

Peer Review File

Elastomers mechanically reinforced and toughened with CO₂ gas



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12th Sep 23

Dear Professor Miwa,

Thank you for submitting your manuscript, "Elastomers mechanically reinforced and toughened with CO₂ gas", to Communications Materials. It has now been seen by 4 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, Reviewer 3 raises of previous reports that may conflict with the current claims in the manuscript, which should be fully addressed and commented upon. Additional experiments are requested, such as a control in air, and further clarifications and details are required.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

- A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

- A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee
Associate Editor
Communications Materials
orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Comments :

The authors report polydimethylsiloxane elastomers with amine groups can be mechanically reinforced and toughened with CO₂ and acidic gases. Specifically, the formation of ionic crosslinks between amines, CO₂ and acidic gases strengthen the elastomers, and the formation of nanodomains via the microphase separation of the ionic components toughen the elastomers by dissipating energy during deformation. The idea of this paper is creative and interesting, and that the experimental design is clear. There are a number of problems in the writing of the paper and the overall logic. In view of these, I consider that the authors should first address the below minor issues before possible to be publication.

1. The research on this material in the paper almost entirely focuses on the performance changes on the introduction of N₂, CO₂, and acidic gases. However, the bulk materials are generally used in atmospheric environments, and the oxygen content in the atmosphere is also high. It requires to supply a group of performance studies in the air as a control group.
2. The authors report CL-D9 with CO₂ gas exhibits the highest toughness among all the materials in this paper just because CL-D9 toughened with CO₂ gas exhibits the largest G'' value at room (25 oC). More evidence needs to solid this conclusion.
3. There are some questions about the choice of words and sentence pattern and expression. And attention should be paid to the singular and plural forms of many words and tense issues. Also, the superposition of many compound sentences would make the entire sentence obscure, difficult to understand, and even incorrect.
4. The logic and expression of the paper need to be strengthened. The examples, summaries, and classifications of some literature are not appropriate, for example, "Various chemical materials including membranes, nanoporous materials, catalysts, and reactive monomers...", and the connection between this sentence and the next sentence is not very strong. Moreover, many analyses in the paper lack strong logic, and the conclusions are summarized too directly and positively, making them difficult to convince.
5. When citing some figures for explanation, it is best to clearly indicate the corresponding specific figures, as some cites are not very clear. And, some figures have chaotic color matching (Figure 1c) and some errors (Figure 4c).
6. The outlook of the paper is too brief, and the significance and value of this work are not clearly

explained.

7. For Figure 1c, it is recommended to replace the “compression” and “release” font colors with other colors to avoid overlapping with the colors of the left and right boxes. The arrow colors on the route should be changed to red and blue to correspond to the following two boxes. For Figure 3, arranging a and b, c and d, e and f vertically, respectively, is more conducive to comparison and aesthetics. Besides, for the overall aesthetic of the figures, many duplicate coordinate axes can be omitted.

Reviewer #2 (Remarks to the Author):

The authors report that weakly crosslinked PDMS rubbers containing amino-modified side chains quickly adsorbed CO₂ and the mechanical property of the rubbers was largely improved by the formation of nano-domains of ammonium carbamates. Overall, this paper is very interesting and to be published in a Nature journal. The fact that microphase separation of ionic components behaves like viscoelastic nanofiller is clearly explained from many of experiments by the authors. Especially, the authors observed large fracture energy of CO₂-exposed rubbers and the high strength even at the compression conditions of 20 MPa. As clearly shown in Figure 4b, the nano-domain interface plays an important role on the toughening of the rubbers. These are very interesting results. CL-D9 show very nice mechanical properties for practical applications under small CO₂ partial pressure of 10%.

My minor comments are as follows:

(1) Crosslinking with BDE (1,4-butanediol diglycidyl ether) should be explained in SI for broad readership.

(2) Page 6, line 244: (Fig. 4d) seems to be (Fig. 5d).

(3) Some water content seems to be essential for carbamate formation. Please explain water content briefly in the main body and SI in detail.

(4) This is question. Tensile stress of CL-T5 is similar with that of CL-D9 (Fig. 4C), but fracture energy of the former is far smaller than the latter. Why?

(5) The location of NH₃⁺ peak of CL-D9/HCl (Fig. S7a) might not be correct. At least, the authors should add one reference for this assignment. N-H peak in Fig. S9a also needs a reference.

Overall, this manuscript is very well-prepared. I fully enjoyed the review process.

Reviewer #3 (Remarks to the Author):

This manuscript reports some very interesting results. However, some of them are not unique to the experiments reported here and have been found elsewhere in related systems. The manuscript actually involves two very different types of polymers—polysiloxanes and polyethylenes. The unifying factor is the use of the same amine substitution along the chains and the use of CO₂ to induce bulk property changes.

Have the authors considered splitting the manuscript into 2 separate ones? I feel that it might make sense to do so.

Specific comments:

1. Lines 22-31— the statement, ‘gels containing a lot of solvents’ is not true in all cases nor are the assertions that follow immediately thereafter; see for example, *Soft Matter*, 2022, 18, 5502. There

are others from the recent literature, but I am unaware of ones with diamines like tris(2-aminoethyl)amine (TAEA). Therefore, the statement/claims in the text should be modified and the list of references should be updated.

2. Lines 110-111—Please be VERY specific about what is taken to be the equilibrium state.

3. Also note that some of the same enhancements in viscoelastic and mechanical properties have been reported by others upon addition of CO₂ to amino-substituted polysiloxanes. The magnitudes of those enhancements should be compared qualitatively and quantitatively with the ones reported here.

4. Again, the property enhancements have been attributed in other publications to the presence of nanodomains. The stretching experiment results reported here place those changes on a nice quantitative basis.

5. I am unaware of a similar use of polyethylene in the literature to demonstrate the enhancements. Thus, the use of TAEA-modified PE film (E-T) opens a whole new range of potential applications not found with polysiloxanes.

6. Lines 294-297—'The obtained CL-Mx sheet was further dried at 90°C for 48 h in a vacuum. In the case of the mixture with PDMS-Dx, the mixture was dried at 35°C for 39 h and then at 60°C for 7 h. The mixture was further heated at 90°C for 14 h in a vacuum to obtain a CL-Dx sheet.' Do films prepared and treated in this way exhibit the same reversibility as those not heated?

7. Surely, the addition of HCl and acetic acid lead to irreversible chemical changes and some of the analogous ones have been reported. The same questions arise for the PE films that were heated to above 100 °C.

8. The compression videos do show that the application of excessive force leads to irreversible film destruction.

Reviewer #4 (Remarks to the Author):

In this study, the authors produced moldable bulk materials that enhance mechanical properties with CO₂ and acidic gases. In the materials, amines form ionic crosslinks with CO₂ and acidic gases mechanically strengthen the materials, and nanodomains formed via the microphase separation of the ionic components dissipate energy during deformation toughening the materials.

The following points should be addressed before publishing.

1. How the nanodomains contribute to the enhancement of mechanical properties?
2. How the volume of nanodomains contributes to mechanical properties of materials?
3. In fig 1, it looks like the volume of elastomers are different under N₂ and CO₂. The information about this should be provided and discussed.
4. The effects of CO₂ concentration on the fracture energy of CL-M10/D5/T5 are not discussed.
5. It's necessary to discuss why the young's modulus of CL-M10 is not improved.
6. The SAXS of PDMS elastomer without CO₂ should be supplemented.
7. Please exhibit the impact of temperature on nanodomains.
8. Please analyze the reason of CL-D9 with CO₂ gas exhibits the highest toughness among all materials.

28 October 2023

According to the reviewer's comments, we revised our manuscript, and our answers to the reviewer's questions are as follows:

Comments from Reviewer 1:

Comments :

The authors report polydimethylsiloxane elastomers with amine groups can be mechanically reinforced and toughened with CO₂ and acidic gases. Specifically, the formation of ionic crosslinks between amines, CO₂ and acidic gases strengthen the elastomers, and the formation of nanodomains via the microphase separation of the ionic components toughen the elastomers by dissipating energy during deformation. The idea of this paper is creative and interesting, and that the experimental design is clear. There are a number of problems in the writing of the paper and the overall logic. In view of these, I consider that the authors should first address the below minor issues before possible to be publication.

Thank you for the Reviewer's constructive comments and kind suggestions. These are helpful to improve the quality of our work. According to the reviewer's comments, we have revised the manuscript. The point-to-point responses to these comments are presented below:

1. The research on this material in the paper almost entirely focuses on the performance changes on the introduction of N₂, CO₂, and acidic gases. However, the bulk materials are generally used in atmospheric environments, and the oxygen content in the atmosphere is also high. It requires to supply a group of performance studies in the air as a control group.

Response: We performed the tensile and tearing tests on the CL-D9 in air. The data are added to Fig. 4a and Fig. 4c. The fracture energy value and tensile behavior of CL-D9 in air are comparable with those in N₂. This indicates that the effect of oxygen and very small amount of CO₂ in atmosphere is considerably small for our materials. We revised the sentence as follows: Our elastomers exhibit considerable brittleness in N₂ gas and in air, where their fracture energy values remained less than 60 J m⁻².

2. The authors report CL-D9 with CO₂ gas exhibits the highest toughness among all the materials in this paper just because CL-D9 toughened with CO₂ gas exhibits the largest G'' value at room (25 °C). More evidence needs to solid this conclusion.

Response: As shown in Fig. 4b in the manuscript, we finally proposed the effect of the interface of nanodomains in addition to the G'' value of the materials to estimate the toughness of our materials. Therefore, we are thinking that CL-D9 exhibits the highest toughness among all the materials because CL-D9 has the largest G''A_{int} value as shown in Fig. 4b (right panel). A sentence "In fact, CL-D9 with CO₂ gas exhibits the highest toughness among all our materials." was revised to "In fact, CL-D9 with CO₂ gas exhibited high toughness as discussed below." in the revised manuscript.

3. There are some questions about the choice of words and sentence pattern and expression. And attention should be paid to the singular and plural forms of many words and tense issues. Also, the superposition of many compound sentences would make the entire sentence obscure, difficult to understand, and even incorrect.

Response: Thank you for the reviewer's comments. We rechecked our manuscript and revised words and sentences. The revised parts were highlighted with yellow.

4. The logic and expression of the paper need to be strengthened. The examples, summaries, and classifications of some literature are not appropriate, for example, "Various chemical materials including membranes, nanoporous materials, catalysts, and reactive monomers...", and the connection between this sentence and the next sentence is not very strong. Moreover, many analyses in the paper lack strong logic, and the conclusions are summarized too directly and positively, making them difficult to convince.

Response: Thank you for the reviewer's comments. We revised the expression of sentences. Also, we added some sentences to explain our opinion more precisely. The revised parts were highlighted with yellow.

5. When citing some figures for explanation, it is best to clearly indicate the corresponding specific figures, as some cites are not very clear. And, some figures have chaotic color matching (Figure 1c) and some errors (Figure 4c).

Response: We rechecked our manuscript and revised some citations of figures. We revised the colors of Fig. 1c. Also, we revised the symbol colors of CL-M10 in Fig. 4c.

6. The outlook of the paper is too brief, and the significance and value of this work are not clearly explained.

Response: We revised the outlook in Conclusion section.

7. For Figure 1c, it is recommended to replace the "compression" and "release" font colors with other colors to avoid overlapping with the colors of the left and right boxes. The arrow colors on the route should be changed to red and blue to correspond to the following two boxes. For Figure 3, arranging a and b, c and d, e and f vertically, respectively, is more conducive to comparison and aesthetics. Besides, for the overall aesthetic of the figures, many duplicate coordinate axes can be omitted.

Response: We changed the font colors of the "compression" and "release" to black. Also, the arrow colors on the route were changed to red and blue. For Fig. 3, a and b, c and d, e and f were arranged vertically, and some coordinate axes were unified.

Comments from Reviewer 2:

The authors report that weakly crosslinked PDMS rubbers containing amino-modified side chains quickly adsorbed CO₂ and the mechanical property of the rubbers was largely improved

by the formation of nano-domains of ammonium carbamates. Overall, this paper is very interesting and to be published in a Nature journal. The fact that microphase separation of ionic components behaves like viscoelastic nanofiller is clearly explained from many of experiments by the authors. Especially, the authors observed large fracture energy of CO₂-exposed rubbers and the high strength even at the compression conditions of 20 MPa. As clearly shown in Figure 4b, the nano-domain interface plays an important role on the toughening of the rubbers. These are very interesting results. CL-D9 show very nice mechanical properties for practical applications under small CO₂ partial pressure of 10%.

My minor comments are as follows:

Thank you for the positive comment and kind suggestions. The point-to-point responses are presented below:

(1) Crosslinking with BDE (1,4-butanediol diglycidyl ether) should be explained in SI for broad readership.

Response: We explained the BDE crosslinking procedure in the revised Supplementary Information.

(2) Page 6, line 244: (Fig. 4d) seems to be (Fig. 5d).

Response: Thank you for the indication. We corrected it in the revised manuscript.

(3) Some water content seems to be essential for carbamate formation. Please explain water content briefly in the main body and SI in detail.

Response: For the formation of carbamate, water is not necessary. We carefully dried samples before the measurements. We added a chemical reaction scheme for the formation of carbamate in Fig. 2a and the explanation about the sample drying was added to the Methods section in the main body and Supplementary Information as follows: Before the measurements, the sample sheets were further vacuum-dried at room temperature for at least 24 h and carefully placed into the instruments to avoid moisture absorption.

(4) This is question. Tensile stress of CL-T5 is similar with that of CL-D9 (Fig. 4C), but fracture energy of the former is far smaller than the latter. Why?

Response: First, we remeasured the tensile and tearing tests for the CL-T5 and CL-D9 to make sure our experimental results. As a result, the experimental results indicated in the manuscript are correct. Namely, the tensile behaviors of CL-T5 and CL-D9 are similar with each other, but CL-D9 has higher fracture energy than CL-T5. Suo et al. studied the relationship between the tensile behavior and fracture energy of various materials (Z. Suo et al. *Extreme Mechanics Letters* 10 (2017) 50–57). In this literature, they pointed out that the relationship between the work to tensile rupture and fracture energy depends on the material property at a small zone around the front of the cut. We speculate that our experimental result is due to the difference of such property between CL-T5 and CL-D9. Anyway, the reviewer's indication is very interesting topic for further study. Thank you very much.

(5) The location of NH₃⁺ peak of CL-D9/HCl (Fig. S7a) might not be correct. At least, the authors should add one reference for this assignment. N-H peak in Fig. S9a also needs a reference.

Response: Thank you for the indication. We corrected the assignment of NH₃⁺ peak of CL-D9/HCl in Fig. S7a. Also, the references are added to Fig. S7 and Fig. S9.

Overall, this manuscript is very well-prepared. I fully enjoyed the review process.

Thank you very much.

Comments from Reviewer 3:

This manuscript reports some very interesting results. However, some of them are not unique to the experiments reported here and have been found elsewhere in related systems. The manuscript actually involves two very different types of polymers—polysiloxanes and polyethylenes. The unifying factor is the use of the same amine substitution along the chains and the use of CO₂ to induce bulk property changes.

Have the authors considered splitting the manuscript into 2 separate ones? I feel that it might make sense to do so.

Thank you for the reviewer's insightful comments and kind suggestions. About splitting the manuscript into two papers, we are thinking that the data for polyethylene is necessary for this manuscript to demonstrate the universality of the present technique. The point-to-point responses to these comments are presented as follows:

Specific comments:

1. Lines 22-31—the statement, ‘gels containing a lot of solvents’ is not true in all cases nor are the assertions that follow immediately thereafter; see for example, Soft Matter, 2022, 18, 5502. There are others from the recent literature, but I am unaware of ones with diamines like tris(2-aminoethyl)amine (TAEA). Therefore, the statement/claims in the text should be modified and the list of references should be updated.

Response: Thank you for the indication. As the reviewer pointed out some gels are not containing solvents. We added new references as ref. 25 and ref. 26 and revised the sentences as follows: However, their practical applications have remained largely limited as they are mostly produced in the form of solutions, liquids, nanoparticles, and gels ~~containing a lot of solvents~~. Herein, the *first* work on gas-responsive **elastomers** that enhance **the** mechanical properties (i.e., modulus, strength, stretchability, and toughness) with CO₂ and acidic gases is reported.

2. Lines 110-111—Please be VERY specific about what is taken to be the equilibrium state.

Response: Here, the equilibrium state means the state at a constant weight in CO₂ atmosphere. In the revised manuscript, we deleted the term “at the equilibrium state”. That is, the sentence has been revised to “The amounts of CO₂ molecules trapped in CL-M5, CL-D9, and CL-T5 were calculated to be 3.3×10^{-4} , 5.1×10^{-4} , and 2.1×10^{-4} mol g⁻¹, respectively.”.

3. Also note that some of the same enhancements in viscoelastic and mechanical properties have been reported by others upon addition of CO₂ to amino-substituted polysiloxanes. The magnitudes of those enhancements should be compared qualitatively and quantitatively with the ones reported here.

Response: In the revised manuscript, we compared our result with the result from a reference 16 (*J. Chem. Phys. C*, **113**, 11546–11553 (2009)) and discussed about the differences between the results. In the reference, the effect of CO₂ on the rheological properties of amino-substituted polysiloxane oils was studied. The G' and G'' of the amino-substituted polysiloxane oils increase with CO₂ gas as well as the case of our materials. However, the values of G' and G'' of the amino-substituted polysiloxane oils with CO₂ are much lower than those of our materials because of the absence of the chemical crosslinks in the amino-substituted polysiloxane oils. In the revised manuscript, we added the following sentence: The increases in G' and G'' with the increasing CO₂ concentration were similarly observed for PDMS oils containing amine groups¹⁶. However, the values of G' and G'' were less than one kPa because of the absence of the chemical crosslinks.

4. Again, the property enhancements have been attributed in other publications to the presence of nanodomains. The stretching experiment results reported here place those changes on a nice quantitative basis.

Response: Thank you for the indication.

5. I am unaware of a similar use of polyethylene in the literature to demonstrate the enhancements. Thus, the use of TAEA-modified PE film (E–T) opens a whole new range of potential applications not found with polysiloxanes.

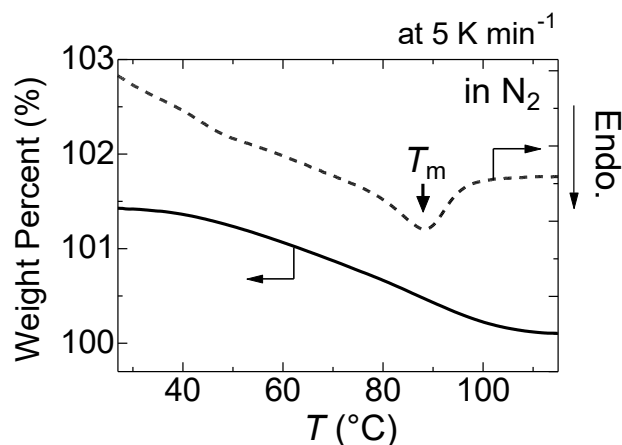
Response: Thank you for the indication. We are currently doing further works on E-T.

6. Lines 294-297–'The obtained CL–Mx sheet was further dried at 90°C for 48 h in a vacuum. In the case of the mixture with PDMS–Dx, the mixture was dried at 35°C for 39 h and then at 60°C for 7 h. The mixture was further heated at 90°C for 14 h in a vacuum to obtain a CL–Dx sheet.' Do films prepared and treated in this way exhibit the same reversibility as those not heated?

Response: We heated the samples to accelerate the reaction. Even without heating, similar CO₂-responsive PDMS sheets can be finally obtained.

7. Surely, the addition of HCl and acetic acid lead to irreversible chemical changes and some of the analogous ones have been reported. The same questions arise for the PE films that were heated to above 100 °C.

Response: To answer against the reviewer's question, we heated the E-T film fully reacted with CO₂ to above 100 °C. The release of CO₂ was accelerated by heating as well as the case of CL–M5 shown in Supplementary Fig. 3. The experimental result was added as Supplementary Fig. 9c in revised Supplementary Information.



8. The compression videos do show that the application of excessive force leads to irreversible film destruction.

Response: Thank you for the indication. We revised the description on the compression test as follows: Upon compression, a block of CL-M5 is completely fractured in N₂ gas (Fig. 4d, Supplementary Movie S3). However, a CL-M5 block reacted with CO₂ gas does not fracture even at high compression (~20 MPa) despite the generation of some cracks (Fig. 4d, Supplementary Movie S4).

Comments from Reviewer 4:

In this study, the authors produced moldable bulk materials that enhance mechanical properties with CO₂ and acidic gases. In the materials, amines form ionic crosslinks with CO₂ and acidic gases mechanically strengthen the materials, and nanodomains formed via the microphase separation of the ionic components dissipate energy during deformation toughening the materials.

The following points should be addressed before publishing.

Thank you very much for Reviewer's very important indications. We revised our manuscript as follows.

1. How the nanodomains contribute to the enhancement of mechanical properties?

Response: Basically, the mechanical properties of our materials are enhanced via formation of the nanodomains because they act as physical crosslinks. In the original manuscript, this explanation was omitted. Therefore, we added the explanation as follows: Contrary to the poor stretchability and fracture stress in N₂ gas, the modulus, stretchability, and fracture stress of our

elastomers drastically increases with the increasing CO₂ concentration owing to the formation of nanodomains that function as physical crosslinks (Fig. 4c).

2. How the volume of nanodomains contributes to mechanical properties of materials?

Response: We are thinking that the volume of nanodomains mainly affect the toughness of our materials. However, as shown in Fig. 4b (right panel), our experimental result demonstrates that the effect of the interface between nanodomains and matrix (A_{int} value) is important for toughening of our materials. Therefore, we believe that the A_{int} value, rather than the volume, mainly influences the toughness of our materials. Of course, the volume of nanodomains relates to the A_{int} value.

3. In fig 1, it looks like the volume of elastomers are different under N₂ and CO₂. The information about this should be provided and discussed.

Response: The sizes of the sample blocks are almost the same in N₂ and CO₂ in Fig. 1c. However, the fractured block looks bigger than the one in CO₂. I think readers can understand the situation by watching the movies. Therefore, we added the below comment in the legend of Fig. 1c. “See Supplementary Movie S3 and Supplementary Movie S4 in detail.”

4. The effects of CO₂ concentration on the fracture energy of CL-M10/D5/T5 are not discussed.

Response: We expect similar effect of CO₂ concentration for CL-M10, CL-D5, and CL-T5 with CL-M5 and CL-D9. We added the following sentence in the revised manuscript: Although the effect of CO₂ gas concentration is examined only for CL-M5 and CL-D9 in this study, a similar trend is expected for the other samples.

5. It's necessary to discuss why the young's modulus of CL-M10 is not be improved.

Response: We remeasured the tensile test of CL-M10 in N₂ and in CO₂ to make sure the result. As a result, the experimental result is correct. As shown in Fig. 3a and Fig. 3b, the relaxation temperature of nanodomains is much lower than room temperature in the cases of CL-M5 and CL-M10. That is, the nanodomains in CL-M5 and CL-M10 are soft at room temperature. Therefore, the Young's modulus of CL-M10 is not improved a lot even in CO₂ gas because the soft nanodomains do not function as effective physical crosslinks. The following sentences were added in the revised manuscript: In case of CL-Mx samples, nanodomains are soft and do not function as effective physical crosslinks at room temperature because the relaxation temperature of nanodomains is considerably lower than room temperature (Fig. 3a and Fig. 3b). Therefore, the modulus of CL-M10 is not remarkably enhanced with CO₂ gas while the stretchability is largely improved owing to the prevention of fracture.

6. The SAXS of PDMS elastomer without CO₂ should be supplemented.

Response: The SAXS for PDMS elastomers without CO₂ gas is presented with black plots in Fig. 2d.

7. Please exhibit the impact of temperature on nanodomains.

Response: As shown in Supplementary Fig. 3, CO₂ trapped by our material is quickly released by heating. This implies that the nanodomains formed with CO₂ gas should be disappeared by heating. To check this behavior, we heated CL-D9 at 85 °C for 30 min under N₂ gas flow after CL-D9 was fully reacted with CO₂ gas. The fracture energy of this treated CL-D9 was almost the same with that of CL-D9 without CO₂. In the revised manuscript, the following description was added: When our elastomer materials were heated, the trapped CO₂ was rapidly released (Supplementary Fig. 3). This result implies that the effect of CO₂ on our materials is easily canceled by heating the materials.

8. Please analyze the reason of CL-D9 with CO₂ gas exhibits the highest toughness among all materials.

Response: CL-D9 exhibits the largest $G''A_{\text{int}}$ value among all materials as shown in Fig. 4b (right panel). We are thinking that this is the main cause for the highest toughness of CL-D9. As discussed in the manuscript, we proposed the effect of the interface of nanodomains (A_{int} value) in addition to the G'' value of the materials to estimate the toughness of our materials.

22nd Nov 23

Dear Professor Miwa,

Thank you for submitting your manuscript, "Elastomers mechanically reinforced and toughened with CO₂ gas", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. Reviewer 1 did not respond to comment on the revisions to their comments but another reviewer thinks that the revisions were suitable. You will see that reviewer 3 still raises some important points. We remain interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, Reviewer 4 thinks that some questions were still not specifically answered, which requires thorough clarification and text rewording, and asks that some results should be compared to polymers of the same molecular weight.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

- A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

- A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

- A clean version of the manuscript. Please select the file type 'Article File'.

- An updated <https://www.nature.com/documents/nr-editorial-policy-checklist.zip> Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

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for reference.

Data availability statements and data citations policy: All Communications Materials manuscripts must include a section titled "Data Availability" at the end of the Methods section or main text (if no Methods). More information on this policy, and a list of examples, is available at http://www.nature.com/authors/policies/data/data-availability-statements-data-citations.pdf.

In particular, the Data availability statement should include:

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DATA SOURCES: We strongly encourage authors to deposit all new data associated with the paper in a persistent repository where they can be freely and enduringly accessed. We recommend submitting the data to discipline-specific, community-recognized repositories, where possible and a list of recommended repositories is provided at http://www.nature.com/sdata/policies/repositories.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be

happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee
Associate Editor
Communications Materials
orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #2 (Remarks to the Author):

I believe this paper is now acceptable for publication. Very nice paper.

Reviewer #3 (Remarks to the Author):

[PLEASE SEE ATTACHMENT]

Reviewer #4 (Remarks to the Author):

My comments have been fully addressed. I therefore endorse its publication in Communications Materials in its current form.

This manuscript reports some very interesting results. However, some of them are not unique to the experiments reported here and have been found elsewhere in related systems. The manuscript actually involves two very different types of polymers—polysiloxanes and polyethylenes. The unifying factor is the use of the same amine substitution along the chains and the use of CO₂ to induce bulk property changes.

Have the authors considered splitting the manuscript into 2 separate ones? I feel that it might make sense to do so.

Thank you for the reviewer’s insightful comments and kind suggestions. About splitting the manuscript into two papers, we are thinking that the data for polyethylene is necessary for this manuscript to demonstrate the universality of the present technique. *In what way do the polyethylene results demonstrate ‘universality’?? I do not think that they do.*

The point-to-point responses
to these comments are presented as follows:

Specific comments:

1. Lines 22-31— the statement, ‘gels containing a lot of solvents’ is not true in all cases nor are the assertions that follow immediately thereafter; see for example, Soft Matter, 2022, 18, 5502. There are others from the recent literature, but I am unaware of ones with diamines like tris(2-aminoethyl)amine (TAEA). Therefore, the statement/claims in the text should be modified and the list of references should be updated.

Response: Thank you for the indication. As the reviewer pointed out some gels are not containing solvents. We added new references as ref. 25 and ref. 26 and revised the sentences as follows: However, their practical applications have remained largely limited as they are mostly produced in the form of solutions, liquids, nanoparticles, and gels containing a lot of solvents. *My comment was specifically about those that do not contain a lot of solvent. It has not been addressed in this response.*

Herein, the first work on gas-responsive elastomers that enhance the mechanical properties (i.e., modulus, strength, stretchability, and toughness) with CO₂ and acidic gases is reported. *Other examples with CO₂ and acid gas-responsive gases that enhance the mechanical properties have been reported in the literature. These are not the first reported examples!!*

2. Lines 110-111—Please be VERY specific about what is taken to be the equilibrium state.

Response: Here, the equilibrium state means the state at a constant weight in CO₂ atmosphere. In the revised manuscript, we deleted the term “at the equilibrium state”. That is, the sentence has been revised to “The amounts of CO₂ molecules trapped in CL–M5, CL–D9, and CL–T5 were

calculated to be 3.3×10^{-4} , 5.1×10^{-4} , and 2.1×10^{-4} mol g⁻¹, respectively.”.

3. Also note that some of the same enhancements in viscoelastic and mechanical properties have been reported by others upon addition of CO₂ to amino-substituted polysiloxanes. The magnitudes of those enhancements should be compared qualitatively and quantitatively with the ones reported here.

Response: In the revised manuscript, we compared our result with the result from a reference 16 (J. Chem. Phys. C, 113, 11546–11553 (2009)) and discussed about the differences between the results. In the reference, the effect of CO₂ on the rheological properties of amino-substituted polysiloxane oils was studied. The G' and G'' of the amino-substituted polysiloxane oils increase with CO₂ gas as well as the case of our materials. However, the values of G' and G'' of the amino-substituted polysiloxane oils with CO₂ are much lower than those of our materials because of the absence of the chemical crosslinks in the amino-substituted polysiloxane oils. In the revised manuscript, we added the following sentence: The increases in G' and G'' with the increasing CO₂ concentration were similarly observed for PDMS oils containing amine groups¹⁶.

However, the values of G' and G'' were less than one kPa because of the absence of the chemical

crosslinks. To make this statement, the results should be compared with polymers of the same molecular weight and degree of amino substitution. Were they comparable???

4. Again, the property enhancements have been attributed in other publications to the presence of nanodomains. The stretching experiment results reported here place those changes on a nice quantitative basis.

Response: Thank you for the indication.

5. I am unaware of a similar use of polyethylene in the literature to demonstrate the enhancements. Thus, the use of TAEA-modified PE film (E-T) opens a whole new range of potential applications not found with polysiloxanes.

Response: Thank you for the indication. We are currently doing further works on E-T.

6. Lines 294-297—'The obtained CL-Mx sheet was further dried at 90°C for 48 h in a vacuum. In the case of the mixture with PDMS-Dx, the mixture was dried at 35°C for 39 h and then at 60°C for 7 h. The mixture was further heated at 90°C for 14 h in a vacuum to obtain a CL-Dx sheet.'

Do films prepared and treated in this way exhibit the same reversibility as those not heated?

Response: *We heated the samples to accelerate the reaction. Even without heating, similar CO₂-responsive PDMS sheets can be finally obtained. This is not an answer to my question. Are they the same???*

7. Surely, the addition of HCl and acetic acid lead to irreversible chemical changes and some of the analogous ones have been reported. The same questions arise for the PE films that were heated to above 100 C.

Response: To answer against the reviewer's question, we heated the E-T film fully reacted with CO₂ to above 100 °C. The release of CO₂ was accelerated by heating as well as the case of CL-M5 shown in Supplementary Fig. 3. The experimental result was added as Supplementary Fig. 9c in revised Supplementary Information. *This is not again, an answer to my question.*

9 December 2023

According to the comments from Reviewer 3, we revised our manuscript, and our answers to the reviewer's questions are as follows:

Comments from Reviewer 3:

This manuscript reports some very interesting results. However, some of them are not unique to the experiments reported here and have been found elsewhere in related systems. The manuscript actually involves two very different types of polymers—polysiloxanes and polyethylenes. The unifying factor is the use of the same amine substitution along the chains and the use of CO₂ to induce bulk property changes. Have the authors considered splitting the manuscript into 2 separate ones? I feel that it might make sense to do so.

Thank you for the reviewer's insightful comments and kind suggestions. About splitting the manuscript into two papers, we are thinking that the data for polyethylene is necessary for this manuscript to demonstrate the universality of the present technique. *In what way do the polyethylene results demonstrate 'universality'? I do not think that they do.*

Our response: Thank you for the indication. "Universality" is certainly an overstatement. In the revised manuscript, we revised the sentence as follows: To demonstrate the applicability of our method to other polymers, the mechanical reinforcement of polyethylene (PE) with CO₂ gas was examined.

The point-to-point responses to these comments are presented as follows:

Specific comments:

1. Lines 22-31— the statement, 'gels containing a lot of solvents' is not true in all cases nor are the assertions that follow immediately thereafter; see for example, Soft Matter, 2022, 18, 5502. There are others from the recent literature, but I am unaware of ones with diamines like tris(2-aminoethyl)amine (TAEA). Therefore, the statement/claims in the text should be modified and the list of references should be updated.

Response: Thank you for the indication. As the reviewer pointed out some gels are not containing solvents. We added new references as ref. 25 and ref. 26 and revised the sentences as follows: However, their practical applications have remained largely limited as they are mostly produced in the form of solutions, liquids, nanoparticles, and gels containing a lot of solvents. *My comment was specifically about those that do not contain a lot of solvent. It has not been addressed in this response.*

Our response: Thank you for the indication. We reevaluated our manuscript and we considered that this sentence is not necessary. Therefore, we deleted the sentence "However, their practical applications have remained largely limited as they are mostly produced in the form of solutions, liquids, nanoparticles, and gels" in the revised manuscript.

Herein, the first work on gas-responsive elastomers that enhance the mechanical properties (i.e.,

modulus, strength, stretchability, and toughness) with CO₂ and acidic gases is reported. *Other examples with CO₂ and acid gas-responsive gases that enhance the mechanical properties have been reported in the literature. These are not the first reported examples!!*

Our response: Thank you for the indication. We deleted the term “the first” and we revised the manuscript as follows: Herein, the gas-responsive elastomers that enhance the mechanical properties (i.e., modulus, strength, stretchability, and toughness) with CO₂ gas is reported.

2. Lines 110-111—Please be VERY specific about what is taken to be the equilibrium state.

Response: Here, the equilibrium state means the state at a constant weight in CO₂ atmosphere. In the revised manuscript, we deleted the term “at the equilibrium state”. That is, the sentence has been revised to “The amounts of CO₂ molecules trapped in CL-M5, CL-D9, and CL-T5 were calculated to be 3.3×10^{-4} , 5.1×10^{-4} , and 2.1×10^{-4} mol g⁻¹, respectively.”.

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However, the values of G' and G'' were less than one kPa because of the absence of the chemical crosslinks. To make this statement, the results should be compared with polymers of the same molecular weight and degree of amino substitution. Were they comparable???

Our response: Thank you for the indication. As the reviewer pointed out, the molecular weights of the polymers are much different in addition to the chemical crosslink. For example, 10PSil in the reference 16 and PDMS-M10 in our work have the same degree of amino substitution. However, the weight-average molecular weights of 10PSil and PDMS-M10 are 9,950 and 98,200, respectively. The PDMS-M10 has much larger molecular weight than 10PSil. Therefore, the differences in the values of G' and G'' are not only from the chemical crosslink but also the molecular weight. We revised the sentence as follows: **However, the values of G' and G'' were less than one kPa because of their small molecular weight and the absence of the chemical crosslinks.**

4. Again, the property enhancements have been attributed in other publications to the presence of nanodomains. The stretching experiment results reported here place those changes on a nice quantitative basis.

Response: Thank you for the indication.

5. I am unaware of a similar use of polyethylene in the literature to demonstrate the enhancements. Thus, the use of TAEA-modified PE film (E-T) opens a whole new range of potential applications not found with polysiloxanes.

Response: Thank you for the indication. We are currently doing further works on E-T.

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Response: We heated the samples to accelerate the reaction. Even without heating, similar CO₂-responsive PDMS sheets can be finally obtained. ***This is not an answer to my question. Are they the same???***

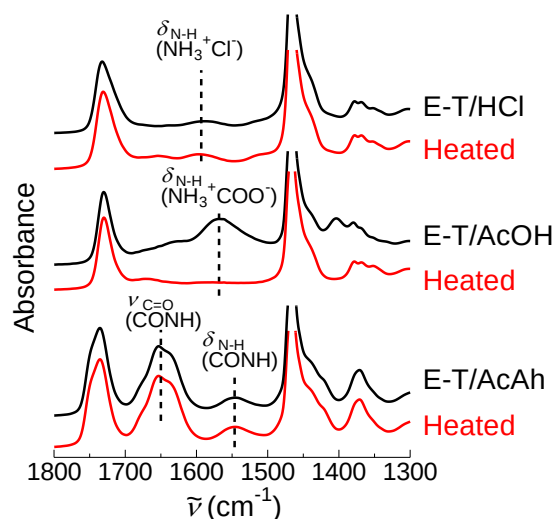
Our response: We sincerely apologize for our poor choice of the word. The same CO₂ responsive PDMS sheet is obtained.

7. Surely, the addition of HCl and acetic acid lead to irreversible chemical changes and some of the analogous ones have been reported. The same questions arise for the PE films that were heated to above 100 °C.

Response: To answer against the reviewer's question, we heated the E-T film fully reacted with CO₂ to above 100 °C. The release of CO₂ was accelerated by heating as well as the case of CL-M5 shown in Supplementary Fig. 3. The experimental result was added as Supplementary Fig. 9c in revised Supplementary Information. ***This is not again, an answer to my question.***

Our response: We are so sorry that we did not understand your question correctly. We did additional FT-IR experiment, and the result is shown in new figure, Supplementary Fig. 10, in the revised Supplementary Information. PE films (E-T) were exposed to HCl, acetic acid (AcOH), and acetic anhydride (AcAh) gases. Furthermore, the films were heated at 110°C for 30 min. Although E-T/HCl and E-T/AcAh are stable even at 110 °C, AcOH molecules are released from E-T upon heating.

Thanks to your indication, we found that we used AcAh instead of AcOH in our experiment in Supplementary Fig. 7. Thank you very much. Although this does not affect the conclusion of our manuscript, we sincerely apologize to this mistake. We carefully rechecked our experiments. Amine groups in our samples change to amide groups with AcAh. We deleted the term "acidic gas" from the revised manuscript. Moreover, we revised Fig. 4a and Supplementary Fig. 7.



24th Jan 24

Dear Professor Miwa,

Your manuscript titled "Elastomers mechanically reinforced and toughened with CO₂ gas" has now been seen again by one of the referees, as Reviewer 3 could not respond to comment. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

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