Annealing and TMOS coating on PSF/ZTC mixed matrix membrane for enhanced CO$_2$/CH$_4$ and H$_2$/CH$_4$ separation

Nurul Widiastuti, Irmariza Shafitri Caralin, Alvin Rahmad Widyanto, Rika Wijiyanti, Triyanda Gunawan, Zulhairun Abdul Karim, Mikihiro Nomura and Yuki Yoshida

Article citation details
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Final acceptance: 24 May 2022

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History
RSOS-211371.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
No

Are the interpretations and conclusions justified by the results?
No

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No
Recommendation?
Reject

Comments to the Author(s)
this work reported that the development of ZTC MMMs for CO2/CH4 and H2/CH4 separations, the topic is very important for industrial application when it is applied to natural gas sweetening, and H2 recovery from the natural gas grid. however, the prepared membranes do not provide a significant improvement compared to the state-of-the-art membranes reported in the literature or industrial applications. therefore, I feel this work did not provide significant scientific novelty for publishing in RSOS.

(1) based on the SEM images in Figure 4. it seems the ZTC particles caused a defect on the surface of the membranes. due to the large finger-like structure of the PSF MMMs, it is unlike the ZTC will provide any contribution neither to gas permeance nor selectivity. by post-treatment with annealing or coating TMOS selective to cause cross-link or make an extra selective layer to enhance the selective might provide some novelties, however, the significant reduction of gas permeance makes it unsuccessful for the post-treatment. as we can see from Figs. 7 and 8, those post-treated membranes do not present a better performance compared to the fresh membrane with respect to the Robeson upper bound. the slightly increased selectivity may not offset the significantly reduced permeance.

(2) the authors need to add the pure PSF membranes as the reference to document the effect of adding ZTC nanoparticles
(3) it is unclear why the membrane coated with 0.03 TMOS presented a much higher H2/CH4 selectivity compared to other membranes (&lt;10). this data point needs to be checked or at least explained. also, the CO2/CH4 selectivity is less than 1- unlikely (it might be the experimental error that there is no selectivity), error bar should be given.
(4) based on the SEM images of Fig. 1H and K, it is clear that the TMOS penetrates deeply into the matrix, which leads to the significant reduction of gas permeance, and of course a slight increase of the selectivity. The reviewer believes that the pore size of fresh PSF/ZTC MMMs is too large for direct coating.

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept with minor revision (please list in comments)
Comments to the Author(s)
The manuscript is more detailed, with clear and crisp tables of photographs. The materials and experimental methods are more complete and will facilitate research by other scholars. I consider it to be a manuscript that could be published.

Review form: Reviewer 3

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
No

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Major revision is needed (please make suggestions in comments)

Comments to the Author(s)
1. In Fig.1, the dense structure formed by the annealing treatment looks like a new layer formed on the PSF matrix, and H2 CO2 CH4 were not marked out.
2. The manuscript lacks the characterization of ZTC itself, including but not limited to the pore size.
3. Whether it is possible to accurately characterize the pore size change range of the membrane before and after annealing.
4. The performance of binary gas H2/CH4 was only carried out using MMM annealed at 190°C, how about other types of membranes?
5. Please illustrate the reason of CH4 increased permeance and CO2 /CH4 increased selectivity occurred on MMM coating with 0.05 mol TMOS.
6. “the excess TMOS concentration on the membrane was able to form multilayers, which could reduce adhesion between the polymer matrix and filler particles.” The analysis is confused.
7. Paragraphs format are inconsistent and the serial number of CONCLUSION is error. Please check the whole manuscript carefully.
8. The logic of the manuscript does not match the order of figures placement and should be adjusted appropriately.
9. The preparation and application of MMM has not been reviewed completely, such as 10.1016/j.cej.2020.127144; 10.1016/j.seppur.2019.05.009; 10.1166/jnn.2017.13914; 10.1016/j.memsci.2016.07.060.
10. In Figure 4, the uppercase and lowercase letters are inconsistent with the legends, and there is no description for fig.4l.
Dear Dr Widiastuti:

Title: Selectivity Improvement of Polysulfone-Zeolite Templated Carbon Membrane by Annealing and Coating Treatment for CO2/CH4 and H2/CH4 Separation

Thank you for your submission to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The editor assigned to your manuscript has now received comments from reviewers. We would like you to revise your paper in accordance with the referee and Subject Editor suggestions which can be found below (not including confidential reports to the Editor). Please note this decision does not guarantee eventual acceptance.

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When submitting your revised manuscript, you must respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". Please use this to document how you have responded to the comments, and the adjustments you have made. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response.

Please also include the following statements alongside the other end statements. As we cannot publish your manuscript without these end statements included, if you feel that a given heading is not relevant to your paper, please nevertheless include the heading and explicitly state that it is not relevant to your work.

• Ethics statement
Please clarify whether you received ethical approval from a local ethics committee to carry out your study. If so please include details of this, including the name of the committee that gave consent in a Research Ethics section after your main text. Please also clarify whether you received informed consent for the participants to participate in the study and state this in your Research Ethics section.

*OR*
Please clarify whether you obtained the necessary licences and approvals from your institutional animal ethics committee before conducting your research. Please provide details of these licences and approvals in an Animal Ethics section after your main text.

*OR*

Please clarify whether you obtained the appropriate permissions and licences to conduct the fieldwork detailed in your study. Please provide details of these in your methods section.

• Data accessibility

It is a condition of publication that you make available the data and research materials supporting the results in the article. Datasets should be deposited in an appropriate publicly available repository and details of the associated accession number, link or DOI to the datasets must be included in the Data Accessibility section of the article (https://royalsocietypublishing.org/rsos/for-authors#question17). Reference(s) to datasets should also be included in the reference list of the article with DOIs (where available).

Please include a Data Availability section after your main text stating where supporting data are available from, or where they will be made available should your article be accepted for publication.

If you wish to submit your supporting data or code to Dryad (http://datadryad.org/), or modify your current submission to dryad, please use the following link: http://datadryad.org/submit?journalID=RSOS&manu=RSOS-211371

• Competing interests

Please include a Competing Interests section after your main text declaring any financial or non-financial competing interests. If you have no competing interests please state 'I/we have no competing interests.'

• Authors' contributions

Please include an Authors' Contributions section at the end of your main text detailing the contribution of each author. All authors should have read and approved the manuscript before submission and this should be stated in the Authors' Contributions section.

The list of Authors should meet all of the following criteria: 1) substantial contributions to conception and design, or acquisition of data, or analysis and interpretation of data; 2) drafting the article or revising it critically for important intellectual content; and 3) final approval of the version to be published.

All contributors who do not meet all of these criteria should be included in the acknowledgements.

We suggest the following format:
AB carried out the molecular lab work, participated in data analysis, carried out sequence alignments, participated in the design of the study and drafted the manuscript; CD carried out the statistical analyses; EF collected field data; GH conceived of the study, designed the study, coordinated the study and helped draft the manuscript. All authors gave final approval for publication.

• Acknowledgements

Please acknowledge anyone who contributed to the study but did not meet the authorship criteria.

• Funding statement
Please include a funding section after your main text which lists the source of funding for each author.

Once again, thank you for submitting your manuscript to Royal Society Open Science and I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Yours sincerely,
Dr Ellis Wilde
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Professor Chaohua Cui.

************************************************

RSC Associate Editor
Comments to the Author:
(There are no comments.)

RSC Subject Editor
Comments to the Author:
(There are no comments.)

************************************************

Reviewers' Comments to Author:
Reviewer: 1
Comments to the Author(s)
this work reported that the development of ZTC MMMs for CO2/CH4 and H2/CH4 separations, the topic is very important for industrial application when it is applied to natural gas sweetening, and H2 recovery from the natural gas grid. however, the prepared membranes do not provide a significant improvement compared to the state-of-the-art membranes reported in the literature or industrial applications. therefore, I feel this work did not provide significant scientific novelty for publishing in RSOS.
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(4) Based on the SEM images of Fig. 1H and K, it is clear that the TMOS penetrates deeply into the matrix, which leads to the significant reduction of gas permeance, and of course a slight increase of the selectivity. The reviewer believes that the pore size of fresh PSF/ZTC MMMs is too large for direct coating.

Reviewer: 2
Comments to the Author(s)
The manuscript is more detailed, with clear and crisp tables of photographs. The materials and experimental methods are more complete and will facilitate research by other scholars. I consider it to be a manuscript that could be published.

Reviewer: 3
Comments to the Author(s)
1. In Fig. 1, the dense structure formed by the annealing treatment looks like a new layer formed on the PSF matrix, and H2 CO2 CH4 were not marked out.
2. The manuscript lacks the characterization of ZTC itself, including but not limited to the pore size.
3. Whether it is possible to accurately characterize the pore size change range of the membrane before and after annealing.
4. The performance of binary gas H2/CH4 was only carried out using MMM annealed at 190°C, how about other types of membranes?
5. Please illustrate the reason of CH4 increased permeance and CO2/CH4 increased selectivity occurred on MMM coating with 0.05 mol TMOS.
6. “the excess TMOS concentration on the membrane was able to form multilayers, which could reduce adhesion between the polymer matrix and filler particles.” The analysis is confused.
7. Paragraphs format are inconsistent and the serial number of CONCLUSION is error. Please check the whole manuscript carefully.
8. The logic of the manuscript does not match the order of figures placement and should be adjusted appropriately.
9. The preparation and application of MMM has not been reviewed completely, such as 10.1016/j.cej.2020.127144; 10.1016/j.seppur.2019.05.009; 10.1166/jnn.2017.13914; 10.1016/j.memsci.2016.07.060.
10. In Figure 4, the uppercase and lowercase letters are inconsistent with the legends, and there is no description for fig. 4l.

Author's Response to Decision Letter for (RSOS-211371.R0)
See Appendix A.

RSOS-211371.R1 (Revision)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes
Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
1) the title might be a bit confusing as the reader might confuse with carbon membranes (in fact this is a PSF/ZTC MMM)
2) the title indicated the enhancement for CO2/CH4 separation by annealing and coating treatment. however, from Table 5, the reviewer cannot clearly see the improvement at least for CO2/CH4 separation, for some cases, it decreases. and the authors may not fully address my comment why CO2/CH4 selectivity is lower than 1. what is the transport mechanism.

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
The author is familiar with is manuscript content and revises it carefully and completely with a serious attitude. The structure of the article is clear. Recommended for acceptance.
Decision letter (RSOS-211371.R1)

We hope you are keeping well at this difficult and unusual time. We continue to value your support of the journal in these challenging circumstances. If Royal Society Open Science can assist you at all, please don't hesitate to let us know at the email address below.

Dear Dr Widiastuti:

Title: Selectivity Improvement of Polysulfone-Zeolite Templated Carbon Membrane by Annealing and Coating Treatment for CO2/CH4 and H2/CH4 Separation
Manuscript ID: RSOS-211371.R1

Thank you for submitting the above manuscript to Royal Society Open Science. On behalf of the Editors and the Royal Society of Chemistry, I am pleased to inform you that your manuscript will be accepted for publication in Royal Society Open Science subject to minor revision in accordance with the referee suggestions. Please find the reviewers' comments at the end of this email.

The reviewers and handling editors have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the comments and revise your manuscript.

Please also include the following statements alongside the other end statements. As we cannot publish your manuscript without these end statements included, if you feel that a given heading is not relevant to your paper, please nevertheless include the heading and explicitly state that it is not relevant to your work. We have included a screenshot example of the end statements for reference.

- Ethics statement
  Please clarify whether you received ethical approval from a local ethics committee to carry out your study. If so please include details of this, including the name of the committee that gave consent in a Research Ethics section after your main text. Please also clarify whether you received informed consent for the participants to participate in the study and state this in your Research Ethics section.
  *OR*
  Please clarify whether you obtained the necessary licences and approvals from your institutional animal ethics committee before conducting your research. Please provide details of these licences and approvals in an Animal Ethics section after your main text.
  *OR*
  Please clarify whether you obtained the appropriate permissions and licences to conduct the fieldwork detailed in your study. Please provide details of these in your methods section.

- Data accessibility
  It is a condition of publication that you make available the data and research materials supporting the results in the article. Datasets should be deposited in an appropriate publicly available repository and details of the associated accession number, link or DOI to the datasets must be included in the Data Accessibility section of the article (https://royalsocietypublishing.org/rsos/for-authors#question17). Reference(s) to datasets should also be included in the reference list of the article with DOIs (where available).

Please include a Data Availability section after your main text stating where supporting data are available from, or where they will be made available should your article be accepted for publication.
If you wish to submit your supporting data or code to Dryad (http://datadryad.org/), or modify your current submission to dryad, please use the following link: http://datadryad.org/submit?journalID=RSOS&manu=RSOS-211371.R1

• Competing interests
Please include a Competing Interests section after your main text declaring any financial or non-financial competing interests. If you have no competing interests please state ‘I/we have no competing interests.

• Authors’ contributions
Please include an Authors’ Contributions section at the end of your main text detailing the contribution of each author. All authors should have read and approved the manuscript before submission and this should be stated in the Authors’ Contributions section.

The list of Authors should meet all of the following criteria: 1) substantial contributions to conception and design, or acquisition of data, or analysis and interpretation of data; 2) drafting the article or revising it critically for important intellectual content; and 3) final approval of the version to be published.

All contributors who do not meet all of these criteria should be included in the acknowledgements.

We suggest the following format:
AB carried out the molecular lab work, participated in data analysis, carried out sequence alignments, participated in the design of the study and drafted the manuscript; CD carried out the statistical analyses; EF collected field data; GH conceived of the study, designed the study, coordinated the study and helped draft the manuscript. All authors gave final approval for publication.

• Acknowledgements
Please acknowledge anyone who contributed to the study but did not meet the authorship criteria.

• Funding statement
Please include a funding section after your main text which lists the source of funding for each author.

Because the schedule for publication is very tight, it is a condition of publication that you submit the revised version of your manuscript before 08-May-2022. Please note that the revision deadline will expire at 00.00am on this date. If you do not think you will be able to meet this date please let me know immediately.

To revise your manuscript, log into https://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under “Manuscripts with Decisions”. Under "Actions," click on "Create a Revision." You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you will be able to respond to the comments made by the referees and upload a file "Response to Referees" in “Section 6 - File Upload”. You can use this to document any changes you make to the original manuscript. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response to the referees.
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2) A separate electronic file of each figure (EPS or print-quality PDF preferred (either format should be produced directly from original creation package), or original software format)
3) Included a 100 word media summary of your paper when requested at submission. Please ensure you have entered correct contact details (email, institution and telephone) in your user account
4) Included the raw data to support the claims made in your paper. You can either include your data as electronic supplementary material or upload to a repository and include the relevant doi within your manuscript
5) All supplementary materials accompanying an accepted article will be treated as in their final form. Note that the Royal Society will neither edit nor typeset supplementary material and it will be hosted as provided. Please ensure that the supplementary material includes the paper details where possible (authors, article title, journal name).

Supplementary files will be published alongside the paper on the journal website and posted on the online figshare repository (https://figshare.com). The heading and legend provided for each supplementary file during the submission process will be used to create the figshare page, so please ensure these are accurate and informative so that your files can be found in searches. Files on figshare will be made available approximately one week before the accompanying article so that the supplementary material can be attributed a unique DOI.

Once again, thank you for submitting your manuscript to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry. I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Kind regards,
Ellis Wilde and Kate Jones
Assistant Editor, Journals
Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Professor Chaohua Cui.

*****************************************************************************

RSC Associate Editor: 1
Comments to the Author:
(There are no comments.)

RSC Associate Editor: 2
Comments to the Author:
(There are no comments.)

*****************************************************************************
Reviewer comments to Author:
Reviewer: 1
Comments to the Author(s)
1) the title might be a bit confusing as the reader might confuse with carbon membranes (in fact this is a PSF/ZTC MMM)
2) the title indicated the enhancement for CO2/CH4 separation by annealing and coating treatment. However, from Table 5, the reviewer cannot clearly see the improvement at least for CO2/CH4 separation, for some cases, it decreases. and the authors may not fully address my comment why CO2/CH4 selectivity is lower than 1. what is the transport mechanism.

Reviewer: 2
Comments to the Author(s)
The author is familiar with is manuscript content and revises it carefully and completely with a serious attitude. The structure of the article is clear. Recommended for acceptance.

Author's Response to Decision Letter for (RSOS-211371.R1)

See Appendix B.

RSOS-211371.R2

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
I'm satisfied with the revision, and recommend to publishing this work.
Decision letter (RSOS-211371.R2)

We hope you are keeping well at this difficult and unusual time. We continue to value your support of the journal in these challenging circumstances. If Royal Society Open Science can assist you at all, please don't hesitate to let us know at the email address below.

Dear Dr Widiastuti:

Title: Annealing and TMOS coating on PSF/ZTC mixed matrix membrane for enhanced CO2/CH4 and H2/CH4 separation
Manuscript ID: RSOS-211371.R2

It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

Where applicable, the comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

If you have not already done so, please ensure that you send to the editorial office (openscience@royalsociety.org) an editable version of your accepted manuscript, and individual files for each figure and table included in your manuscript. You can send these in a zip folder if more convenient. Failure to provide these files may delay the processing of your proof.

Please remember to make any data sets or code libraries 'live' prior to publication, and update any links as needed when you receive a proof to check - for instance, from a private 'for review' URL to a publicly accessible 'for publication' URL. It is also good practice to add data sets, code and other digital materials to your reference list.

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The proof of your paper will be available for review using the Royal Society online proofing system and you will receive details of how to access this in the near future from our production office (openscience_proofs@royalsociety.org). We aim to maintain rapid times to publication after acceptance of your manuscript and we would ask you to please contact both the production office and editorial office if you are likely to be away from e-mail contact to minimise delays to publication. If you are going to be away, please nominate a co-author (if available) to manage the proofing process, and ensure they are copied into your email to the journal.

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Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,
Raffaele Egizio
On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Professor Chaohua Cui.

********

RSC Associate Editor
Comments to the Author:
(There are no comments.)

RSC Subject Editor
Comments to the Author:
(There are no comments.)

********

Reviewer(s)' Comments to Author:
Reviewer: 1
Comments to the Author(s)
I'm satisfied with the revision, and recommend to publishing this work.
Response to Reviewers of Royal Society Open Science

Reviewer #1: this work reported that the development of ZTC MMMs for CO$_2$/CH$_4$ and H$_2$/CH$_4$ separations, the topic is very important for industrial application when it is applied to natural gas sweetening, and H$_2$ recovery from the natural gas grid. however, the prepared membranes do not provide a significant improvement compared to the state-of-the-art membranes reported in the literature or industrial applications. therefore, I feel this work did not provide significant scientific novelty for publishing in RSOS.

1: based on the SEM images in Figure 4, it seems the ZTC particles caused a defect on the surface of the membranes. due to the large finger-like structure of the PSF MMMs, it is unlike the ZTC will provide any contribution neither to gas permeance nor selectivity. by post-treatment with annealing or coating TMOS selective to cause cross-link or make an extra selective layer to enhance the selective might provide some novelties, however, the significant reduction of gas permeance makes it unsuccessful for the posttreatment. as we can see from Figs. 7 and 8, those post-treated membranes do not present a better performance compared to the fresh membrane with respect to the Robeson upper bound. the slightly increased selectivity may not offset the significantly reduced permeance.

Response

First of all, thank you for your time to review this manuscript.

We greatly appreciate the reviewer’s positive comments. Our response to your comments is below:

There is no relationship between the defects and the finger-like structure. Based on Wijiyanti et al. [1], the neat membrane does have finger-like pores similar to this study. The finger-like pore was obtained as a result of phase inversion between coagulation
liquid and polymer solution during the dry/wet-spinning process. Thus, it cannot be expressed as a defect. The defect that occurs in MMM is in the form of interfacial voids, which is shown in Figure b. However, in this study, there is no visible defect on the membrane, as shown in Figures 4b1, d1, f1.

Page 5 Line 36-39.
According to the SEM observation, the finger-like pore was formed during the dry/wet-spinning process as a consequence of phase inversion between the coagulation liquid and polymer solution. On the other hand, the presence of voids in MMM PSF/ZTC without annealing, as shown in Wijiyanti et al. [1], was due to the low adhesion between the polymer matrix and the ZTC.

Figure. SEM Image of (a) neat PSF membrane (cross-section), (b) unmodified MMM PSF/ZTC (surface) from [1]; 150 °C annealed MMM PSF/ZTC (c) cross-section, and (d) surface in this study.

Indeed, the annealing and TMOS coating process does not provide a significant increment in gas separation performance. However, it should be noted that annealing is important in improving the mechanical properties of membranes by promoting the strengthened interactions among polymer chains, and a higher degree of crystallinity in the polymer matrix. Pham et al. [2] reported annealing at 100, 150, and 200 °C can increase the mechanical strength of membrane from 372 to 586, 734, and 743 MPa, respectively.
On the other hand, annealing improved the mechanical characteristics of polymeric membranes by encouraging stronger connections between polymer chains and a greater degree of crystallinity in the polymer matrix. Annealing the membrane at 100, 150, or 200°C enhanced its mechanical strength from 372 to 586, 734, or 743 MPa, respectively [2].

On the other hand, the addition of TMOS did cause a decrease in permeability, which can be shown by SEM images which are much denser in structure (Figure 4g, h). This led to a significant increase in selectivity in the membrane with 0.03 mol TMOS for the studied gas separation. Furthermore, a significant increase in selectivity occurred in the gas separation process with different gas sizes, especially in the H₂/CH₄ gas separation. As a result, the addition of TMOS in an optimum composition could increase membrane performance. For instance, the membrane coated with 0.03 mol TMOS exhibits superior H₂/CH₄ separation performance.

| Authors need to add the pure PSF membranes as the reference to document the effect of adding ZTC nanoparticles. |
|---|
| **Response** |
| We highly recognize the reviewer’s positive comments. However, in this study, we focus on the investigation of post-treatment MMM PSF/ZTC to improve gas separation performance. We have been discussed the effect of adding ZTC fillers in the PSF membrane, as well as the neat PSF membrane characterization that has been exhibited in the previous studies [1,3]. Furthermore, we have discussed the addition ZTC nanoparticle could enhanced CO₂/CH₄ and H₂/CH₄ gasses separation performance of polysulfone membrane. |
| Page 2 Line 39-41. Our result showed that the presence of ZTC as filler in the MMM-based polysulfone increased the selectivity of CO₂/CH₄ from 2.56 to 9.99 and selectivity of H₂/CH₄ from 7.77 to 28.88 [1]. |
| it is unclear why the membrane coated with 0.03 TMOS presented a much higher H₂/CH₄ selectivity compared to other membranes (<10). This data point needs to be checked or at least explained. Also, the CO₂/CH₄ selectivity is less than 1- unlikely (it might be the experimental error that there is no selectivity), error bar should be given. |
We highly recognize the reviewer’s positive comments, we have added error bar in all Figures and standard deviation in Table 2.

Table 2. Permeation and selectivity of single gases on MMM PSF/ZTC with variations of annealing temperature, coating treatment and its combination.

| Membranes                      | Permeation (GPU) | Selectivity |
|--------------------------------|------------------|-------------|
|                                | H₂      | CO₂      | CH₄      | H₂/CH₄  | CO₂/CH₄ |
| MMM PSF/ZTC                   | 389775.2 | 116361.0 | 85088.9 | 4.58    | 1.37    |
|                                | 9 ±     | 3 ±      | 1 ±     |         |         |
|                                | 46321.49| 3477.65  | 3392.87 |         |         |
| MMM PSF/ZTC annealed at 120°C | 4.69 ±  | 1.63 ±   | 1.01 ±  | 4.63    | 1.61    |
|                                | 0.041   | 0.007    | 0.013   |         | (0.97%) |
|                                | (-99%)  | (-99%)   | (-99%)  |         | (17%)   |
| MMM PSF/ZTC annealed at 150°C | 3.89 ±  | 1.41 ±   | 0.42 ±  | 9.26    | 3.35    |
|                                | 0.054   | 0.003    | 0.001   |         | (102%)  |
|                                | (-99%)  | (-99%)   | (-99%)  |         | (144%)  |
| MMM PSF/ZTC annealed at 190°C | 107433.2| 41229.82 | 30293.3 | 3.55    | 1.36    |
|                                | 0 ±     | 3 ±      |         | (-22%)  |         |
|                                | 13317.84| 1683.41  | 1033.68 |         | (-0.48%)|
| MMM PSF/ZTC coated with 0.01 mol TMOS | 13818.57| 2887.87 | 5297.68 | 2.61    | 0.55    |
|                                | 420.95  | 36.64    | 58.03   | (-43%)  | (-60%)  |
|                                | (-96%)  | (-97%)   | (-93%)  |         |         |
| MMM PSF/ZTC coated with 0.03 mol TMOS | 444.11 ± | 5.42 ± | 6.75 ±  | 65.76   | 0.80    |
|                                | 7.76    | 0.10     | 0.10    | (1335.52%)| (-41%)|
|                                | (-99%)  | (-99%)   | (-99%)  |         |         |
| MMM PSF/ZTC coated with 0.05 mol TMOS | 423.67 ± | 157.35 ± | 125.88 ± | 3.37    | 1.25    |
|                                | 17.83   | 2.27     | 2.57    | (-26%)  | (-8%)   |
|                                | (-99%)  | (-99%)   | (-99%)  |         |         |
We suggest that 0.03 mol TMOS addition is provided an ideal coating for the membrane to separate H$_2$/CH$_4$. Furthermore, for CO$_2$/CH$_4$ gas separation, the addition of 0.05 TMOS gives the best results in terms of selectivity, but if we look at the trend, it is actually still necessary to carry out further variations on the higher addition of TMOS concentration (which will be considered in future research). According to the H$_2$/CH$_4$ separation performance, the addition of TMOS is optimal at 0.03 mol. We guess the increase in concentration is the optimal condition to produce a membrane with the appropriate structure in the H$_2$/CH$_4$ separation process. It is also exhibit similar result from Kagari et al. [4], in which they study coating PEI membrane utilizes PDMS at various concentrations (5-17 wt%). The selectivity of H$_2$/CH$_4$ was increased utilizing coating solutions up to 15.0 wt%, but thereafter decreased as the concentration increased. Further increasing the coating solution concentration seems to have resulted in a thicker layer with low gas permeance. On the other hand, the selection size of the silane coating agent influences the gas diffusion compatibility. For example, PVP was not suited for surface modification of microporous inorganic fillers since polymer sizing on the particle surface is prone to causing pore blockage [5]. This argument is used for 0.03 mol TMOS utilization, which could be disturbing the diffusion of higher size of gas molecules (i.e., CO$_2$ and CH$_4$) due to the membrane pores are getting narrower, while H$_2$ penetration not affected considerably.

We have added discussion.

On the other hand, the selection size of the silane coating agent influences the gas diffusion compatibility. For example, PVP was not suited for surface modification of microporous inorganic fillers since polymer sizing on the particle surface is prone to

|                          | MMM PSF/ZTC 190°C | 0.01 mol TMOS | 0.03 mol TMOS | 0.05 mol TMOS | Knudsen selectivity |
|--------------------------|--------------------|---------------|---------------|---------------|---------------------|
|                          | 128.08 ± 58.55 ± 58.47 ± 2.19 1.00 | (-99%) (-99%) (-99%) (-52%) (-26%) | 0.02 ± 0.01 ± 0.002 ± 10.83 5.90 | 0.00002 0.0001 0.0001 (136%) (331%) | 0.11 ± 0.037 ± 0.040 ± 2.79 0.93 | 0.0006 0.0002 0.0007 (-39%) (-32%) | 2.83 0.6 |
causing pore blockage [5]. Thus, this study discovered the other potential coating material which has unique properties to enhance gas separation performance.

Page 8 Line 34-36.
It suggests that at 0.03 mol TMOS utilization could be disturbing the diffusion of higher size of gas molecules (i.e., CO₂ and CH₄) due to the membrane pores are getting narrower, while H₂ penetration not affected considerably. As seen in Figure 7 (a-c), the MMM pore was smaller.

| 4 | based on the SEM images of Fig. 1H and K, it is clear that the TMOS penetrates deeply into the matrix, which leads to the significant reduction of gas permeance, and of course a slight increase of the selectivity. The reviewer believes that the pore size of fresh PSF/ZTC MMMs is too large for direct coating. |
|---|---|
| **Response** | We are aware of it and we also would like to suggest for coating should only be dyed. We do it under reflux expecting a cross link between the TMOS and the membrane. However, we did not find the cross-linking behavior according to the FTIR spectra. |

Reviewer #2: The manuscript is more detailed, with clear and crisp tables of photographs. The materials and experimental methods are more complete and will facilitate research by other scholars. I consider it to be a manuscript that could be published.

| **Response** | First of all, thank you for your time to review this manuscript. Thank you for your positive feedback. We highly appreciate it. |

Reviewer #3:

| 1 | In Fig.1, the dense structure formed by the annealing treatment looks like a new layer formed on the PSF matrix, and H₂ CO₂ CH₄ were not marked out. |
|---|---|
| **Response** | First of all, thank you for your time to review this manuscript. The reviewer raises an interesting concern. Thank you very much for your positive comment, we have been redrawing the figure. Sorry for making it confusing, but it’s not. Please kindly see the revised illustration for a better understanding. |
Figure. Revised illustration which exhibited in Fig 1.

2 The manuscript lacks the characterization of ZTC itself, including but not limited to the pore size.

Response

We highly recognize the reviewer’s positive comments. However, we have been discussed more detailed ZTC characterization in previous research in [1,3,6].

3 Whether it is possible to accurately characterize the pore size change range of the membrane before and after annealing.

Response

We highly recognize the reviewer’s positive comments. Tsuru and coworkers have been reported the utilization of nanopermoporometry apparatus to determine the membrane pore size [7–11]. However, we did not have access to conducting this characterization currently. We would consider studying the pore size change analysis of the mixed matrix membrane in further research as it is also the important feature for aid elucidating the separation processes in membrane.

4 The performance of binary gas H2/CH4 was only carried out using MMM annealed at 190°C, how about other types of membranes?

Response

We highly recognize the reviewer’s positive comments. We chose a membrane that has been annealed at 190 °C since it has the highest separation performance in single gas separation, and we presume that mixed gas separation is not much different.

5 Please illustrate the reason of CH4 increased permeance and CO2/CH4 increased selectivity occurred on MMM coating with 0.05 mol TMOS.

Response

We apologize with the data drawn on the graph is upside down for CO2 and CH4 permeation (Figure 6a). Thus, we have redrawn it and rechecked all data carefully.
As the concentration of the TMOS coating increases, it covers the membrane pores so that the most influential diffusion is solution diffusion, which is more influenced by the solubility of the gas. Therefore, the H\textsubscript{2} gas permeation decreased while the CO\textsubscript{2} and CH\textsubscript{4} gas permeation increased. Furthermore, we suggest that the addition of silane which consist of oxygen atom promotes physical interaction due to higher polarity \cite{12,13}. Thus, CO\textsubscript{2} permeation higher than CH\textsubscript{4} as well as the CO\textsubscript{2}/CH\textsubscript{4} selectivity increase following by increasing TMOS concentration coating.

We have added this discussion below, Page 8 Line 44-50:

However, at 0.05 mol TMOS coating it observed a unique pattern that the penetration of H\textsubscript{2} gas reduced while the permeability of CO\textsubscript{2} and CH\textsubscript{4} gas climbed. Because this concentration of the TMOS coating rises, it completely covers the membrane pores, favoring solution diffusion, which is more dependent on the gas's solubility. Moreover, it suggests that the incorporation of silane, which contains oxygen atoms, facilitates physical contact owing to its increased polarity \cite{12,13}. Thus, increasing the TMOS concentration coating leads to a rise in CO\textsubscript{2} permeation greater than CH\textsubscript{4} permeation, as a result, CO\textsubscript{2}/CH\textsubscript{4} selectivity improved.

“the excess TMOS concentration on the membrane was able to form multilayers, which could reduce adhesion between the polymer matrix and filler particles.” The analysis is confused.

Response

We highly recognize the reviewer’s positive comments. Thank you for your concern. We have revised the sentences.

Page 8 Line 40-41.
the excess TMOS concentration on the membrane was able to form multilayers, which can not only cover the voids but also block the gas diffusion path.

Furthermore, higher Pebax coating concentration (9wt%) on PSF membrane decreased CO₂ permeation to 11.55 GPU from 47.73 GPU (1wt%) [14].

- **Paragraphs format are inconsistent and the serial number of CONCLUSION is error. Please check the whole manuscript carefully.**

**Response**

Thank you for your feedback, we have revised it, Page 12 Line 13.

5. Conclusion

- **The logic of the manuscript does not match the order of figures placement and should be adjusted appropriately.**

**Response**

We highly recognize the reviewer’s positive comments, our response to your comments below:

Thank you for the constructive suggestion, we have reorganized it.

From Figure 4.

**Figure 4.** SEM morphology of MMM PSF/KTZ’s cross-section annealed at (a) 120 °C, (c) 150 °C, (e) 190 °C, and its surfaces annealed at (b) 120 °C; and (b1) zoom-in of (b), (d) 150 °C; and (d1) zoom-in of (d), (f) 190 °C; and (f1) zoom-in of (f), with magnification of 850-33000x; coated TMOS (g, h) cross-section and its surface (i) with magnification of 180-2000x; annealed at 190 °C and coated TMOS (j, k) cross section, and its surface (e) with magnification of 230-2600x.

Removed the figure 4(g-k) to other section, becoming:

Page 6 Line 19-20.
Figure 4. SEM morphology of MMM PSF/KTZ’s cross-section annealed at (a) 120 °C, (c) 150 °C, (e) 190 °C, and its surfaces annealed at (b) 120 °C; and (b1) zoom-in of (b), (d) 150 °C; and (d1) zoom-in of (d), (f) 190 °C; and (f1) zoom-in of (f).

In addition, Figure 5 create from combining of XRD, TGA and AFM characterization of annealing membrane.

Page 7 Line 32.
Figure 5. MMM PSF/ZTC characterizations of (a) XRD diffractogram ((a) without annealing, annealed at (b) 120 °C, (c) 150 °C, and (d) 190 °C); (b) TGA curve; AFM Images of (c) without modification; annealed at (d) 120 °C, (e) 150 °C, and (f) 190 °C.

Furthermore, Figure 7 create from combining of SEM, AFM and FTIR characterization of coating membrane.

Page 9 Line 5.

Figure 7. Coated MMM PSF/ZTC characterization of (a,b) cross-section, and (c) its surface SEM Images; (d) AFM Images; and (e) FTIR spectra.

Additionally, Figure 9 create from combining of SEM, and AFM characterization of annealing and coating combination post-treatment in membrane.

Page 10 Line 24.

Figure 9. Double post-treatment (annealing and coating) on MMM PSF/ZTC characterization of (a,b) cross-section and (c) its surface SEM images; and (d) AFM images.

Lastly, the Robeson upper bound discussion move to Page
The comparison between the performance of CO₂/CH₄ and H₂/CH₄ gas separation, and the Robeson upper bound curve can be seen in Figure 11. MMM PSF/ZTC without annealing and MMM PSF/ZTC annealed at 190 °C had a gas separation performance of CO₂/CH₄ close to the Robeson upper bound curve and H₂/CH₄ gas separation performance, which was above the Robeson upper bound curve. Those exhibited a good separation performance, but the selectivity was still relatively low. On the other hand, The MMM PSF/ZTC without coating and MMM PSF/ZTC coated with 0.01 and 0.03 mol TMOS had H₂/CH₄ gas separation performance was above the Robeson upper limit, indicating good gas separation performance. Unlike the case with the CO₂/CH₄ gas separation performance, which was quite far from the Robeson upper limit. Furthermore, the gas separation performance of MMM PSF/ZTC modified with combinations of annealing and coating was no better than MMM PSF/ZTC modified by annealing or coating only. Therefore, the appropriate membrane modification to improve the performance of MMM PSF/ZTC was annealing at 190 °C or coating with 0.03 mol TMOS.

Figure 11. MMM PSF/ZTC gas separation performance with variations in heating temperature, coating concentration, and its combination for gas pairs (a) CO₂/CH₄ and (b) H₂/CH₄, compared to the Robeson curve [15] and other studies [16–18].
The preparation and application of MMM has not been reviewed completely, such as 10.1016/j.cej.2020.127144; 10.1016/j.seppur.2019.05.009; 10.1166/jnn.2017.13914; 10.1016/j.memsci.2016.07.060.

Response

We highly recognize the reviewer’s positive comments. However, the cited paper is not relevant with this study. In this study we focused on mixed matrix membrane PSF/ZTC for gas separation application. The study from (10.1016/j.cej.2020.127144; 10.1016/j.seppur.2019.05.009; 10.1166/jnn.2017.13914; 10.1016/j.memsci.2016.07.060) was focus on nanofiltration and ultrafiltration. Therefore, we regret that we could not cite it since the topics discussed are wide and do not focus on gas separation applications.

Furthermore, we have been reviewed the previous study of MMM for gas separation. Our result showed that the presence of ZTC as filler in the MMM-based polysulfone increased the selectivity of CO2/CH4 from 2.56 to 9.99 and selectivity of H2/CH4 from 7.77 to 28.88 [1]. The other fillers applied in MMM based polysulfone have been reported by several researchers such as zeolite and silica. Mohamat et al. [19] reported that the incorporation of 3wt% zeolite T in polysulfone membrane enhanced CO2/CH4 selectivity from 2.63 to 3.37 with CO2 permeability as 78.90 GPU. On the other hand, the presence 2wt% of KIT-6 (KIT: Korea Advanced Institute of Science and Technology), a silica mesoporous, could improve CO2/CH4 selectivity for 32.4 with CO2 permeability as 5.4 Barrer [20].

On the other hand, thought the preparation method of this study is utilizing phase inversion, it’s quite different preparation technique in this study and the cited literature. Since in this study was used hollow fiber module and utilizing different solvent and polymer matrix, the cited literatures (10.1016/j.cej.2020.127144; 10.1016/j.seppur.2019.05.009; 10.1166/jnn.2017.13914; 10.1016/j.memsci.2016.07.060) used DMAc as a solvent to produce flat sheet mixed matrix membranes based PVDF or PES polymer matrix.

In addition, we have been cited more similar preparation of hollow fiber MMM that adopted from previous studies.

Page 4 Line 36-37.
The membrane preparation is adopted from the previous literatures [1,3].

Response

In Figure 4, the uppercase and lowercase letters are inconsistent with the legends, and there is no description for fig.4l.

Response
Thank you for your concern about it, we have revised it. Please kindly see revised Figure 4.

Page 6 Line 19.

Furthermore, we have added legend for zoom in image of (b,d, and f).

Page 6 Line 20-22.

**Figure 4.** SEM morphology of MMM PSF/KTZ’s cross-section annealed at (a) 120 °C, (c) 150 °C, (e) 190 °C, and its surfaces annealed at (b) 120 °C; and (b1) zoom-in of (b), (d) 150 °C; and (d1) zoom-in of (d), (f) 190 °C; and (f1) zoom-in of (f).

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Response to Reviewers of Royal Society Open Science

|Reviewer #1: |  
|---|---|
|1  | The title might be a bit confusing as the reader might confuse with carbon membranes (in fact this is a PSF/ZTC MMM) |
|  | Response |
|  | We highly appreciate the reviewer’s constructive comment. We have been changed the title becomes “Annealing and TMOS coating on PSF/ZTC mixed matrix membrane for enhanced CO₂/CH₄ and H₂/CH₄ separation” |
|2  | The title indicated the enhancement for CO₂/CH₄ separation by annealing and coating treatment. However, from Table 5, the reviewer cannot clearly see the improvement at least for CO₂/CH₄ separation, for some cases, it decreases and the authors may not fully address my comment why CO₂/CH₄ selectivity is lower than 1. what is the transport mechanism? |
|  | Response |
|  | We highly recognize the reviewer’s positive comments, our response to your comments below: |
|  | According to gas separation performance data in Table 2, annealed at 190 °C and TMOS coating with 0.03 mol produce CO₂/CH₄ selectivity improvement by 331%, from 1.37 to 5.90. |
|  | However, different TMOS coating concentrations (0.01 and 0.05 mol) on annealed MMM exhibited low CO₂/CH₄ selectivity, which are 1.00 and 0.93, respectively. The
low selectivity (similar to CO$_2$/CH$_4$ Knudsen selectivity of 0.6) indicates that the most gas diffusion contributor is Knudsen diffusion, in which the gas permeance was inversely related to the molecular weight of the penetrated species [1]. In addition, the gas diffusion depended on the mean free path length as the average distance traveled by a gas molecule before colliding with another gas molecule [2]. Thus, it supposes the reason why CO$_2$/CH$_4$ selectivity on the membrane with 0.01 mol TMOS coating and annealed at 190 °C below one. Additionally, its selectivity is less than annealed at 190 °C MMM (1.36). It suggests that membrane surfaces are typically covered by TMOS coating, resulting in tighter polymer chain packing and a decrease in free volume.

Interestingly, there is an additional factor that leads to the poor selectivity of MMM with 0.05 mol TMOS coating and annealed at 190 °C. Excess TMOS concentration would diminish selectivity due to the multilayer, which can reduce adhesion between the polymer matrix and filler particles [3]. Furthermore, another diffusion mechanism that gives a major impact is solution diffusion due to the dense structure of the membrane after annealing.

Therefore, we add the discussion below.

Page 10, Line 24-26.
Moreover, its selectivity is less than annealed at 190 °C MMM (1.36). It suggests that membrane surfaces are typically covered by TMOS coating, resulting in tighter polymer chain packing and a decrease in free volume.

Page 11, Line 25-42.

The proposed diffusion mechanism on MMM PSF/ZTC annealed at 190 °C and TMOS coating is a combination of Knudsen diffusion, surface flux, and solution diffusion. Different TMOS coating concentrations (0.01 and 0.05 mol) on annealed MMM exhibited low CO$_2$/CH$_4$ selectivity, namely 1.00 and 0.93, respectively. The low selectivity (similar to CO$_2$/CH$_4$ Knudsen selectivity of 0.6) indicates that the major gas diffusion contributor is Knudsen diffusion, in which the gas permeance is inversely related to the molecular weight of the penetrated species [1]. Furthermore, gas diffusion is influenced by the mean free path length, which is the average distance travelled by a gas molecule before colliding with another gas molecule [2]. Additionally, a similar trend was observed for H$_2$/CH$_4$ separation for 0.01 and 0.05 mol TMOS coating concentration on annealed MMM, which means its selectivity is close to the H$_2$/CH$_4$ Knudsen selectivity (2.83). Hence, the Knudsen diffusion mechanism exerts a crucial influence on the gas separation mechanism. On the other hand, membrane selectivity beyond Knudsen selectivity was observed on an annealed MMM coating with 0.03 mol TMOS. Because the optimal silane coating on the membrane surface provides an electrical charge distribution on the membrane, it implies that the electric charge produces a difference in gas separation behavior [4]. Takahashi et al. studied that at the surface of the porous alumina structure, oppositely charged atoms promote a physical interaction between the CO$_2$ molecule and the silane coupling agent [4]. Due to the fact that the CH$_4$ molecule is non-polar, while CO$_2$ has a polarity, thus providing a higher permeation of CO$_2$ molecules than CH$_4$. Therefore, the other diffusion mechanism that makes a contribution is surface flux or facilitated diffusion.

Reviewer #2: The author is familiar with is manuscript content and revises it carefully and completely with a serious attitude. The structure of the article is clear. Recommended for acceptance.
Response

Thank you for your positive feedback. We highly appreciate it.

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