that the 10 fold increase of the fatigue threshold should be stressed clearer in the abstract (at least be mentioned in words, as opposed to now where one has to go back and compare numbers).

Response: Thank you for your suggestion. We have modified the abstract to state this comparison directly. The modified sentence is:

"This composite achieves a fatigue threshold of ~1,000 J m^{-2}, a 10-fold improvement over existing filled rubbers."

Comment: The data & methodology is sound. The approach is really nice. There is high quality of data, and the article reads very nicely. With respect to the presentation, as a suggestion, I think that there should really be a picture of the tearing process of the elastomers. It is so visual in the videos, and it is really a

shame that there is no real figure of it in the main text. One could maybe take out after x seconds where normal material tears and the new material does not (does not even show that it is in its way to it).

Response: Thank you for your suggestion. We have revised Figure 4d as shown below.

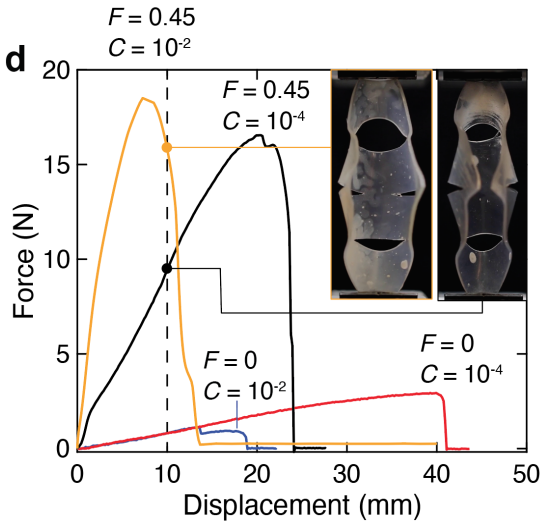


Figure 4. (**d**) The force is measured as a function of displacement for grippers of various *C* and *F*. The dashed line indicates when the grippers are closed, and the inset photos show the grippers at this displacement.

Comment: There is an appropriate use of statistics and treatment of uncertainties.

Response: N/A.

Comment: The conclusions are scientifically sound. The manuscript stands out as a manuscript that in my opinion is ready to publish, maybe with a few of the changes suggested above. As such they are not necessary but I think that they will improve the understanding of the importance of this article.

Response: Thank you for your suggestions.

Comment: With respect to citations, I find a single reference missing, namely that it has previously been shown that a silicone polymer network where entanglements greatly outnumber crosslinks that superior stretchability is achieved (Hu et al, Nature Communications volume 13, Article number: 370 (2022)). I think this should be mentioned as background knowledge.

Response: Thank you for pointing to this article. It reports a technique to synthesize silicone elastomers with very long chains. This overcomes the difficulty of preparing long chain polymer networks from prepolymers. We expect that such a technique can be used with the mechanism of multiscale stress deconcentration developed in this work. We have added the following sentence to the manuscript:

"A recently developed technique has enabled the synthesis of highly entangled elastomers from prepolymers, which can be potentially used to make particle filled elastomers of high fatigue resistance.[27]"

Comment: The references have a few missing details, see e.g. ref 5 that misses an issue/vol number. Likewise, with reference 18 – it spreads over four volumes? Ref 35 has no issue number.

Response: We have added missing details to all references, which primarily included issue numbers. All changes to the references have been marked red in the manuscript.

Comment: Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions.

Comment: I therefore recommend that the publication is accepted after a few minor corrections, as suggested above.

Response: Thank you for recommending our paper to be published in *Nature*. We hope our responses address your comments.

Referee #2

Comment: To address the challenge of low fatigue threshold in rubber (~ 100 J m-2), the authors have proposed utilizing entangled polymer network and percolated particle network in silica-nanoparticle reinforced PEA elastomers for achieving simultaneous high modulus and high fatigue threshold (~ 1,000 J m-2). Through systematic experimental studies, the authors explored the effects of two governing parameters volume fraction of silica particles F and crosslinker-to-monomer molar ratio C on stress-strain curves, modulus, cyclical mechanical responses, and fatigue thresholds etc. The mechanism for both high modulus and high fatigue threshold is proposed from the multiscale synergistic effects of both polymer network and nanoparticle percolation networks. Lastly, the authors demonstrated the application of high modulus and high fatigue resistant composite elastomers in a compliant kirigami gripper for high cyclic life.

Response: Thank you for the summary of our work.

Comment: The manuscript is well written. This reviewer enjoyed reading through the flow of the story. The mechanisms governing the high fatigue threshold are well explained from the proposed synergy of two networks and examined by parametric mechanical testing. It is an excellent work.

Response: Thank you.

Comment: However, the reviewer has several major comments on this work:

Response: We will address the comments below.

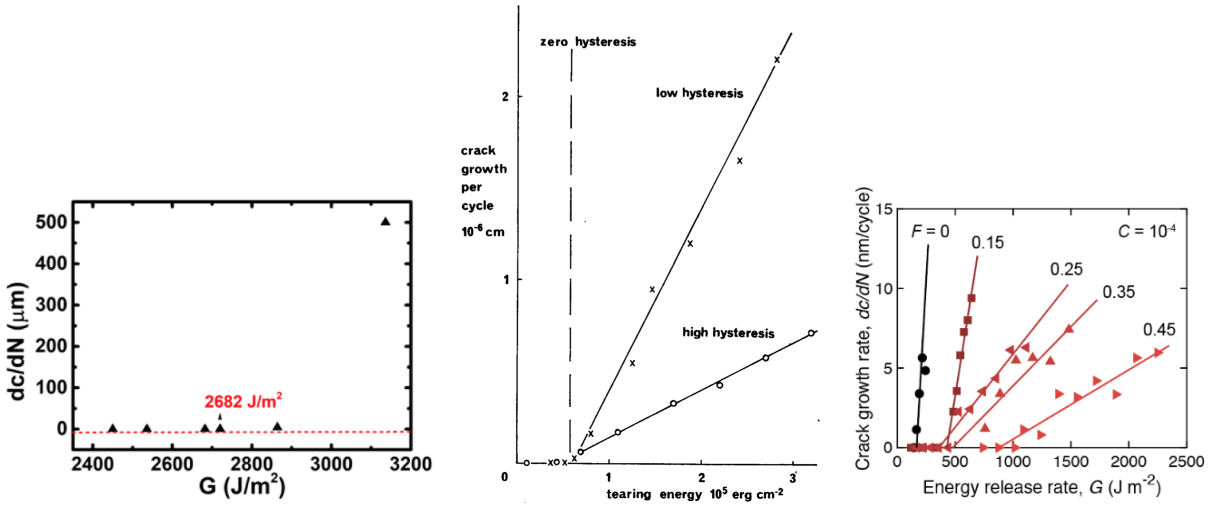
Comment: First, there is a recent closely related work by Li et al., that reported the achievement of both high modulus and high fatigue resistant in a different composite elastomer, see Li et al., Superstretchable, yet stiff, fatigue-resistant ligament-like elastomers, Nature Communications, 13, 2279 (2022).

Li et al. reported a ligament-like composite elastomer (rigid PMMA nanodomains and soft PEGA) that achieves a high Young's modulus of 18 MPa and high fatigue threshold of 2682 J m^{-2} via a hierarchal crosslinking design to deconcentrate the stress. Despite the different mechanisms, the performances of both Young's modulus and fatigue threshold in Li et al.'s work are superior to the reported values of 14 MPa and 1020 J m^{-2} in this work, especially for the fatigue threshold value, which is over 2.6 times higher than the current work. In addition, Li et al.'s work can also simultaneously achieve a high stretchability of 3,000% and high self-healing efficiency (98%).

The authors may consider justifying their performances by comparing their work with Li et al.'s work.

Response: Li et al.'s work reports data for dc/dN in the range of 100 μm/cycle, which greatly overestimates the fatigue threshold (left figure). At such a range, dc/dN values below ~10 μm/cycle would be observed as zero, even though the crack growth is relatively fast (~1 cm growth over 1,000 cycles). By contrast, we measure the fatigue crack growth in the 10 nm/cycle range, following the majority of literature in this field (Lake, Thomas, 1967; center figure). At G = 2,500 J/m^2, the value of dc/dN of our

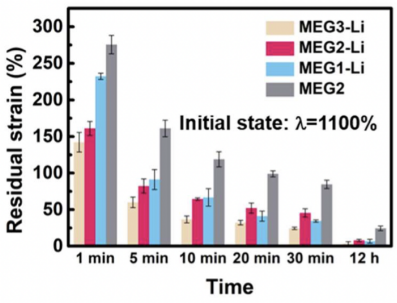
nanocomposite is ~10 nm/cycle (right figure, F = 0.45), which is one thousand times lower than the resolution of dc/dN in the literature mentioned.



Furthermore, G in fatigue loading must be calculated using the stress-stretch curves in steady state. We have been careful in following this requirement in our work, as noted by all three reviewers. However, Li et al.'s work calculates G using stress-stretch curves of samples that have healed for 12 hours (see their description in **Supplementary Discussion 5**). Conspicuously, the authors do not provide stress-stretch curves in the steady state (e.g., **Supplementary Figure 9** only provides data after healing, and the W curve in **Supplementary Figure 10** is identical to that in **Supplementary Figure 9**). Since this material is self-healing (e.g., **Supplementary Figure 5**), G calculated after healing will be much greater than G calculated in the steady state. Overall, this will lead to a greatly overestimated fatigue threshold.

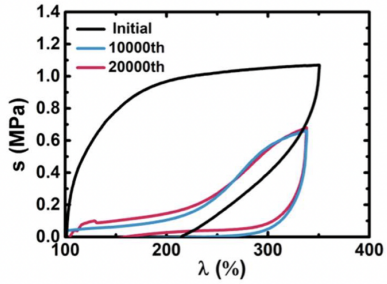
Our response above cited several parts of Li et al., which we reproduce below for the convenience of reviewers.

> **Supplementary Discussion 5: The definition of fatigue threshold**
>
> The loading-unloading hysteresis loop is decreased after thousands of cycles due to the segmental motion and partial reformation of Li^+-O interactions. After about successive 10,000 cycles, the steady stress-strain curve can be obtained. But after 12 hours, the MEG-Li can return to the 60% of its initial stress. Even after another 10,000 cycles and relaxation time of 12 hours, the property can still recover (Fig. S6). The anti-fatigue mechanism of the MEG2-Li is different from the conventional covalently-bonded networks which comply with the classical Lake-Thomas theory. When the material was placed for 12 h, most of the Li^+-O interactions in the material could be restored. Here, we choose the tensile curve of the material after recovery for 12 h to calculate the fatigue threshold. The synergy of physical crosslinking and strong dissipative ability can help continuously recover the anti-fatigue properties of the material, thus greatly improving the service life of the material.



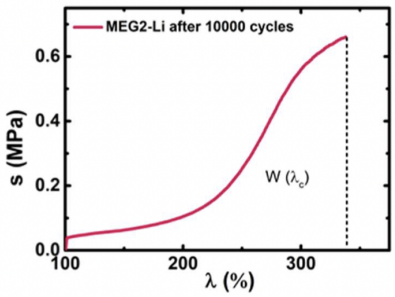
Supplementary Figure 5.

Residual strain statistic for MEG1-Li, MEG2-Li, MEG3-Li and MEG2 under λ=1,100% for different relaxation time, error bars represent standard deviation.



Supplementary Figure 9.

The mechanical properties of MEG2-Li reached a steady state when N=10,000 (the stress-strain cycling curve of the $10{,}000_{th}$ almost overlapped with that of the $20{,}000_{th}$) with the relaxation time of 12 h. When the material was placed for 12 h, most of the Li^{+}-O interactions could be restored, thus the mechanical properties recovered partly.



Supplementary Figure 10.

The stress-strain curve of unnotched MEG2-Li specimen after 10,000 cycles, the $W(\lambda_c)$ was the elastic strain energy density of MEG2-Li when λ = 337.5%.

It is surprising that these two oversights were not addressed in the peer review. For these reasons, we are confident that the work does not challenge the significance of our work.

We also note that our paper studies particle filled rubbers, a class of materials with decades-long history and numerous high-volume applications. Each system has different applications. We have already discussed other classes of promising materials, including interpenetrating polymer networks, fiber-reinforced composites, fabrics, and thermoplastic elastomers. Li et al. reports data for phase separated rubbers. We have expanded the discussion to include semi-crystalline and phase separated polymers.

We have added the following sentences to the manuscript on page 10:

"Semi-crystalline rubbers can have both high modulus and high fatigue threshold. For example, filled natural rubber crystallizes under strain and, when loaded under non-relaxing conditions, strain-induced crystallization greatly enhances the fatigue threshold.[32,33] However, these strain-induced crystals melt when the stretch is fully relaxed each cycle, resulting in a fatigue threshold of ~100 J/m^2 regardless of the presence of particles. Phase separation in immiscible polymer blends can also enhance the fatigue threshold.[7]"

Comment: Second, the proposed key mechanism of two synergistic networks for both high modulus and fatigue threshold are indirectly examined by the experimental mechanical testing on the macroscopic level.

Direct evidence from the microstructured level may be needed to validate the proposed mechanisms as schematically illustrated in Fig. 1.

Response: We conducted the following experiments to characterize the microstructure. First, we imaged the particles in the composites with scanning electron microscopy (SEM) (**Fig. 1c**). This figure was previously in the Supplementary Information. The SEM images show that the particles are well dispersed and percolate near $F = 0.25$.

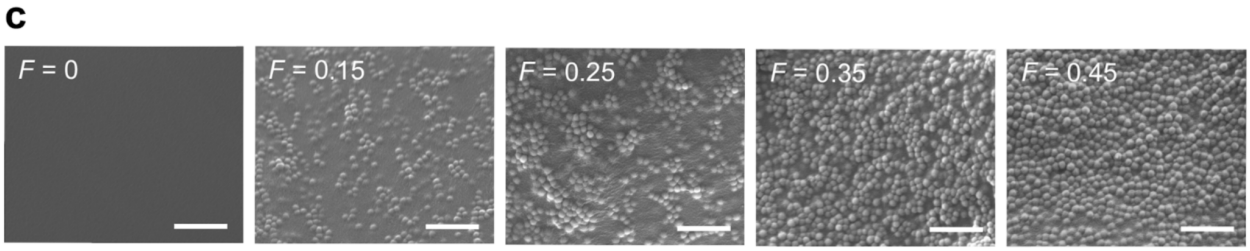


Figure 1. (c) Scanning electron microscope images of cross-sections of PEA elastomers reinforced with various volume fractions of silica nanoparticles, F, and a fixed crosslinker-to-monomer molar ratio, $C = 10^{-4}$. The scale bars are 1 μm.

Second, the density of functional groups on the particle surfaces is provided by the manufacturer, which is 2.7 TPM molecules per nm^2. This was mentioned in the Materials and Methods section in the original manuscript. We now have added the following sentence on page 3:

"On the surfaces of the silica particles, the number density of TPM groups is 2.7 nm^{-2}, which is measured by the manufacturer."

Third, direct observation of the polymer network is not feasible for us. Therefore, in **Fig. 2d** and the accompanying text, we use established techniques to correlate the mechanical properties to the structure of the polymer network. Our measurements show that the polymer chains are long and highly entangled when C is below $10^{-2.5}$. We have added a section titled "Supplementary Note 2. Experimental crosslink density" to the Supplementary Information that discusses the crosslinking density of the polymer network. We add the following sentence to page 4:

"We discuss the experimental crosslink density in **Supplementary Note 2**."

"**Supplementary Note 2. Experimental crosslink density**

The experimental crosslink density is defined by the experiment used to measure it. For a polymer network with negligible entanglements, the elastic modulus is related to the crosslink density as $E = 3\rho N_{Av}kT/M_s$, where ρ is the density, N_{Av} is Avogadro's number, kT is the temperature in unit of energy, and M_s is the molecular weight of polymer strands between crosslinks (Ref. 12, Eqn. (7.31)). Therefore, the experimental crosslink density can be estimated from the elastic modulus. For example, at $F = 0$ and $C = 10^{-2.5}$, the modulus is 0.7 MPa. This modulus gives the molecular weight of 12,070 g/mol or 109 monomers per chain. In the manuscript, we estimated the length of the polymer chain as $1/(2C) = 158$ monomers, which is similar to the crosslink density estimated by the modulus.

For a highly entangled polymer network, by contrast, the elastic modulus is related to the entanglement density as $E = 3\rho kT/M_e$, where M_e is the molecular weight of polymer strands between entanglements (Ref. 12, Eqn. (7.47)). Therefore, the elastic modulus does not provide experimental crosslink density. Instead, the crosslink density can be related to the fatigue threshold for a highly entangled polymer network. The Lake-Thomas model relates the fatigue threshold to the crosslink density as $G_0 = \alpha l n^{1/2} J V^{-1}$, where α is a pre-factor of order of unity, l is the length of each monomer unit, n is the number of monomer units in a polymer chain, J is the C-C bond energy, and V is the volume of each monomer unit (Ref. 4). Therefore, the experimental crosslink density of a highly entangled polymer network can be calculated by scaling ($G_0 \sim n^{1/2}$). This scaling corresponds to our data ($G_0 \sim C^{-1/2}$, see **Fig. 3g**), as $n \sim C^{-1}$. For example, the fatigue thresholds of pure PEA elastomers at $C = 10^{-2}$ and $C = 10^{-4}$ are ~20 J/m^2 and ~200 J/m^2, respectively. Therefore, the values of n are expected to be different by 100 times. As n at $C = 10^{-2}$ is estimated as ~100 monomers per chain from the modulus, n at $C = 10^{-4}$ is ~10,000 monomers per chain."

Comment: For the percolation networks, several basic questions arise including how the silica nanoparticles percolate, how the percolate nanoparticle network look like and how they are correlated to the stiffness and enhance the fatigue resistance with the entangled polymer network, etc.

Response: Thank you for these questions, which we answer one by one.

How do the silica nanoparticles percolate and how does the percolate nanoparticle network look like?

We have discussed the SEM images above. We now move the SEM images from the Supplementary Information to **Fig. 1c**.

How does the percolated silica network correlate to the stiffness?

We have amplified the introductory paragraphs and added a schematic in **Fig. S2**:

"Our experimental data will also show that polymers and particles synergize to amplify modulus (**Fig. S2**). We choose a polymer with a low entanglement molecular weight, such that a polymer chain between two crosslinks forms many entanglements. Even though the polymer network is sparsely crosslinked, dense entanglements set the modulus of the matrix. In turn, the modulus of the matrix scales the modulus of the composite. The scaling factor increases steeply when the particles percolate, since the percolated particle network is much stiffer than the polymer network. In effect, the percolated particle network acts like stretchable but stiff fibers.

The requirements for high modulus differ from those for high fatigue threshold. High modulus requires densely entangled polymers and percolated particles. By contrast, high fatigue threshold requires long polymers and clustered particles, regardless of whether polymers are entangled or particles are percolated. To attain both high modulus and high fatigue threshold requires a network of densely entangled long polymers and a network of percolated particles. Also required are low friction between polymer chains, and strong interlinks between polymers and particles."

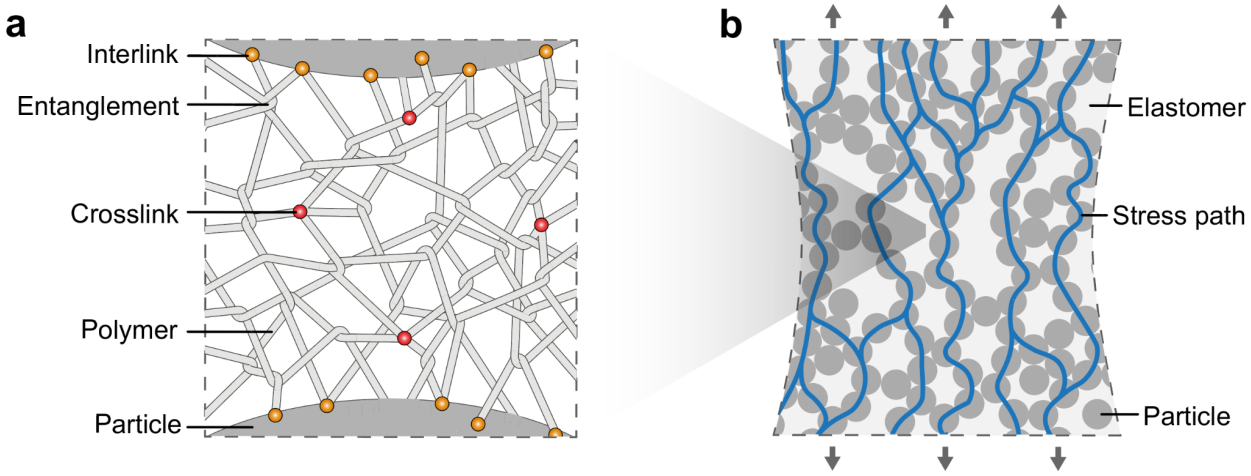


Figure S2. Modulus is amplified by synergy of entangled polymer network and percolated particle network. (**a**) Long polymer chains form a network of sparse crosslinks and dense entanglements. Some of the polymer chains interlink with particles. (**b**) When particles form a percolated network, high stress transmits through the stiff particle network.

In the original manuscript, we discussed how particle percolation correlates with the modulus as follows. We have also added two sentences in red.

"...We compare our data with the Guth-Gold model for rigid spherical particles in a linear elastic matrix, $E(C, F) = E_0(C)(1 + 2.5F + 14.1F^2)$ (the dashed line in **Fig. 2e**).[15,16] This solution follows the data approximately at low F, but deviates greatly at high F, when particles form a percolated network. This deviation in modulus from the Guth-Gold model suggests that the percolated particle network greatly

affects the modulus at high particle volume fractions.[2,17,18] Indeed, this deviation from the Guth-Gold model occurs near the percolation threshold of randomly dispersed impenetrable spheres, which percolate at $F = 0.20$.[19]"

We also observe that the modulus decreases with stretch amplitude in cyclic loading (**Fig. S14a**). Decreasing modulus with stretch amplitude is referred to as the Payne effect, and is commonly attributed to a percolated particle network (e.g., Refs. 2, 3 and 21). From Ref. 2: "It has widely been accepted that the Payne effect is mainly, if not only, related to the filler network formed in the polymer matrix." These observations support the material structure depicted in **Fig. 1b**, where particles form a percolated network. We have modified the sentence on page 5 to:

"This behavior, called the Payne effect, further indicates that particles form a percolated network at high F.[2,21]"

How does the percolated silica network correlate to fatigue resistance?

We have rewritten the introductory paragraph.

"Our experimental data will show that polymers and particles synergize to amplify fatigue threshold. Consider a crack impinging on a polymer chain (**Fig. 1a**). We choose a polymer network with low friction between polymer chains, such that stress deconcentrates over the entire polymer chain. Rupture of a single bond on the chain dissipates the energy stored in every bond along the chain.[4] Next, consider a crack impinging on a particle cluster (**Fig. 1b**). Because the particles are rigid and the gaps between the particles are thin, stress deconcentrates over many particle-particle gaps in the cluster. Strong adhesion between polymers and particles makes this stress high. Rupture of a single gap dissipates energy stored in many gaps. Consequently, stress deconcentrates over two scales: polymer chains and particle clusters. This multiscale stress deconcentration amplifies the energy dissipated when the crack grows, leading to a high fatigue threshold (**Supplementary Note 1**)."

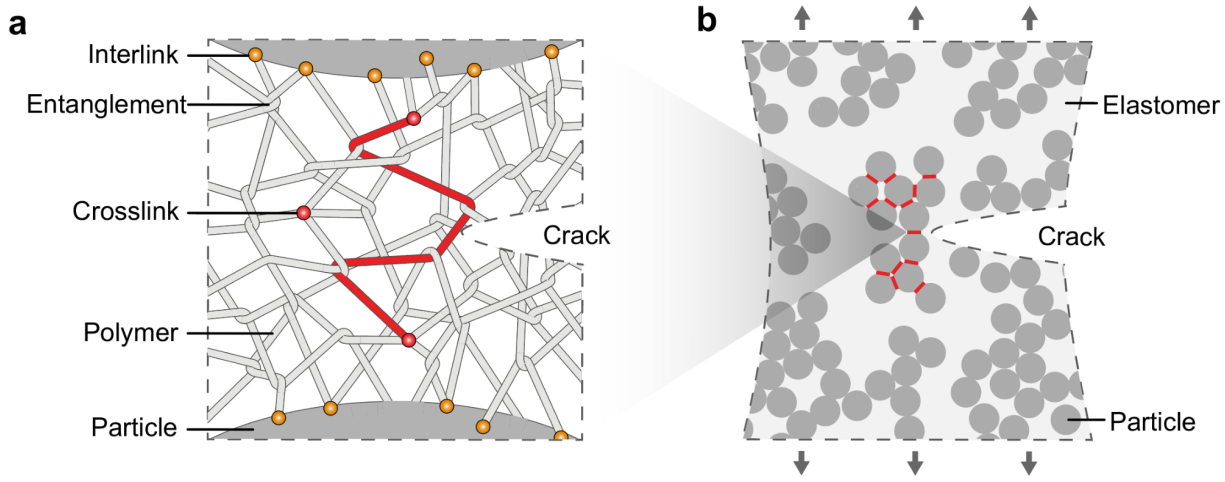


Figure 1. Fatigue threshold is amplified by synergy of long polymer chains and clustered particles. (**a**) When a crack impinges on a polymer chain, the rupture of a single bond on the chain dissipates the energy stored in all the bonds along the chain. (**b**) When a crack impinges on a cluster of particles, the

rupture of a single particle-particle gap dissipates the energy stored in many particle-particle gaps in the cluster."

Our data show that fatigue threshold is high when interlinks are strong (**Fig. 3d**), polymer chains are long (**Fig. 3e**), and particles are concentrated (**Fig. 3h**). These experimental data are consistent with the proposed synergy of polymers and particles, as discussed in the original manuscript:

"Without covalent interlinks, the fatigue threshold is the same as the polymer matrix, G_{th} = 170 J m^{-2}. By contrast, the composite with covalent interlinks has a fatigue threshold of G_{th} = 420 J m^{-2}. Strong interlinks enable clustered particles to carry high stress. Second, we measure the dc/dN–G curves of composites with F = 0.45 and various values of C (**Fig. 3e**). As C decreases, the fatigue threshold increases. We repeat this procedure for F = 0, F = 0.15, F = 0.25, and F = 0.35 and observe the same trends in C (**Fig. S17**). Long polymer chains deconcentrate stress. Third, we measure the dc/dN–G curves of composites with $C = 10^{-4}$ and various values of F (**Fig. 3f**). While the polymer matrix without particles has a fatigue threshold of G_{th} = 170 J m^{-2}, a composite of F = 0.45 forms dense clustered particles and has a fatigue threshold of G_{th} = 1,020 J m^{-2}. Clustered particles further deconcentrate stress. Taken together, these experiments support the mechanism of multiscale stress deconcentration."

We have added the following sentences to page 7 of the manuscript:

"The fatigue threshold is high when polymers are long and particles are concentrated (**Fig. 3g**). For all composites, the threshold scales approximately as $G_{th} \sim C^{-1/2}$, following the Lake-Thomas model.[4] For any given value of C, G_{th} increases with F. Even at F = 0.15, the fatigue threshold is about a factor of two higher than pure PEA. At F = 0.15, particles do not percolate, but cluster (**Fig. 1c**). These observations are consistent with stress deconcentration over multiple thin layers of polymers between particles in a cluster (**Fig. S1, Supplementary Note 1**). It appears that the percolation threshold plays no special role in enhancing the fatigue threshold."

This is the Supplementary Note:

"**Supplementary Note 1. Mechanics of multiscale stress deconcentration**

Consider an elastomer filled with rigid particles of volume fraction F. A crack in the composite impinges both on polymer chains (**Fig. 1a**) and clusters of particles (**Fig. 1b**). Near the crack tip, stress deconcentrates across both long polymer chains and clustered particles.

First consider a crack growing in the elastomer network (**Fig. 1a**). Before a polymer chain breaks, stress is deconcentrated over the entire length of the chain. Rupture of a single bond along the chain dissipates energy stored in every bond along the chain. According to Lake and Thomas,[4] the fatigue threshold of the polymer matrix, $G_{th,m}$, is the covalent energy per unit area of one layer of polymer chains.

Next consider a crack growing in a particle filled elastomer (**Fig. 1b**). Particles cluster and percolate. Within a cluster, the thickness of the gap between two particles is small, comparable to a layer of polymer chains. The fatigue threshold of each gap is $G_{th,m}$. Because the particles are rigid compared to the polymer matrix, the stress to rupture one gap is deconcentrated to several other gaps in the particle cluster. When the crack grows through one gap, the energy stored in many gaps is released. The fatigue threshold of a cluster of particles is $N_g G_{th,m}$, where N_g is the number of gaps in the cluster that participate in stress deconcentration.

By rule of mixture, write the threshold of the composite as $G_{th} = FN_gG_{th,m} + (1 - F)G_{th,m}$. Like modulus, the fatigue threshold takes a separable form $G_{th}(C, F) = G_{th,m}(C)R_{th}(F)$, where the particles amplify the fatigue threshold by a factor

$$R_{th}(F) = F\left(N_g - 1\right) + 1 \quad (1)$$

The threshold of the matrix scales the threshold of the composite, $G_{th} \sim G_{th,m}$. Therefore, the threshold of the composite will follow the scaling of the Lake-Thomas model, $G_{th} \sim C^{-1/2}$. Long polymer chains and clustered particles synergize to increase the threshold of the composite.

We plot the threshold reinforcement ratio R_{th} at various values of F and C (**Fig. S1a**). R_{th} is not sensitive to changes in C, as changing C by 100 times changes R_{th} by at most a factor of 3. Consistent with Eqn. (1), we write the fatigue threshold of the composite in a separable form: $G_{th} = G_{th,m}(C)R_{th}(F)$. Using Eqn. (1), we estimate the number of gaps N_g that participate in stress deconcentration (**Fig. S1b**). Unlike R_{th}, N_g does not vary significantly with F. These observations show that R_{th} is more strongly a function of the volume fraction of particles than N_g. Across all C and F, we measure an average value of $N_g = 13.6$. We note that if the adhesion between particles and polymers is not strong, the threshold of the composite is not increased with particle reinforcement (**Fig. 3d**). Without strong adhesion, stress is not deconcentrated from the scale of a polymer chain to that of clustered particles.

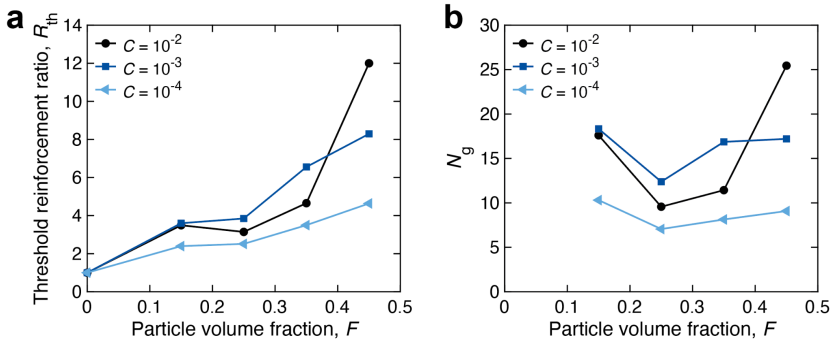
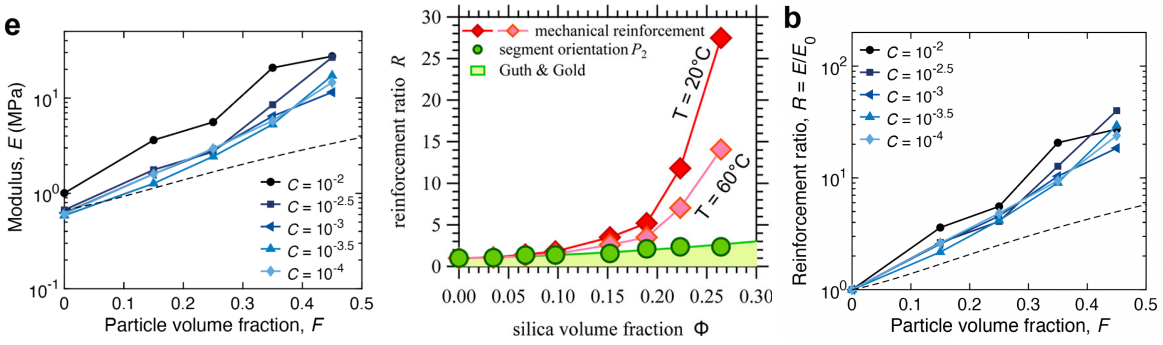


Figure S1. Reinforcement of fatigue threshold. (a) Threshold reinforcement ratio, $R_{th} = G_{th}/G_{th,m}$, and (b) N_g plotted as functions of F. The value of N_g is evaluated from R_{th} and Eqn. (1) for each value of F."

Comment: Third, theoretically, how to understand the synergistic effects considering the development of percolation network theory?

Response: Percolation in filled rubbers can be predicted by percolation theory. Our system can be modeled most simply as randomly dispersed impenetrable spheres.[1] For this model, percolation theory predicts that percolation occurs at a particle volume fraction of $F = 0.20$.[2,3] Our data show that the modulus deviates significantly from the Guth-Gold elastic solution above this value of F (**Fig. 2e**, left

figure). This result is consistent with the literature (e.g., Ref. 2; Ref. 17, center figure).



We modify the following sentences on page 5:

"...We compare our data with the Guth-Gold model for rigid spherical particles in a linear elastic matrix, $E(C, F) = E_0(C)(1 + 2.5F + 14.1F^2)$ (the dashed line in **Fig. 2e**).[15,16] This solution follows the data approximately at low F, but deviates greatly at high F, when particles form a percolated network. This deviation in modulus from the Guth-Gold model suggests that the percolated particle network greatly affects the modulus at high particle volume fractions.[2,17,18] Indeed, this deviation from the Guth-Gold model occurs near the percolation threshold of randomly dispersed impenetrable spheres, which percolate at $F = 0.20$.[19]

Inside the plateau, entanglements and particles synergize to increase the modulus of the composite. To characterize this synergy, we quantify the amplification of the modulus by the reinforcement ratio, $R = E/E_0$, where E is the modulus of the composite and E_0 is the modulus of pure PEA. The reinforcement ratio is a function of F but not a function of C (**Fig. S10**). These observations indicate that the modulus of the composite takes the separable form $E(C, F) = E_0(C)R(F)$. Inside the plateau, the synergy between entanglements and particles is multiplicative: $E(F) = E_0R(F)$, where E_0 is set by entanglements, and $R(F)$ increases steeply when particles percolate. We interpret this scaling as follows. The composite has three microscopic length scales: the diameter of individual particles ($D \sim 110$ nm), the average distance between neighboring entanglements ($\xi \sim 10$ nm), and the thickness of a layer of polymer of reduced mobility near the particles ($\varepsilon \sim 2$ nm).[20] In the limit of $D >> \xi, \varepsilon$, the composite can be treated as rigid particles in a continuum matrix, where ξ is contained in the modulus of the matrix E_0, and ε modifies D negligibly. Dimensional analysis indicates that the only remaining length scale, D, does not affect the modulus of the composite. Consequently, the modulus of the composite is proportional to the modulus of the matrix, $E = E_0R$, which corresponds to our observation. The scaling factor R depends on the volume fraction of particles F and their arrangement, such as when the particles form a percolated network. We note that, although modulus increases steeply when particles percolate, percolation theory by itself does not explain how entangled polymers and percolated particles synergize to increase modulus."

We observe that fatigue threshold does not increase dramatically when the particles percolate (**Fig. 3g**). This behavior is in contrast to that observed for modulus. Modulus is a global quantity related to the transmission of load from one side of the material to another, while fatigue threshold is a local quantity related to the material behavior near the crack tip. The synergy to increase fatigue threshold is interpreted in Supplementary Note 1, provided in our response to the previous comment. We have added the following sentences on page 7.

"Even at $F = 0.15$, the fatigue threshold is about a factor of two higher than pure PEA. At $F = 0.15$, particles do not percolate, but cluster (**Fig. 1c**). These observations are consistent with stress deconcentration over multiple thin layers of polymers between particles in a cluster (**Fig. S1, Supplementary Note 1**). It appears that the percolation threshold plays no special role in enhancing the fatigue threshold."

Comment: Fourth, regarding the application in kirigami grippers, it is true that high fatigue resistance and high stiffness are beneficial for the elastomer kirigami gripper. However, a kirigami gripper (e.g., Ref. 26) normally employs a rigid, thin, less-stretchable sheet like PET to favor the out-of-plane buckling deformation to release the stress concentration at the cut tip. The benefit of an elastomer kirigami gripper compared to less-stretchable rigid elastic sheets may need to be justified. Minor comment: the thickness of kirigami gripper is not specified in the manuscript.

Response: As noted in the original manuscript, our choice of kirigami grippers as a demonstration was inspired by a recent paper (Yang, Y., Vella, K. & Holmes, D. P. Grasping with kirigami shells. *Sci. Robot.* **6**, eabd6426 (2021)). Specifically, kirigami requires cuts by design and grippers need to sustain cyclic deformation. Furthermore, the paper by Yang et al. reported that their elastomer kirigami grippers were too compliant and prone to crack growth, and needed to reinforce the gripper with cellulose paper. They used an elastomer in their work because it enabled them to incorporate magnetic particles into the gripper. Furthermore, functional elastomers such as liquid crystal elastomers have recently been used for soft actuators (Ref. 27).

Kirigami grippers made of our elastomers highlight two main features: high modulus and high fatigue threshold. The demonstration of kirigami grippers does not highlight all features of particle filled elastomers important for other applications. For example, particle filled elastomers are essential for treads of tires and seals.

We have expanded our paragraph as follows.

"Many applications require materials to bear load over many cycles. For example, in soft robotics, materials need to bear loads over large and repeated displacements.[24,25] For an elastic material, the load-bearing capacity is scaled by modulus, and a large number of cycles is enabled by high fatigue threshold. Here we demonstrate the significance of both high modulus and high fatigue threshold using a recent design of a compliant gripper (**Fig. 4c**).[26] We choose this application because kirigami requires cuts by design, and grippers need to sustain cyclic deformation. The gripper is made using a square sheet with cuts parallel to a diagonal. When pulled along the other diagonal, the sheet buckles out of plane, gripping an object. Grippers with particles require larger forces to close than those without particles (**Fig. 4d**). We cyclically close and open the grippers. A gripper with $F = 0.45$ and $C = 10^{-2}$ fractures in only a few cycles (**Movie S1**). However, a gripper with $F = 0.45$ and $C = 10^{-4}$ has negligible permanent deformation after $N = 350{,}000$ cycles, and the crack does not advance appreciably (**Fig. 4e**). Next, we use a gripper to grasp a sphere, and measure the force required to lift the sphere at a constant velocity (**Fig. 4f, Movie S2**). A gripper with long polymer chains and percolated particles lifts a load six times that of a gripper made of

pure PEA (**Fig. 4g**), and maintains this lift force over many cycles (**Fig. 4h**). We discuss design considerations for kirigami grippers in **Supplementary Note 3**."

We also have added the following sentences in the Supplementary Note 3.

"Structural design: elastomers of high fatigue resistance, high stiffness, and stretchability open doors to new possibilities in the design of kirigami structures. For example, recent works have developed elastomeric kirigami structures that can be actuated by nonmechanical means, such as magnets or temperature.[26,46] We look forward to seeing new kirigami applications."

We modify our manuscript to show the thickness of our composite film explicitly.

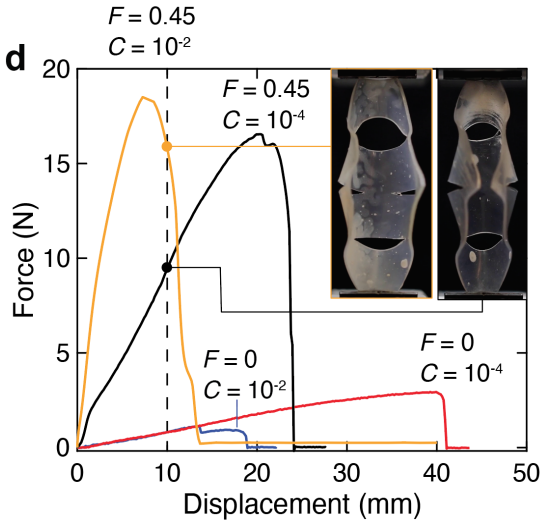
"Molds consisted of glass plates (8476K15, McMaster) separated by a silicone sheet (1460N11, McMaster, thickness = 0.79 mm)."

"A gripper was cut from a film of composite (thickness = 0.79 mm) using a razor blade."

Comment: The authors showed the comparison between two sample grippers: one is C= 10^{-4}, F=0.45 and C = 10^{-2}, and F = 0.45. What are the displacement applied to stretch both samples for the reported cyclic fatigue life? The magnitude of stretching displacement is highly related to the fatigue life since the gripper samples have largely different tensile strength as shown in Fig. 4d.

Response: The displacement is 10 mm, which is shown in **Fig. 4d** as a dotted line. We applied this displacement as it closes the gripper. Our fatigue test was done with this displacement as well. As noted in the manuscript, when we open and close the gripper for multiple cycles, the sample of $C = 10^{-2}$ and $F = 0.45$ fails after a few cycles, whereas the sample of $C = 10^{-4}$ and $F = 0.45$ last without noticeable damage (**Movie S1** and **Fig. 4e**).

We have revised **Fig. 4d** as shown below.



Comment: There is a compromise for design the kirigami elastomer gripper: on one hand, an applied large stretching displacement/strain is preferred to even potentially close the two "arms" for accommodating different sizes of grasped objects. On the other hand, the materials may failure under large stretching as shown in Fig. 4d. How to synergistically integrate stiffness, fatigue, materials stretchability, and deformed gripper shapes for grasping may be considered for its potential applications as a kirigami gripper.

Response: We have added the following sentence to page 8 and **Supplementary Note 3** to the Supplementary Information.

"We discuss design considerations for kirigami grippers in **Supplementary Note 3**."

"**Supplementary Note 3: Design of mechanical properties of kirigami grippers**

In designing elastomeric kirigami grippers, one may consider the following.

- Stretchability: the displacement required to close the gripper is ~10 mm and excess stretchability is redundant. As described in Ref. 26, the actuation displacement is a geometric quantity unrelated to the mechanical properties of the material, assuming fracture does not occur.

- Fatigue resistance: the higher the fatigue resistance, the better the durability and reliability. The fatigue resistance increases with F and decreases with C.

- Stiffness: the gripping force and lift force scale with the stiffness. The required force will differ depending on the application. Provided that low C provides high fatigue resistance while the stiffness is maintained by entanglements, one can tune F to design the stiffness. For example, varying F from 0 to 0.45 at $C = 10^{-4}$ varies the modulus from 0.6 MPa to 14 MPa. While reducing F decreases the fatigue resistance, the threshold can still be relatively high with low C. Furthermore, the energy release rate G at a fixed strain scales with modulus, making fatigue threshold requirements for stiff materials greater than for soft materials. For example, G scales with E for a linear elastic material at fixed applied strain.

- Structural design: elastomers of high fatigue resistance, high stiffness, and stretchability open doors to new possibilities in the design of kirigami structures. For example, recent works have developed elastomeric kirigami structures that can be actuated by nonmechanical means, such as magnets or temperature.[26,46] We look forward to seeing new kirigami applications."

Comment: Another comparison on the fatigue life between two cases may also be needed to justify the high fatigue life, i.e., gripper with C= 10^{-4}, F = 0.45, and C= 10^{-4}, F = 0 despite its lower modulus. As mentioned above, the lower modulus and higher stretchabilty in C=10^{-4} and F = 0 could have other applications in grasping lightweight objects.

Response: We agree that a gripper with $C = 10^{-4}$ and $F = 0$ is more stretchable and softer than a gripper with $C = 10^{-4}$ and $F = 0.45$. When a soft gripper is needed, then one can decrease F. See the discussion in the previous comment.

Referee #3

Comment: A. Steck et al propose to study model elastomers obtained by coreacting acrylate monomers (chain extender and crosslinker) with functionalized filler. The idea is to systematically vary the content of fillers and crosslinks, at high entanglement ratio, to study the fatigue of the materials.

Response: We present a principle of multiscale stress deconcentration to improve the fatigue resistance of particle filled rubbers (**Fig. 1**). We identify for the first time multiscale stress deconcentration in particle filled rubbers, and demonstrate that this principle improves fatigue threshold by an order of magnitude. No works have reported particle filled rubbers with comparably high fatigue thresholds. We use filled rubbers in which polymer chains are ~100 times longer than those in typical rubbers. We show that the high fatigue threshold requires stress deconcentration not only along long polymers, but also through clustered particles. The latter has never been suggested in the literature.

To validate the principle of multiscale stress deconcentration, we conduct extensive systematic studies by varying synthesis parameters. Our data support the principle. Since this principle is not material-specific, it would be generally applicable to many other polymers and particles.

Comment: B. Even if the paper is very didactic and the work perfectly executed and discussed, the proposed materials are not new. In fact, rubber industry working on NR, silicones or EPDM systems, has long introduced in their materials functionalized silica or carbon black for both reinforcement and fatigue resistance.

Response: Thank you for appreciating our writing, experiments, and discussion. As we noted in the manuscript, particle filled elastomers have high-volume applications, including tires and seals.

The difference between our design and existing filled rubbers is the molecular structure of the polymer matrix. Existing particle filled rubbers do not have chain lengths as long as those reported in this work. For example, most commercial rubbers use crosslinker-to-monomer molar ratios on the order of $C \sim 10^{-2}$. See Ref. 4, Ref. 5, Ref. 7, and (Mzabi, S., et al. A Critical Local Energy Release Rate Criterion for Fatigue Fracture of Elastomers, *J. Polymer Sci. B: Polymer Phys.* **49**, 1518-1524 (2011)). In our paper, we test rubbers of C two orders of magnitude lower. Furthermore, we show that $C \sim 10^{-2}$ is insufficient to achieve a high fatigue threshold. This is consistent with the fatigue thresholds of existing filled rubbers, which are on the order of ~100 J m^{-2}.

There are practical reasons why previous works have used short polymer chains. First, before crosslinking, long polymer chains form entangled polymer melts and require processing to incorporate particles and reagents. This is commonly achieved by mechanical mixing, or mastication, which is known to reduce the molecular weight of the polymers (Pike, M. & Watson W. F., Mastication of Rubber. I. Mechanism of Plasticizing by Cold Mastication, *J. Polymer Sci.* **9**, 3, 229-251 (1952)). Moreover, if the polymer chains are initially short, then the concentration of the crosslinker must be high enough to crosslink all chains. For example, crosslinking an SBR melt with a molecular weight of 120 kg/mol (e.g., that used in Mzabi, et al., 2011) requires $C > 10^{-3}$ to form a polymer network. This lower limit will be

higher if crosslinking efficiency is low or if crosslinks are not uniformly distributed across all chains. By synthesizing PEA from EA monomer, we avoid these complications.

We add the following sentences to the manuscript:

"Functionalized nanoparticles have long been used as reinforcing fillers in industrial applications.[1,2] Additionally, TPM-functionalized silica nanoparticles have been used as reinforcing fillers in PEA elastomers,[8,9] but these works used polymer chains much shorter than reported here, and did not report fatigue threshold."

Additionally, we add a sentence discussing a recent technique to overcome some of these limitations:

"A recently developed technique has enabled the synthesis of highly entangled elastomers from prepolymers, which can be potentially used to make particle filled elastomers of high fatigue resistance.[27]"

Comment: The figure 3i does not acknowledge some works that actually show materials that outperform the presented performances (see e.g. two reviews that the authors know because they actually cited it in other works: Rep. Prog. Phys. 79 046601, 2016 and J. Phys.: Condens. Matter 17 (2005) R1071–R1142). In particular, prestretched NR filled with carbon black show G threshold of more than 3000J/m^2 at dc/dn of few nanometers. This is ascribed to strain-induced crystallization. I advise the authors to really go deep into the literature of reinforced fillers so that not to rediscover already existing knowledge.

Response: Thank you for mentioning strain-induced crystallization. Some materials such as natural rubbers induce local crystallization near the crack tip as polymer chains highly align. When the sample is not fully relaxed during the fatigue test, the strain-induced crystal domains remain at the crack tip, which resists the crack from propagation. Consequently, prestretched natural rubbers filled with carbon black can show fatigue thresholds on the order of 3,000 J m^{-2}. However, a prestretched natural rubber is a natural rubber at prestretched state, not a different material. Note that the fatigue threshold of relaxed rubber, regardless of particles, is ~100 J m^{-2}. By contrast, we show how to improve the fatigue resistance of relaxed particle filled elastomers, which has never been discovered before.

To discuss strain-induced crystallization in natural rubbers, we have added the following sentences.

"Semi-crystalline rubbers can have both high modulus and high fatigue threshold. For example, filled natural rubber crystallizes under strain and, when loaded under non-relaxing conditions, strain-induced crystallization greatly enhances the fatigue threshold.[32,33] However, these strain-induced crystals melt when the stretch is fully relaxed each cycle, resulting in a fatigue threshold of ~100 J/m^2 regardless of the presence of particles. Phase separation in immiscible polymer blends can also enhance the fatigue threshold.[7]"

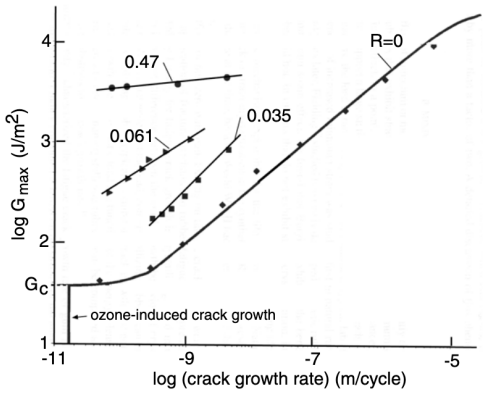


Figure 29. Fatigue crack growth for unfilled natural rubber. The (maximal) crack propagation energy G_{max} is shown as a function of the crack velocity. Results are for different ratios $R = F_{min}/F_{max}$ between the minimal and maximal loading force. Adapted from [54].

Comment: By the way, the materials presented here have a high level of viscoelasticity that would not be accepted by industry (very bad elastic return, large deformation with low level of strain, what would it give at 300% deformation?)

Response: In general, different polymer and particle chemistries can be used to reduce viscoelasticity and hysteresis. The object of this paper is to propose the principle of multiscale stress deconcentration (**Fig. 1**) and to demonstrate that the principle greatly amplifies fatigue threshold. The claim of novelty in this work is this general principle, which we have demonstrated using a model system: PEA filled with monodisperse silica nanoparticles. We have selected this system as a model following many previous works including Refs. 8, 9, 13, and 29. Specifically, our proposed principle enhances fatigue threshold without requiring any effect of viscoelasticity. The object of this paper is not to design a rubber with comprehensive material properties for any given application.

Comment: C. Data are good and very well presented, presentation is good and methodology is good as well. I have however some reserves on the description of the chemistry applied here that, IMHO, is totally eluded. We don't know the conversion in monomers after polymerization, the level of functionalization of fillers, their specific surface and their reactivity, the experimental crosslink density. All explanation are based on theoretical values: this is not acceptable for a paper in Nature.

Response: Thank you for appreciating our data and how we present them. We respond to your comments as follows.

1) Conversion in monomers after polymerization.

Following your comments, we have characterized the monomer-to-polymer conversion ratio gravimetrically and added the following sentence and supporting figure in the manuscript.

"Most monomers polymerize at all values of C (**Fig. S4**)"

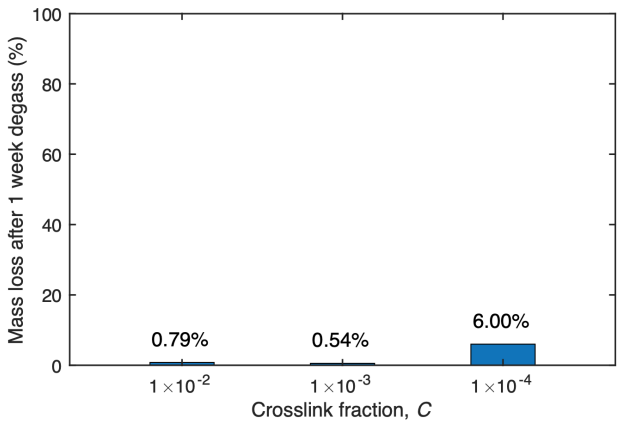


Figure S4. The monomer-to-polymer conversion ratio. The composite is weighed right after polymerization and one week after polymerization. Since EA monomers are volatile at room temperature, the mass loss represents the amount of unreacted monomers.

2) Level of functionalization of fillers

We specified the level of functionalization of particles in the original Materials and Methods section, which is provided from the Cabot Corporation.

"Silica nanoparticles functionalized with 3-(trimethoxysilyl)propyl methacrylate (TPM) of areal density 2.7 molecules per nm^2 were used as reinforcing particles (Cabot Corporation, Silica A), …"

We have also added the following sentence in the main text:

"On the surfaces of the silica particles, the number density of TPM groups is 2.7 nm^{-2}, which is measured by the manufacturer."

3) Specific area

We have calculated the specific area of the particles based on the diameter of the particles measured by TEM. We have added the following sentence to the Materials and Methods.

"From the diameter of the nanoparticles, the specific area is calculated as 26 m^2 g^{-1}."

4) Reactivity of fillers

We confirmed the reactivity of silica functionalized with TPM by conducting experiments to compare silica functionalized by TPM and silica functionalized by TMS.

"First, we prepare a composite with silica nanoparticles functionalized with trimethylsilyl (TMS) groups. Such particles do not form covalent interlinks with PEA polymers. The stress-stretch curves for such composites coincide with the stress-stretch curve of pure PEA, suggesting weak particle-matrix adhesion

(**Fig. S16a**). The stress-stretch curves do not change significantly with cycles (**Fig. S16b-d**). … Without covalent interlinks, the fatigue threshold is the same as the polymer matrix, G_{th} = 170 J m^{-2}. By contrast, the composite with covalent interlinks has a fatigue threshold of G_{th} = 420 J m^{-2}. Strong interlinks enable the particle network to carry high stress."

Unlike particles with grafted linear polymers, which can be extracted from the ungrafted polymers (e.g. soxhlet), the particles in our composite are hard to be extracted as they strongly adhere to the crosslinked polymer network. This limits the measurement of reactivity of the particles. However, because the silica particles are functionalized with methacrylate groups very similar to the monomers and the monomer-to-polymer conversion ratio is high, we assume that most functional groups react. We also find that those who have studied the same chemistry (grafting ethyl acrylate onto TPM-functionalized silica) assumed full consumption of the anchored methacrylate units (Espiard, Ph., Guyot, A. Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 2. Grafting process onto silica. *Polymer* **36**, 4391–4395 (1995)). Additionally, Refs. 8 and 9 report that, for a nearly identical system (EA monomers and TPM-functionalized silica nanoparticles), dense covalent interlinks are formed between the silica surfaces and PEA.

5) Experimental crosslink density

We have added the following discussion in the Supplementary Information.

"**Supplementary Note 2. Experimental crosslink density**

The experimental crosslink density is defined by the experiment used to measure it. For a polymer network with negligible entanglements, the elastic modulus is related to the crosslink density as $E = 3\rho N_{Av}kT/M_s$, where ρ is the density, N_{Av} is Avogadro's number, kT is the temperature in unit of energy, and M_s is the molecular weight of polymer strands between crosslinks (Ref. 12, Eqn. (7.31)). Therefore, the experimental crosslink density can be estimated from the elastic modulus. For example, at $F = 0$ and $C = 10^{-2.5}$, the modulus is 0.7 MPa. This modulus gives the molecular weight of 12,070 g/mol or 109 monomers per chain. In the manuscript, we estimated the length of the polymer chain as $1/(2C)$ = 158 monomers, which is similar to the crosslink density estimated by the modulus.

For a highly entangled polymer network, by contrast, the elastic modulus is related to the entanglement density as $E = 3\rho kT/M_e$, where M_e is the molecular weight of polymer strands between entanglements (Ref. 12, Eqn. (7.47)). Therefore, the elastic modulus does not provide experimental crosslink density. Instead, the crosslink density can be related to the fatigue threshold for a highly entangled polymer network. The Lake-Thomas model relates the fatigue threshold to the crosslink density as $G_0 = \alpha l n^{1/2} J V^{-1}$, where α is a pre-factor of order of unity, l is the length of each monomer unit, n is the number of monomer units in a polymer chain, J is the C-C bond energy, and V is the volume of each monomer unit (Ref. 4). Therefore, the experimental crosslink density of a highly entangled polymer network can be calculated by scaling ($G_0 \sim n^{1/2}$). This scaling corresponds to our data ($G_0 \sim C^{-1/2}$, see **Fig. 3g**), as $n \sim C^{-1}$. For example, the fatigue thresholds of pure PEA elastomers at $C = 10^{-2}$ and $C = 10^{-4}$ are ~20 J/m^2 and ~200 J/m^2, respectively. Therefore, the values of n are expected to be different by 100 times. As n at $C = 10^{-2}$ is estimated as ~100 monomers per chain from the modulus, n at $C = 10^{-4}$ is ~10,000 monomers per chain."

Comment: D. Not appropriate here.

Comment: E. Conclusions are going to far on tire pollution and claiming of totally new materials, this is not true. Introduction about skin and cartilage mimicking is overstretched as well.

Response: Here the reviewer made three comments, which we address one by one.

"Tire pollution" Our manuscript mentions tire pollution in discussion, and not in conclusion. The intent is to remind the reader that tire pollution is an important and current problem. As noted in the manuscript, "it has long been appreciated that wear resistance correlates with fatigue resistance.[40–42]" It seems natural that one should examine if multiscale stress deconcentration will also enhance wear resistance. We add a sentence to the paragraph.

"Furthermore, tires of high molecular weight are under development to improve many properties related to their performance.[43,44]"

"Totally new materials". Our manuscript does not claim totally new materials. As we noted in the manuscript and in this response, the novelty here is the principle that multiscale stress deconcentration can greatly amplify fatigue threshold. We add the following sentences to the manuscript.

"Functionalized nanoparticles have long been used as reinforcing fillers in industrial applications.[1,2] Additionally, TPM-functionalized silica nanoparticles have been used as reinforcing fillers in PEA elastomers,[8,9] but these works used polymer chains much shorter than reported here, and did not report fatigue threshold."

"Skin and cartilage". We agree that a proper discussion on the analogy of biological tissues and particle filled elastomers would require more than a single sentence. We have removed the following sentence from page 2: "This architecture is analogous to structures found in load-bearing tissues, such as skin, cartilage, and ligaments."

Comment: F. I advise the authors to submit their work in a specialized journal, after they improved the literature survey and chemistry description. I also suggest to correct the quotes to supporting information, the numbers were not correct.

Response: We have corrected all references to the Supplementary Information.

Comment: I have also minor comments that again show the paper is not at the level of Nature: DSC is differential scanning calorimetry, not dynamic! and deltaH are better comparison than Tgs.

Response: We have corrected the labels of DSC in the Supplementary Information and in **Fig. S20**. The updated text is:

Differential scanning calorimetry

We characterized the composites with a differential scanning calorimeter (DSC, TA Discover DSC 250). Using the DSC, samples were heated to 75 °C, cooled to -75 °C, and heated to 75 °C, while measuring the heat flow through the samples. The heat flow normalized by the mass of the sample is plotted as a function of temperature for various composites (**Fig. S20**).

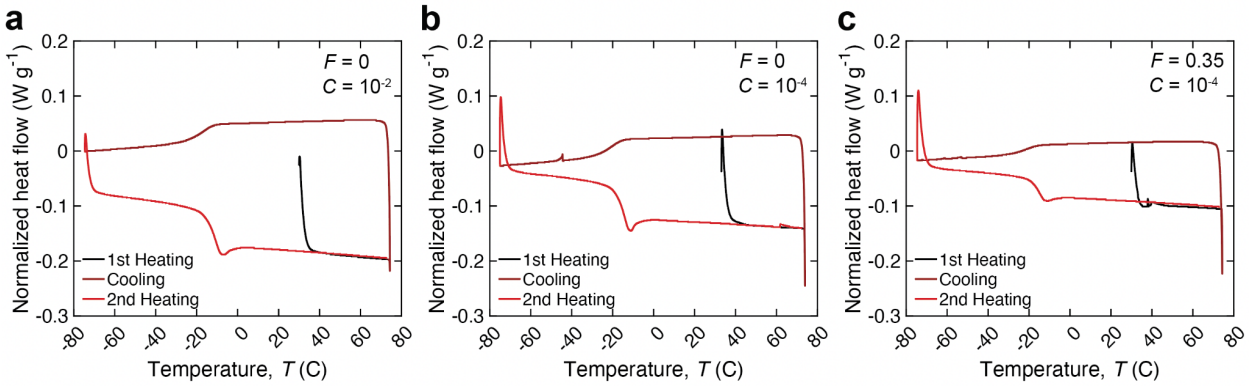


Figure S20. Differential scanning calorimetry of composites. The mass normalized heat flow is plotted as a function of temperature for (**a**) $C = 10^{-2}$ and $F = 0$, (**b**) $C = 10^{-4}$ and $F = 0$, and (**c**) $C = 10^{-4}$ and $F = 0.35$, where the glass transition temperature upon cooling is measured, respectively, to be T_g = -17.49 °C, T_g = -20.96 °C, and T_g = -21.93 °C. For pure PEA of $C = 10^{-4}$, T_g upon cooling is -20.96 °C, which agrees with the expected values for PEA.

Our conclusion from this experiment is that the glass transition temperature of PEA with low C matches the expected value for uncrosslinked PEA. We agree with the reviewer that it is challenging to interpret the effect of C or F on glass transition temperature. We have removed the following sentence: "Increasing C increases T_g, while adding particles decreases T_g."

Comment: Most likely, some chains break with strain, and this is not evoked at all in the paper.

Response: We mention partial debonding between particles and void formation on page 6. We did not explicitly mention breaking some chains with strain due to PEA elastomer being highly elastic until large strains (e.g., Ref. 11). However, it is possible that stretching particle-filled samples can break PEA chains. We have modified the text on page 6 to acknowledge this:

"These observations suggest changes in microstructure, such as partial debonding between the particles and matrix, breaking polymer chains, or formation of voids in the matrix."

Comment: G. see above.

Comment: H. This didactic study is nice for comprehension of model systems, but cannot shade other materials that have been optimized for more than 70 years now.

Response: Our claim is that multiscale stress deconcentration provides new opportunities in the development of fatigue resistant rubbers. To test our hypothesis, we used a known chemistry of polymers,

particles, and their adhesion. We demonstrate that our principle achieves previously unattainable fatigue threshold in relaxing conditions. We have not found any mention in the literature of the principle of multiscale stress deconcentration–that is, fatigue threshold is amplified by stress deconcentration through not only long polymers, but also clustered particles.

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

The manuscript has improved significantly. The authors clearly communicate the great findings of their study. As mentioned in my first review of this manuscript, I took some time to reach an understanding of the novelty of this work but this time it was clear from the beginning. I will definitely use these findings in my future work and explore them further.

I suggest accepting it as is.

Referee #2 (Remarks to the Author):

The reviewer's major comment is on the recent work that reported similar both high modulus and high fatigue resistant (Nat. Commun. 13, 2279, 2022), which needs justification for the novelty conserving the similar major report despite different materials systems.

After carefully reading through the authors' response and the NC paper, the reviewer agrees with the authors that the NC paper greatly overestimates the reported fatigue threshold considering its over 1000 times higher dc/dN than the authors' work. The reviewer also agrees that it is not reasonable to calculate the fatigue resistant using the healed samples rather than the steady state. The reviewer's major concern is cleared.

The reviewer's other comments on the mechanisms of how two synergistic networks lead to high modulus and fatigue are also well addressed in the response letter through related experimental images, discussions, and simplified models. The reviewer is clear on these comments.

Last part of the reviewer's comment is on the potential broad impact of this work with one example demonstration of application in kirigami gripper. The reviewer's technical comments on the design are addressed in the revised version.

The reviewer agrees with the authors that the kirigami gripper example does not showcase all the unprecedented features. As the authors mentioned and motivated in the introduction and discussion for treads of tires and seals, this work could have potential applications in resistant tires. Since wear resistance is correlated with fatigue resistance, the reviewer wonders if possible to conduct wear resistance test of their particle filled rubber to showcase the power and broad impact of the particle-filled elastomers.

In sum, the reviewer's major comment on the similar work is cleared and other comments on the mechanisms and kirigami gripper are well addressed. After clearing the concerns and comments, the reviewer supports that it is an excellent piece of work in terms of unprecedented performance and

uncovered fundamental sciences.

Regarding its potential broad impact, the kirigami gripper is a good example to showcase the high stiffness and high fatigue properties, but it is a bit off the introduction and motivation in the challenge of rubber industry. The reviewer suggests to find one more example or test to showcase its potential broad impact and application in resistant tires by conducting the wear resistance test if possible. Such an example or test would be more convincing.

Referee #3 (Remarks to the Author):

Steck et al propose a new version of their paper submitted to nature about elastomers that show exceptional fatigue resistance. Their study follows up an article published in 2021 in Science where they polymerized EA in a manner to encourage high entanglements. Here, they have introduced functionalized silica particles to add a new component of stress release, allowing large fatigue treshold to be reached in pure shear tests.

As I said before, the study shows many data and interesting fatigue results, but again I cannot accept the manuscript, since I have serious doubts about the chemistry; obviously, my first shot may not have been clear enough, so here we go again.
The major drawback that I emphasized last time was the fact that the polymerization scheme was not looked at and is actually likely wrong.

First, to measure the molar mass between crosslink (Mc), researchers from the rubber field carry out swelling measurements, in presence or not of fume ammonia to disrupt specific interactions between filler particles and polymer chains. This was not done here, and the proposed Mc calculation by stress strain curves is not relevant, particularly in presence of a filler.

I also asked more about the polymerization by itself, and did not receive the answers I expected. First, looking at volatiles does not allow to conclude on polymerization and crosslinking reactions. Swelling to extract uncrosslinked chains would be again more adapted, as well as to estimate a true Mc.
Besides, the authors now added references to support their view on a 'conventional system' very close to theirs (only the crosslinker is different). Actually, in Berriot's studies, it is clearly shown how important it is to measure true Mc's, there for instance by low field NMR.

In Espiard and Guyot's paper, not added in the main text, these authors show that:
1. reaction of methacrylate groups on the filler is faster than acrylate monomers (typically, reactivity ratios are 2 for 0.2, respectively), so that grafting reaction occurs majoritarely at the beginning of the polymerization, generating loops on the filler. Then, polymer chains grow independently at larger conversions. The blank experiments with non-functionalized silica in the present paper do not prove anything in terms of polymerization and crosslinking reactions of functionalized fillers;
2. Maximal molar masses obtained in emulsion (best system for generating high molar masses) and deduced from extraction are 200kg/mol, not the million that the present authors claim here to

explain the properties of their materials.

Another important point is the presence of side reactions that complicate the chemistry. All chemists practicing polymerization know that transfer reaction to the monomer is systematically occuring with acrylates (see e.g. Castignolles et al, Polymer 50 (2009) 2373–2383). Long branches are generated by initiation from the polymer chains and thus, at large conversion, gelation by crosslinking is systematically seen. This occurs mostly at moderate temperature (40°C and above), but it is also pregnant at room temperature. By the way, I expect that you see an exotherm here while you make the polymerization, this is not mentioned in the text.

This last information contradicts with the view of the authors that long chains are formed in their system that end-link with the filler; not only it is not the case, but even more, crosslinking ratio is certainly above the calculated values they propose (again, swelling would prove that, since most of the entanglements would desentangle with solvent).

I suggest that the authors make a blank experiment in absence of crosslinker and with non functionalized silica to prove this gelation effect. I expect that with functional silica and no crosslinker, they will also generate a fatigue resistant material.

Note that changing the ratio I/C is not what polymer chemists usually practice (see cited papers above). They first set a constant initiator/monomer ratio and then change the crosslinker concentration according to the network they want to produce. Decreasing both C and I is more likely to decrease the polymerization rate and thus to modulate the final network.

In short, even if the presented materials have certainly encouraging fatigue properties, the storytelling based on idealized polymerization scheme is not correct. Several works of rubbers' specialists have proven that more precise structure determination is needed before interpreting the properties as you do it here.

I have also some comments on the mechanical analyses of the systems. The authors have added the Figure S9 that shows DMA results. First, the technique is not presented in the experimental section, so we don't know what they did exactly. Second, the steep increase in tan(delta) at high stretch frequency clearly shows that the material exhibit a large viscoelasticity that participate to stress release. This is confirmed by the strong Payne effect shown in Figure 14a.
Besides, the fact that the percolation treshold does not globally change the fatigue resistance advocates against the 'ideal network' proposed here.
Third, invoking that thermoplastic polymers suffer from creep is certainly true, but this is also what one would anticipate from your viscoelastic system.

To pursue, several comments directly related to the answers:
- p.20 'Since this principle is not material-specific': I believe exactly the contrary, but since the pure shear experiments are not very developed in the rubber community (apart in industry,but they don't publish their results generally), it is difficult to say if it is the best material ever that the present authors propose.
- p. 20 'Existing particle filled rubbers do not have chain lengths as long as those reported in this

work': well, actually, you did not measure them so how do you know, other than guessing?
- p. 22 'The object of this paper is not to design a rubber with comprehensive material properties for any given application': if generating high fatigue treshold is accompanied by huge viscoelasticity, then there is no point claiming in the abstract 'elastomeric materials of both high modulus and high fatigue resistance expand the space of materials design, opening doors to curtailing polymer pollution and building high performance machines'.
- p. 24 'the particles in our composite are hard to be extracted...': swelling experiments, though certainly not extracting silica, would allow measuring 'true' Mc's, the content of extractible material that could further be analysed by SEC for instance.
- p. 24 'methacrylate groups very similar to the monomers': not the same reactivity at all (a decade difference in propagation rate and so cross-reaction versus homopropagation).
- p. 26: 'we used a known chemistry of polymers': you did not look at it thoroughly actually.

Last points of detail:
In the field of polymer materials, we name 'composite' a hard and brittle material made of long fibers and a thermoset polymer such as in an epoxy amine system. Soft materials are named rubbers or elastomers, depending on how elastic and stress resistant they are.
Finally, in the y axis in Figure S8b, stretch at rupture has no unit (not MPa).

Author Rebuttals to First Revision:

Point-by-point response to the referees:

Referee #1:

Comment: The manuscript has improved significantly. The authors clearly communicate the great findings of their study. As mentioned in my first review of this manuscript, I took some time to reach an understanding of the novelty of this work but this time it was clear from the beginning. I will definitely use these findings in my future work and explore them further.

I suggest accepting it as is.

Response: We appreciate your kind words on our work. We are pleased to hear that you will use these findings in your own work. Thank you so much for making specific suggestions in the previous review to help us bring out the novelty and significance of this work more clearly to the readers. Also thank you for suggesting that this version of the paper be accepted as it is.

Referee #2:

Comment: The reviewer's major comment is on the recent work that reported similar both high modulus and high fatigue resistant (Nat. Commun. 13, 2279, 2022), which needs justification for the novelty conserving the similar major report despite different materials systems.

After carefully reading through the authors' response and the NC paper, the reviewer agrees with the authors that the NC paper greatly overestimates the reported fatigue threshold considering its over 1000 times higher dc/dN than the authors' work. The reviewer also agrees that it is not reasonable to calculate the fatigue resistant using the healed samples rather than the steady state. The reviewer's major concern is cleared.

Response: Thank you for bringing our attention to this 2022 Nature Communications paper. The lack of attention to certain significant details in that paper helped us appreciate the practice which we inherited from Thomas and others. We are delighted that you find our response helpful.

Comment: The reviewer's other comments on the mechanisms of how two synergistic networks lead to high modulus and fatigue (resistance) are also well addressed in the response letter through related experimental images, discussions, and simplified models. The reviewer is clear on these comments.

Response: Thank you for making comments in the previous review regarding the synergistic effects in our system. Your comments helped make it clear to us questions from a reader's perspective, and sharpen our description of multiscale stress deconcentration. These comments helped us appreciate the effects of percolation in modulus and fatigue threshold, and we feel the paper was improved by clarifying these points. We are pleased to hear that the revised manuscript has addressed your concerns.

Comment: Last part of the reviewer's comment is on the potential broad impact of this work with one example demonstration of application in kirigami gripper. The reviewer's technical comments on the design are addressed in the revised version.

Response: We are delighted that your concerns about our demonstration are addressed. We hope the discussion about the design of kirigami grippers is helpful to those who are interested in using particle reinforced elastomer to design kirigami structures. This demonstration of a kirigami gripper shows the benefits of having high fatigue threshold and high modulus.

The kirigami grippers demonstrated in the paper by Yang, Vella, and Holmes in Science Robotics (2021) have intrigued us. The paper by Yang et al. shows that deformation of a simple, well-designed structure can serve useful functions. The kirigami grippers by definition contain cuts and need to lift weights repeatedly. Consequently, the kirigami grippers highlight two main attributes of the particle reinforced elastomer: high stiffness and high fatigue threshold.

Comment: The reviewer agrees with the authors that the kirigami gripper example does not showcase all the unprecedented features. As the authors mentioned and motivated in the introduction and discussion for treads of tires and seals, this work could have potential applications in resistant tires. Since wear

resistance is correlated with fatigue resistance, the reviewer wonders if possible to conduct wear resistance test of their particle filled rubber to showcase the power and broad impact of the particle-filled elastomers.

Response:

We have designed our experiments to support two main findings:

(1) Entangled polymers and percolated particles synergize to increase modulus;
(2) Long polymers and clustered particles synergize to increase fatigue threshold.

To ascertain these main findings, we have systematically varied the experimental parameters (crosslinker-to-monomer molar ratio C, particle volume fraction F, and chemistry of interlinks between particles and polymers).

Kirigami gripper is a demonstration, which showcases two outstanding properties: high modulus and high fatigue threshold. High modulus enables the gripper to lift a high load, and high fatigue threshold enables the gripper to operate over many cycles.

We share the referee's enthusiasm and hope that multiscale stress deconcentration may also lead to wear-resistant elastomers. We believe that the general thesis developed in this paper and its conclusions will be used in the broad field of reinforced elastomers to develop new materials and applications, including wear-resistant tires. However, each such application will require separate work to develop reinforced elastomers specific for that application.

It has long been appreciated that wear resistance and fatigue resistance are related.[40–42] However, wear is a complex phenomenon, and is also related to other properties, including toughness, endurance limit, strength, viscoelasticity, friction coefficient, filler content, and the severity of testing conditions (Muhr, A. H. & Roberts, A. D. Rubber abrasion and wear. *Wear* **158**, 213–228 (1992)). Various properties are often in trade-off relations. For example, for materials with the same fatigue resistance, the wear resistance will be lower if the friction coefficient increases, since the shear stress increases at the given normal load.[44] For car tires specifically, the three major properties are wear resistance, wet traction, and rolling resistance. These properties must be considered simultaneously in what is known as the 'magic triangle' (Araujo-Morera, J., Verdejo, R., López-Manchado, M. A. & Santana, M. H. Sustainable mobility: The route of tires through the circular economy model. *Waste Management*. **126**, 309–322 (2021)). For these reasons, studying the effect of multiscale stress deconcentration on wear resistance requires extensive work dedicated to choice of polymers, design of experiments to control material properties, and proper test methods for wear resistance.

We have modified the paragraph on page 10 to alert readers to this opportunity for research.

"Polymers pollute our planet, and part of this pollution comes from wear of tires.[38,39] Tires wear by chipping off micron-sized pieces of rubber. Despite decades of effort to reduce rubber pollution on roads, the pollution has persisted and become even more severe with electric vehicles.[40] It does not escape our attention that fatigue resistance and wear resistance are related.[41–43] However, their relation is complex, so that wear resistance in practice is a distinct property characterized by separate experiments.[43–45] It is hoped that work will soon succeed in taking advantage of multiscale stress deconcentration to reduce rubber pollution on roads."

Instead of studying wear resistance, we have added a demonstration of a rubber mount to showcase the power and broad impact of our material. This mount is analogous to vibration dampers, seals, and o-rings. We have added the following paragraph to page 8, modified **Fig. 4**, and added **Movie S1** and **Movie S2**:

"Many applications require materials to bear load over many cycles. For example, in vibration dampers, seals, and o-rings, materials need to bear loads over large and repeated deformations.[1] For an elastic material, the load-bearing capacity is scaled by modulus, and a large number of cycles is enabled by high fatigue threshold. Here we demonstrate the significance of both high modulus and high fatigue threshold using a cylindrical rubber mount with a crack (**Fig. 4c**). The crack opens when the mount is compressed. The mounts without particles are soft, and either fracture at a low stress or deform excessively (**Fig. 4d**, **Movie S1**). The mount with particles and short chains is stiff, but fractures at a modest load. By contrast, the mount with particles and long chains (F = 0.45 and C = 10^{-4}) is stiff and can support large loads repeatedly. For this mount, the crack does not advance appreciably after 33,000 cycles (**Fig. 4e**, **Movie S2**).

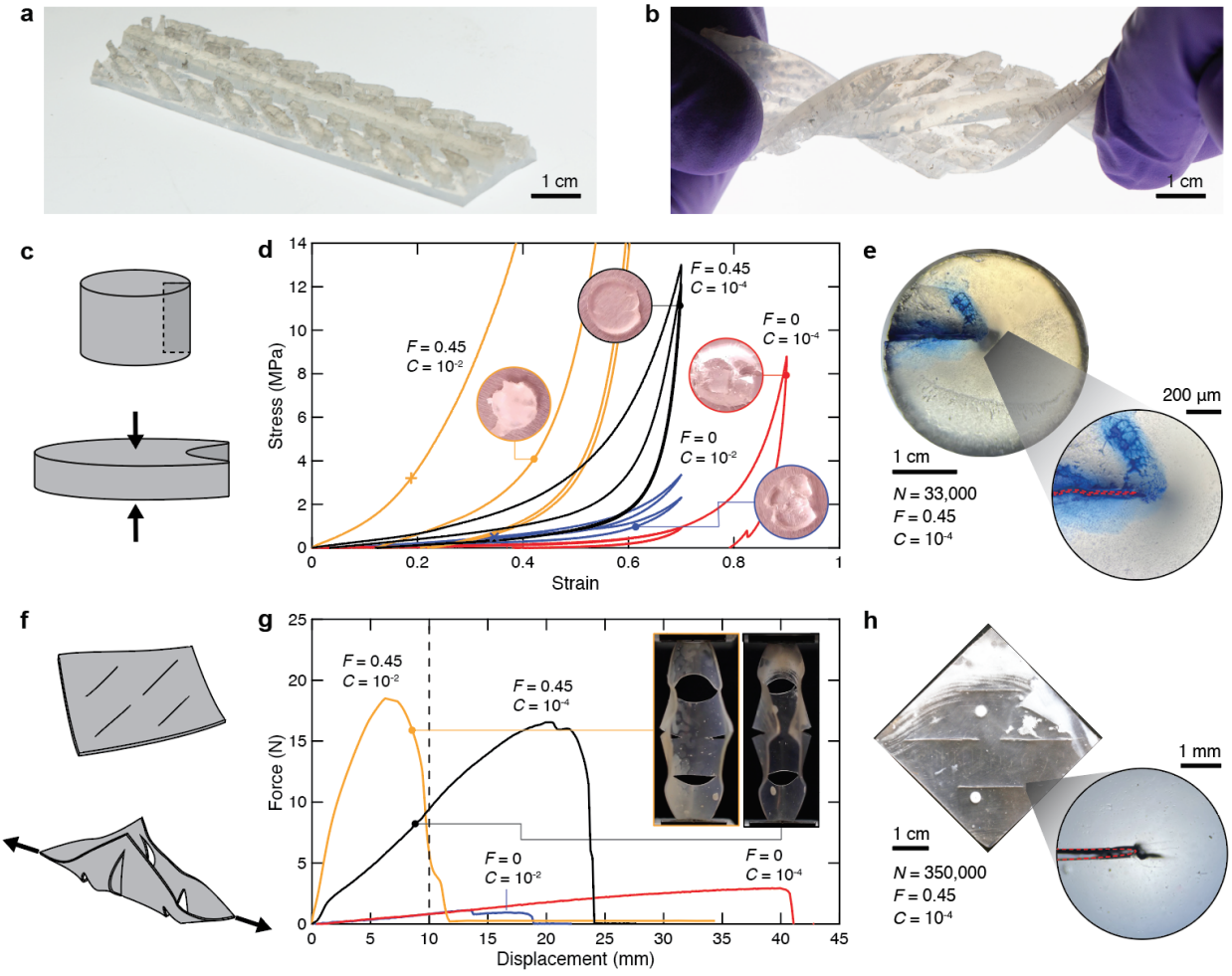


Figure 4. Applications of particle reinforced elastomers with high stiffness and fatigue resistance. (**a**) A particle reinforced elastomer is molded into a complex shape. (**b**) The molded sample can undergo large deformation. (**c**) Schematic of a mount with a crack. The crack opens when the mount is compressed. (**d**) The stress is measured as a function of strain for mounts of various C and F. The point of

fracture is marked on the plot. (**e**) A mount of $C = 10^{-4}$ and $F = 0.45$ after $N = 33{,}000$ cycles. The red dotted line shows the initial crack. (**f**) Schematic of a gripper made of a flat sheet with cuts. When pulled, the sheet buckles out of plane. (**g**) The force is measured as a function of displacement for grippers of various C and F. The dashed line indicates when the grippers are closed, and the inset photos show the grippers at this displacement. (**h**) A gripper of $C = 10^{-4}$ and $F = 0.45$ after $N = 350{,}000$ cycles. The red dotted line shows the initial crack."

Comment: In sum, the reviewer's major comment on the similar work is cleared and other comments on the mechanisms and kirigami gripper are well addressed. After clearing the concerns and comments, the reviewer supports that it is an excellent piece of work in terms of unprecedented performance and uncovered fundamental sciences.

Response: We appreciate your kind remarks.

Comment: Regarding its potential broad impact, the kirigami gripper is a good example to showcase the high stiffness and high fatigue properties, but it is a bit off the introduction and motivation in the challenge of rubber industry. The reviewer suggests to find one more example or test to showcase its potential broad impact and application in resistant tires by conducting the wear resistance test if possible. Such an example or test would be more convincing.

Response: Thank you for the suggestion. We hope that our new demonstration of a mount showcases the power and broad impact of stiff and fatigue-resistant rubbers.

Referee #3:

Comment: Steck et al propose a new version of their paper submitted to nature about elastomers that show exceptional fatigue resistance. Their study follows up an article published in 2021 in Science where they polymerized EA in a manner to encourage high entanglements. Here, they have introduced functionalized silica particles to add a new component of stress release, allowing large fatigue treshold to be reached in pure shear tests.

Response: Thank you for noting that we have identified a new component of stress release, and that the fatigue threshold reported in our work is large.

Your statement above also resonates with the main thesis of our manuscript: **Long polymers and clustered particles deconcentrate stress at multiple scales, synergizing to increase fatigue threshold.** Before we respond to your comments point-by-point, we summarize our reading of your comments in forms that challenge this thesis, as well as our responses.

Challenge 1: No long polymers.

> Long polymers are evident in our experiment. We use the Lake-Thomas model to show that we produce long polymers. The Lake-Thomas model gives a scaling relation between fatigue threshold and polymer chain length. A high fatigue threshold corresponds to long polymers. Furthermore, the method suggested by Referee 3, which is based on the Flory-Rehner model, cannot characterize the polymer chain length when entanglements greatly outnumber crosslinks. As a background note, the Lake-Thomas model is as extensively validated as the Flory-Rehner model.

Challenge 2: No covalent interlinks between particles and the polymer network.

> Covalent interlinks are evident in our experiment. We prepare a control sample with particles that do not form covalent interlinks with the polymer network. Our material has much higher modulus than the control sample. These experiments confirm that strong adhesion forms between the matrix and the particles. The TPM-functionalized particles and the PEA matrix can adhere by two mechanisms. First, TPM copolymerizes with PEA in the matrix, such that covalent bonds form between particles and the polymer matrix. Second, a PEA loop anchored on a particle can form trapped entanglements with PEA chains in the matrix. Both types of adhesion are illustrated in **Fig. 1a.**

Comment: As I said before, the study shows many data and interesting fatigue results, but again I cannot accept the manuscript, since I have serious doubts about the chemistry; obviously, my first shot may not have been clear enough, so here we go again.

Response: Included below are your comment and our response from the last round, which may provide a reference for some of the points in this round of response.

> **Comment:** C. Data are good and very well presented, presentation is good and methodology is good as well. I have however some reserves on the description of the chemistry applied here that, IMHO, is totally eluded. We don't know the conversion in monomers after

polymerization, the level of functionalization of fillers, their specific surface and their reactivity, the experimental crosslink density. All explanation are based on theoretical values: this is not acceptable for a paper in Nature.

Response: Thank you for appreciating our data and how we present them. We respond to your comments as follows.

1) Conversion in monomers after polymerization.

Following your comments, we have characterized the monomer-to-polymer conversion ratio gravimetrically and added the following sentence and supporting figure in the manuscript.

"Most monomers polymerize at all values of C (**Fig. S4**)"

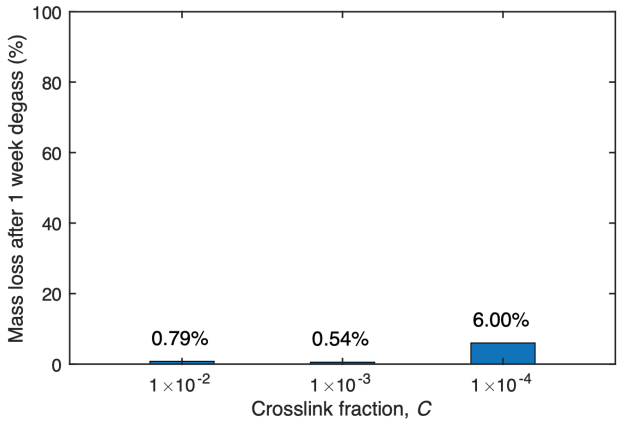


Figure S4. The monomer-to-polymer conversion ratio. The composite is weighed right after polymerization and one week after polymerization. Since EA monomers are volatile at room temperature, the mass loss represents the amount of unreacted monomers.

2) Level of functionalization of fillers

We specified the level of functionalization of particles in the original Materials and Methods section, which is provided from the Cabot Corporation.

"Silica nanoparticles functionalized with 3-(trimethoxysilyl)propyl methacrylate (TPM) of areal density 2.7 molecules per nm^2 were used as reinforcing particles (Cabot Corporation, Silica A), …"

We have also added the following sentence in the main text:

"On the surfaces of the silica particles, the number density of TPM groups is 2.7 nm^{-2}, which is measured by the manufacturer."

3) Specific area

We have calculated the specific area of the particles based on the diameter of the particles measured by TEM. We have added the following sentence to the Materials and Methods.

"From the diameter of the nanoparticles, the specific area is calculated as 26 m^2 g^{-1}."

4) Reactivity of fillers

We confirmed the reactivity of silica functionalized with TPM by conducting experiments to compare silica functionalized by TPM and silica functionalized by TMS.

"First, we prepare a composite with silica nanoparticles functionalized with trimethylsilyl (TMS) groups. Such particles do not form covalent interlinks with PEA polymers. The stress-stretch curves for such composites coincide with the stress-stretch curve of pure PEA, suggesting weak particle-matrix adhesion (**Fig. S16a**). The stress-stretch curves do not change significantly with cycles (**Fig. S16b-d**). … Without covalent interlinks, the fatigue threshold is the same as the polymer matrix, G_{th} = 170 J m^{-2}. By contrast, the composite with covalent interlinks has a fatigue threshold of G_{th} = 420 J m^{-2}. Strong interlinks enable the particle network to carry high stress."

Unlike particles with grafted linear polymers, which can be extracted from the ungrafted polymers (e.g. soxhlet), the particles in our composite are hard to be extracted as they strongly adhere to the crosslinked polymer network. This limits the measurement of reactivity of the particles. However, because the silica particles are functionalized with methacrylate groups very similar to the monomers and the monomer-to-polymer conversion ratio is high, we assume that most functional groups react. We also find that those who have studied the same chemistry (grafting ethyl acrylate onto TPM-functionalized silica) assumed full consumption of the anchored methacrylate units (Espiard, Ph., Guyot, A. Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 2. Grafting process onto silica. *Polymer* **36**, 4391–4395 (1995)). Additionally, Refs. 8 and 9 report that, for a nearly identical system (EA monomers and TPM-functionalized silica nanoparticles), dense covalent interlinks are formed between the silica surfaces and PEA.

5) Experimental crosslink density

We have added the following discussion in the Supplementary Information.

"**Supplementary Note 2. Experimental crosslink density**

The experimental crosslink density is defined by the experiment used to measure it. For a polymer network with negligible entanglements, the elastic modulus is related to the crosslink density as $E = 3\rho N_{Av}kT/M_s$, where ρ is the density, N_{Av} is Avogadro's number, kT is the temperature in unit of energy, and M_s is the molecular weight of polymer strands between crosslinks (Ref. 12, Eqn. (7.31)). Therefore, the experimental crosslink density can be estimated from the elastic modulus. For example, at F = 0 and $C = 10^{-2.5}$, the modulus is 0.7 MPa. This modulus gives the molecular weight of 12,070 g/mol or 109 monomers per chain.

In the manuscript, we estimated the length of the polymer chain as $1/(2C) = 158$ monomers, which is similar to the crosslink density estimated by the modulus.

For a highly entangled polymer network, by contrast, the elastic modulus is related to the entanglement density as $E = 3\rho kT/M_e$, where M_e is the molecular weight of polymer strands between entanglements (Ref. 12, Eqn. (7.47)). Therefore, the elastic modulus does not provide experimental crosslink density. Instead, the crosslink density can be related to the fatigue threshold for a highly entangled polymer network. The Lake-Thomas model relates the fatigue threshold to the crosslink density as $G_0 = \alpha l n^{1/2} J V^{-1}$, where α is a pre-factor of order of unity, l is the length of each monomer unit, n is the number of monomer units in a polymer chain, J is the C-C bond energy, and V is the volume of each monomer unit (Ref. 4). Therefore, the experimental crosslink density of a highly entangled polymer network can be calculated by scaling ($G_0 \sim n^{1/2}$). This scaling corresponds to our data ($G_0 \sim C^{1/2}$, see **Fig. 3g**), as $n \sim C^{-1}$. For example, the fatigue thresholds of pure PEA elastomers at $C = 10^{-2}$ and $C = 10^{-4}$ are ~20 J/m^2 and ~200 J/m^2, respectively. Therefore, the values of n are expected to be different by 100 times. As n at $C = 10^{-2}$ is estimated as ~100 monomers per chain from the modulus, n at $C = 10^{-4}$ is ~10,000 monomers per chain."

Comment: The major drawback that I emphasized last time was the fact that the polymerization scheme was not looked at and is actually likely wrong.

First, to measure the molar mass between crosslink (Mc), researchers from the rubber field carry out swelling measurements, in presence or not of fume ammonia to disrupt specific interactions between filler particles and polymer chains. This was not done here, and the proposed Mc calculation by stress strain curves is not relevant, particularly in presence of a filler.

Response: Swelling experiments cannot measure the molecular weight between crosslinks in the polymer network, M_C, when entanglements greatly outnumber crosslinks. The measurement of M_C by swelling is based on the Flory-Rehner model (Flory, P.J., Rehner, J., 1943. Statistical mechanics of cross-linked polymer networks II. Swelling. J. Chem. Phys. 11, 521–526). This model relates swelling to the elastic modulus E. When the modulus is set by crosslinks, the modulus relates to M_C as $E = 3\rho N_{Av} kT/M_C$.[12] However, when entanglements outnumber crosslinks, the modulus is set by entanglements. Therefore, the molecular weight calculated from a swelling experiment would be the molecular weight of the polymer segment between two adjacent entanglements, as we have shown in our 2021 Science paper. For this reason, when entanglements outnumber crosslinks, we estimate the chain length using the fatigue threshold on the basis of the Lake-Thomas model. This point was discussed in Supplementary Note 2, provided in response to the first round of review:

"**Supplementary Note 2. Experimental crosslink density**

For a highly entangled polymer network, by contrast, the elastic modulus is related to the entanglement density as $E = 3\rho kT/M_e$, where M_e is the molecular weight of polymer strands between entanglements (Ref. 12, Eqn. (7.47)). Therefore, the elastic modulus does not provide experimental crosslink density. Instead, the crosslink density can be related to the fatigue threshold for a highly entangled polymer network. The Lake-Thomas model relates the fatigue threshold to the crosslink density as $G_0 = \alpha l n^{1/2} J V^{-1}$,

where α is a pre-factor of order of unity, l is the length of each monomer unit, n is the number of monomer units in a polymer chain, J is the C-C bond energy, and V is the volume of each monomer unit (Ref. 4). Therefore, the experimental crosslink density of a highly entangled polymer network can be calculated by scaling ($G_0 \sim n^{1/2}$). This scaling corresponds to our data ($G_0 \sim C^{-1/2}$, see **Fig. 3g**), as $n \sim C^{-1}$. For example, the fatigue thresholds of pure PEA elastomers at $C = 10^{-2}$ and $C = 10^{-4}$ are ~20 J/m^2 and ~200 J/m^2, respectively. Therefore, the values of n are expected to be different by 100 times. As n at $C = 10^{-2}$ is estimated as ~100 monomers per chain from the modulus, n at $C = 10^{-4}$ is ~10,000 monomers per chain."

The effect of filler is unlikely to be removed under swelling. The polymer network and the silica nanoparticles form covalent bonds. The presence of solvent will not cause a covalent bond to dissociate. Particles will not be fully chemically detached from the polymer network upon swelling. The modulus of the filled rubber will be much higher than the pure polymer network, and the calculated molecular weight M_C will be greatly underestimated.

The polymer matrix can be characterized by using a pure PEA network. The transition to plateau modulus agrees with this estimate for pure PEA and with that reported from literature (**Fig. 2b**). At this point, $M_e \sim M_e$. Data for pure PEA was also shown in the 2021 Science paper. This transition is the same when particles are added, suggesting that the matrix in the composite is the same as that of pure PEA.

Comment: I also asked more about the polymerization by itself, and did not receive the answers I expected. First, looking at volatiles does not allow to conclude on polymerization and crosslinking reactions. Swelling to extract uncrosslinked chains would be again more adapted, as well as to estimate a true Mc.

Response: Your Comment C in the first round of review asked for "the conversion in monomers after polymerization". This comment led us to measure the change in mass due to evaporation of volatile species (**Fig. S4**). Monomers that do not polymerize will be volatile. This experiment measures the conversion in monomers after polymerization.

We have not performed a swelling experiment to extract uncrosslinked chains. But we have discussed measuring M_C in our responses to the previous comments.

Comment: Besides, the authors now added references to support their view on a 'conventional system' very close to theirs (only the crosslinker is different).

Response: We cite Berriot on page 3:

"Additionally, TPM-functionalized silica nanoparticles have been used as reinforcing fillers in PEA elastomers,[8,9] but these works used polymer chains much shorter than reported here, and did not report fatigue threshold."

We cite the papers by Berriot because they use the same monomer (EA), the same type of particle (silica nanoparticles), and same functional groups (TPM). They use different crosslinkers, so we do not use these papers in any other way.

Comment: Actually, in Berriot's studies, it is clearly shown how important it is to measure true Mc's, there for instance by low field NMR.

Response: Berriot measured M_C by NMR and concluded:

"The density of additional topological constraints increases proportionally to the surface area introduced in the matrix. This result shows that far from the particles, the polymer network is not affected by the covalent bonds connecting the polymer chains and the particles. Its mesh size is essentially controlled by the cross-linker concentration and the entanglement density."

Berriot's conclusion reinforces our point that the structure of the polymer network on the surfaces of the particles is not relevant to the properties of the matrix.

Comment: In Espiard and Guyot's paper, not added in the main text, these authors show that:

1. reaction of methacrylate groups on the filler is faster than acrylate monomers (typically, reactivity ratios are 2 for 0.2, respectively), so that grafting reaction occurs majoritarely at the beginning of the polymerization, generating loops on the filler. Then, polymer chains grow independently at larger conversions.

Response: Thank you for the comment. We add the following sentences to the manuscript.

"See additional discussion on polymerization (**Supplementary Note 3**)."

"**Supplementary Note 3. Additional discussion on polymerization**

Adhesion between particles and polymer matrix

The reaction between methacrylate groups on the particles and acrylate monomers is faster than the reaction between acrylate monomers.[46] In principle, all the methacrylate groups on the particles could be consumed without coupling the particles to polymer chains in the matrix. However, our experiments indicate that particles do adhere to the matrix. PEA filled with TPM-functionalized silica particles has a much higher modulus and fatigue threshold than PEA filled with TMS-functionalized silica particles (**Fig. S12h**, **Fig. S16c**, and **Fig. 3d**). The TPM-functionalized particles and the PEA matrix can adhere by two mechanisms. First, TPM copolymerizes with PEA in the matrix, such that covalent bonds form between particles and the polymer matrix. Second, a PEA loop anchored on a particle can form trapped entanglements with PEA chains in the matrix. Both types of adhesion are illustrated in **Fig. 1a.**"

Comment: The blank experiments with non-functionalized silica in the present paper do not prove anything in terms of polymerization and crosslinking reactions of functionalized fillers;

Response: It is not our intention to use experiments with TMS-functionalized silica to test polymerization or crosslinking of polymer. Rather, these experiments show that adhesion between the matrix and TPM-functionalized silica is stronger than adhesion between the matrix and TMS-functionalized silica.

Comment: 2. Maximal molar masses obtained in emulsion (best system for generating high molar masses) and deduced from extraction are 200kg/mol, not the million that the present authors claim here to explain the properties of their materials.

Response: In the Espiard-Guyot paper, the initiator-to-monomer molar ratio, I, is much larger than ours. For the synthesis conditions in the Espiard-Guyot paper, we calculate:

Monomer (EA, 0.918 g/mL, 100 g/mol): 51 mL ~ 0.47 mol
Initiator (Potassium Pursurfate, 270 g/mol): 1.05 g ~ 0.0039 mol

$I = 8.3 \times 10^{-3}$.

By comparison, although the types of polymerization and initiators are different, our value of I is much smaller: $I = 4 \times 10^{-5}$. Low values of I are known to lead to long polymer chains (McGrath, J. E. Chain reaction polymerization. *J Chem Educ* **58**, 844 (1981)). See further discussion in our response to your comment regarding I/C.

Comment: Another important point is the presence of side reactions that complicate the chemistry. All chemists practicing polymerization know that transfer reaction to the monomer is systematically occuring with acrylates (see e.g. Castignolles et al, Polymer 50 (2009) 2373–2383). Long branches are generated by initiation from the polymer chains and thus, at large conversion, gelation by crosslinking is systematically seen. This occurs mostly at moderate temperature (40°C and above), but it is also pregnant at room temperature. By the way, I expect that you see an exotherm here while you make the polymerization, this is not mentioned in the text.

Response: Thank you for this comment. We have added the following text.

"See additional discussion on polymerization (**Supplementary Note 3**)."

"**Supplementary Note 3. Additional discussion on polymerization**

Side reaction

Radical polymerization of polyacrylates such as PEA is accompanied by side reactions that cause polymer chains to branch.[47] Like crosslinks, branches reduce the chain length, and branches can even form a network in the absence of crosslinkers. As an additional experiment, we prepare pure PEA without crosslinker, $C = 0$, but with initiator, $I = 4 \times 10^{-5}$. This sample dissolves in propylene carbonate, indicating that a network did not form. By contrast, pure PEA forms a network at $C = 1 \times 10^{-4}$ and $I = 4 \times 10^{-5}$, and even forms a network at much lower concentrations of crosslinker and initiator, $C = 1 \times 10^{-6}$ and $I = 4 \times 10^{-7}$.[13] These observations indicate that, under the conditions of this work, $I/C = 0.4$, side reactions occur less frequently than reactions with crosslinkers. We surmise that branching is insignificant in our samples because they are prepared with $I < C$ and with unusually low concentrations of initiator."

Comment: This last information contradicts with the view of the authors that long chains are formed in their system that end-link with the filler; not only it is not the case, but even more, crosslinking ratio is certainly above the calculated values they propose (again, swelling would prove that, since most of the entanglements would desentangle with solvent).

Response: As we discussed above, side reactions are not significant in our system. We do provide experimental evidence that long chains are formed, and that polymer chains strongly adhere to the particles.

Trapped entanglements do not disentangle upon swelling. Our 2021 Science paper showed a clear example. One polymer network is synthesized from a precursor having a lot of solvent. As the polymer chains are sparse, the polymer chains barely entangle. A second polymer network is synthesized from a precursor having a small amount of solvent. As the polymer chains are crowded, the polymer chains densely entangle. Both precursors have the same crosslink-to-monomer molar ratio and initiator-to-monomer molar ratio. If most entanglements were disentangled under swelling, the two polymer networks should reach the same equilibrium state in a solvent. However, the two polymer networks behave very differently, showing that the dense entanglements are trapped by the crosslinks so that entanglements greatly outnumber crosslinks even at the fully swollen state. The same is true in our system. We can not use a swelling experiment to measure M_C.

Comment: I suggest that the authors make a blank experiment in absence of crosslinker and with non functionalized silica to prove this gelation effect. I expect that with functional silica and no crosslinker, they will also generate a fatigue resistant material.

Response: See our previous comment regarding gelation due to side reactions. PEA without crosslinker and with low concentration of initiator does not gelate.

Comment: Note that changing the ratio I/C is not what polymer chemists usually practice (see cited papers above). They first set a constant initiator/monomer ratio and then change the crosslinker concentration according to the network they want to produce. Decreasing both C and I is more likely to decrease the polymerization rate and thus to modulate the final network.

Response: Thank you for this comment. We have added the following text.

"See additional discussion on polymerization (**Supplementary Note 3**)."

"**Supplementary Note 3. Additional discussion on polymerization**

Initiator concentration

The molar ratio of initiator to crosslinker was set to $I/C = 0.4$ for all samples. This value of I/C was chosen based on the following considerations. When initiators are triggered, they form radicals. The radicals drive polymerization by reacting with either monomers or crosslinkers. Assume that polymerization is terminated by recombination and ignore side reactions. After polymerization, polymer strands connect either two crosslinks, one initiator and one crosslink, or two initiators. These three types

of polymer strands are often called network chain, dangling chain, and linear chain, respectively. Only network chains carry load when the polymer network is stretched.

When I is much lower than C, the number of dangling chains and linear chains is negligible compared to the number of network chains. By contrast, when I is much higher than C, dangling chains and linear chains can outnumber network chains, resulting in a poor polymer network where most of the polymer strands do not carry load. Therefore, to produce a polymer network in which most polymer strands carry load, I should be low enough compared to C. Our previous work showed that PEA prepared with $I/C = 10$ creeps when subject to a constant load.[13] In this work, we set $I/C = 0.4$ for all samples.

Furthermore, if I is too low, then polymerization will be quenched by oxygen dissolved in the precursor, and the sample will not cure. As C is reduced, it becomes increasingly difficult to satisfy $I/C = 0.4$ while maintaining an I high enough to cure the sample. In our experiments, composites with $C < 10^{-4}$ do not cure."

We studied the effect of the concentration of initiator in our previous paper published in 2021 at Science as follows.

In our 2021 Science paper, we prepared PAAm in two ways: changing I and C proportionally with a fixed I/C, and changing I and C independently. We showed that I should decrease proportionally with C to form a highly entangled polymer network. When C decreases with fixed $I = 8 \times 10^{-5}$, swelling and modulus start to decrease when $C \sim I$ (Fig. S1D, purple line). However, when $C < 10^{-4}$, the polymer content and modulus are expected to plateau since the polymer chains are longer than the entanglement molecular weight. We suppose that this deviation is because too many polymer chains are initiated, which form a polymer network of many dangling chains. Therefore, in the 2021 Science paper, we fixed I/C to be low enough to avoid this issue. Decreasing I together with C was essential for polymer content and modulus to plateau as expected.

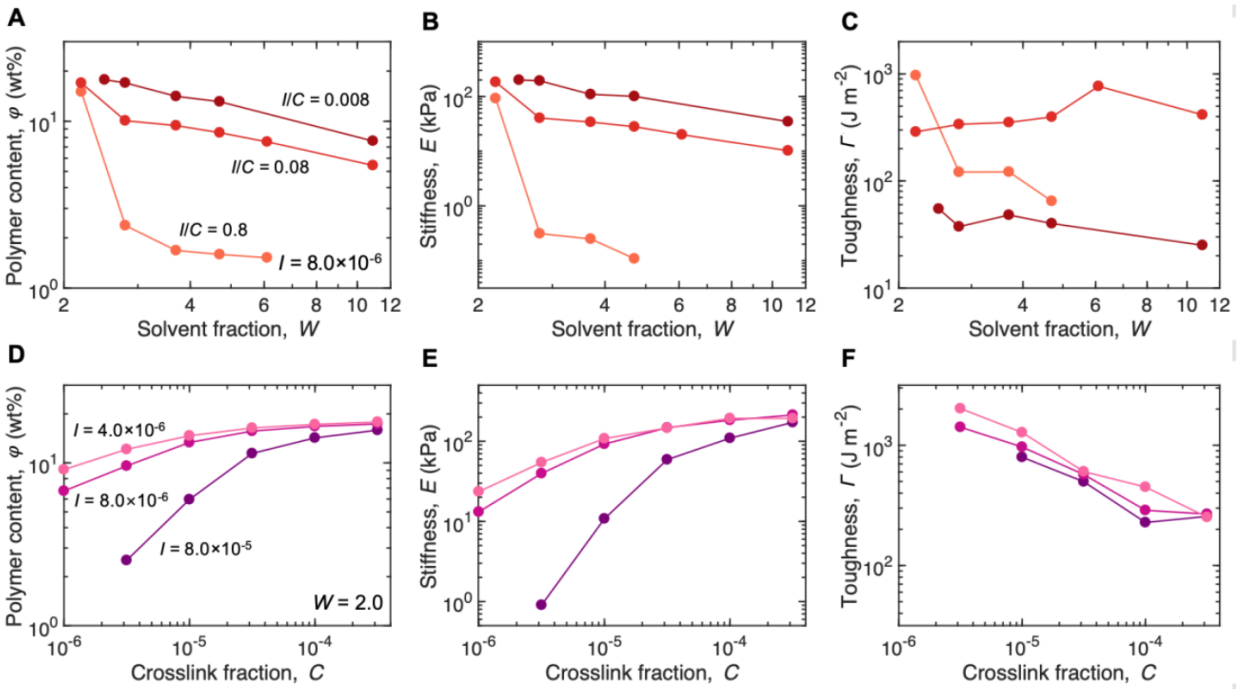


Fig. S1

The polymer content φ, stiffness E, and toughness Γ of hydrogels prepared with precursors of various compositions. Let W, C, and I be the molar ratios of water, crosslinker, and initiator to monomer. After synthesis, each hydrogel is submerged in water to swell to equilibrium, and is then characterized by various tests. **(A-C)** φ, E, and Γ as functions of W. We fix $I = 8.0\times10^{-6}$ and $C = 1.0\times10^{-5}$, 1.0×10^{-4}, and 1.0×10^{-3}, which gives $I/C = 0.8$, 0.08, and 0.008. When I/C is too high ($I/C = 0.8$), too many polymer chains are initiated, which form a hydrogel of many dangling chains, and causes low values of φ, E, and Γ with enormous swelling. Hydrogels made with precursors of the low values of I/C of 0.08 and 0.008 show almost the same trends as those made with precursors of $I/C = 0.4$ (Fig. 2). **(D-F)** φ, E, and Γ as functions of C with different values of I at $W = 2.0$. At any I, φ and E drop when I/C is higher than ~ 0.5, leading to inelastic solids with enormous swelling. Toughness is less sensitive to I but high I/C lowers the minimum C required to obtain a well-formed network, suggesting that the toughness is limited by I. For example, the maximum toughness is ~2,000 J/m^2 at $I = 4.0\times10^{-6}$, but is ~800 J/m^2 at $I = 8.0\times10^{-5}$.

Our data for PEA shows a similar trend that I/C needs to be low enough to form a highly entangled long-chain polymer network. Attached below is Fig. S8 of the 2021 Science paper.

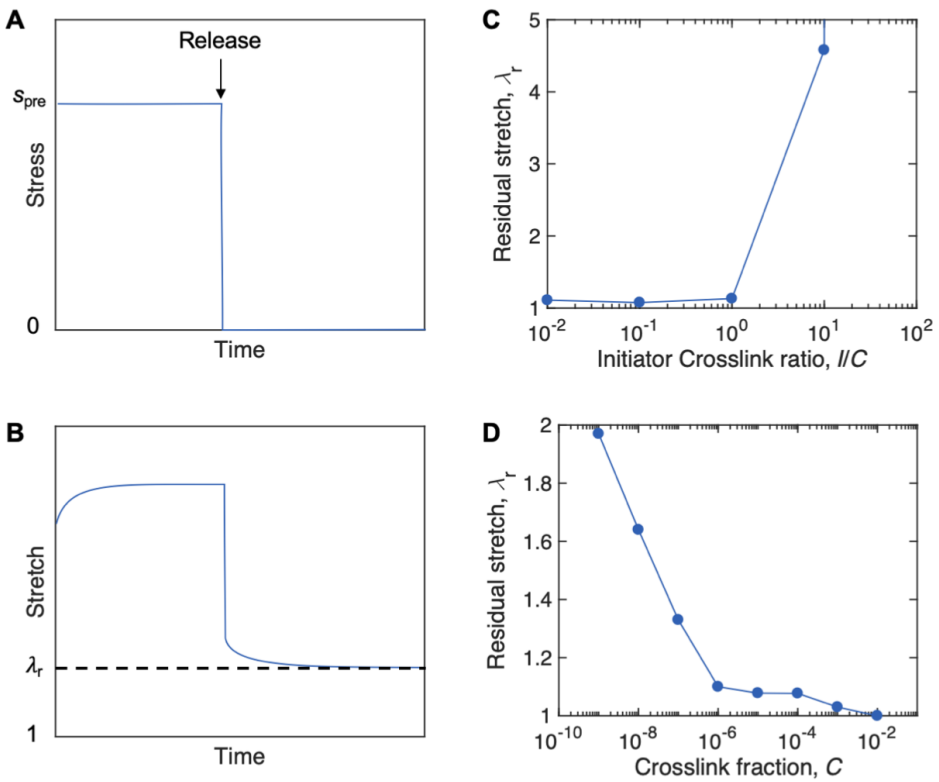


Fig. S8.
The stress relaxation and recovery of a highly entangled elastomer. (A) A dead load of 360 kPa is applied for 48 hours and relaxed for 24 hours. **(B)** The schematic of the stretch as a function time. The residual stretch λ_r is measured after the relaxation of 24 hours. The residual stretch is used as a measure of invariance of polymer topology after relaxation. **(C)** The residual stretch at different I/C values at $C = 10^{-5}$. When I/C exceeds 10^1, the sample creeps. When I/C is below 10^0, the residual stretch is small. **(D)** The residual stretch at various C at $I/C = 0.1$. The residual stretch is low at high C and rapidly increases below $C = 10^{-6}$.

Comment: In short, even if the presented materials have certainly encouraging fatigue properties, the storytelling based on idealized polymerization scheme is not correct. Several works of rubbers' specialists have proven that more precise structure determination is needed before interpreting the properties as you do it here.

Response: Our schematic illustrates the roles of long chains, interlinks, and particles (**Fig. 1**). The function of the schematic is to communicate multiscale stress deconcentration to the reader. Other detailed polymer network structures are not studied in our work.

For any given system, one can certainly do more experiments to learn more. In this paper, we have designed our experiments to support our conclusions:

(1) entanglements and percolated particles synergize to increase modulus;
(2) long polymer chains and clustered particles synergize to increase fatigue threshold.

It is well established that entanglements increase the modulus of the polymer matrix and that percolated particles amplify the modulus of the matrix. The referee has not challenged this point.

The Lake-Thomas model predicts that long polymer chains increase the fatigue threshold of the matrix (Ref. 4). This model is supported by decades of experimental data (Refs. 4–7, 13, 23, 31–33). We use this model to validate that the polymer chains are long. We identify, for the first time, that clustered particles amplify the fatigue threshold of the matrix. Our experiments support this conclusion.

Comment: I have also some comments on the mechanical analyses of the systems. The authors have added the Figure S9 that shows DMA results. First, the technique is not presented in the experimental section, so we don't know what they did exactly. Second, the steep increase in tan(delta) at high stretch frequency clearly shows that the material exhibit a large viscoelasticity that participate to stress release. This is confirmed by the strong Payne effect shown in Figure 14a.

Response: The details of the DMA experiment are on page 18:

"Dynamic mechanical analysis tests were performed using a DMA 1 instrument (Mettler Toledo) and the tension geometry. The stretch amplitude was fixed at $\lambda = 0.01$ and the temperature was 25 °C."

Our material is viscoelastic. We addressed this point in the previous revision:

> **Comment:** By the way, the materials presented here have a high level of viscoelasticity that would not be accepted by industry (very bad elastic return, large deformation with low level of strain, what would it give at 300% deformation?)
>
> **Response:** In general, different polymer and particle chemistries can be used to reduce viscoelasticity and hysteresis. The object of this paper is to propose the principle of multiscale stress deconcentration (**Fig. 1**) and to demonstrate that the principle greatly amplifies fatigue threshold. The claim of novelty in this work is this general principle, which we have demonstrated using a model system: PEA filled with monodisperse silica nanoparticles. We have selected this system as a model following many previous works including Refs. 8, 9, 13, and 29. Specifically, our proposed principle enhances fatigue threshold without requiring any effect of viscoelasticity. The object of this paper is not to design a rubber with comprehensive material properties for any given application.

We note that our previous response did not explicitly state that viscoelasticity does not contribute to fatigue threshold (Lake and Thomas, 1967). We have added the following sentence to page 7:

"Therefore, further changes in microstructure are negligible in the steady state, and both hysteresis and residual stretch indicate viscoelasticity. We note that although the filled rubber shows viscoelasticity, viscoelasticity does not increase fatigue threshold.[4]"

Comment: Besides, the fact that the percolation treshold does not globally change the fatigue resistance advocates against the 'ideal network' proposed here.

Response: We do not claim that our material contains an 'ideal network', nor does our manuscript use the words 'ideal' or 'ideal network'. We discuss the relationship between percolation and fatigue threshold on page 7 and in Supplementary Note 1.

Comment: Third, invoking that thermoplastic polymers suffer from creep is certainly true, but this is also what one would anticipate from your viscoelastic system.

Response: Our system does not dissolve in solvent over long periods of time. Unlike an uncrosslinked thermoplastic, a crosslinked rubbery network will not creep indefinitely.

Comment: To pursue, several comments directly related to the answers:

- p.20 'Since this principle is not material-specific': I believe exactly the contrary, but since the pure shear experiments are not very developed in the rubber community (apart in industry,but they don't publish their results generally), it is difficult to say if it is the best material ever that the present authors propose.

Response: We do not claim that our material is the best. We propose and test a mechanism. Since the mechanism of multiscale stress deconcentration is based on mechanics, it does not require specific chemistry.

Pure shear experiments have been done by numerous groups to characterize fatigue of rubber, starting with the pioneering papers by Thomas and colleagues.

Comment: - p. 20 'Existing particle filled rubbers do not have chain lengths as long as those reported in this work': well, actually, you did not measure them so how do you know, other than guessing?

Response: We discuss measuring M_C in Supplementary Note 2.

Comment: - p. 22 'The object of this paper is not to design a rubber with comprehensive material properties for any given application': if generating high fatigue treshold is accompanied by huge viscoelasticity, then there is no point claiming in the abstract 'elastomeric materials of both high modulus and high fatigue resistance expand the space of materials design, opening doors to curtailing polymer pollution and building high performance machines'.

Response: We do not claim that there is no viscoelasticity. We show materials with high modulus and high fatigue threshold. As pointed out by Lake and Thomas, and substantiated by decades of subsequent work, viscoelasticity does not contribute to fatigue threshold (Ref. 4).

Comment: - p. 24 'the particles in our composite are hard to be extracted...': swelling experiments, though certainly not extracting silica, would allow measuring 'true' Mc's, the content of extractible material that could further be analysed by SEC for instance.

Response: Since our materials are highly entangled, swelling measurements cannot provide M_C. See the previous comments regarding M_C and Supplementary Note 2.

Extractible polymers will not be the same as polymer strands crosslinked into the polymer network. To measure chain lengths in the polymer network by chromatography, we would need to break all crosslinks to turn crosslinked polymer chains into linear polymers. This is unavailable in most polymer networks.

Comment: - p. 24 'methacrylate groups very similar to the monomers': not the same reactivity at all (a decade difference in propagation rate and so cross-reaction versus homopropagation).

Response: In principle, all the reaction sites on a particle could be consumed by the fast reaction, so that the particle would not form any covalent bonds with polymer chains in the matrix. This does not happen in our system, because particles strongly adhere with the matrix. See the previous comment regarding adhesion and Supplementary Note 3. The difference in reaction rates does not affect the conclusions of our paper.

Comment: - p. 26: 'we used a known chemistry of polymers': you did not look at it thoroughly actually.

Response: The intention of the quoted sentence is as follows. The object of our study is a mechanical principle, and we have used a system that has previously been studied chemically. We do not claim to invent crosslinked PEA or functionalized silica.

Comment: Last points of detail:

In the field of polymer materials, we name 'composite' a hard and brittle material made of long fibers and a thermoset polymer such as in an epoxy amine system. Soft materials are named rubbers or elastomers, depending on how elastic and stress resistant they are.

Response: In this paper, the word “composite” is first used in the Abstract as follows. “A filled rubber, also called particle reinforced elastomer, or composite for brevity, consists of a network of crosslinked polymer chains and a network of percolated rigid particles.” The word “composite” has been used in the literature in this context (Ref. 18; *Macromolecules* 2013, 46, 22, 8964–8972, doi:10.1021/ma401910c; *Polymers* **2021**, *13*(22), 3922, doi.org/10.3390/polym13223922; Nanomaterials 2019, 9, 12, doi:10.3390/nano9010012).

Comment: Finally, in the y axis in Figure S8b, stretch at rupture has no unit (not MPa).

Response: We have corrected the unit on the vertical axis of **Fig. S8b**.

Reviewer Reports on the Second Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

Figure s4 is not a proper way to determine the conversion, I completely agree with reviewer 3. This figure should be taken out, at least in its current state. A proper characterization of the network is needed, since reviewer 3 is bringing forth several good points. Ensuring that these have been experimentall addressed will bring most more credibility to the paper seen from a polymer scientist's perspective. Networks are not just networks as long as they behave like one. And I agree with reviewer 3's points on the lack of experimental proof that the structure is what the authors claim it to be.

I think that this opinion will also be clear through the next page or so, where I discuss some of the other comments that go hand in hand with this. After that, I propose some methods to aid the authors and reviewer 3 to come to a common agreement. I think that the two parts come from "different research worlds" and therefore there is some miscommunication (I find part parts communicate clearly but they do not always talk about the same thing).

I disagree with the following comment from the authors "Monomers that do not polymerize will be volatile. This experiment measures the conversion in monomers after polymerization". There is an inherent issue with their experimental approach since there is no determination of the solubility of the monomer in the polymer, so basically there could still be plenty of monomer present in the polymer, and this would alter the properties significantly, actually making the elastomer more stretchable. Even at a low concentration, this could change the properties.
And secondly, or maybe rather in the opposite case where the monomer is highly volatile, there could be significant evaporation of the monomer before successful curing. If the monomer is this volatile, the polymer/network will become ill-defined.
And as a last and less important issue, the conversion should be defined with respect to what takes part in the network structure. This links back to the reviewer's request for swelling experiments.

Reviewer 3 has not specified specifically what he/she wants to know from the swelling data (I agree with the authors that the modulus prediction is close to worthless in most cases, but I am not sure that this is what is asked), however, as the reviewer points out then proper characterizations of elastomer structures entail swelling experiments. In my opinion, this is to get an idea about the sol and the gel fractions with the sol fraction being an important part of the network, especially if softer materials with higher elongation are sought. The removal of the sol fraction from certain elastomers can make the elastomer brittle/fragile, so in the context of this paper, it is necessary to know how large the sol fraction is.

I agree with the authors on their comment "The polymer matrix can be characterized by using a pure PEA network. The transition to plateau modulus agrees with this estimate for pure PEA and that reported from literature (Fig. 2b). At this point, Mc ~ Me . Data for pure PEA was also shown in the 2021 Science paper. This transition is the same when particles are added, suggesting that the matrix

in the composite is the same as that of pure PEA."

They have a well-entangled network and thus the discussion of using the crosslinking density to determine the molecular weight between crosslinks becomes irrelevant (as we will get back to the molecular entanglement weight and not the polymer length). But again, I think that reviewer 3 is asking for knowledge about how much of the network is a true network.

Here is my suggestion on how to address the questions from reviewer 3 with respect to identifying the network structure and ensure that a "true" network has been prepared:

1. Figure s3a could be used if data for the solubility of the monomer in the polymer can be shown (or experiments can be conducted). If there is no solubility of the monomer in the polymer, Figure s3a regains its meaning. Otherwise, there will be a significant amount of solvent (plasticizer in a sense). Ideally, the mass of the system should also be measured during the reaction to prove that there is no significant evaporation during the reaction (could just be done for a simple experiment).
2. Swell the samples in suitable to do simple swelling experiments to determine the sol fraction/gel fraction of the samples. Do not do Soxleth extraction as this will br If you have e.g. 5-10% of sol fraction, then this is comparable to other network systems. On the other hand, then if you end up having +20% of sol fraction then maybe this is the driving force for the good properties. I will guess from your data that you will have maximum 10% but I am just "guessing qualifiedly".

By the two above experiments, you will have me convinced that the "multiscale stress deconcentration phenomenon" is correct.

Author Rebuttals to Second Revision:

Point-by-point response to the referees:

Referee #1:

Comment: Figure s4 is not a proper way to determine the conversion, I completely agree with reviewer 3. This figure should be taken out, at least in its current state. A proper characterization of the network is needed, since reviewer 3 is bringing forth several good points. Ensuring that these have been experimentally addressed will bring most more credibility to the paper seen from a polymer scientist's perspective. Networks are not just networks as long as they behave like one. And I agree with reviewer 3's points on the lack of experimental proof that the structure is what the authors claim it to be.

I think that this opinion will also be clear through the next page or so, where I discuss some of the other comments that go hand in hand with this. After that, I propose some methods to aid the authors and reviewer 3 to come to a common agreement. I think that the two parts come from "different research worlds" and therefore there is some miscommunication (I find part parts communicate clearly but they do not always talk about the same thing).

I disagree with the following comment from the authors "Monomers that do not polymerize will be volatile. This experiment measures the conversion in monomers after polymerization". There is an inherent issue with their experimental approach since there is no determination of the solubility of the monomer in the polymer, so basically there could still be plenty of monomer present in the polymer, and this would alter the properties significantly, actually making the elastomer more stretchable. Even at a low concentration, this could change the properties.

Response: Thank you for your reading of the communication between reviewer 3 and ourselves. Your comments have helped us experimentally verify the formation of the polymer networks in our materials, which we detail below. We hope the new data will help us come to a common agreement.

We agree with the reviewer that we did not determine the solubility of ethyl acrylate in poly(ethyl acrylate). In the prior version, we assumed that the concentration of monomer in the air is zero, so any monomers in the elastomer will evaporate if allowed to reach equilibrium. We have replaced Figure S4 using data from new experiments:

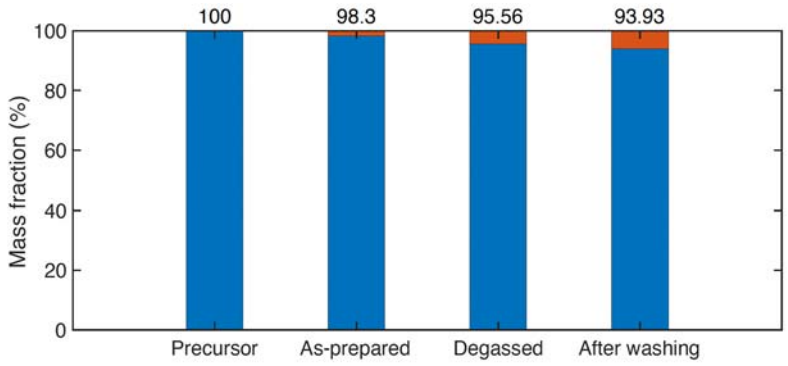


Figure S4. The fraction of PEA chains that crosslink into a network. The mass of precursor for a PEA elastomer of $C = 10^{-4}$ is measured before curing. The PEA elastomer is then weighed after polymerization, as well as after degassing in air for two days. The degassed sample is submerged in ethyl acetate for one week, after which the sample is removed from the solvent and the solvent in the sample is allowed to fully

evaporate in air. The gel fraction is 95.54 wt%, calculated as the mass of washed sample divided by the mass of the as-prepared sample. Most polymer chains are crosslinked into a polymer network.

In response to the second action item below, we have measured the sol and gel fractions of PEA. Any monomers dissolved in the elastomer after curing will be contained in the sol fraction. The sol fraction is 4.46 wt%, suggesting that the concentration of monomers in the elastomers is small.

We note that the fatigue threshold, as shown by Lake-Thomas in Ref. 4, is insensitive to hysteresis or viscoelasticity. For example, swelling an elastomer in solvent changes its stretchability and modulus, but not its fatigue threshold (Ref. 5). The presence of monomers should have a similar effect.

Comment: And secondly, or maybe rather in the opposite case where the monomer is highly volatile, there could be significant evaporation of the monomer before successful curing. If the monomer is this volatile, the polymer/network will become ill-defined.

Response: We measure the mass during curing in response to action item 1 below (**Fig. S4**). The mass of a PEA precursor with $C = 10^{-4}$ reduces by 1.7% while curing in a glass mold with silicone rubber spacers.

Comment: And as a last and less important issue, the conversion should be defined with respect to what takes part in the network structure. This links back to the reviewer's request for swelling experiments.

Response: We use a swelling experiment to measure the sol and gel fractions of the PEA elastomer in response to action item 2 below (**Fig. S4**).

Comment: Reviewer 3 has not specified specifically what he/she wants to know from the swelling data (I agree with the authors that the modulus prediction is close to worthless in most cases, but I am not sure that this is what is asked), however, as the reviewer points out then proper characterizations of elastomer structures entail swelling experiments. In my opinion, this is to get an idea about the sol and the gel fractions with the sol fraction being an important part of the network, especially if softer materials with higher elongation are sought. The removal of the sol fraction from certain elastomers can make the elastomer brittle/fragile, so in the context of this paper, it is necessary to know how large the sol fraction is.

I agree with the authors on their comment "The polymer matrix can be characterized by using a pure PEA network. The transition to plateau modulus agrees with this estimate for pure PEA and that reported from literature (Fig. 2b). At this point, Mc ~ Me . Data for pure PEA was also shown in the 2021 Science paper. This transition is the same when particles are added, suggesting that the matrix in the composite is the same as that of pure PEA."

They have a well-entangled network and thus the discussion of using the crosslinking density to determine the molecular weight between crosslinks becomes irrelevant (as we will get back to the molecular entanglement weight and not the polymer length). But again, I think that reviewer 3 is asking for knowledge about how much of the network is a true network.

Response: Thank you for providing your interpretation of reviewer 3's request for swelling experiments. We agree that although swelling experiments can not provide the molecular weight between crosslinks,

they can provide the fraction of polymers crosslinked into the network. The sol and gel fractions are valuable data points for our system, since entangled but not crosslinked chains may alter the mechanical properties. We use a swelling experiment to measure the sol and gel fractions of the PEA elastomer in response to the second action item below.

Comment: Here is my suggestion on how to address the questions from reviewer 3 with respect to identifying the network structure and ensure that a "true" network has been prepared:

1. Figure s3a could be used if data for the solubility of the monomer in the polymer can be shown (or experiments can be conducted). If there is no solubility of the monomer in the polymer, Figure s3a regains its meaning. Otherwise, there will be a significant amount of solvent (plasticizer in a sense). Ideally, the mass of the system should also be measured during the reaction to prove that there is no significant evaporation during the reaction (could just be done for a simple experiment).

Response: We measured the mass before and after the reaction (**Fig. S4**). The mass decreases by 1.7% during curing, suggesting that evaporation is not significant while the samples cure. This finding may be expected since the permeability of the glass mold is low.

We also measured the change in mass after the sample was removed from the glass mold and degassed in air for two days. The mass of PEA with $C = 10^{-4}$ decreased by 2.8% after degassing. However, as the referee suggests, this measurement does not provide the monomer-to-polymer conversion ratio if monomers are still present in the sample. We will return to this point in response to the following comment.

We added one sentence to page 3 of the manuscript, new text in the methods section, and Figure S4:

"Most monomers polymerize, and most polymers crosslink into the polymer network (**Fig. S4**)."

"The precursor solution was then poured into a mold and sealed with a glass plate. Binder clips were attached along the perimeter of the mold. The mold was placed in a plastic bag (Minigrip Redline, VWR) filled with nitrogen gas, and excess gas was pressed out of the bag before it was sealed. The mold was then irradiated with a UV lamp (8 ea, Sankyo Denki, F8T5BL) for at least 12 hours with an intensity of 1.5 mW cm^{-2}. After curing, the sample was removed from the mold, the mass of the as-prepared sample was measured, and the sample was placed for 1 day in a fume hood to allow unreacted monomers and DMF to evaporate. To construct **Fig. S4**, we measure the mass of the mold assembly before and after curing. The percent mass lost during curing was calculated as the difference between the mold before and after curing, divided by the mass of the as-prepared sample. Since mass was lost by degassing, we expect that some monomers did not polymerize during the reaction. We measure the thickness with digital calipers and do not observe a change in thickness after evaporation. The thickness of all samples was 0.8 mm."

Comment: 2. Swell the samples in suitable solvent to do simple swelling experiments to determine the sol fraction/gel fraction of the samples. Do not do Soxleth extraction as this will br If you have e.g. 5-10% of sol fraction, then this is comparable to other network systems. On the other hand, then if you end up having

+20% of sol fraction then maybe this is the driving force for the good properties. I will guess from your data that you will have maximum 10% but I am just "guessing qualifiedly".

Response: To measure the sol fraction of polymer in our materials, we prepare a sample of PEA with $C = 10^{-4}$ and $I/C = 0.4$. This sample is representative of the matrix in filled samples with $C = 10^{-4}$. We swell this sample in ethyl acetate for 1 week (Ref. 49 and 50). The solvent swells the elastomer and is volatile in air. The mass fraction of polymer in the fully swollen sample is 11.8 wt%. While swollen, polymer chains not crosslinked into the polymer network will diffuse into the solvent. The sample is then removed from the solvent, and the solvent in the sample is allowed to evaporate in air for 3 days. The sol fraction is calculated as the mass lost during this procedure divided by the mass of the as-prepared sample. We calculate the sol fraction to be 4.46 wt%, meaning most polymers crosslink into a polymer network. We conclude that long polymer chains form highly entangled polymer networks in our materials.

We have added Figure S4, provided in response to the previous comment, as well as the following text to page 3 of the manuscript and the supplementary information:

"Most monomers polymerize, and most polymers crosslink into the polymer network (**Fig. S4**)."

"Sol and gel fraction

We prepare a PEA elastomer of $F = 0$ and $C = 10^{-4}$. We measure the mass of the sample before and after curing, and after degassing in air for 48 hours. We then submerge the degassed sample in a reservoir of ethyl acetate solvent.[49,50] The sample swells in the solvent, where the mass fraction of polymer in the fully swollen sample is 11.8 wt%. While submerged in the solvent, uncrosslinked polymers and monomers diffuse out of the elastomer and into the reservoir of ethyl acetate. After 1 week, we remove the elastomer from the solvent and allow the solvent in the sample to evaporate in air for 3 days. We measure the mass of the washed sample. The gel fraction is calculated from the mass of the washed sample divided by the mass of the as-prepared sample, and the sol fraction is calculated as one minus the gel fraction. Most polymer chains are crosslinked into a polymer network (**Fig. S4**).

49. Nandi, S. & Winter, H. H., Swelling behavior of partially cross-linked polymers: a ternary system. *Macromolecules*. **38**, 10, 4447-4455 (2005).

50. Frankær, S. M. G., Jensen, M. K., Bejenariu, A. G., & Skov, A. L. Investigation of the properties of fully reacted unstoichiometric polydimethylsiloxane networks and their extracted network fractions. *Rheol. Acta.* **51**, 559-567 (2012)."

Comment: By the two above experiments, you will have me convinced that the "multiscale stress deconcentration phenomenon" is correct.

Response: We hope that these experiments provide the needed data.