nature portfolio

Peer Review File

Enhanced High-Temperature Energy Storage Performances in Polymer Dielectrics by Synergistically Optimizing Band-gap and Polarization of Dipolar Glass

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This work developed a bifunctional dipolar glass (DG) filler containing two molecule components with large dipole moment and large band gap to enhance the high temperature capacitive energy storage performances of polymer dielectrics. The introduction of DG remarkably improves the dielectric constant and breakdown strength of polymers from 2.78 to 3.36 and from 551.11 MV m-1 to 761.21 MV m-1 at 200 ºC, respectively. The thermal stability of composite dielectric is also well maintained. A high energy density with the efficiency of 90% of 8.34 J cm-3 (150 ºC) and 6.21 J cm-3 (200 ºC) are achieved. This work is well organized and helpful for the peers, so I would like to recommend its publication after minor revision of the following issues:
[1] The chemical structures of FPI, PEI, and sPI should be included.
[2] In Figure 3A and 3B, the test frequency should be indicated.
[3] There are some errors that should be corrected, such as the area numbers in Figure 4D and “DG-NS” (should be “FPI-NS”) in Line 159.
[4] I’d like to know what the yellow stripes in Figure 2c are?
[5] Why the dielectric constant and loss in FPI-molecules composites vary much more sharply than FPI-DG composites versus temperature in the inset of Figure 2A?
[6] The raw data of the statistical results should be provided, such as average spacing around SO2 group in Figure 2B.
[7] I’d like to know the distribution form of small molecules in polymers, e.g., uniformly dispersion or phase separation?

Reviewer #2 (Remarks to the Author):

This review is well formatted in the annex.

Review of the manuscript: Enhanced High-Temperature Energy Storage Performances in Composite Dielectrics by Synergistically Optimizing Band-gap and Polarization of Dipolar Glass Fillers

The authors presented an interesting manuscript describing a symbiotic relationship between ab initio simulations and the properties of dipolar glass fillers within polymeric dielectric composites to increase the dielectric constant and energy gap concomitantly.
The manuscript is well presented and generally well written (typos remain on pages 1 and 2). Some points need to be understood or improved:

1 – The authors state in the abstract and along the text referring to Fig. 4: “The composite dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200C @ 600 MV m-1”.

However, we cannot compare cycles in the manuscript or supplement, such as, for example, the 1st, 100, 1000, 10,000, and 50,000.
The other important point is the temperature. What are the applications for an energy storage polymer composite at 200°C?

2 – The authors state, “thus leading to more homogeneous distribution of local electric field hence less stress concentration at interface”, however, the concentration at the interface

depends on the materials in contact with the polymer composite as well as the nature of their charges. The charges accumulate due to the difference in chemical potentials μ_(i,) the presence of at least one insulator unable to exchange electrons, and the necessity to align the electrochemical potentials μ¯_i. The charges accumulate in agreement with the equation: If two species i and j (element, phase, material, cathode, anode, electrolyte, semiconductor,…) come into electrical contact:
μ¯_i-μ¯_j=μ_i 〖-μ〗_j+z_i e(ϕ_i-ϕ_j)
When equilibrium is reached, μ¯_i-μ¯_j=0=μ_i 〖-μ〗_j+z_i e(ϕ_i-ϕ_j) where ∆V_ij= ϕ_i-ϕ_j. If the surface chemical potentials align (or equalized), ϕ_i-ϕ_j=0⟹ μ_i 〖-μ〗_j=-z_i e(ϕ_i-ϕ_j)=0 then the chemical potentials equalize (for more info, first pages 691-692: Beatriz Moura Gomes, J. Francisco Ribeiro Moutinho, Maria Helena Braga Journal of Materials Chemistry A, 2024, 12, 690-722 A perspective on the building blocks of a solid-state-battery: from solid electrolytes to quantum power harvesting and storage doi: https://doi.org/10.1039/d3ta04228f)

3 – The authors state, "As a result, polymer-DG composites exhibit concomitant enhancement of εr from 2.78 to 3.36 (@103 Hz, 25 °C)". However, the enhancement in the dielectric constant is not significant, especially if considering that polymer composites can reach εr = 120 (Reference: "High Dielectric Constant (High k) Polymer Composites" Encyclopedia of Polymer Science and Technology https://doi.org/10.1002/0471440264.pst674).
The other point left to clarify is the frequency, which should also be given for, 0.1 Hz, since experiments should compare to DC as well. At low frequencies, such as 0.1 Hz, the dielectric constant typically includes contributions from all possible polarization mechanisms: electronic, ionic, dipolar (orientational), and space charge polarization. This is because, at very low frequencies, all these mechanisms have enough time to respond to the changing electric field. Measurements at very low frequencies can capture the maximum dielectric response of the material.

4 — The breakdown strength of polymer dielectrics was measured at 200 °C; the reason why the measurements were not made at 25 °C was not discussed in the context of applications.

5 – In Fig. 1B, it is partially understood how the energy of the band gap (width) was obtained from ab initio simulations, but not how to place the gap in the absolute scale was calculated. In other words, for example, for NS, how was LUMO energy -1.27 eV obtained? Moreover, no numbers are given for Density functional theory (DFT) calculations, including plane-wave cut-offs, structural parameters, spacing of k points, etc.

6—The desired characteristic in thermally stimulated depolarization current TSDC curves of FPI composites is typically a low current at the operational temperature range, indicating stable and minimal charge release (Fig. 2). While high current peaks provide useful information about the trapping sites, they may signal potential issues with charge stability at those temperatures. Here, the authors should discuss their temperature test choices.

7 - The results demonstrate that the FPI-DG combination outperforms PEI-DG and SPI-DG. Why were the polymers FPI, PEI, and SPI specifically chosen to be tested with this organic filler? Additionally, would the selection of different polymers affect the performance improvements attributed to the DG organic filler?

8 - Overall, the authors compared the results from NS, DS, and HPMA with different polymers like FPI, PEI, and SPI, where the selected weight percentage was 8%. Was the performance ever compared to other polymer-inorganic composites?

9 — There are basically no performance tests for the polymer composites in capacitor cells where the electrodes are capacitor electrodes. Functional analysis in a cell is paramount for reliable assessment of the materials' functional capacity.

Reviewer #3 (Remarks to the Author):

This work englobes the design and development of a polymer-based dielectric material for use as active layers in electrostatic capacitor devices. Currently, the development of these types of systems represents a productive and highly interesting area within materials science, mainly due to its direct involvement in the energy field. In this sense, it has become evident that moving towards creating new technologies and materials that guarantee efficient energy storage is as crucial as obtaining it. Thereby, all efforts invested in the development of new ways of extracting energy are useless if we are not able to ensure correct and efficient storage of it once obtained. For this reason, as a first comment, I consider that the topic in which this work is framed is of high interest and might be very attractive to the reading community.
In the present work, Yang and coworkers prepared and studied a class of all-organic composite dielectrics fabricated by incorporating macromolecular fillers into a PI matrix. Importantly, these fillers - named by them as Dipolar Glass fillers - were designed looking for the incorporation of entities having a wide band-gap (Eg) along with the presence of high dipole moment functional groups. The requirement for a wide Eg is sustained by the need to diminish charge migration phenomena. At the same time, high dipole moment structures will endow the final material with an adequate dipolar density and, consequently, an increased polarization property. So, in search of the above conditions, the authors came up with the condensation of HPMDA and NS units as building blocks for this class of filler, merging the aliphatic nature of the first one (favoring the Eg condition) with the dipolar character of sulfonyl groups present in the NS. It is worth mentioning that although the strategy reported here cannot be considered novel or pioneering since it involves the mere blending of two polymeric systems, Its simplicity, accompanied by some clearly non-trivial and outstanding results (e.g. homogeneity, synergy, high discharge energy density, high efficiency, reliability and scalability, among others) deserves the attention. However, there are some relevant flaws in terms of discussions and correlation between characterization techniques. This work cannot be accepted in its current form and might be considered for publication only after a deep and careful inspection and the repetition of some of the experiments. Trying to solve the following points can orient the authors to achieve the above:
Abstract Section
1) It is confusing the fact that this section mentions the limitations of using “small molecules” as fillers, followed by the description of the filler used in this work as an "assembly of two molecule components" and as a “bifunctional dipolar glass filler”. It could give the false idea that the DG filler is small in size when, indeed, it has macromolecular features (Mn 38.577 g/mol, n= 88). Please, be clear on the polymeric nature of DG. Also, it would be advisable to avoid the term "assembling" when, actually, it is a covalent polymer made by multiple condensation reactions.
2) In Line 23 there is an extra “space” in “.The**composite”

Introduction Section

The authors provide a clear and brief introduction, pointing out in an organized way the theory, literature voids and, therefore, the motivations behind proposing the present project. However:

3) Within the field of polymer dielectrics, the concept of “dipolar glass polymer” is one of the most relevant strategies when affording suitable and efficient materials. More importantly, the use of sulfones as dipolar entities for improving the dielectric properties of polymers has been successfully demonstrated thanks to this concept. So, I was wondering if the idea of "dipolar glass polymers" motivated, to some extent, this project and, for example, the use of the NS molecule. If so, it would be important to include some relevant references such as:

- Zhu, L. (2014). Exploring strategies for high dielectric constant and low loss polymer dielectrics. The journal of physical chemistry letters, 5(21), 3677-3687.
- Wei, J., Zhang, Z., Tseng, J. K., Treufeld, I., Liu, X., Litt, M. H., & Zhu, L. (2015). Achieving high dielectric constant and low loss property in a dipolar glass polymer containing strongly dipolar and small-sized sulfone groups. ACS Applied Materials & Interfaces, 7(9), 5248-5257.
- Baer, E., & Zhu, L. (2017). 50th anniversary perspective: dielectric phenomena in polymers and multilayered dielectric films. Macromolecules, 50(6), 2239-2256.

To name a few

4) Related to the above, and sustained by the vast amount of literature, I find it more correct to refer to DG as a dipolar glass polymer rather than a “dipolar glass filler” or “organic filler” (line 66). It must be considered that the material developed in this work fits properly with the definition of a polymer blend. In this sense, if both components are organic polymers, even coming from the same type of family, why call this material a composite? (see the title of the manuscript). Please explain.

Results and Discussion Section:

5) Line 82: PI is not defined.

6) Figure S1: Any explanation why homo and lumo orbital are so localized in DG? This could be not trivial for a non-expert audience

7) Regarding DSC analysis and Tg calculations (Figures S3 and S10): In most cases, the DSC curves are not so well resolved and with an appreciable level of signal noise that would definitely affect the correct identification of Tg. Also, there is no clear information about the thermal treatment and cycles performed on samples during DSC analysis. Were the Tg values obtained from the last heating run? How many heating, cooling and isothermal processes were included? And most importantly, what was the temperature interval chosen for studying these samples? This data is not suitable for calculating Tg values. Consider redoing these experiments.

8) Due the importance of DG, in addition to FTIR spectroscopy (Figure S4), it is required to include proton and carbon NMR analysis of the polymer, as well as the GPC traces from which its Mn, Mw and dispersity were calculated.

9) Regarding interchain spacing of composites calculated from XRD results, please consider mentioning the error associated with these calculations and how accurate it is to discuss the notably low-value differences in some cases (< 0.01 nm).

10) In the same line with the above, how many samples were analyzed for each specimen during mechanical analysis? No error bars were included in Figure 1E for Young's modulus, making the analysis of the values given in lines 136 and 137 difficult.

11) Line 155: For polymer materials, the current requirements are set to be above 4.0 to be considered a high dielectric constant, and there are some reports that place this value even above 5.0. Therefore, the phrase "a high er of 3.56" is not correct.

12) Line 171 it should be Figure 1E instead of 1C

13) Can be related the interchain spacing reported in Figure 1E to the average spacing

referred in between lines 180 and 182? I ask this because those trends are not well correlated, creating a mismatch between the experimental and theoretical results.
14) Regarding the AFM-IR analysis depicted in lines 183 – 189, the mobility of groups understood as their ability to reorient themself under the influence of an external electric field should not be directly associated with the vibration of their chemical bonds. That is the reason why the orientational polarization and the atomic (vibrational) polarization exhibit remarkable differences in terms of contributions.
15) Insets in Figure 2 are unclear, making difficult the analysis of the displayed information.
16) Considering that the authors were successfully able to calculate the electrical breakdown, why is it relevant to provide and compare Eg values of materials calculated from UV-Vis spectroscopy? Did you use the Taffel model to achieve this? Honestly, I believe that the Eg calculation and the discussion from it is useless in this case. For example, how can you support a rise of Eb from 579.32 MV/m to 784.1 MV/m when the increment of Eg for the same specimens is just 0.04 eV? In this sense, if authors feel motivated to include Eg in the discussion, it should be calculated using electrochemistry tools.
17) I find very interesting the use of TSDC for estimating charge-related phenomena. Can the authors provide a clearer explanation or at least an idea about the noticeable enhanced suppression of charge injection observed for FPI-DG when compared to the other systems? Considering that in all cases, at least 90 % of the material is FPI.
18) I consider the sections related to energy storage performance, reliability, and scalability are the strongest in this work; the results shown in these sections are the ones that demonstrate the novelty as well as the impact that these specimens could exert on the field. Both sections are well-organized and well-written, accompanied by a proper level of discussions extracted from the employed characterization techniques (contrary to the previous sections). The observed values for the energy densities are above those usually found in the literature, and the same for the efficiencies, outperforming very recent reports such as Journal of Materials Chemistry A, 2023, 11(37), 20021-20030. Moreover, these results gain relevance when considered they were measured at temperatures as high as 200 °C, showing the real applicability of the system. Figure 4 summarizes the high impact of the achieved results. Thanks to these two sections, I believe that the manuscript deserves a second chance to be corrected and improved, instead of being rejected, to find a suitable version to be considered for publication.
Experimental section
19) Regarding the synthesis of DG: Because of the importance of the DG polymer in the confection of the final material, it is mandatory to present all the details related to its synthesis, aiming to facilitate its reproducibility. In this sense, please provide the purity degree of reactants involved, the amount of reactants (HPMDA and NS), isoquinoline and solvent during the synthesis.
20) Regarding the preparation of films: In line 370, it is mentioned that a uniform dispersion must be obtained, while in line 371, it is indicated as an “as-prepared solution.” Is DG soluble in the mixture?
21) Also, are solvents completely removed during these heating processes? Considering that even traces of them can notably modify the dielectric performance of materials. Personally, I have struggled a lot trying to remove DMF, NMP, DMSO and other high boiling point solvents from these types of materials. By re-dissolving the material and carrying out an H-NMR analysis of the final material would help to demonstrate the purity of the material
22) The characterization section must be improved by detailing every aspect of the technique employed. For example, for GPC analysis, which solvent was used as eluent? Also indicate the temperature of the measurement, calibration curve information, how many and what type of columns were used. In a similar manner, for DSC, XPS, AFM (in tapping mode?). What were the dimensions of the employed samples during Young’s moduli

determination? Did you have access to thermogravimetric analysis? If so, it would help to ensure that no degradation is taking place during the heating process in DSC measurements. Also, as mentioned in comment 7), include a complete description of the DSC program used.
Conclusion section
23) Remove terms associated with “assembled” and “composite”, also in the rest of the manuscript.
24) Also, lines 340-342, small molecules are mentioned again when DG is NOT small at all. Please, re-write this section considering all the above mentioned comments.

Reviewer #4 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts

Review of the manuscript: **Enhanced High-Temperature Energy Storage Performances in Composite Dielectrics by Synergistically Optimizing Band-gap and Polarization of Dipolar Glass Fillers**

The authors presented an interesting manuscript describing a symbiotic relationship between *ab initio* simulations and the properties of dipolar glass fillers within polymeric dielectric composites to increase the dielectric constant and energy gap concomitantly.

The manuscript is well presented and generally well written (typos remain on pages 1 and 2). Some points need to be understood or improved:

1 – The authors state in the abstract and along the text referring to Fig. 4: "The composite dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200 °C @ 600 MV m^{-1}".

However, we cannot compare cycles in the manuscript or supplement, such as, for example, the 1st, 100, 1000, 10,000, and 50,000.

The other important point is the temperature. What are the applications for an energy storage polymer composite at 200°C?

2 – The authors state, "thus leading to more homogeneous distribution of local electric field hence less stress concentration at interface", however, the concentration at the interface depends on the materials in contact with the polymer composite as well as the nature of their charges. The charges accumulate due to the difference in chemical potentials $\mu_{i,}$ the presence of at least one insulator unable to exchange electrons, and the necessity to align the electrochemical potentials $\bar{\mu}_i$. The charges accumulate in agreement with the equation:

If two species i and j (element, phase, material, cathode, anode, electrolyte, semiconductor,...) come into electrical contact:

$$\bar{\mu}_i - \bar{\mu}_j = \mu_i - \mu_j + z_i e(\phi_i - \phi_j)$$

When equilibrium is reached, $\bar{\mu}_i - \bar{\mu}_j = 0 = \mu_i - \mu_j + z_i e(\phi_i - \phi_j)$ where $\Delta V_{ij} = \phi_i - \phi_j$. If the surface chemical potentials align (or equalized), $\phi_i - \phi_j = 0 \Longrightarrow \mu_i - \mu_j = -z_i e(\phi_i - \phi_j) = 0$ then the chemical potentials equalize (for more info, first pages 691-692: Beatriz Moura Gomes, J. Francisco Ribeiro Moutinho, Maria Helena Braga **Journal of Materials Chemistry A**,

2024, 12, 690-722 *A perspective on the building blocks of a solid-state-battery: from solid electrolytes to quantum power harvesting and storage* doi: https://doi.org/10.1039/d3ta04228f)

3 – The authors state, "As a result, polymer-DG composites exhibit concomitant enhancement of ε_r from 2.78 to 3.36 (@10^3 Hz, 25 °C)". However, the enhancement in the dielectric constant is not significant, especially if considering that polymer composites can reach ε_r = 120 (Reference: "High Dielectric Constant (High k) Polymer Composites" **Encyclopedia of Polymer Science and Technology** https://doi.org/10.1002/0471440264.pst674).

The other point left to clarify is the frequency, which should also be given for, 0.1 Hz, since experiments should compare to DC as well. At low frequencies, such as 0.1 Hz, the dielectric constant typically includes contributions from all possible polarization mechanisms: electronic, ionic, dipolar (orientational), and space charge polarization. This is because, at very low frequencies, all these mechanisms have enough time to respond to the changing electric field. Measurements at very low frequencies can capture the maximum dielectric response of the material.

4 — The breakdown strength of polymer dielectrics was measured at 200 °C; the reason why the measurements were not made at 25 °C was not discussed in the context of applications.

5 – In Fig. 1B, it is partially understood how the energy of the band gap (width) was obtained from *ab initio* simulations, but not how to place the gap in the absolute scale was calculated. In other words, for example, for NS, how was LUMO energy -1.27 eV obtained? Moreover, no numbers are given for Density functional theory (DFT) calculations, including plane-wave cut-offs, structural parameters, spacing of k points, etc.

6—The desired characteristic in thermally stimulated depolarization current TSDC curves of FPI composites is typically a low current at the operational temperature range, indicating stable and minimal charge release (Fig. 2). While high current peaks provide useful information about the trapping sites, they may signal potential issues with charge stability at those temperatures. Here, the authors should discuss their temperature test choices.

7 - The results demonstrate that the FPI-DG combination outperforms PEI-DG and SPI-DG. Why were the polymers FPI, PEI, and SPI specifically chosen to be tested with this organic filler?

Additionally, would the selection of different polymers affect the performance improvements attributed to the DG organic filler?

8 - Overall, the authors compared the results from NS, DS, and HPMA with different polymers like FPI, PEI, and SPI, where the selected weight percentage was 8%. Was the performance ever compared to other polymer-inorganic composites?

9 — There are basically no performance tests for the polymer composites in capacitor cells where the electrodes are capacitor electrodes. Functional analysis in a cell is paramount for reliable assessment of the materials' functional capacity.

Journal: Nature Communications
Number: 24-35430
Title: Enhanced High-Temperature Energy Storage Performances in Polymer Dielectrics by Synergistically Optimizing Band-gap and Polarization of Dipolar Glass

We sincerely appreciate the reviewers for their time and efforts on carefully reviewing our manuscript. The comments and suggestions are very valuable, and we have accordingly conducted a large number of experiments and simulations. The manuscript has been revised according to these comments and suggestions. The revisions are highlighted in the manuscript in response to reviewers' comments. We also listed the detailed revisions and responses in the followings, with the page numbers of the manuscript where we made the corresponding revisions.

Reviewer #1 (Remarks to the Author):

This work developed a bifunctional dipolar glass (DG) filler containing two molecule components with large dipole moment and large band gap to enhance the high temperature capacitive energy storage performances of polymer dielectrics. The introduction of DG remarkably improves the dielectric constant and breakdown strength of polymers from 2.78 to 3.36 and from 551.11 MV m-1 to 761.21 MV m-1 at 200 ºC, respectively. The thermal stability of composite dielectric is also well maintained. A high energy density with the efficiency of 90% of 8.34 J cm-3 (150 ºC) and 6.21 J cm-3 (200 ºC) are achieved. This work is well organized and helpful for the peers, so I would like to recommend its publication after minor revision of the following issues:

Reply: We really appreciate the reviewer's positive comments and suggestions. Following the comments, we have revised the manuscript and the revisions are listed below.

[1] The chemical structures of FPI, PEI, and sPI should be included.

Reply: We thank the reviewer for the valuable comment. We have added the monomer structures of three polymers in the SI.

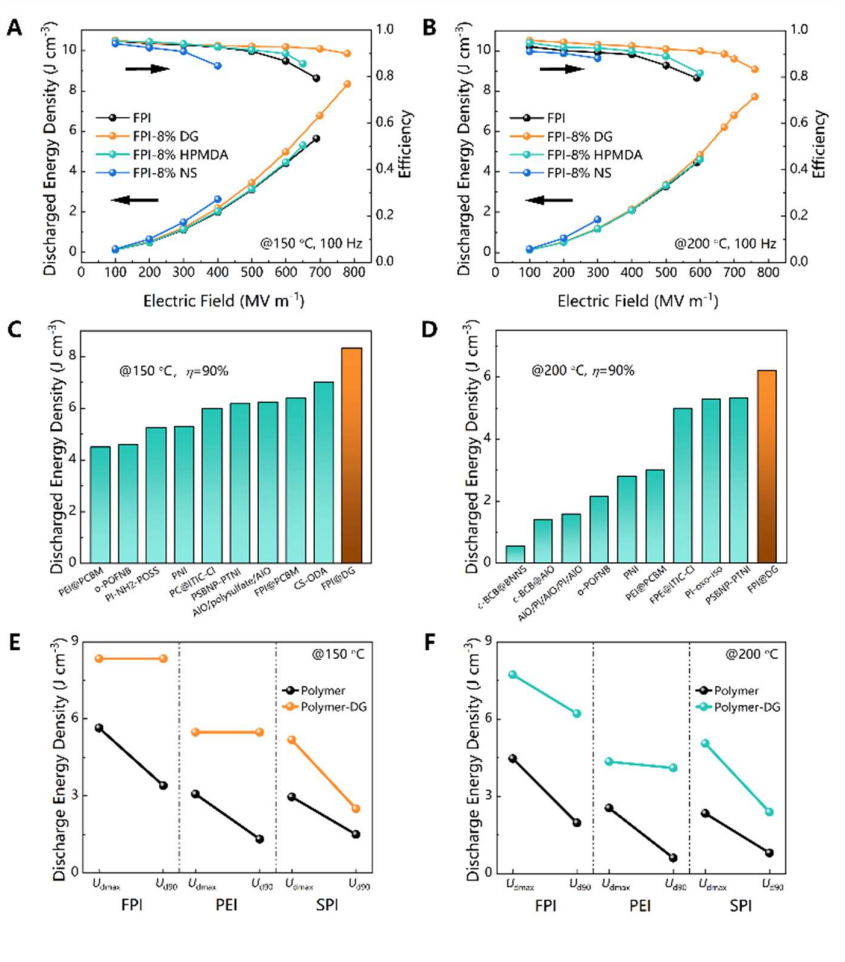
Revision: (1) (Line 104) Its chemical structure is shown in Figure S2.
(2) (Line 305) The chemical structures of these two polymers are shown in Figure S2.
(3) (SI)

Figure S2. Chemical structures of PIs: (a) FPI, (b) PEI, and (c) SPI.

[2] In Figure 3A and 3B, the test frequency should be indicated.

Reply: We thank the reviewer for the valuable comment. The test frequency is 100 Hz and we have added it in the Figure 3A and Figure 3B.

Revision:

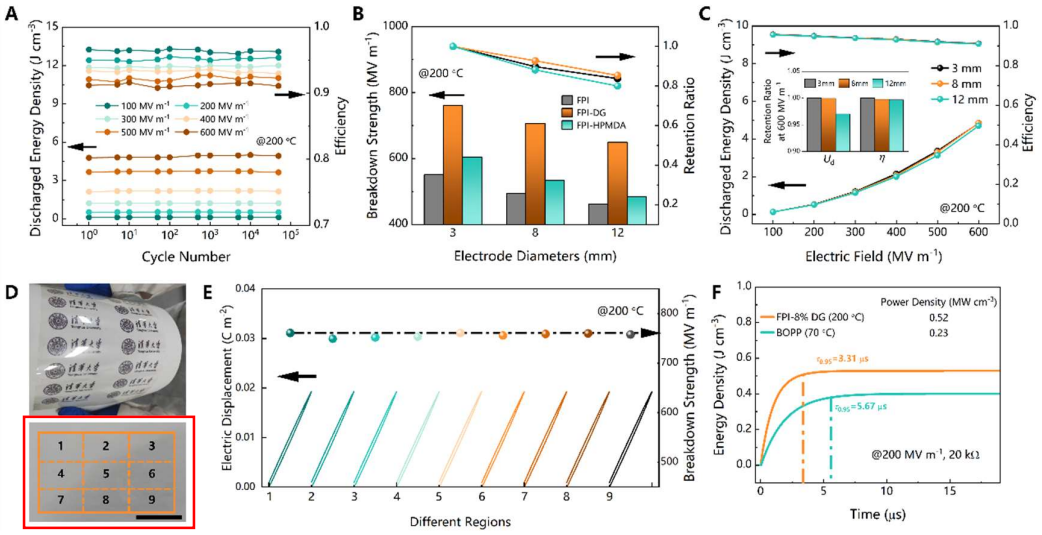


[3] There are some errors that should be corrected, such as the area numbers in Figure 4D and "DG-NS" (should be "FPI-NS") in Line 159.

Reply: We thank the reviewer for the kind remind. We have reviewed the whole manuscript and revised the errors.

Revisions: (1) (Line 177) More notably, the dielectric properties of FPI-DG are much more stable than FPI-HPMDA and FPI-NS at wider temperature ranges.

(2)



(3) (Line 19) The bifunctional dipolar glass with a large-molecular-weight high than 30000 g mol^{-1} not only maintains the thermal stability of polymer blends even at a high loading of 10 wt%,…

(4) (Line 24) The polymer blend dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200 ºC @ 600 MV m^{-1}.

(5) (Line 31) With ever increasing demand for device miniaturization, system integration and higher reliability[7], it is imperative to increase the discharged energy density (U_d) of dielectric materials. In general, U_d can be expressed as:…

(6) (Line 154) These results are all in line with our hypotheses that the DG with large-molecular-weight can enhance the structural stability of polymers more efficiently than its monomer components.

[4] I'd like to know what the yellow stripes in Figure 2c are?

Reply: We thank the reviewer for the valuable question. The yellow stripes in Fig. 2c are regions where IR absorption is slightly higher than the other regions. Due to the topographic crosstalk as well as the surface adsorbates during the sample fabrication process, the IR absorption exhibits a certain degree of fluctuation even in regions of pure polymers, as can be seen in Fig. 2d in ref. 1[R1], Fig. 1b in ref. 2[R2], Fig. 4b in ref. 3[R3], and Fig. 2 in ref. 4[R4]. In our study, since the cross-sectional samples exhibit striped morphology (Fig. 1c and Supplementary S15), the IR absorption images also show striped pattern. Similar striped morphology and IR absorption results can refer to Fig. 4b and Fig. S4a in ref. 3, where PEI-based nanocomposites were studied.

[5] Why the dielectric constant and loss in FPI-molecules composites vary much more sharply than FPI-DG composites versus temperature in the inset of Figure 2A?

Reply: We thank the reviewer for the valuable question. When the small molecules are dispersed in the polymer matrix, they will weaken the cohesive energy of polymers due to their lack of intrinsic interactions and small molecular weight. As a result, the composite dielectrics feature deteriorated structural stability after external stimuli, such as high temperature and electric field. For example, the polymer chains possess high mobility under high temperature thus exhibiting enhanced polarization and relaxation-induced loss. On the contrary, as the small molecules are synthesized into dipolar glass polymer with large molecular weight, the cohesive energy of polymer matrix can

be well maintained. Therefore, the loss of FPI-HPMDA and FPI-NS at high temperature is remarkably higher than that of FPI-DG.

[6] The raw data of the statistical results should be provided, such as average spacing around SO_2 group in Figure 2B.

Reply: We thank the reviewer for the kind remind. The raw data of the average spacing around SO_2 is shown as below. We took 10 points in each simulation cells and calculated the average value and standard deviation. We will provide it as the individual file after the manuscript is accepted.

	Tested points									Average	Standard deviation
FPI-NS	4.776	3.374	3.405	2.439	4.355	4.325	2.859	4.625	3.248	3.72	0.78
FPI-DG	7.767	9.914	3.518	3.959	3.363	4.907	3.258	6.242	4.918	5.32	2.15

[7] I'd like to know the distribution form of small molecules in polymers, e.g., uniformly dispersion or phase separation?

Reply: We thank the reviewer for the valuable question. As shown in the TEM images, the small molecules and bifunctional dipolar glass both disperse uniformly in polymer matrix without aggregations.

Revision: (Line 124) In addition, there is no phase separations of DG, HPMDA, or NS in polymers according to above results.

Reviewer #2 (Remarks to the Author):

The authors presented an interesting manuscript describing a symbiotic relationship between ab initio simulations and the properties of dipolar glass fillers within polymeric dielectric composites to increase the dielectric constant and energy gap concomitantly.

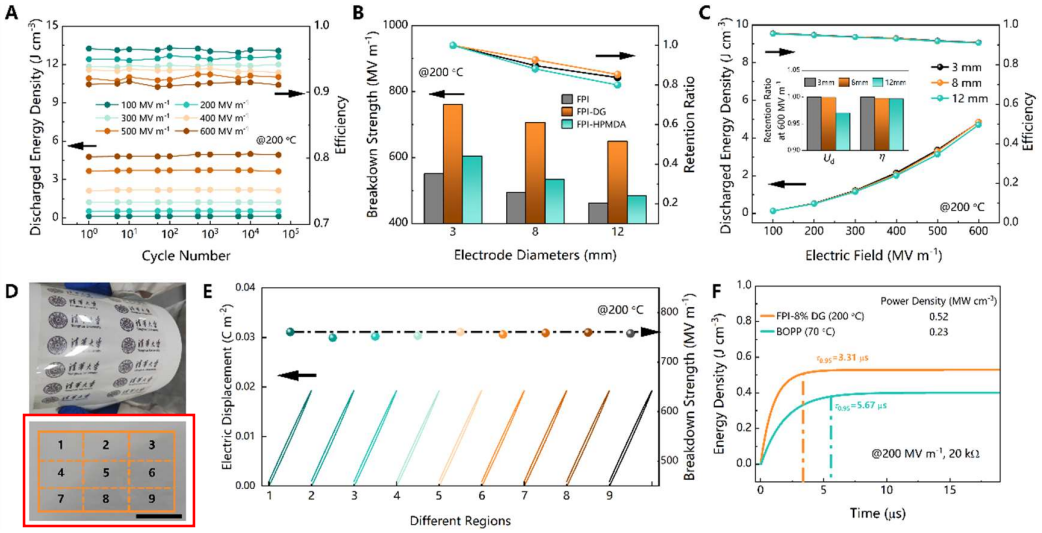
The manuscript is well presented and generally well written (typos remain on pages 1 and 2).

Some points need to be understood or improved:

Reply: We thank the reviewer for the comments. Following the comments, we have revised the manuscript and the revisions are listed below. We also reviewed the whole manuscript and revised the typos and other errors.

Revisions: (1) (Line 177) More notably, the dielectric properties of FPI-DG are much more stable than FPI-HPMDA and FPI-NS at wider temperature ranges.

(2)



(3) (Line 19) The bifunctional dipolar glass with a large-molecular-weight high than 30000 g mol^{-1} not only maintains the thermal stability of polymer blends even at a high loading of 10 wt%,…

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1 – The authors state in the abstract and along the text referring to Fig. 4: "The composite dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200C @ 600 MV m-1".

However, we cannot compare cycles in the manuscript or supplement, such as, for example, the 1st, 100, 1000, 10,000, and 50,000.

The other important point is the temperature. What are the applications for an energy storage polymer composite at 200C?

Reply: We thank the reviewer for the kind remind and valuable question. The charge-discharge cycling tests is operated through repeatedly applying and removing the electric field onto dielectrics. The U_d and η points in Figure 4A, which are calculated through integrating the tested *D-E* loops, indicate the actual performance of FPI-DG in a certain cycle, such as 1st cycle, 10th cycle and so on. For a clearer comparison of the performance in different cycles, we added the *D-E* loops of the 1st cycle, 10th cycle, 100th cycle, 1000th cycle, 10000th cycle, and 50000th cycle under the highest electric field (600 MV m^{-1}) into the SI.

Then, we have summarized the typical application scenarios of the polymer dielectrics with an operation temperature around 200 ºC as shown in the Table below[R5-7].

Application scenarios of capacitors	Temperature Requirement
Power converter	150-250 ºC
Oil & gas exploration	175-250 ºC
Aircraft engine	180-250 ºC
Geothermal	200-320 ºC

In addition, the application scenarios of capacitors with the operation temperature around 150 ºC are more common, such as the hybrid electric vehicle and pulsed power sources in electromagnetic launch systems. Therefore, in the field of capacitive energy storage polymer dielectrics, the energy density and cyclic stability at 150/200 ºC are the most common parameters to assess the performances of polymer dielectrics. The higher temperature, higher electric field and more charge-discharge cycles a dielectric can tolerance, the higher operation reliability it can achieve. We have added the related content in the manuscript.

Revisions: (1) (Line 28) Polymer dielectrics are considered promising candidate as energy storage media in electrostatic capacitors, which play critical roles in power electrical systems involving elevated temperatures, such as hybrid electric vehicles, oil & gas exploration, aircraft, and geothermal facilities[1-6].

(2) (Line 343) The *D-E* loops of different cycles and corresponding U_d and η were summarized in Figure S36 and Figure 4A, respectively.

(3) (SI)

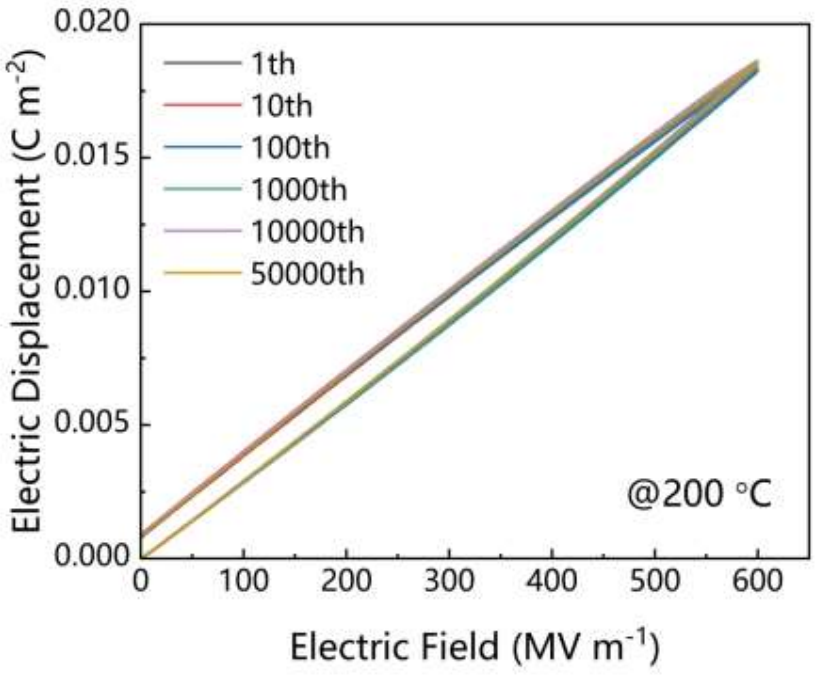


Figure S36. *D-E* loops at different cycles of FPI-8 wt% DG under 600 MV m^{-1} at 200 °C.

2 – The authors state, "thus leading to more homogeneous distribution of local electric field hence less stress concentration at interface", however, the concentration at the interface depends on the materials in contact with the polymer composite as well as the nature of their charges. The charges accumulate due to the difference in chemical potentials μ_(i,) the presence of at least one insulator unable to exchange electrons, and the necessity to align the electrochemical potentials μ¯_i. The charges accumulate in agreement with the equation:

If two species i and j (element, phase, material, cathode, anode, electrolyte, semiconductor,…) come into electrical contact:

μ¯_i-μ¯_j=μ_i 〖-μ〗_j+z_i e(ϕ_i-ϕ_j)

When equilibrium is reached, μ¯_i-μ¯_j=0=μ_i 〖-μ〗_j+z_i e(ϕ_i-ϕ_j) where ΔV_ij= ϕ_i-ϕ_j. If the surface chemical potentials align (or equalized), ϕ_i-ϕ_j=0⟹ μ_i 〖-μ〗_j=-z_i e(ϕ_i-ϕ_j)=0 then the chemical potentials equalize (for more info, first pages 691-692: Beatriz Moura Gomes, J. Francisco Ribeiro Moutinho, Maria Helena Braga Journal of Materials Chemistry A, 2024, 12, 690-722 A perspective on the building blocks of a solid-state-battery: from solid electrolytes to quantum power harvesting and storage doi: https://doi.org/10.1039/d3ta04228f)

Reply: We thank the reviewer for the valuable question and sincerely apologize for our ambiguous statement. In the sentence mentioned, we aim to explain the interfacial concentration of mechanical stress instead of charges. The breakdown of polymer dielectrics can be represented by the propagation of a crack (named as "breakdown path") across the dielectrics, which is driven by the coulomb force between electrodes. Any stress concentration in dielectrics may accelerate the propagation of breakdown path hence the final breakdown. In the polymer-nanosized inorganic composites, there are two types of stress concentration at the interfaces. First, due to the electric displacement ($D=\varepsilon_0\varepsilon_r E$) is continuous across the interface, the two components there with different ε_r should withstand different electric field. This distortion of electric field may make low-ε_r polymers

much more vulnerable under a low nominal electric field. Secondly, the thermal expansion and electrostriction coefficient of polymers and inorganics are both different, which also contributes the stress concentration at interface and form interfacial defects, such as voids and cracks, especially at high temperatures and high electric field. As the nano-sized inorganics feature rigid structures and much large size than polymer chains, above interfacial stress concentration cannot be easily mitigated, which results in premature breakdown at interface and decreased overall breakdown strength of polymer-inorganic composite dielectrics. On the contrary, the organic small molecules possess comparable size and good structural compatibility with polymer chains. Therefore, the mechanical stress concentration at polymer-organic molecule interface can be much more mitigated. And the common interfacial defects that tend to induce stress concentration, such as voids and cracks, can be also greatly reduced due to the flexibility of small molecules. As a result, under the electric field, the generation of breakdown path driven by concentrated stress at interface will be largely delayed, which resulting in higher breakdown strength of the overall dielectrics.

Even so, we found that the references mentioned above is instructive to describe the characteristics of charge distribution at polymer-filler interfaces and its effect on the breakdown. Different from electrolytes, the ions in dielectrics cannot migrate along a long distance, but delocalize with a short range under the electric field. However, similarly, the electrical double-layer model has also been proposed at the polymer-inorganic interface[R8,9]. If a filler particle in polymer holds certain charges, there are a Stern layer with tightly packed opposite charges and a diffuse layer with loosely distributed charges forming around the particle. And the charge characteristics (positive/negative) are determined by the triboelectricity nature of fillers and polymers. The opposite charges in filler surface-stern layer actually form an inner electric field. According to the model, the local electric field of polymers may be further increased due to the inner electric field, which confirms the advantages of small, flexible organic molecules. We believe the electrochemical potential also play a role in the distribution of interfacial charges in insulating dielectrics even though the ions and electrons cannot move along a long distance. We have revised the related sentences and cited the important references.

Revision: (1) (Line 55) Plus, small molecules possess smaller sizes (~1 nm) and better flexibility than rigid nano-sized inorganics (10-100 nm), thus exhibiting more effective mitigation of the distorted interfacial electric field, which is induced by the mismatch of ε_r and interfacial charge concentration[23,24].

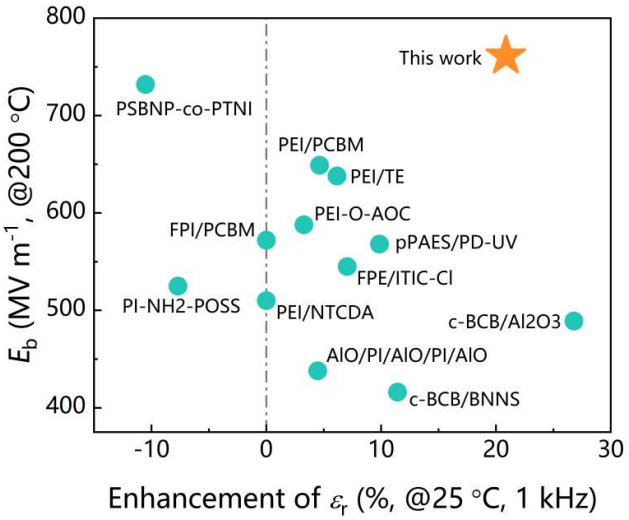
(2) (Line 576) 23 Gomes, B. M., Ribeiro Moutinho, J. F. & Braga, M. H. A perspective on the building blocks of a solid-state battery: from solid electrolytes to quantum power harvesting and storage. *J. Mater. Chem. A* **12**, 690-722, doi:10.1039/D3TA04228F (2024).

3 – The authors state, "As a result, polymer-DG composites exhibit concomitant enhancement of εr from 2.78 to 3.36 (@103 Hz, 25C)". However, the enhancement in the dielectric constant is not significant, especially if considering that polymer composites can reach εr = 120 (Reference: "High Dielectric Constant (High k) Polymer Composites" Encyclopedia of Polymer Science and Technology https://doi.org/10.1002/0471440264.pst674).

The other point left to clarify is the frequency, which should also be given for, 0.1 Hz, since experiments should compare to DC as well. At low frequencies, such as 0.1 Hz, the dielectric constant typically includes contributions from all possible polarization mechanisms: electronic, ionic, dipolar (orientational), and space charge polarization. This is because, at very low frequencies,

all these mechanisms have enough time to respond to the changing electric field. Measurements at very low frequencies can capture the maximum dielectric response of the material.

Reply: We thank the reviewer for the valuable comment and kind suggestion. We would like to introduce the difference between the capacitive energy storage polymer-based dielectrics at room temperature and elevated temperature. As for the polymer dielectrics for room temperature energy storage, ferroelectric polymers (such as PVDF and its copolymers) with a high ε_r of ~10 are usually used. If we fill them with inorganic ferroelectrics (such as $BaTiO_3$ with a ε_r nearly 10^4) and even conductors (the ε_r can be regarded as infinite), the ε_r of these composite dielectrics can be further increased. In the reference above, several polymer-based composites achieve a ε_r of ~120, such as, P(VDF-HFP) with 50 vol% $BaTiO_3$@TiO_2 core-shell particles (E_b = 200 MV m^{-1} at room temperature)[R10], epoxy with 18 vol% $BaTiO_3$ framework (loss is ~0.045)[R11], PVDF with 18 vol% Zn flakes in parallel direction (loss is ~0.04)[R12]. These high ε_r can all be attributed to the of high loading of $BaTiO_3$ and metal fillers with ultrahigh ε_r. However, at the same time, due to the poor insulating properties of ferroelectrics (band gap ≈ 1.8 eV) and conductors, the overall breakdown strength and energy density of this composites will be sharply deteriorated and the loss will be sharply increased. Even though some modulation strategies, such as filler surface modification and topological structure design, have been applied to enhance the energy density at room temperature of PVDF-based composites and an energy density of ~40 J cm^{-3} has been achieved, PVDF and its copolymers have met their application bottleneck at elevated temperatures. PVDF melts at ~180 ºC and its loss will sharply raise at high temperature. If $BaTiO_3$ or metals are introduced, the situation will be even worse. Therefore, no matter how high the ε_r of above systems achieves, they cannot be applied in practical condition, which always involves elevated temperatures as shown in the Reply to comment (1). Instead, only heat-resistant polymers, such as polyimides, and insulating fillers can be taken into account for capacitive energy storage at high temperatures. In this context, our FPI-DG blend exhibits advantages among recently reported polymer composites and polymer blend dielectrics as shown in Figure below.



As seen, the enhancement of ε_r of FPI-DG surpass most polymer composites or multi-component dielectrics. In addition, there are some novel dipolar glass polymers have been synthesized, which

are directly used as energy storage dielectrics rather than blended with other polymers. Because more than 90 wt% of our dielectrics is low-ε_r FPI, the absolute ε_r value of 3.36 may be lower than a few publications. However, they will face much higher synthesis cost as the synthesized DG is only 8 wt% of the blend dielectrics in our study. More importantly, our high ε_r is companied with the notable enhancement of E_b, and yields a high U_d with high efficiency (90%) that surpass most of other reports.

We also tested the ε_r and loss at low frequency range down to 0.1 Hz at different temperatures to examine their performances in DC conditions as shown in the Revisions. As seen, there are no significant variation in ε_r of FPI-DG, FPI-HPMDA, and FPI-NS versus frequency. As temperature increase, the ε_r and loss of these dielectrics monotonically rise, and the FPI-DG exhibits the most stable dielectric properties due to the large molecular weight and enhanced intra-/interchain interaction of DG.

We have revised the related content and added these data.

Revisions: (1) (Line 78) As a result, polymer-DG blends exhibit improved ε_r from 2.78 to 3.36 (@10^3 Hz, 25 ºC) and E_b from 551.11 MV m^{-1} to 761.21 MV m^{-1} (@200 ºC) concomitantly, which boosts an ultrahigh U_d with the charge-discharge efficiency of 90% (U_{d90}) of 8.34 J cm^{-3} (150 ºC) and 6.21 J cm^{-3} (200 ºC).

(2) (Line 171) It can be seen that FPI-DG, FPI-HPMDA, and FPI-NS all exhibit a stable ε_r among the frequency range from 10^{-1} to 10^6 Hz.

(3) (SI)

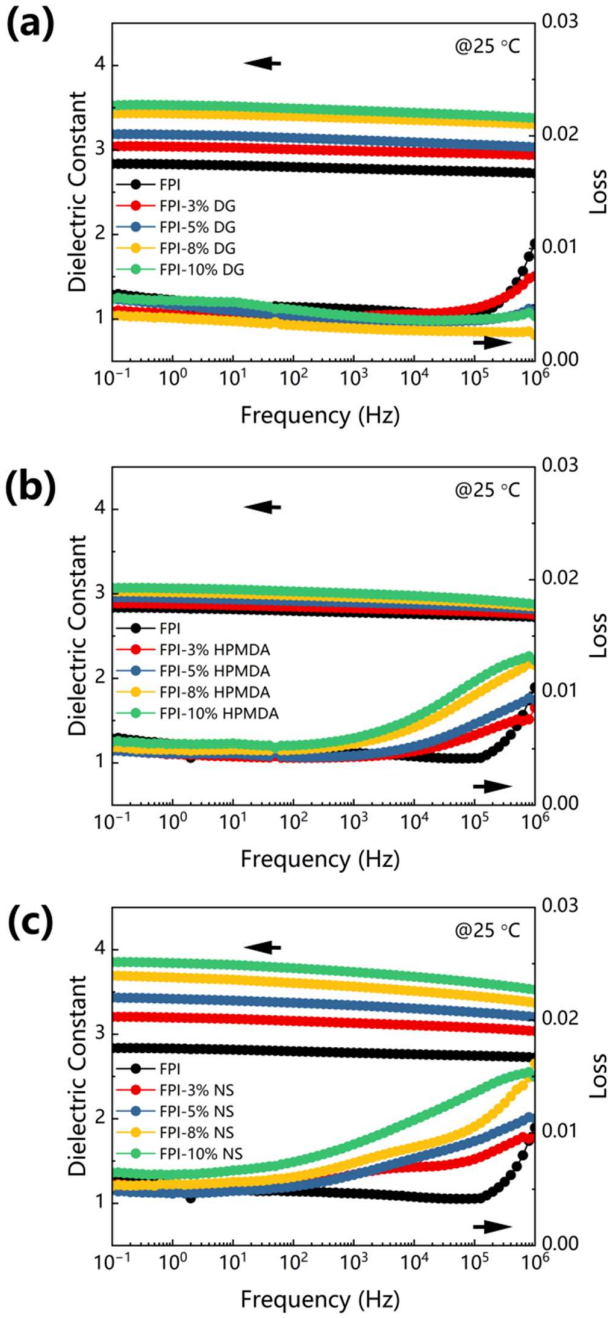


Figure S17. Dielectric spectra versus frequency of (a) FPI-DG, (b) FPI-HPMDA, and (c) FPI-NS at 25 °C.

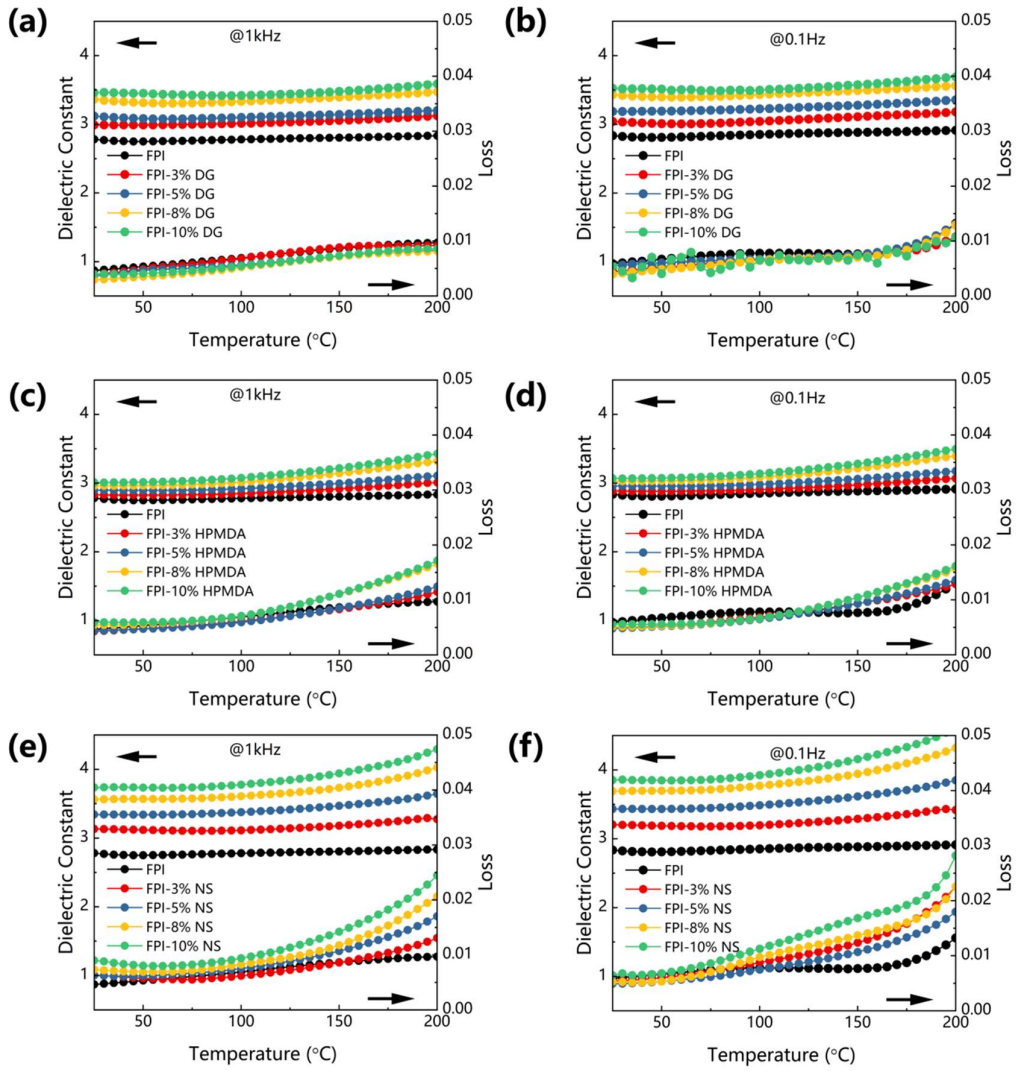


Figure S18. Dielectric spectra versus temperature of (a, b) FPI-DG, (c, d) FPI-HPMDA, and (e, f) FPI-NS at 1000 Hz and 0.1 Hz.

4 — The breakdown strength of polymer dielectrics was measured at 200C; the reason why the measurements were not made at 25C was not discussed in the context of applications.

Reply: We thank the reviewer for the valuable question. As the Reply to comment (1) and comment (3), most of the operation condition of capacitive energy storage polymer dielectrics involves high temperature, which is induced by external environment or inner Joule heat under electric field. Therefore, it is meaningless to pursue high E_b and U_d at room temperature for polyimide-based dielectrics. We have added the related explanation in the Introduction sections.

On the other hand, note that as the ε_r of polyimide-based dielectrics are almost unchanged among the temperature range from 25 ºC to 200 ºC as shown in the Reply to comment (3), the ε_r at 25 ºC can be used to reflect the actual properties in practical conditions.

Revision: (Line 225) As most of the operation conditions of polymer dielectrics involve high temperatures, we tested the high temperature E_b of FPI composites as shown in Figure 2D and Figure

S16.

5 – In Fig. 1B, it is partially understood how the energy of the band gap (width) was obtained from ab initio simulations, but not how to place the gap in the absolute scale was calculated. In other words, for example, for NS, how was LUMO energy -1.27 eV obtained? Moreover, no numbers are given for Density functional theory (DFT) calculations, including plane-wave cut-offs, structural parameters, spacing of k points, etc.

Reply: We thank the reviewer for the valuable question. For obtaining the locations of energy levels, the vacuum level is set as 0 eV at first. Then, we determined the LUMO, HOMO energy as the Method section. Fundamentally, the energy required to move an electron from the vacuum level to a level is the energy value corresponding to that level. Above process can be easily implemented by computation softwares. In this study, we used the Dmol3 module in Materials Studio software. After that, the band gap can be obtained as $E_{LUMO} - E_{HOMO}$. When calculating HOMO and LUMO using Dmol3, the long-chain structure of polymers used is a non-periodic structure rather than a crystalline structure, so it doesn't involve plane wave cutoff energy or cell parameters setting. The key parameters include the degree of polymerization of DG chain of 4, and the self-consistent field (SCF) convergence limit of 1.0e-5. We have added the related content about DFT calculation.

Revision: (Line 482) The vacuum level is aligned with 0. The DG chain has a degree of polymerization of 4, and the self-consistent field (SCF) convergence limit is 1.0e-5.

6—The desired characteristic in thermally stimulated depolarization current TSDC curves of FPI composites is typically a low current at the operational temperature range, indicating stable and minimal charge release (Fig. 2). While high current peaks provide useful information about the trapping sites, they may signal potential issues with charge stability at those temperatures. Here, the authors should discuss their temperature test choices.

Reply: We thank the reviewer for the valuable question. We would like to introduce the operation mechanism of TSDC test. First, an electric field at high temperature is applied on the sample for a while to inject sufficient charges (mostly electrons) into it. In this work, we choose the parameters of 40 MV m^{-1}, 200 ºC, and 10 min. After this "polarization" stage, all the traps in the sample are full of trapped charges. Then, the sample undergoes rapid cooling to an ultralow temperature with the electric field kept to freeze the trapped charges in traps. The cooling speed and the cooling temperature are set as 10 ºC min^{-1} and -100 ºC. Afterwards, the sample are short-circuited without external electric field and heated with a relatively low speed (3 ºC min^{-1} in this work) and the current across the sample is recorded. During this stage, the trapped charges will obtain thermal energy which are positively related to the temperature. When the obtained energy reaches the depth of a type of traps, these trapped charges can jump out and migration across the dielectric, resulting in a TSDC peak. Finally, a complete TSDC curve that indicates the depth and density of all types of traps can be obtained. Therefore, the TSDC peaks indicate the charges that are trapped in dielectrics, rather than the leakage current under electric field (Shown in Figure S23). And the relationships between TSDC peak area and the insulating properties of dielectrics depends on the nature of corresponding traps.

Besides FPI, FPI-DG, FPI-HPMDA, and FPI-NS, we tested SPI, SPI-DG, PEI, PEI-DG to systematically compare and analyze their TSDC characteristics as shown below. As for the pure polyimides, such as FPI, SPI, and PEI, only two TSDC peaks can be observed. The peak fitted by

dashed black line is named as "peak 1", which indicates the β relaxation of polymers[R13]. The peak fitted by dashed red line is named as "peak 2", suggesting the charge injected from electrode into dielectrics and is related to the overall insulating properties of dielectrics[R14]. When the small molecules or DG are introduced into polymers, the peak 1 will not change much but the peak 2 may change a lot due to the effect of introduced components on the overall insulating properties. What's more, the introduced components induce new traps at interfaces, which are named as "peak 3" and highlighted by dashed blue lines in TSDC curves. As for peak 3, high temperature is desired as it reflects deep charge traps induced by new components. As for peak 2, smaller area and higher temperature are preferred which indicates less injected charges and higher injection obstacles.

We calculated the trap parameters according to TSDC curves as shown below[R15]. As seen, the introduction of DG improves the trap depth (i.e., peak temperature) and decrease the trap density (i.e., TSDC peak area) of peak 2 in all three polyimides, which means the DG enhance the overall insulating properties of polymer dielectrics and reduce injected charges. Then, the new peak 3 with high location temperatures can be also observed in all three TSDC curves of polyimide-DG blends. Note that the trap depth and trap density of peak 3 is determined by the energy band structures, interaction, distribution of DG and polyimides. And, compared to trap density of peak 3, trap depth of peak 3 is much more important to indicates the charge trapping capability of new component. Therefore, the trap density of peak 3 in different systems, such as FPI-8 wt% DG vs. SPI-8 wt% DG and FPI-8 wt% DG vs. FPI-8 wt% HPMDA, are rarely compared. In the original manuscript, we have compared the TSDC curves of FPI-DG, FPI-HPMDA, and FPI-NS. Briefly, besides the new peak 3, HPMDA can also enhance the insulating properties, but exhibit much weaker effect than DG. Even though NS introduce a peak 3 due to its energy level mismatch to FPI at interfaces, it reversely decreases the location temperature and increases the area of peak 2, indicating the overall insulating properties are deteriorated in FPI-NS. This deterioration is induced by the high quantity of SO_2 groups in small-sized NS, which possess extremely high mobility to facilitate the charge migration.

In summary, the results of TSDC tests match well with the results of E_b, leakage current, and U_d. We revised the related content for a better understanding of TSDC test and added TSDC results of SPI, SPI-DG, PEI, PEI-DG into SI.

Revisions: (1) (Line 254) As for peak 2, higher temperature and smaller area are preferred which indicate higher injection barrier and less injected charges.

(2) (Line 257) For this peak, high temperature is desired for better charge trapping capability.

(3) (Line 313) The TSDC curves with the trap parameters of PEI, SPI, and their blends are shown in Figure S33 and Table S4. As seen, the introduction of DG induces a new peak (peak 3) with a high temperature of 208.77 ºC for SPI-8 wt% DG and 212.04 ºC for PEI-8 wt% DG, respectively. Moreover, the suppressed charge injections can be observed both blends according to higher temperature and lower area of peak 2.

(4) (SI)

Table S3. Trap depth and trap density of FPI and FPI-based dielectrics.

	Trap depth of Peak 2 (°C)	**Trap Density of Peak 2 (10^{20} m^{-3})**	**Trap depth of Peak 3 (°C)**
FPI	199.12	0.58	

FPI-8% DG	220.47	0.468	228.09
FPI-8% HPMDA	215.38	0.504	216.28
FPI-8% NS	184.38	0.958	226.50
FPI-3% BN	193.69	1.164	209.18

(5) (SI)

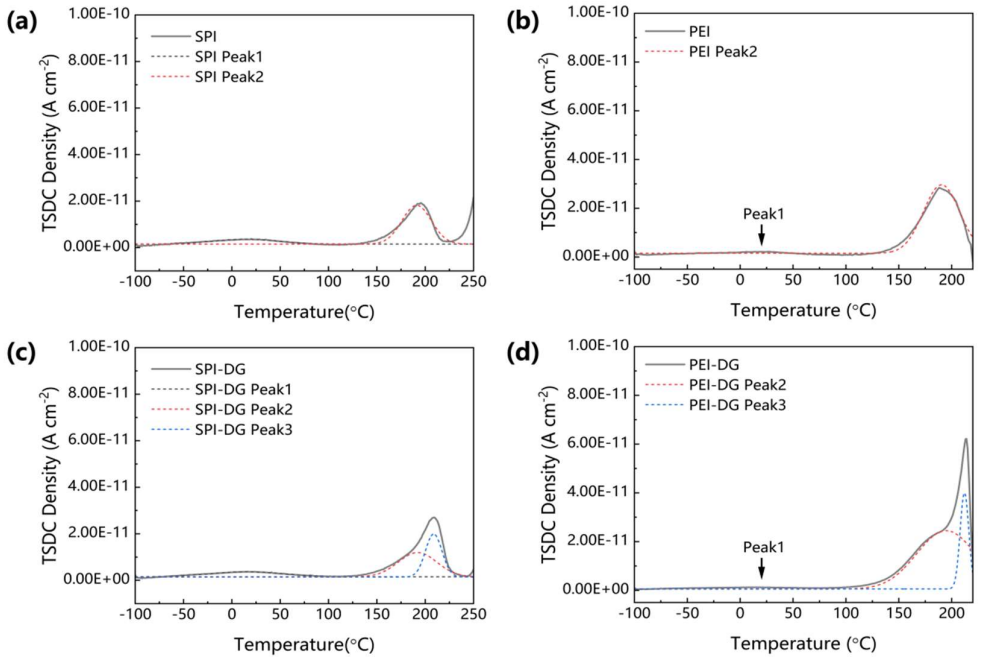


Figure S33. TSDC curves of (a) SPI, (b) PEI, (c) SPI-8 wt% DG, and (d) PEI-8 wt% DG.

Table S4 Trap parameters of TSDC curves of SPI, PEI, and their blends.

	Trap depth of Peak 2 (°C)	**Trap Density of Peak 2 (10^{20} m^{-3})**	**Trap depth of Peak 3 (°C)**
SPI	191.12	0.607	-
SPI-8% DG	192.09	0.499	208.77
PEI	190.21	1.284	-
PEI-8% DG	194.65	1.238	212.04

7 - The results demonstrate that the FPI-DG combination outperforms PEI-DG and SPI-DG. Why were the polymers FPI, PEI, and SPI specifically chosen to be tested with this organic filler? Additionally, would the selection of different polymers affect the performance improvements attributed to the DG organic filler?

Reply: We thank the reviewer for the valuable question. As mentioned above, heat-resistant

polyimides are intensively studied for high temperature capacitive energy storage with good thermal structural stability[R16]. In this context, as we aimed to utilize solution casting process to prepare polyimide-DG dielectrics, the PEI, FPI, and SPI, which are all common soluble polyimides, were selected as the polymer candidates.

As shown in the Figure 3E and 3F, DG significantly improves the energy density of all three polyimides, and the enhancements are obviously different. Therefore, we think the polyimides indeed affect the enhancing effect of DG, which may be attributed to their band structures, own thermal structural stability and energy storage performances, and interactions between the groups of them and DG.

8 - Overall, the authors compared the results from NS, DS, and HPMA with different polymers like FPI, PEI, and SPI, where the selected weight percentage was 8%. Was the performance ever compared to other polymer-inorganic composites?

Reply: We thank the reviewer for the valuable question. We took boron nitride nanoparticles (BN) as the comparison, which is a common inorganic filler of high temperature energy storage polymer dielectrics[R17-19]. We prepared FPI-BN composites using the same solution casting process as FPI-DG. According to that $U_d=1/2\varepsilon_0\varepsilon_r E_b^2$, we firstly tested their high temperature E_b and determined its optimal content of 3 wt% as shown in the Revisions. We then tested the TSDC curves and energy density of FPI-3 wt% BN as a comparison to FPI-8 wt% DG as shown in the Revisions. It can be seen that BN increases the trap density and decreases the trap depth of peak 2, which indicates the deteriorated insulating properties. Moreover, 3 wt% BN slightly improves the energy density and efficiency of FPI at 200 ºC, yielding a U_{d90} of 3 J cm$^{-3,}$ which are much lower than that of FPI-8 wt% (6.12 J cm^{-3}). The enhanced E_b and U_d of BN can be mainly attributed to its high mechanical strength and wide band gap (5.72 eV). As mentioned above, high mechanical strength is conducive to prevent the propagation of breakdown path. The introduction of BN can strengthen the whole polymer matrix and serve as rigid blocks against breakdown path. In addition, wide band gap enables BN to effectively trap charges. However, above effects are both compromised by the deteriorated interfacial insulating properties as shown in the results of TSDC tests.

The BN actually exhibits the common characteristics of insulating inorganic fillers, such as Al_2O_3 and SiO_2. They feature high mechanical strength and wide band gap, but poor structural compatibility with organic polymers. As a result, there will be a lot of defects and stress concentration at interface, which deteriorate insulating properties at interface and limits the performance enhancement of inorganic fillers.

We have added the data about FPI-BN composites.

Revisions: (1) (Line 264) To highlight the advantages of organic DG over inorganic components, we prepared FPI-boron nitride (BN, has a similar band gap of 5.72 eV) composites with an optimal content of 3 wt% (determined by the high temperature E_b, Figure S27). The TSDC curve and trap parameters of FPI-3 wt% BN can be seen in Figure S26 and Table S3. Even though BN introduces new traps with a temperature location of 209.18 ºC (peak 3), its peak 2 exhibits a lower temperature (193.69 ºC) and larger area (1.164×10^{20} m^{-3}) than pure FPI, which can be attributed to the polymer-inorganic interface with dense defects and poor insulating properties.

(2) (Line 293) As a comparison, we tested the U_d of FPI-3 wt% BN composites at 200 ºC as shown in Figure S30 and only a U_{d90} of 3 J cm^{-3} is achieved, confirming the excellent effect of our polymer-DG blending strategy.

(3) (SI)

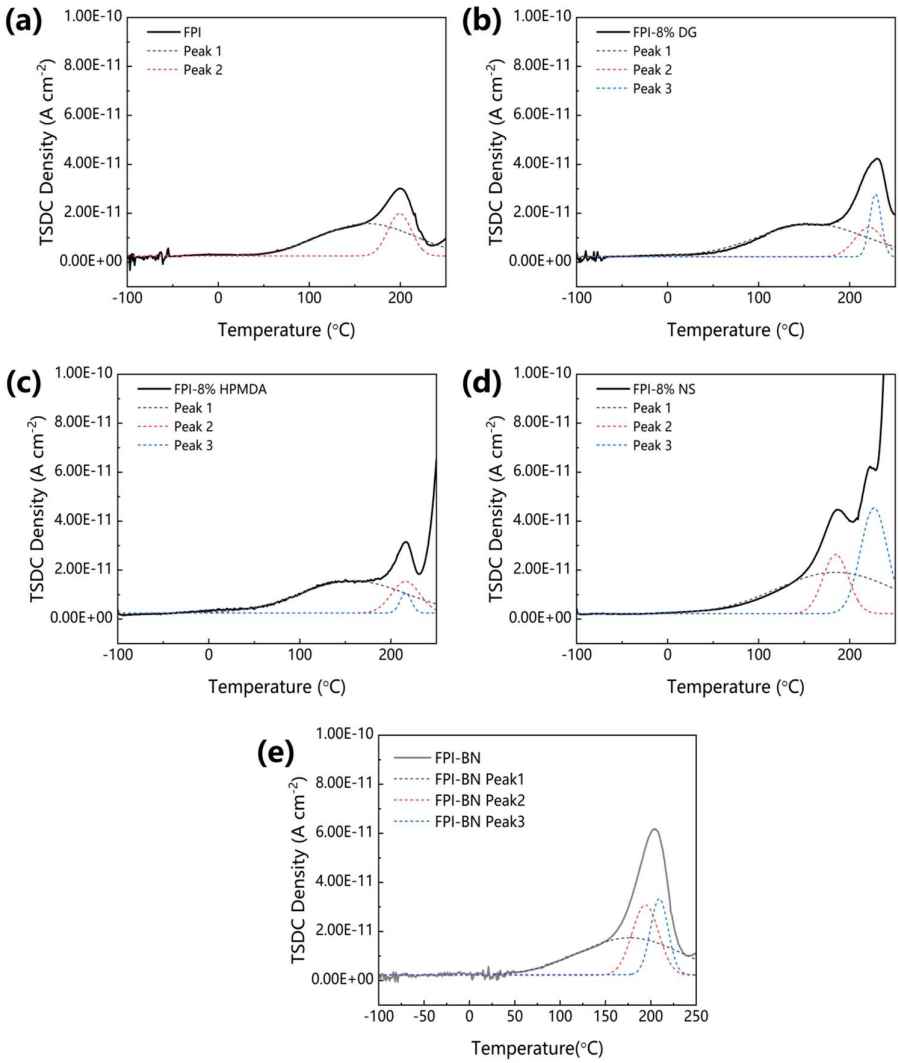


Figure S26. TSDC curves of (a) FPI, (b) FPI-8 wt% DG, (c) FPI-8 wt% HPMDA, and (d) FPI-8 wt% NS, (e) FPI-3 wt% BN.

Table S3. Trap depth and trap density of FPI and FPI-based dielectrics.

	Trap depth of Peak 2 (°C)	**Trap Density of Peak 2 (10^{20} m^{-3})**	**Trap depth of Peak 3 (°C)**
FPI	199.12	0.58	
FPI-8% DG	220.47	0.468	228.09
FPI-8% HPMDA	215.38	0.504	216.28
FPI-8% NS	184.38	0.958	226.50
FPI-3% BN	193.69	1.164	209.18

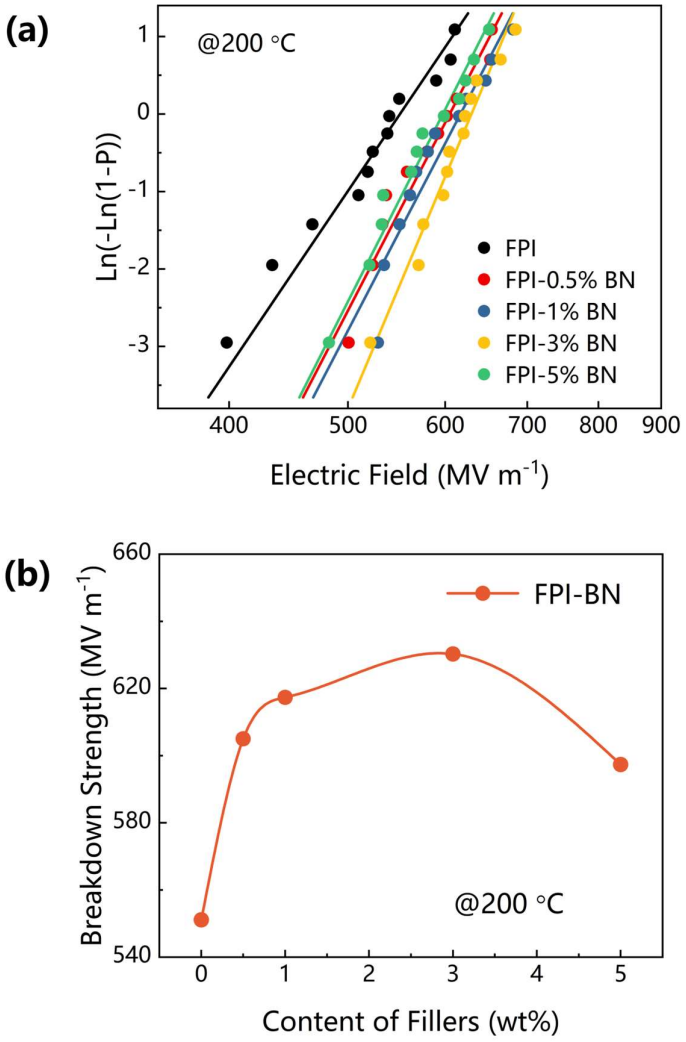


Figure S27. (a) Breakdown electric field Weibull distribution of FPI-BN composites with different filler content at 200 °C. (b) Breakdown strength of FPI-BN composites versus filler content at 200 °C.

(4) (SI)

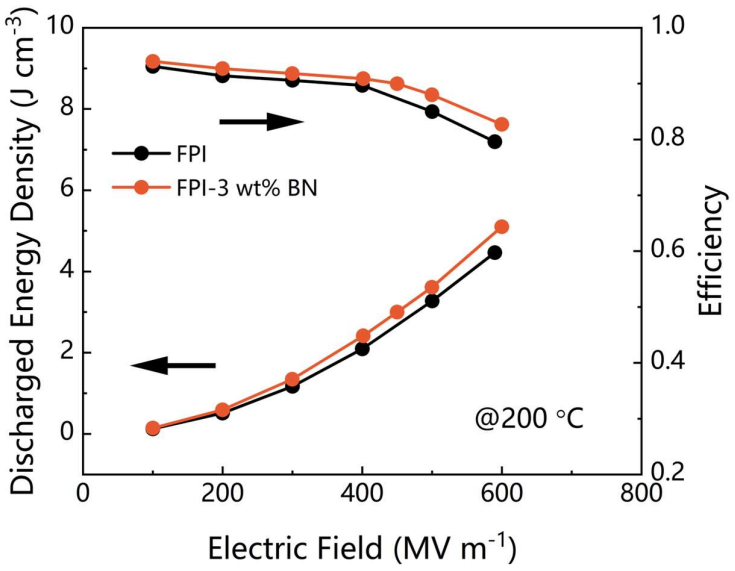


Figure S30. U_d and η versus electric field of FPI and FPI-3 wt% BN at 200 °C.

9 — There are basically no performance tests for the polymer composites in capacitor cells where the electrodes are capacitor electrodes. Functional analysis in a cell is paramount for reliable assessment of the materials' functional capacity.

Reply: We thank the reviewer for the kind suggestion. However, we are really sorry to say that the polyimide-based capacitor prototypes that meet industrial standards cannot be produced yet. The laboratory-level sample we made can be seen as a simple metallized film capacitor prototype, which consists of a polymer film and the evaporated copper electrodes on its two sides. If we want to get a standard capacitor prototype, we should first manufacture a kilometers-long polyimide film. Then, the film needs to undergo roll-to-roll metallization, slitting, winding, electrical end test, terminal welding, healing, and terminal metallization to yield a capacitor[R20].

Currently, the mostly used polymer dielectrics in industrial capacitors is biaxial oriented polypropylene (BOPP) which is produced by melt extrusion technology. Due to the biaxial orientation process, the BOPP films exhibit good mechanical strength and can tolerance roll-to-roll tension during following manufacturing steps, such as metallization. On the contrary, the polyimides in our study, such as FPI, PEI, SPI, and their composites or blends, cannot be produced using melt extrusion due to their high glass transition temperature (T_g) and filler aggregation and degradation in molten state polymers. Instead, they can only be produced by solution casting process without orientation stage, which makes their mechanical strength lower than those of BOPP. Therefore, the solution cast polyimide films are vulnerable and easy to fracture during the roll-to-roll metallization process. For now, this technical problem has not been solved so the standard polyimide capacitors are still out to reach in both academia and industry. In recent years, our team has devoted great effort to overcome this issue towards the industrialization of our polyimide-based dielectrics. In last year, we first fabricated the industrial polymer-based composite film with the lengths higher than 100 m with a roll-to-roll solution casting manufacturing line[R21]. We hope the issue of film fracture during metallization can be handled soon so we can follow the guide of the reviewer to examine the practical performances of our polymer dielectrics.

Even so, impressed by the reviewer's suggestion, we switched the copper electrodes to aluminum electrodes, which are more commonly applied for industrial metallized polymer film capacitors, to get as close as the practical operation conditions. We evaporated aluminum electrodes onto the surface of FPI-8 wt% DG films and tested their energy storage performances at high temperature as shown in the Revisions. FPI-8 wt% DG exhibits much higher E_b than FPI. An E_b of 769.62 J cm^{-3} and 748.10 J cm^{-3} are achieved at 150 ºC and 200 ºC, which are very close to those for copper electrodes (784.10 MV m^{-1} and 761.21 MV m^{-1}). We also tested the high temperature energy density of FPI-8 wt% DG with aluminum electrodes as shown below. As seen, the U_{d90} of FPI-8 wt% reaches 8.21 J cm^{-3} and 5.90 J cm^{-3} at 150 ºC and 200 ºC, which are comparable to those for copper electrodes (8.34 J cm^{-3} and 6.21 J cm^{-3}). The lower E_b and U_d of polymer dielectrics with aluminum electrodes can be attributed to the rapid oxidation of aluminum at high temperatures. Honestly, it is also the reason why we used copper electrodes in our study. In the practical capacitors, polymers and aluminum electrodes will be packaged to isolate air so the energy storage performances can be further improved. We added the data about FPI-8 wt% DG with aluminum electrodes into the manuscript.

Revisions: (1) (Line 355) In order to examine the performances of our blend dielectrics in practical operation conditions, we tested the E_b and U_d of FPI-8 wt% DG blends at high temperatures with aluminum electrodes that are more commonly used in polymer film capacitors. As shown in Figure S38, FPI-8 wt% DG has a E_b of 769.62 MV m^{-1} and 748.10 MV m^{-1} at 150 ºC and 200 ºC, respectively, which are comparable to those for copper electrodes. A high U_{d90} of 8.21 J cm^{-3} and 5.90 J cm^{-3} is also achieved at 150 ºC and 200 ºC as shown in Figure S39.

(2) (SI)

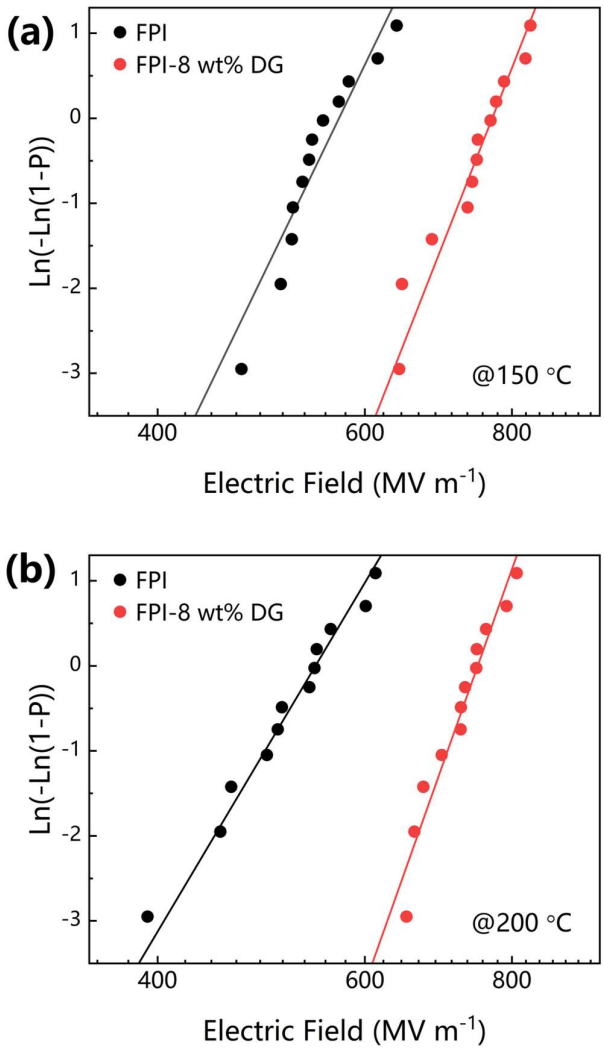


Figure S38. Breakdown electric field Weibull distribution of FPI and FPI-8 wt% DG with aluminum electrodes at (a) 150 °C and (b) 200 °C.

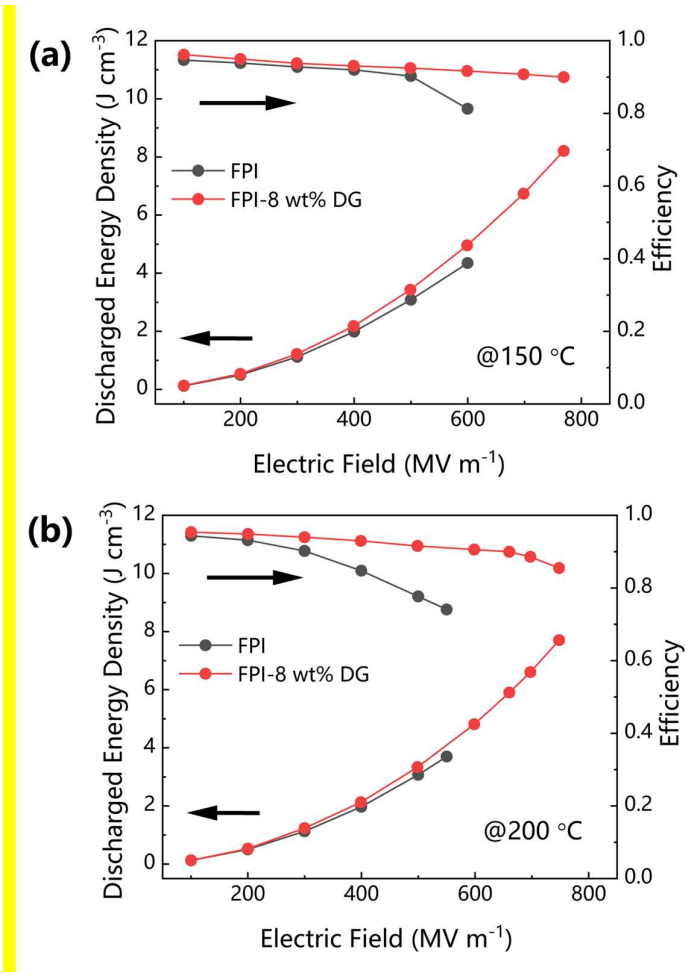


Figure S39. U_d and η versus electric field of FPI and FPI-8 wt% DG with aluminum electrodes at (a) 150 °C and (b) 200 °C.

Reviewer #3 (Remarks to the Author):

This work englobes the design and development of a polymer-based dielectric material for use as active layers in electrostatic capacitor devices. Currently, the development of these types of systems represents a productive and highly interesting area within materials science, mainly due to its direct involvement in the energy field. In this sense, it has become evident that moving towards creating new technologies and materials that guarantee efficient energy storage is as crucial as obtaining it. Thereby, all efforts invested in the development of new ways of extracting energy are useless if we are not able to ensure correct and efficient storage of it once obtained. For this reason, as a first comment, I consider that the topic in which this work is framed is of high interest and might be very attractive to the reading community.

In the present work, Yang and coworkers prepared and studied a class of all-organic composite dielectrics fabricated by incorporating macromolecular fillers into a PI matrix. Importantly, these fillers - named by them as Dipolar Glass fillers - were designed looking for the incorporation of entities having a wide band-gap (Eg) along with the presence of high dipole moment functional groups. The requirement for a wide Eg is sustained by the need to diminish charge migration phenomena. At the same time, high dipole moment structures will endow the final material with an adequate dipolar density and, consequently, an increased polarization property. So, in search of the above conditions, the authors came up with the condensation of HPMDA and NS units as building blocks for this class of filler, merging the aliphatic nature of the first one (favoring the Eg condition) with the dipolar character of sulfonyl groups present in the NS. It is worth mentioning that although the strategy reported here cannot be considered novel or pioneering since it involves the mere blending of two polymeric systems, Its simplicity, accompanied by some clearly non-trivial and outstanding results (e.g. homogeneity, synergy, high discharge energy density, high efficiency, reliability and scalability, among others) deserves the attention. However, there are some relevant flaws in terms of discussions and correlation between characterization techniques. This work cannot be accepted in its current form and might be considered for publication only after a deep and careful inspection and the repetition of some of the experiments. Trying to solve the following points can orient the authors to achieve the above:

Reply: We sincerely thank the reviewer for the careful review. These issues and comments are really helpful for improving this manuscript. We have revised the manuscript according to each comment as shown below.

Abstract Section

1) It is confusing the fact that this section mentions the limitations of using “small molecules” as fillers, followed by the description of the filler used in this work as an "assembly of two molecule components" and as a “bifunctional dipolar glass filler”. It could give the false idea that the DG filler is small in size when, indeed, it has macromolecular features (Mn 38.577 g/mol, n= 88). Please, be clear on the polymeric nature of DG. Also, it would be advisable to avoid the term "assembling" when, actually, it is a covalent polymer made by multiple condensation reactions.

Reply: We thank the reviewer for the valuable comment. In the original manuscript, we would like to highlight the comparison between the FPI-DG and FPI-small molecule composites. Therefore, the FPI-DG in original manuscript follows the term “composite”. Thanks for reminding that the FPI-DG is essentially a polymer blend. As a result, we revised the Title, Abstract, and related content

in the whole manuscript to clarify the difference between FPI-DG blends and FPI-small molecule composites.

Revision: **To save space, we only summarized the typical revisions in the manuscript here. Other revisions can be seen in the revised manuscript.**

(1) (Line 1, Title) Enhanced High-Temperature Energy Storage Performances in Polymer Dielectrics by Synergistically Optimizing Band-gap and Polarization of Dipolar Glass

(2) (Line 11, Abstract) Electrostatic capacitors are widely used as capacitive energy storage devices in electric vehicles and oil & gas exploration facilities. As the key energy storage media of capacitors, polymer dielectrics have been intensively studied with their polarization and breakdown strength (E_b) optimized for high discharged energy density (U_d) at elevated temperatures. Small molecules have been explored as fillers for enhanced polarization and E_b, yet they deteriorate the thermal stability of matrix which limits their optimal loading to ~1 wt% in composite dielectrics. Herein, instead, we developed a polymer blend dielectric consisting of common polyimide and a bifunctional dipolar glass polymer which are synthesized through condensation polymerization of two small molecule components with wide band-gap and large dipole moment. The bifunctional dipolar glass with a large-molecular-weight high than 30000 g mol^{-1} not only maintains the thermal stability of polymer blends even at a high loading of 10 wt%, but also induces substantial enhancement in polarization and E_b than any of the individual components does, giving rise to an ultrahigh U_d of 8.34 J cm^{-3} (150 ºC) and 6.21 J cm^{-3} (200 ºC) with a charge-discharge efficiency of 90%. The polymer blend dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200 ºC @ 600 MV m^{-1}.

(3) (Line 28) Polymer dielectrics are considered promising candidate as energy storage media in electrostatic capacitors, which play critical roles in power electrical systems involving elevated temperatures, such as hybrid electric vehicles, oil & gas exploration, aircraft, and geothermal facilities[1-6].

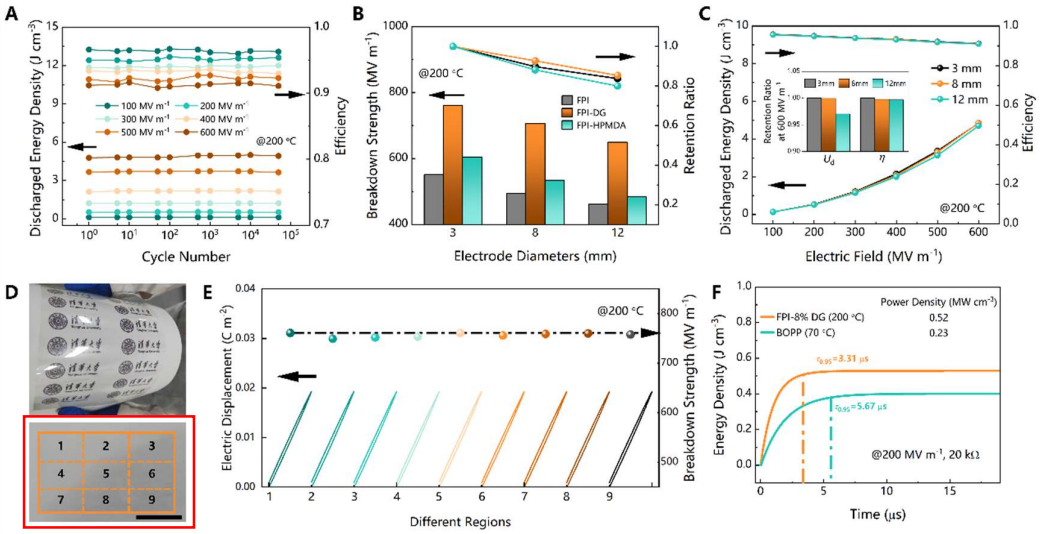
(5) (Line 66) The structural thermal stability of polymer-based dielectrics is closely correlated with the interaction between molecules[2, 34]. Compared to small molecules, high-molecular-weight additives, such as another polymer, are conducive to achieve strong interchain interactions and high cohesive energy, and thus providing new opportunity of maintaining high structural stability in polymer blend dielectrics at elevated temperatures. In this work, we employed 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) with wide E_g and 3,3'-sulfonyldianiline (NS) containing high-μ group as the functional components and polymerized them to synthesize a bifunctional dipolar glass (DG) polymer. A series of polymer blend dielectrics were then fabricated through blending the DG and common polyimides (PI). The DG possesses the molecular weight larger than 30000 g mol^{-1}, thus maintaining the T_g above 300 ºC and performance thermal stability of polymer blend dielectrics with its content up to 10 wt%. Besides, the functional components respectively enhance the polarization and charge trapping, which can be further promoted by the non-linear chain configuration of DG. As a result, polymer-DG blends exhibit improved ε_r from 2.78 to 3.36 (@10^3 Hz, 25 ºC) and E_b from 551.11 MV m^{-1} to 761.21 MV m^{-1} (@200 ºC) concomitantly, which boosts an ultrahigh U_d with the charge-discharge efficiency of 90% (U_{d90}) of 8.34 J cm^{-3} (150 ºC) and 6.21 J cm^{-3} (200 ºC). In addition, charge-discharge cycling stability up to 5×10^4 cycles under high electric field of 600 MV m^{-1} at 200 ºC and large-scale preparation prospects are also achieved in the polymer-DG blend dielectrics.

2) In Line 23 there is an extra “space” in “.The**composite”

Reply: We thank the reviewer for the kind remind. We have revised the issues and examine the whole manuscript as shown below.

Revisions: (1) (Line 177) More notably, the dielectric properties of FPI-DG are much more stable than FPI-HPMDA and FPI-NS at wider temperature ranges.

(2)



(3) (Line 19) The bifunctional dipolar glass with a large-molecular-weight high than 30000 g mol^{-1} not only maintains the thermal stability of polymer blends even at a high loading of 10 wt%,…

(4) (Line 24) The polymer blend dielectrics can be mass produced and exhibit charge-discharge cyclic stability of 50000 cycles at 200 ºC @ 600 MV m^{-1}.

(5) (Line 31) With ever increasing demand for device miniaturization, system integration and higher reliability[7], it is imperative to increase the discharged energy density (U_d) of dielectric materials. In general, U_d can be expressed as:…

(6) (Line 154) These results are all in line with our hypotheses that the DG with large-molecular-weight can enhance the structural stability of polymers more efficiently than its monomer components.

Introduction Section

The authors provide a clear and brief introduction, pointing out in an organized way the theory, literature voids and, therefore, the motivations behind proposing the present project. However:

3) Within the field of polymer dielectrics, the concept of “dipolar glass polymer” is one of the most relevant strategies when affording suitable and efficient materials. More importantly, the use of sulfones as dipolar entities for improving the dielectric properties of polymers has been successfully demonstrated thanks to this concept. So, I was wondering if the idea of "dipolar glass polymers" motivated, to some extent, this project and, for example, the use of the NS molecule. If so, it would be important to include some relevant references such as:

- Zhu, L. (2014). Exploring strategies for high dielectric constant and low loss polymer dielectrics. The journal of physical chemistry letters, 5(21), 3677-3687.

- Wei, J., Zhang, Z., Tseng, J. K., Treufeld, I., Liu, X., Litt, M. H., & Zhu, L. (2015). Achieving high dielectric constant and low loss property in a dipolar glass polymer containing strongly dipolar and

small-sized sulfone groups. ACS Applied Materials & Interfaces, 7(9), 5248-5257.
- Baer, E., & Zhu, L. (2017). 50th anniversary perspective: dielectric phenomena in polymers and multilayered dielectric films. Macromolecules, 50(6), 2239-2256.
To name a few

Reply: We thank the reviewer for the kind remind. We totally agree that our idea is inspired by the dipolar glass design strategy. We have read the above references long ago and received great help and guidance. Therefore, these references have been included in our previous review articles[R22,23]. We have added these references in this manuscript as shown below.

Revisions: (1) (Line 95) NS contains a sulfone group, which possesses a large μ of 4.5 D and has been extensively grafted into polymer chains to fabricate dipolar glass polymers with enhanced polarization[26,38-43].

(2) (Line 622) 41 Wei, J. *et al.* Achieving High Dielectric Constant and Low Loss Property in a Dipolar Glass Polymer Containing Strongly Dipolar and Small-Sized Sulfone Groups. *ACS Appl. Mater. Interfaces* **7**, 5248-5257, doi:10.1021/am508488w (2015).

42 Zhu, L. Exploring Strategies for High Dielectric Constant and Low Loss Polymer Dielectrics. *J. Phys. Chem. Lett.* **5**, 3677-3687, doi:10.1021/jz501831q (2014).

43 Baer, E. & Zhu, L. 50th Anniversary Perspective: Dielectric Phenomena in Polymers and Multilayered Dielectric Films. *Macromolecules* **50**, 2239-2256, doi:10.1021/acs.macromol.6b02669 (2017).

4) Related to the above, and sustained by the vast amount of literature, I find it more correct to refer to DG as a dipolar glass polymer rather than a “dipolar glass filler” or “organic filler” (line 66). It must be considered that the material developed in this work fits properly with the definition of a polymer blend. In this sense, if both components are organic polymers, even coming from the same type of family, why call this material a composite? (see the title of the manuscript). Please explain.

Reply: We thank the reviewer for the valuable remind. We indeed realized that the term “composite” and “dipolar glass filler” here is inappropriate. Therefore, just as the Reply to comment (1), we revised the whole manuscript including Title, Abstract, and text to correct the related content. And, to distinguish the synthesized dipolar glass polymer and original polyimides (such as FPI, SPI, and PEI), we used the term “dipolar glass” rather than “dipolar glass polymer”, and used the term “polymer-dipolar glass blends” to define the FPI-DG, PEI-DG, and SPI-DG in the manuscript.

Revision: The typical revisions can be seen in the Reply to comment (1).

Results and Discussion Section:

5) Line 82: PI is not defined.

Reply: We thank the reviewer for the kind remind and revised the issue.

Revision: (Line 73) A series of polymer blend dielectrics are then fabricated though blending the DG and different common polyimides (PI).

6) Figure S1: Any explanation why homo and lumo orbital are so localized in DG? This could be not trivial for a non-expert audience

Reply: Thank the reviewer for the kind remind. As for a polymer chain with infinite length in which each monomer has the same orientation and conformation, the same positions in different monomers should be located to the equivalent degenerate orbitals and have the identical energy value. However,

above situation cannot be realized in actual materials. In this study, we used a DG chain segment containing 4 monomers as shown in Figure S1(g) and (h) for energy level calculation. The structure optimization process before calculation induces twist of the chain segment to achieve the most stable state, which results in the change of orientation, conformations, and electron cloud distribution of 4 monomers. Therefore, HOMO and LUMO of the whole chain segment are located in two individual monomers but not 4 monomers[R24,25]. Nevertheless, the difference between HOMO of 4 monomers are very small, and so is the LUMO. We have added related content into the SI.

Revision: (SI) Figure S1. Energy level distribution of (a) HOMO and (b) LUMO of HPMDA, (c) HOMO and (d) LUMO of PMDA, (e) HOMO and (f) LUMO of NS, (g) HOMO and (h) LUMO of DG. Note that the localization of HOMO and LUMO in DG chain is induced by the structure optimization for a most stable state of the polymer chain. In the ideal polymer chain containing infinite monomers with same conformation and orientation, same positions in each monomer should have identical energy.

7) Regarding DSC analysis and Tg calculations (Figures S3 and S10): In most cases, the DSC curves are not so well resolved and with an appreciable level of signal noise that would definitely affect the correct identification of Tg. Also, there is no clear information about the thermal treatment and cycles performed on samples during DSC analysis. Were the Tg values obtained from the last heating run? How many heating, cooling and isothermal processes were included? And most importantly, what was the temperature interval chosen for studying these samples? This data is not suitable for calculating Tg values. Consider redoing these experiments.

Reply: We thank the reviewer for the valuable suggestion. We indeed realized that the original DSC curves contain noises that may mislead the determination of T_g. Therefore, we increased the weight of all the samples including pure HPMDA and NS by 10 times and retested their DSC curves as shown in Revisions. HPMDA and NS show a melting point (T_m) of 285 ºC and 173 ºC, respectively. DSC curves of FPI-based composites and blends all exhibit a step in the range of 225-250 ºC, which may be attributed to the variation the distribution form of FPI chains and is not the focus of this study. The glass transition peaks of FPI, FPI-DG, and FPI-NS show similar shapes. Among the curves of FPI-DG, all peak positions are very close, indicating the maintained T_g. As for FPI-NS, the T_g undergoes a sharp decrease versus NS content and the NS melting has no significant effect on the DSC curves of FPI-NS. The DSC curves of FPI-HPMDA composites are more irregular, in which a new peak appears in the range of 150-200 ºC next to the original step (225-250 ºC). Since the peak area is positively correlative to the HPMDA content, we think the peak can be attributed to the variation of HPMDA existence or distribution form, which is also not the focus of this study. It can be seen that the DSC peaks of pure HPMDA doesn't affect the trend of DSC curves of FPI-HPMDA, either. Therefore, we can determine the T_g in these curves and a sharp decrease tendency of T_g versus HPMDA content can be observed in FPI-HPMDA just like FPI-NS.

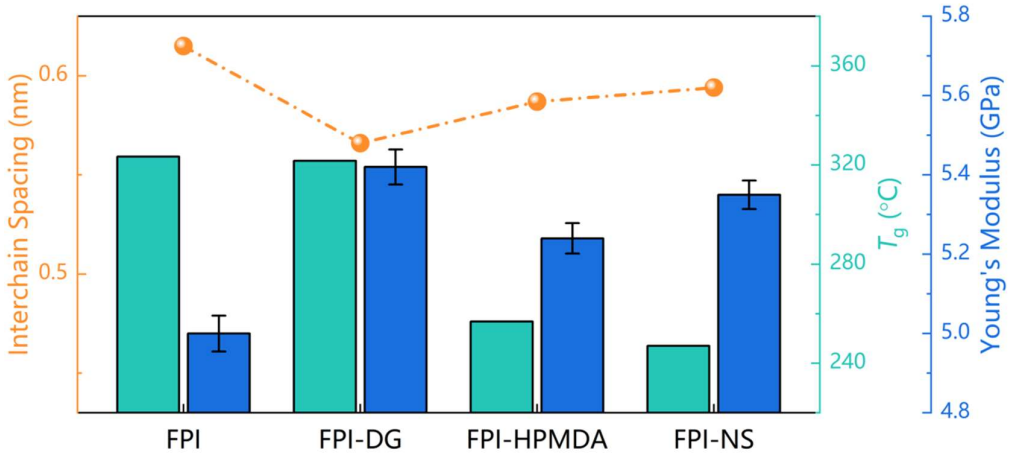
We also carried out the TGA characterizations of these dielectrics as shown in the Revisions. It can be seen that FPI and DG polymers exhibit no significant weight loss until 400 ºC. HPMDA and NS have a degradation process since 260 ºC, which can be also observed as a peak in their DSC curves. However, considering the $T_{d5\%}$ of HPMDA and NS (>290 ºC) are higher than the determined T_g from their FPI-based composites and their DSC peaks have no significant influence on DSC curve trend of their composites. The determined T_g should be reasonable to indicate the glass transition of FPI chains in FPI composites and blends.

We added the retested DSC curves and TGA curves into the manuscript and revised the related content. We also added test parameters in the Method section. Note that as the heat treatments of the samples during preparation are same, their heat history can be regarded identical. And HPMDA and NS will thermally degrade once the temperature is higher than 260 ºC. Therefore, we didn't operate preheating process but only heated samples once to record DSC curves.

Revision: (1) (Line 128) According to the thermogravimetric analysis (TGA) curve (Figure S11), FPI-HPMDA, FPI-NS, FPI-DG dielectrics exhibits no significant weight loss among wide temperature range up to 200 ºC, indicating good thermal stability in practical operation conditions.

(2) (Line 147) As the addition of HPMDA or NS, the T_g of FPI-HPMDA and FPI-NS composites sharply fall from 323.4 ºC to 256.9 ºC for FPI-8 wt% HPMDA and 247.0 ºC for FPI-8 wt% NS, respectively. By contrast, FPI-DG blends maintain thermal stability well and a T_g of 321.7 ºC for FPI-8 wt% DG is obtained.

(3) (Line 158)



(4) (Line 440) Differential scanning calorimetry (DSC) curves were obtained by a DSC Q2000 (TA Instrument). The samples were first cooled down to 25 ºC with a rate of 10 ºC min^{-1}. After another isothermal stage for 5 min, the DSC curves were recorded by heating the samples up to 450 ºC with a rate of 10 °C min^{-1}. All stages were carried out in nitrogen atmosphere. The data sampling interval is 0.2 s pt^{-1}.

(5) (Line 452) TGA curves were obtained using a Q5000IR (TA instrument) with a heating speed of 10 ºC min^{-1} in nitrogen atmosphere from room temperature to 900 ºC.

(6) (SI)

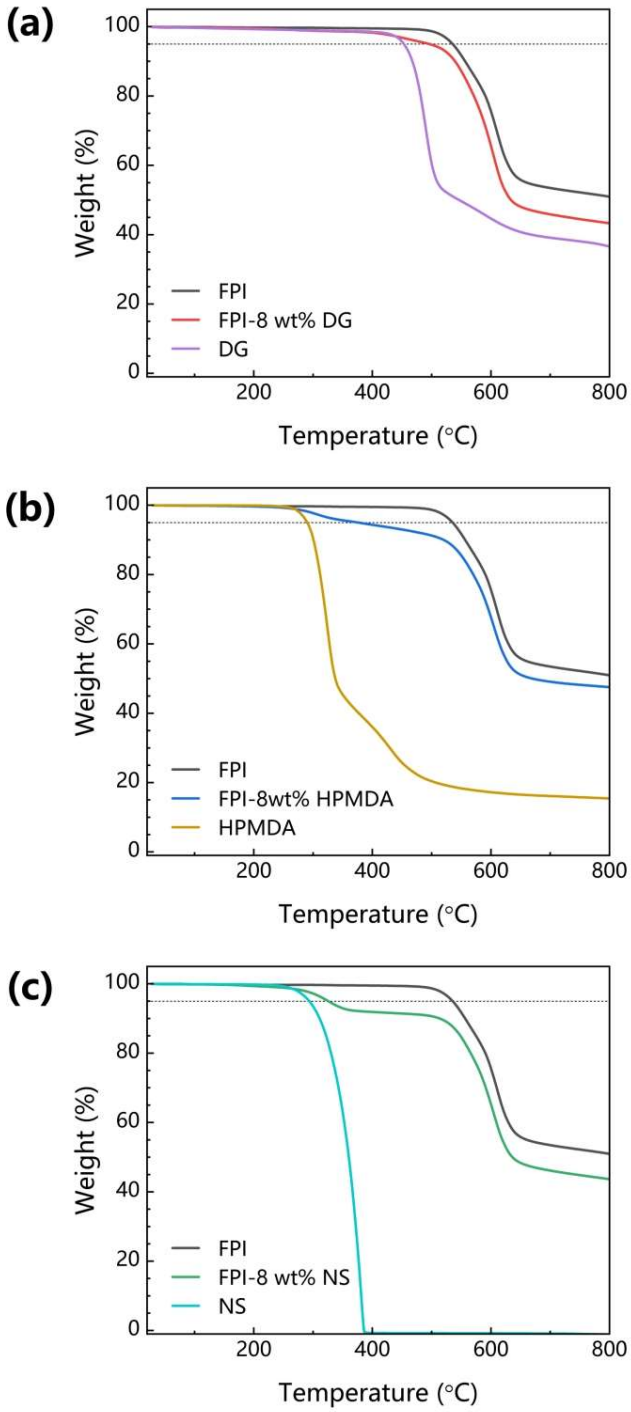


Figure S11. TGA curves of FPI and (a) FPI-8 wt% DG and DG, (b) FPI-8 wt% HPMDA and HPMDA, and (c) FPI-8 wt% NS and NS.

(7) (SI)

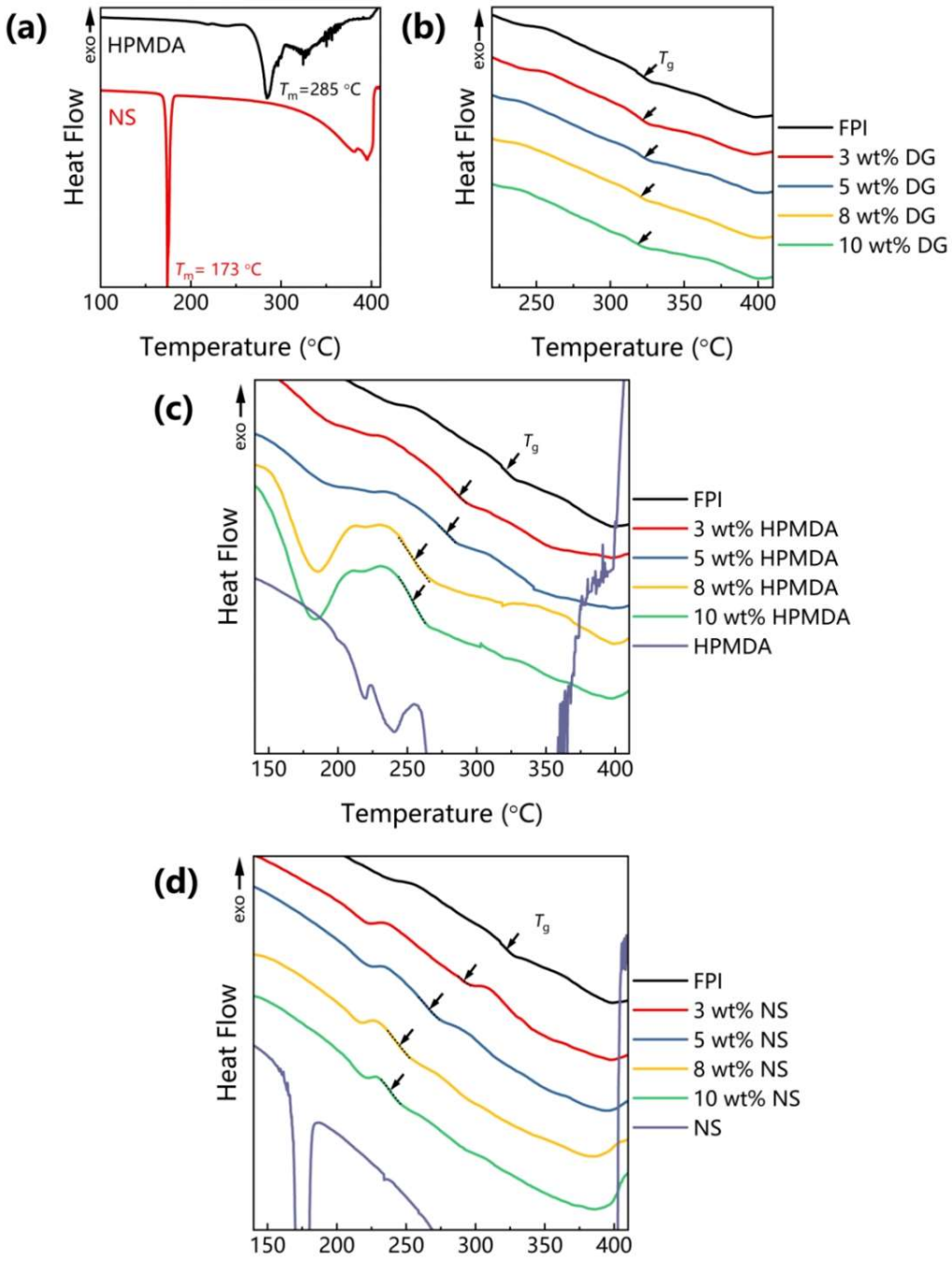


Figure S15. DSC curves of (a) pure HPMDA and NS, (b) FPI-DG, (c) FPI-HPMDA, and (d) FPI-NS.

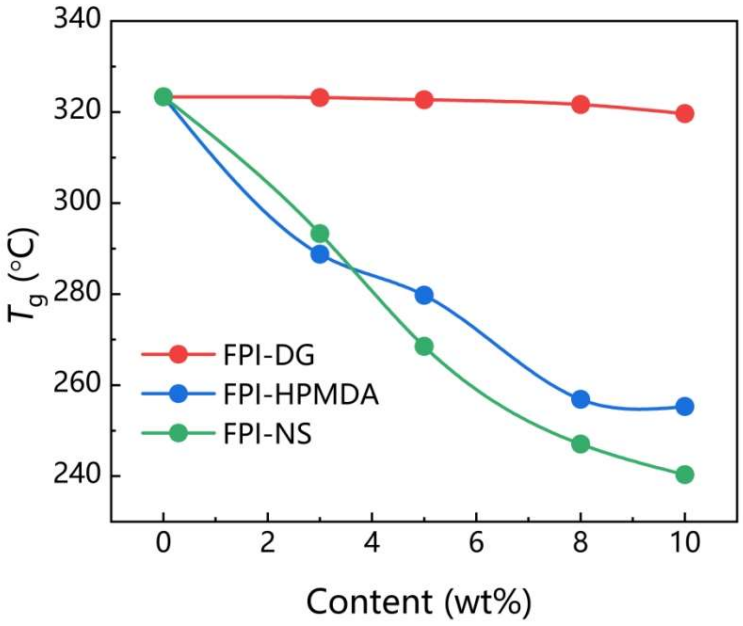


Figure S16. T_g values of FPI-DG, FPI-HPMDA, and FPI-NS.

8) Due the importance of DG, in addition to FTIR spectroscopy (Figure S4), it is required to include proton and carbon NMR analysis of the polymer, as well as the GPC traces from which its Mn, Mw and dispersity were calculated.

Reply: We thank for the valuable suggestions and have added the data in SI.

Revisions: (1) (Line 111) Based on the gel permeation chromatography (GPC) results (Figure S5), the number-average molecular weight of DG reaches 38577 g mol^{-1}, yielding a degree of polymerization of 88, which is close to that of FPI (120, Table S1).

(2) (Line 116) ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of synthesized DG are shown in Figure S7. It can be seen that all peaks can correspond to H or C atoms in certain positions in DG.

(3) (SI)

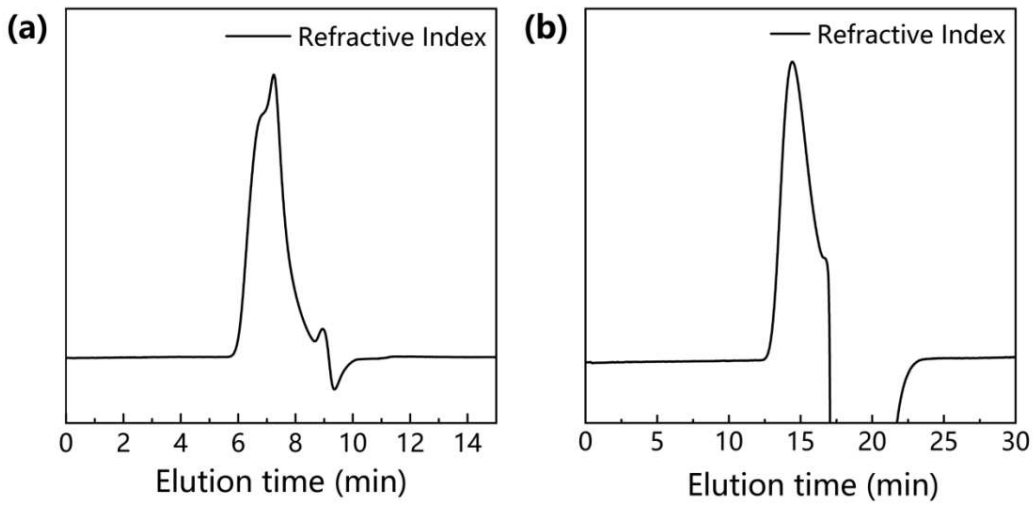


Figure S5. GPC traces of (a) FPI and (b) DG.

(4) (SI)

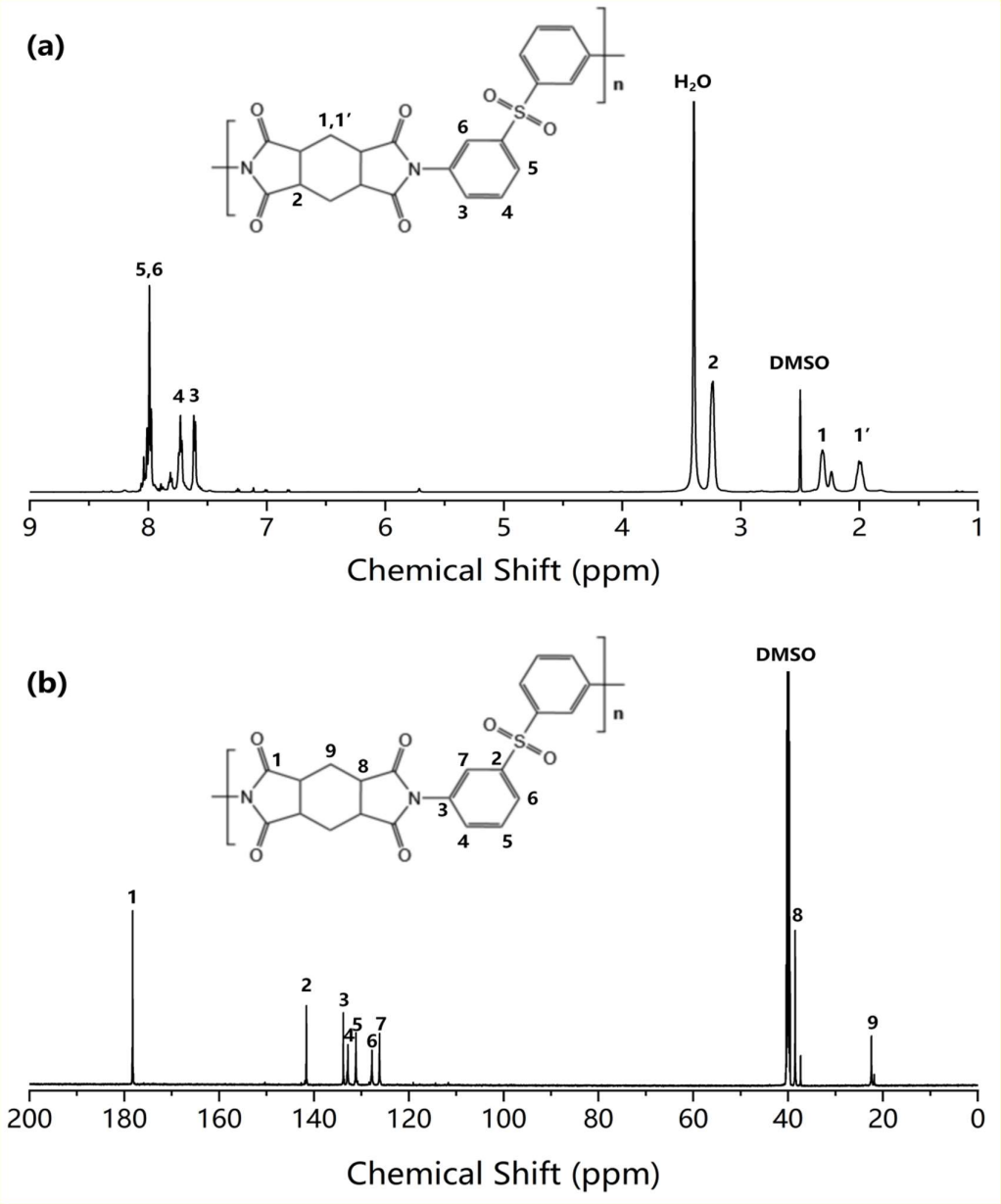


Figure S7. (a) ^{1}H and (b) ^{13}C NMR spectrum of DG.

9) Regarding interchain spacing of composites calculated from XRD results, please consider mentioning the error associated with these calculations and how accurate it is to discuss the notably low-value differences in some cases (< 0.01 nm).

Reply: We thank for the valuable suggestion. We have added the fitting lines in the original XRD results for a clear identification of peak points. The statement about the potential data deviation between fitting results and actual values have also been added in SI.

Revision: (1) (SI)

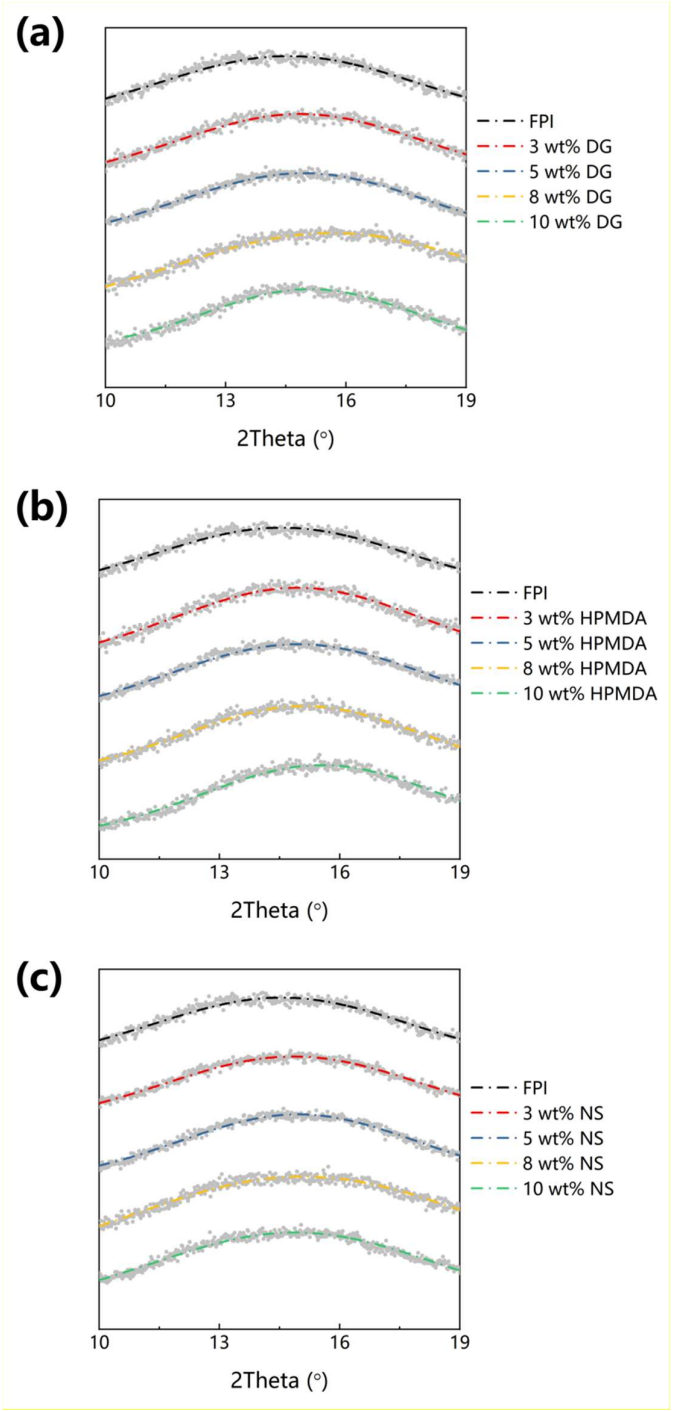


Figure S13. XRD curves of (a) FPI-DG, (b) FPI-HPMDA, and (c) FPI-NS.

(2) (SI) Figure S14. Interchain spacing values of FPI-DG, FPI-HPMDA, and FPI-NS. Considering that the data points were fitted from the XRD curves and the differences between some data points are too small (< 0.01 nm), the size relationships between a few data points may not be very accurate. However, FPI-DG obviously exhibits lower interchain spacing than FPI-HPMDA and FPI-NS, which is the most important and desired result of XRD characterization in this study.

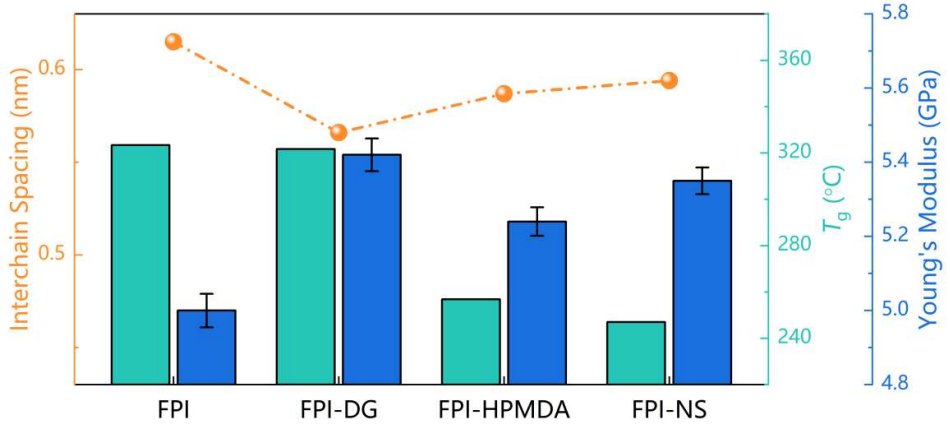
10) In the same line with the above, how many samples were analyzed for each specimen during

mechanical analysis? No error bars were included in Figure 1E for Young's modulus, making the analysis of the values given in lines 136 and 137 difficult.

Reply: We thank the reviewer for the kind remind. 5 specimens were tested for each sample. We have added the error bars and the test parameters as shown in the Revisions. The raw data are shown in the Table below, we will provide it as an individual file after the manuscript is accepted.

	Raw Data					Average Value	Standard deviation
FPI	4.97	4.93	5.02	5.04	5.05	**5.002**	0.045343
FPI-8% DG	5.39	5.42	5.36	5.48	5.46	**5.422**	0.044
FPI-8% HPMDA	5.28	5.21	5.22	5.3	5.21	**5.244**	0.038262
FPI-8% NS	5.39	5.29	5.34	5.38	5.33	**5.346**	0.036111

Revisions: (1)



(2) (Line 443) Young's moduli were measured by a nano-indenter (Keysight Technologies G200) using a diamond indenter with a Triangular pyramid shape (TB26375). The nominal radius of indenter is 20 nm and the indentation depth is 500 nm. 5 samples were tested for each data point. Square polymeric films with the size of 2 cm × 2 cm were used for Young's moduli tests.

11) Line 155: For polymer materials, the current requirements are set to be above 4.0 to be considered a high dielectric constant, and there are some reports that place this value even above 5.0. Therefore, the phrase "a high er of 3.56" is not correct.

Reply: We thank the reviewer for the kind remind. This sentence and other similar content have been revised.

Revisions: (1) (Line 173) For example, an improved ε_r of 3.56 is obtained for FPI-8 wt% NS versus 2.78 for FPI (1 kHz, 25 ºC).

(2) (Line 175) As for the FPI-DG blends, 8 wt% of DG in FPI can induce a ~~high~~ ε_r of 3.36, which is 20% higher than that of FPI.

12) Line 171 it should be Figure 1E instead of 1C

Reply: We thank the reviewer for the kind remind. The 1C there should be replaced by 1D. We have revised the issue.

Revision: (Line 188) giving rise to a big void in the simulation cell as shown in the left inset of Figure 2B and a decreased calculated density of FPI-8 wt% NS as depicted in Figure 1D.

13) Can be related the interchain spacing reported in Figure 1E to the average spacing referred in between lines 180 and 182? I ask this because those trends are not well correlated, creating a mismatch between the experimental and theoretical results.

Reply: We thank the reviewer for the valuable comment. We would like to explain the difference between the tested interchain spacing and statistical average spacing around SO_2 in simulation cells. The interchain spacing is determined from the XRD curves based on Bragg's law ($2d\sin\theta=\lambda$). The value indicates the average distance between adjacent polymer chains. The introduction of DG or small molecules (HPMDA/NS) can both fill the free volume around FPI chains, thus resulting in a lower interchain spacing in FPI-DG, FPI-HPMDA, and FPI-NS. However, the large-molecular-weight DG exhibit much higher intra-/interchain interactions than its monomer components, which resulting in a denser polymer chain packing. Therefore, the interchain spacing of FPI-DG is lower than those of FPI-HPMDA and FPI-NS, which is in line with cohesive energy calculation results in Figure 1D.

The average spacing around SO_2 is determined by measuring the distance between SO_2 group to the nearest atom in adjacent FPI chains. We randomly took 9 SO_2 groups in each simulation cell to calculated the average value and standard deviation as shown below (The data will be also provided individually after the manuscript is accepted).

	Tested points									Average	Standard deviation
FPI-NS	4.776	3.374	3.405	2.439	4.355	4.325	2.859	4.625	3.248	3.72	0.78
FPI-DG	7.767	9.914	3.518	3.959	3.363	4.907	3.258	6.242	4.918	5.32	2.15

Therefore, the average spacing around SO_2 here cannot reflect the overall distribution of polymer chains. And the higher spacing in FPI-DG can be attributed to the non-linear configuration and large molecular weight of DG. Note that NS possess much smaller size and weight than DG, so they may be attracted to FPI chains easily due to the interactions between FPI chains and high polar SO_2 groups, resulting in crowded space around SO_2 groups. On the contrary, DG with large size/weight and non-linear configuration can provide their SO_2 groups with larger surrounding free volume even though other parts of DG may get closer to adjacent FPI chains. According to the reference of Professor Zhu, the reserved free volume is helpful for orientation of SO_2 groups under electric field and higher polarization[R26].

We added the related explanation about above data and added the Professor Zhu's publication into the manuscript.

Revision: (Line 201) thus further confirming that DG chains with non-linear configuration generate more free volume around polar groups due to steric hindrance for promoting polarization[44]. Note that the average spacing here indicates the local free volume around SO_2, but not the average distance between adjacent DG and FPI chains.

14) Regarding the AFM-IR analysis depicted in lines 183 – 189, the mobility of groups understood as their ability to reorient themself under the influence of an external electric field should not be directly associated with the vibration of their chemical bonds. That is the reason why the orientational polarization and the atomic (vibrational) polarization exhibit remarkable differences in terms of contributions.

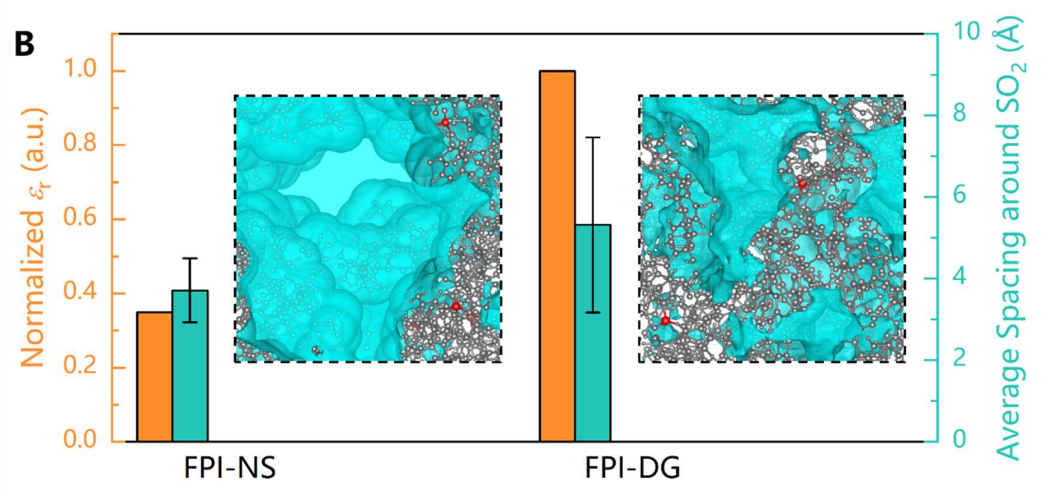
Reply: We thank the reviewer for the valuable comment. We have realized our misunderstanding of the relationships between group mobility and IR absorption intensity of chemical bonds, which are actually at two different levels. According to the publication of Professor Zhu[R27], the vibration of polar chemical bonds in polymers is correlated with the vibrational polarization of them. In this manuscript, the comparable IR absorption intensity of S=O vibration band in FPI-NS and FPI-DG can only suggest the similar contribution of their SO_2 groups to overall vibrational polarization rather than orientational polarization[R3,28]. We have revised the related content and cited the important reference.

Revisions: (1) (Line 207) It is noteworthy that the former contains only about half the quantity of SO_2 groups in the latter, indicating a significantly enhanced contribution to the vibrational polarization of each SO_2 group in FPI-DG blends.

(2) (Line 633) 45 Wei, J. & Zhu, L. Intrinsic polymer dielectrics for high energy density and low loss electric energy storage. *Prog. Polym. Sci.* **106**, 101254, doi:10.1016/j.progpolymsci.2020.101254 (2020).

15) Insets in Figure 2 are unclear, making difficult the analysis of the displayed information.

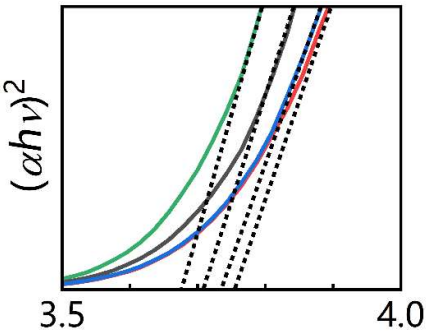
Reply: We thank the reviewer for the kind remind. We have updated the figures as shown below. And it should be noted that the figures in word file are always unclear due to the limited figure size. After the manuscript is accepted, we will upload clear versions as individual files for editing.



16) Considering that the authors were successfully able to calculate the electrical breakdown, why is it relevant to provide and compare Eg values of materials calculated from UV-Vis spectroscopy? Did you use the Taffel model to achieve this? Honestly, I believe that the Eg calculation and the discussion from it is useless in this case. For example, how can you support a rise of Eb from 579.32 MV/m to 784.1 MV/m when the increment of Eg for the same specimens is just 0.04 eV? In this

sense, if authors feel motivated to include Eg in the discussion, it should be calculated using electrochemistry tools.

Reply: We thank the reviewer for the valuable question. We noticed that the UV-Vis spectroscopy is a common method to examine the E_g and insulating properties of capacitive energy storage polymer dielectrics[R29-34]. According to these publications, even though there is a gap between tested optical E_g, simulated E_g and real E_g of dielectrics, the comparison of the optical E_g in single publication still make sense if their test conditions are same. For example, in a study published on Nature[R33], researchers used UV-Vis spectroscopy to compare the optical E_g of poly(N-4-aminophenyl trifluoroethyl-norbornene imide) (PTNI) and poly[N-4-aminophenyl sulfuryl-bis(norbornene pyrrolidine)] (PSBNP), which are 4.67 eV and 3.91 eV, respectively. These data motivate him to copolymerize the two components to enhance the insulating properties and E_b of PSBNP, and an increased E_b of 732 MV m^{-1} were achieved in PSBNP-co-PTNI versus 688 MV m^{-1} of pure PSBNP at 200 ºC. Therefore, we also tested the UV-Vis spectroscopy of FPI, FPI-DG, FPI-HPMDA, FPI-NS to compare their optical E_g. Different from the direct comparison of two pure polymers in above references, 90 wt% of the four dielectrics is FPI, so the difference between their optical E_g should be slight. However, the rank of optical E_g: FPI-DG > FPI-HPMDA > FPI > FPI-NS is right as shown in the partial enlarged Figure of UV-Vis spectroscopy below.



We would like to mention that the optical E_g results are just a piece of evidence, which are combined with other data, such as leakage current and TSDC test, to confirm the enhanced insulating properties hence higher E_b. In addition, the mechanical strengthening also play a role in increasing E_b, which can be evidenced by the improved Young's modulus. We have added the partial enlarged figure in SI for a clear comparison the optical E_g of different dielectrics and mention the potential differences between tested optical E_g and real E_g.

Revisions: (1) (Line 243) Note that even though there may be a difference between tested optical E_g and real E_g, comparison of the four values of same test conditions still makes sense for analyzing the insulating properties of polymer dielectrics[40]. And, since the 92 wt% of these dielectrics is FPI, the difference between their optical E_g should be slight. However, the size relationships of them are clear, which are highlighted in the inset of Figure S24.

(2) (SI)

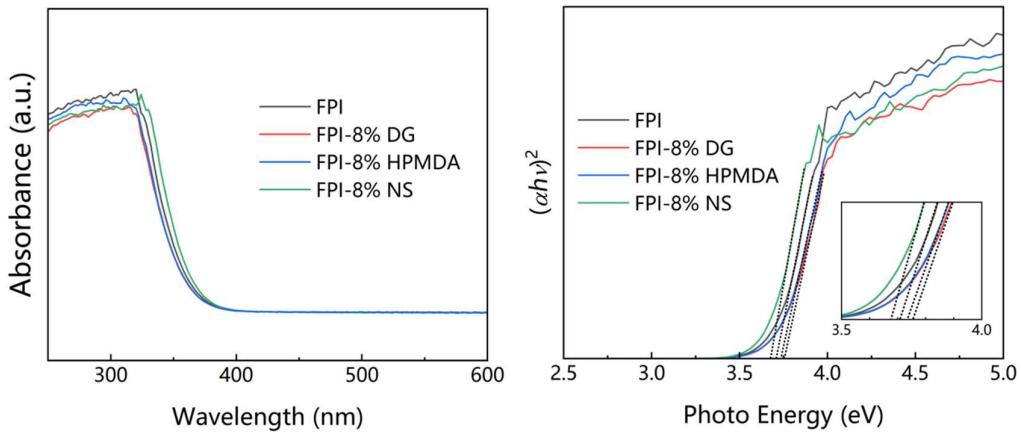


Figure S24. UV-Vis spectra of FPI-8 wt% DG, FPI-8 wt% HPMDA, and FPI-8 wt% NS.

17) I find very interesting the use of TSDC for estimating charge-related phenomena. Can the authors provide a clearer explanation or at least an idea about the noticeable enhanced suppression of charge injection observed for FPI-DG when compared to the other systems? Considering that in all cases, at least 90 % of the material is FPI.

Reply: We thank the reviewer for the valuable question. Firstly, we would like to mention that 8 wt% is actually a high content. Considering DG has similar density to FPI, the volume content of DG should also be ~8 %, which is comparable to many polymer-inorganic composites. As the DG chains are distributed uniformly without aggregations, the surrounding regions affected by DG chains, i.e., interface regions, should be enormous.

The charge injection in a practical dielectric is a complicate process which can be influenced by both the charge injection from electrodes and charge migration within the dielectrics. For example, if the injected electrons are soon trapped in dielectrics, subsequent electrons will be subject to coulomb repulsion from them, which plays a role in suppression charge injections. In this context, we believe the suppression of charge injection in FPI-DG can be attributed to three aspects: high insulating properties, enhanced interaction and good interfacial properties.

The high insulating properties means that DG itself has wide band gap, which can be proved by simulations and characterizations (such as UV-Vis spectroscopy). When high content DG is introduced into FPI, the overall insulating properties will not be deteriorated but enhanced due to wider band gap of DG than FPI. Therefore, the energy barrier of charge injection will rise in FPI-DG.

The enhanced interaction means the DG can improve the cohesive energy density of polymer dielectrics due to their large molecular weight versus small molecules. Therefore, the polymer chains in FPI-DG will form a denser packing at polymer-electrode interface and within the polymers, which facilitates to charge injection blocking. It is also the reason why DG exhibits more remarkable effect on increasing the trap depth and decreasing the trap density of peak 2 than HPMDA and NS as shown in the Revisions.

The good interfacial property is the common advantage of all-organic polymer composites and blends. Compared to the inorganic fillers, such as BN, SiO_2, and Al_2O_3, the organic molecules exhibit smaller size, better flexibility, and structural compatibility with polymers. As a result, the contact between polymer and introduced organic components will be robust with minimal defects

such as voids and cracks, which cannot be achieved in polymer-inorganic composites. As a comparison, in polymer-inorganic composites, the interfaces regions with numerous defects near polymer-electrode interface will act as the "weak point" of charge injections with decreased injection barrier.

To compare the charge injection suppression of FPI-DG blends and FPI-inorganic composites, we prepared FPI-BN composites (the optimal BN content is determined by high temperature E_b to be 3 wt%) as shown in the Revisions. We tested the TSDC curve of FPI-3 wt% BN and compare the trap parameters as shown in the Revisions. As seen, even though BN introduces a new peak (peak 3) due to its wide band gap, it increases the trap density and decreases the trap depth of peak 2, which means more injected charges and lower injection barrier. Considering the similar band gap of BN (5.72 eV) and DG (5.31 eV), the deterioration of charge blocking of BN can be attributed to the poor insulating properties at interfaces.

In addition, to prove the universality of charge injection suppression of DG, we tested the TSDC curves of PEI, SPI, PEI-8 wt% DG, and SPI-8 wt% DG and extracted trap parameters as shown in the Revisions. As seen, besides the newly induced peak 3, DG increases the trap depth and decreases the trap density of both polymers, confirming its great effect on charge injection suppression.

We have added the data about FPI-BN, PEI, SPI, PEI-8 wt% DG, and SPI-8 wt% DG into manuscript and added the discussion about the charge suppression of DG.

Revisions: (1) (Line 260) Besides, peak 2 of FPI-DG is also observed at higher temperature and exhibits smaller area (220.47 ºC and 0.468 × 10^{20} m^{-3}) than FPI (199.12 ºC and 0.58 × 10^{20} m^{-3}), FPI-HPMDA (215.38 ºC and 0.504 × 10^{20} m^{-3}), and FPI-NS (184.38 ºC and 0.958 × 10^{20} m^{-3}), indicating better charge injection suppression of DG with enhanced intra-/interchain interactions and wide band gap. To highlight the advantages of organic DG over inorganic components, we prepared FPI-boron nitride (BN, has a similar band gap of 5.72 eV) composites with an optimal content of 3 wt% (determined by the high temperature E_b, Figure S27). The TSDC curve and trap parameters of FPI-3 wt% BN can be seen in Figure S26 and Table S3. Even though BN introduces new traps with a temperature location of 209.18 ºC (peak 3), its peak 2 exhibits a lower temperature (193.69 ºC) and larger area (1.164 × 10^{20} m^{-3}) than pure FPI, which can be attributed to the polymer-inorganic interface with dense defects and poor insulating properties.

(2) (Line 313) The TSDC curves with the trap parameters of PEI, SPI, and their blends are shown in Figure S33 and Table S4. As seen, the introduction of DG induces a new peak (peak 3) with a high temperature of 208.77 ºC for SPI-8 wt% DG and 212.04 ºC for PEI-8 wt% DG, respectively. Moreover, the suppressed charge injections can be observed both blends according to higher temperature and lower area of peak 2.

(3) (SI)

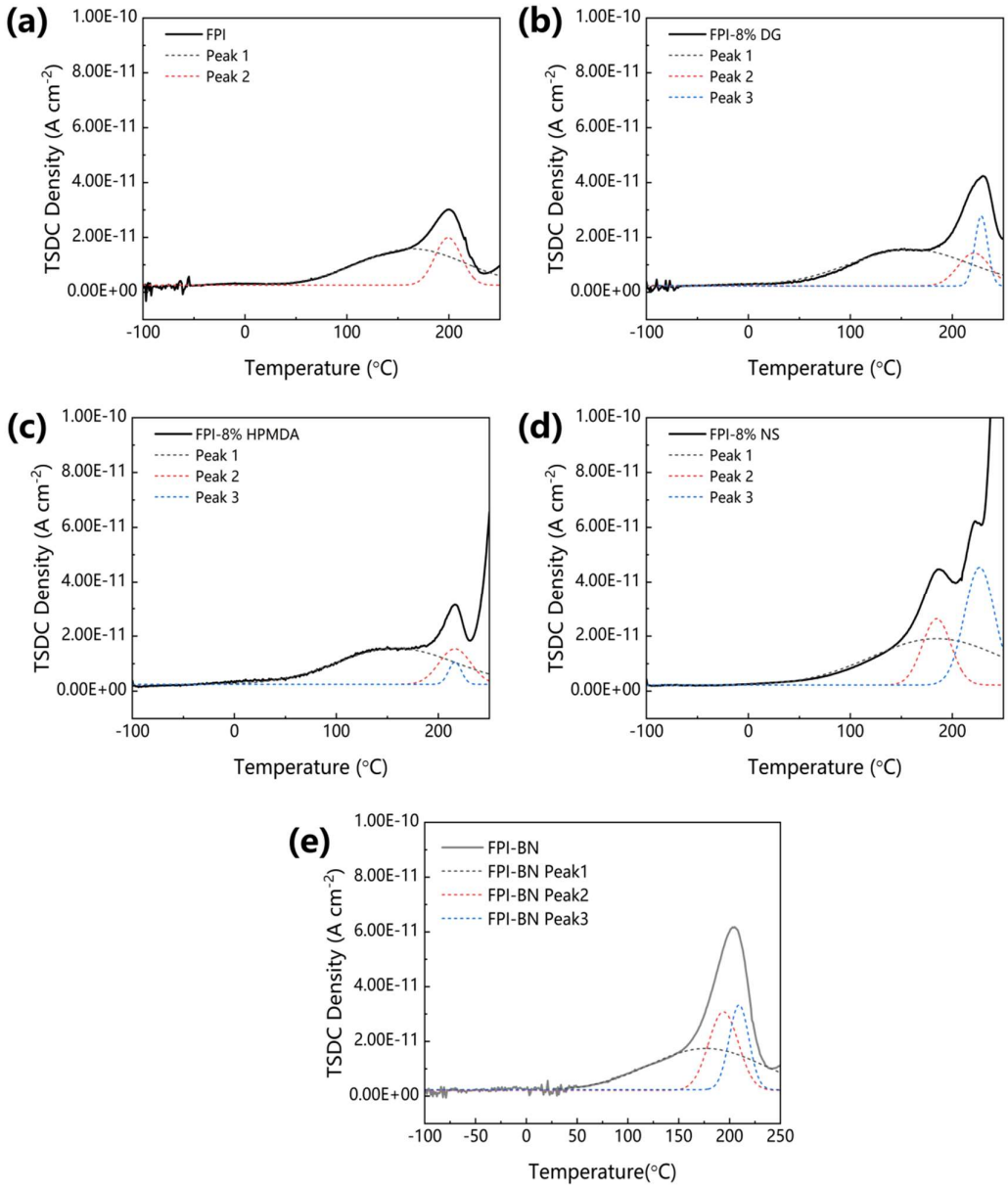


Figure S26. TSDC curves of (a) FPI, (b) FPI-8 wt% DG, (c) FPI-8 wt% HPMDA, and (d) FPI-8 wt% NS, (e) FPI-3 wt% BN.

Table S3. Trap depth and trap density of FPI and FPI-based dielectrics.

	Trap depth of Peak 2 (°C)	**Trap Density of Peak 2 (10^{20} m^{-3})**	**Trap depth of Peak 3 (°C)**
FPI	199.12	0.58	
FPI-8% DG	220.47	0.468	228.09
FPI-8% HPMDA	215.38	0.504	216.28

FPI-8% NS	184.38	0.958	226.50
FPI-3% BN	193.69	1.164	209.18

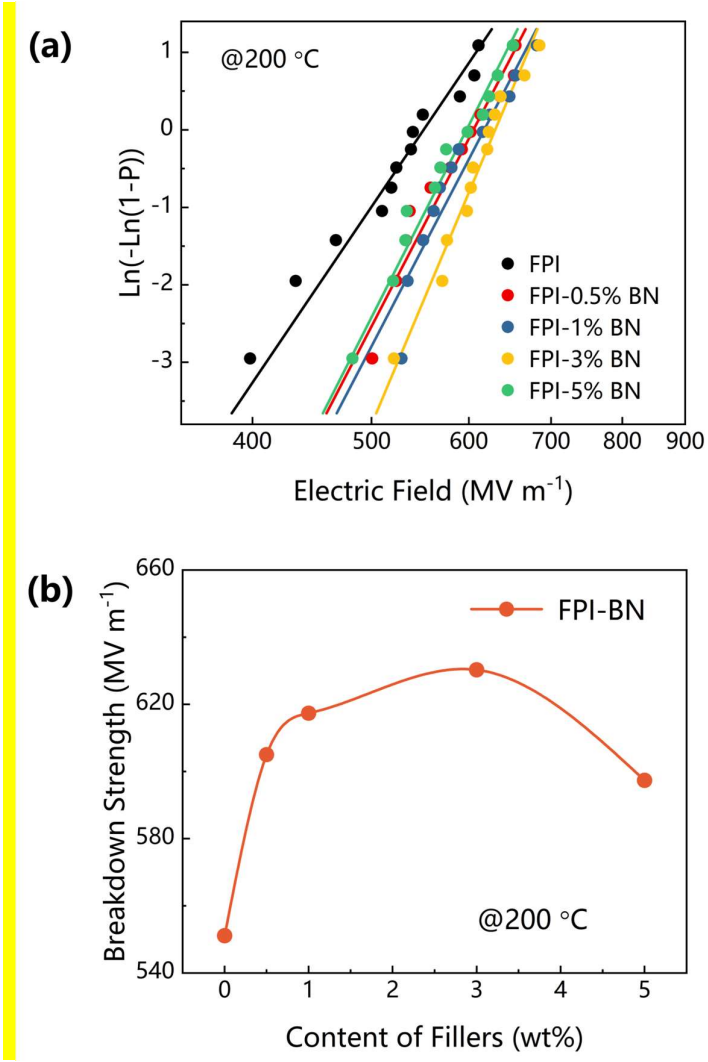


Figure S27. (a) Breakdown electric field Weibull distribution of FPI-BN composites with different filler content at 200 °C. (b) Breakdown strength of FPI-BN composites versus filler content at 200 °C.

(4) (SI)

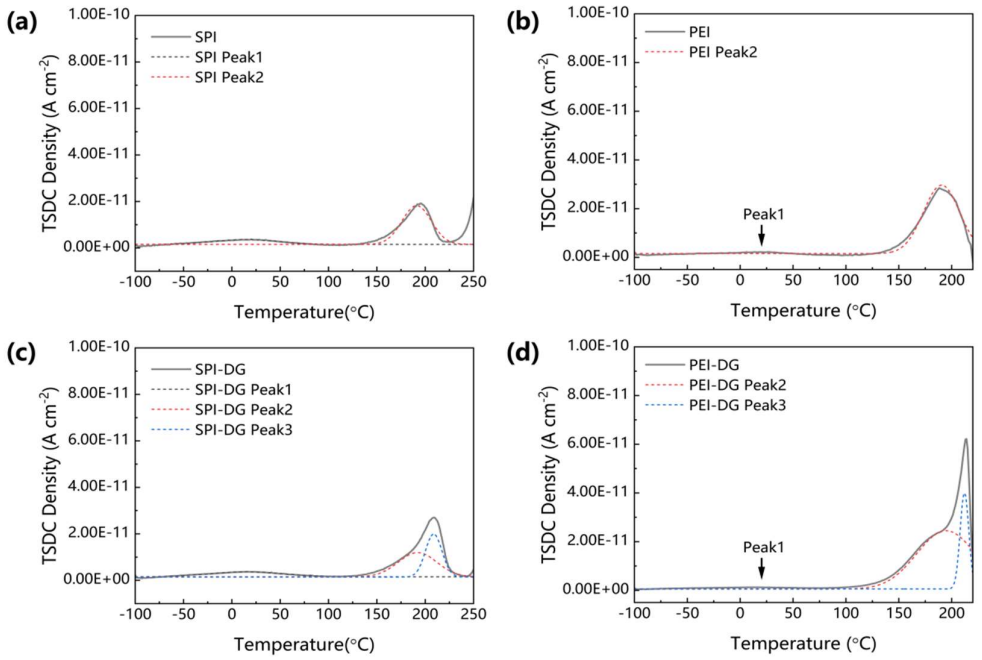


Figure S33. TSDC curves of (a) SPI, (b) PEI, (c) SPI-8 wt% DG, and (d) PEI-8 wt% DG.

Table S4 Trap parameters of TSDC curves of SPI, PEI, and their blends.

	Trap depth of Peak 2 (°C)	**Trap Density of Peak 2 (10^{20} m^{-3})**	**Trap depth of Peak 3 (°C)**
SPI	191.12	0.607	-
SPI-8% DG	192.09	0.499	208.77
PEI	190.21	1.284	-
PEI-8% DG	194.65	1.238	212.04

18) I consider the sections related to energy storage performance, reliability, and scalability are the strongest in this work; the results shown in these sections are the ones that demonstrate the novelty as well as the impact that these specimens could exert on the field. Both sections are well-organized and well-written, accompanied by a proper level of discussions extracted from the employed characterization techniques (contrary to the previous sections). The observed values for the energy densities are above those usually found in the literature, and the same for the efficiencies, outperforming very recent reports such as Journal of Materials Chemistry A, 2023, 11(37), 20021-20030. Moreover, these results gain relevance when considered they were measured at temperatures as high as 200 °C, showing the real applicability of the system. Figure 4 summarizes the high impact of the achieved results. Thanks to these two sections, I believe that the manuscript deserves a second chance to be corrected and improved, instead of being rejected, to find a suitable version to be considered for publication.

Reply: We thank the reviewer for the positive comment. We have read the mentioned reference and found it very impressive and instructive. We added the reference into our manuscript as shown below.

Revision: (1) (Line 28) Polymer dielectrics are considered promising candidate as energy storage media in electrostatic capacitors, which play critical roles in power electrical systems involving elevated temperatures, such as hybrid electric vehicles, oil & gas exploration, aircraft, and geothermal facilities[1-6].

(2) (Line 527) 6 Duan, Y. *et al.* High-temperature resistant polyetherimides containing a twisted spirane structure for capacitive energy storage. *J. Mater. Chem. A* **11**, 20021-20030, doi:10.1039/D3TA02534A (2023).

Experimental section

19) Regarding the synthesis of DG: Because of the importance of the DG polymer in the confection of the final material, it is mandatory to present all the details related to its synthesis, aiming to facilitate its reproducibility. In this sense, please provide the purity degree of reactants involved, the amount of reactants (HPMDA and NS), isoquinoline and solvent during the synthesis.

Reply: We thank the reviewer for the kind remind. We have added related data.

Revision: (Line 407) The bifunctional DG was prepared through a one-step method, involving the dissolution of equal molar amounts of HPMDA (10 mmol, 2.242 g, 98%) and NS (10 mmol, 2.483 g, 98%) in NMP (15 ml, super dry). The mixture was then subjected to reaction with isoquinoline (5 mmol, 0.646g, 98%) as an imidization catalyst under a nitrogen atmosphere.

20) Regarding the preparation of films: In line 370, it is mentioned that a uniform dispersion must be obtained, while in line 371, it is indicated as an "as-prepared solution." Is DG soluble in the mixture?

Reply: We thank the reviewer for the valuable question. The DG, HPMD, and NS can all dissolve in NMP and DMF. We have revised the related content.

Revision: (Line 377) As for polymer composite and blend samples, a certain amount of DG/HPMDA/NS was added into the solution and the final clear solution were obtained after vigorous stirring at 60 °C for 4 h.

21) Also, are solvents completely removed during these heating processes? Considering that even traces of them can notably modify the dielectric performance of materials. Personally, I have struggled a lot trying to remove DMF, NMP, DMSO and other high boiling point solvents from these types of materials. By re-dissolving the material and carrying out an H-NMR analysis of the final material would help to demonstrate the purity of the material.

Reply: We thank the reviewer for the valuable question. We tested the ^{1}H-NMR spectrum of FPI-8 wt% DG, PEI-8 wt% DG, and SPI-8 wt% DG as shown in Revisions, and the characteristics peaks of DG have been highlighted. The FPI-8 wt% DG was cast using DMF, which has the strongest peak around 2.9 ppm. As seen, there is no obvious peak around 2.9 ppm. The solvent NMP for PEI-8 wt% DG and SPI-8 wt% DG possesses the peak of 2.03, 2.37, 2.85 (the strongest), and 3.39 ppm. And the spectra of blends show no obvious peak at those positions. Therefore, the residual solvent is minimal in our polymer blends.

Revisions: (1) (Line 125) To examine the residual solvent of polymer blends, we tested the ^{1}H NMR spectrum as shown in Figure S10. As seen, no obvious peak corresponding to DMF (~2.9 ppm) or NMP (~2.85 ppm) is observed, indicating high purity of the dielectrics.

(2) (SI)

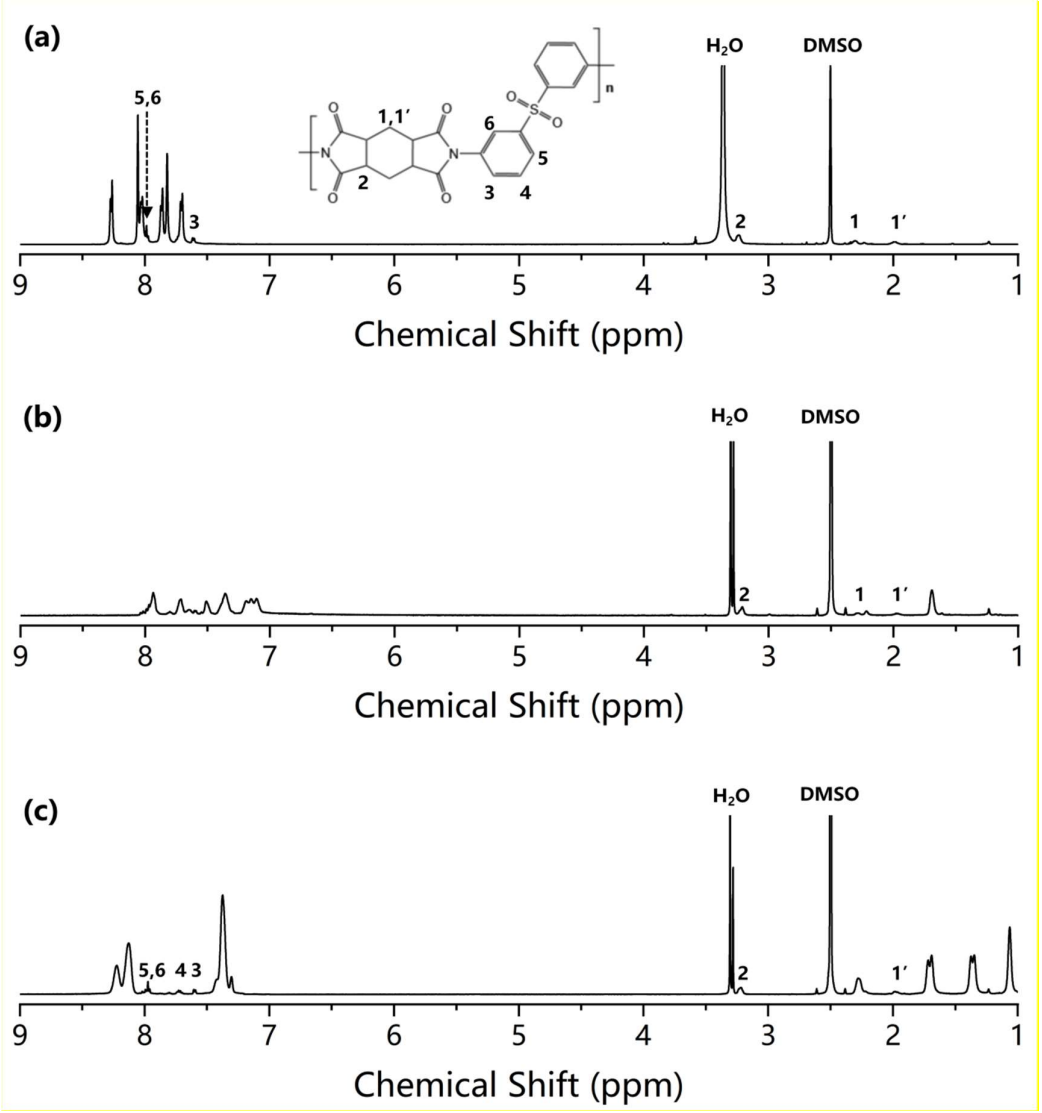


Figure S10. ^{1}H NMR spectrum of (a) FPI-8 wt% DG, (b) PEI-8 wt% DG (c) SPI-8 wt% DG. The characteristic peaks of DG that do not overlap with the peaks of other polymers are marked. The preparation of FPI-DG involves DMF, and the preparation of PEI-DG and SPI-DG involves NMP. The characteristic peaks of DMF include 2.9 (the strongest) and 8.0 ppm. The characteristic peaks of NMP include 2.03, 2.37, 2.85 (the strongest), and 3.39 ppm. As seen, there is no obvious peak at these positions. The two small peaks symmetrical along the DMSO peaks in (b) and (c) are the satellite peaks, which is induced by the couplings of ^{13}C to H atoms.

22) The characterization section must be improved by detailing every aspect of the technique employed. For example, for GPC analysis, which solvent was used as eluent? Also indicate the temperature of the measurement, calibration curve information, how many and what type of columns were used. In a similar manner, for DSC, XPS, AFM (in tapping mode?). What were the dimensions of the employed samples during Young's moduli determination? Did you have access to thermogravimetric analysis? If so, it would help to ensure that no degradation is taking place

during the heating process in DSC measurements. Also, as mentioned in comment 7), include a complete description of the DSC program used.

Reply: We thank the reviewer for the kind suggestion. We have added the details of all characterizations. We would like to mention that XPS characterization were not used but UV-Vis spectroscopy and detailed discussion about the TGA tests can be seen in Reply to comment (7).

Revision: (Line 429) SEM cross-sectional micromorphology of films was characterized by a ZEISS MWRLIN compact. TEM images were acquired with a JEOL JEM2010 electron microscope. AFM topology images were obtained with a commercial scanning probe microscope (Asylum Research MFP-3D) in the tapping mode. Silicon cantilevers with a conducting Pt/Ir coating layer (PPP-EFM, Nanosensors) were used. The relative molecular weight and molecular-weight distribution were determined by GPC Agilent PL-GPC50 with differential refractive index (RI) detector. One and two mixed-C columns (Plgel mixed, 5 μm pore size, 300 mm × 7.5 mm) were utilized for FPI and DG, respectively. GPC measurements were performed at 40 °C using HPLC grade DMF as the eluent with a flow rate of 1.0 ml min^{-1}. Polystyrene standards were used for conventional calibration. XRD patterns were measured by a Rigaku D/max-2550 in a 2theta range of 5-30 º. DSC curves were obtained by a DSC Q2000 (TA Instrument). The samples were first cooled down to 25 ºC with a rate of 10 ºC min^{-1}. After an isothermal stage for 5 min, the DSC curves were recorded by heating the samples up to 450 ºC with a rate of 10 °C min^{-1}. All stages were carried out in nitrogen atmosphere. The data sampling interval is 0.2 s pt^{-1}. Young's moduli were measured by a nano-indenter (Keysight Technologies G200) using a diamond indenter with a Triangular pyramid shape (TB26375). The nominal radius of indenter is 20 nm and the indentation depth is 500 nm. 5 samples were tested for each data point. Square polymeric films with the size of 2 cm × 2 cm were used for Young's moduli tests. AFM-IR measurements were implemented using a NanoIR3 (Bruker, USA). Contact-mode Si tips coated with gold of spring constant 0.07-0.4 N m^{-1} (PR-EX-NIR2-10, radius ≈ 20 nm) were used. UV-Vis spectroscopy were carried out using a Lambda 1050+ instrument (PerkinElmer) with a 150 mm-diameter sphere and slit width of 2 nm. The data is recorded in the absorption mode with a wavelength of 250-800 nm and a data interval of 2 nm. TGA curves were obtained using a Q5000IR (TA instrument) with a heating speed of 10 ºC min^{-1} in nitrogen atmosphere from room temperature to 900 ºC. FT-IR spectra were obtained in a Thermo. Nicolt Is50 FT-IR spectrometer over a wavenumber range of 450-4000 cm^{-1}. NMR spectra were tested using a Quantum-I^{Plus} 600-2 instrument. The test frequency for proton and carbon NMR are 600 MHz and 150 MHz, respectively. The DMSO-d_6 were used for solvents.

Conclusion section

23) Remove terms associated with "assembled" and "composite", also in the rest of the manuscript.

24) Also, lines 340-342, small molecules are mentioned again when DG is NOT small at all. Please, re-write this section considering all the above mentioned comments.

Reply: We thank the reviewer for the valuable suggestion. Just as the Reply to comment (1), we have realized the misusing of term "assembled", "composite", "dipolar glass filler" and so on. We have re-write the whole conclusion section as shown below.

Revision: (Line 376) We synthesized a bifunctional DG polymer through condensation polymerization of two small molecules, i.e., HPMDA with wide E_g and NS with high μ, and developed a polymer-DG blend dielectric with a well-maintained thermal stability in wide temperature range. The DG has the large molecular weight over 30000 g mol^{-1} to guarantee the

structural stability of overall dielectrics at elevated temperatures which can be proved by the maintained cohesive energy density, T_g, and improved density in polymer-DG blends. Besides, the HPMDA and NS in DG act as functional components to boost the E_b and ε_r of polymers simultaneously. More notably, the non-linear configuration of DG further enhances these two effects through mechanically strengthening the polymer, trapping charges and modulating the free volume around polar groups. As a result, the FPI-8 wt% DG blend achieves an ultrahigh U_{d90} of 8.34 J cm^{-3} at 150 ºC and 6.21 J cm^{-3} at 200 ºC, which surpass most of the reported polymer-based dielectrics. Furthermore, the FPI-8 wt% DG exhibits stable performances during the long charge-discharge cycling of 50000 cycles under the electric field as high as 600 MV m^{-1} at 200 ºC and potential in large scale manufacturing. This work demonstrates the remarkable comprehensive improvement of the bifunctional DG on high temperature capacitive energy storage properties of polymer dielectrics, and indicates a polymer blend strategy to develop high performance polymer-based dielectrics.

Reviewer #4 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts

Reply: We thank the reviewer for the effort to improve the manuscript. The replies and revisions of all comments can be found above.

Reference

R1 Liu, Y. *et al.* Chirality-induced relaxor properties in ferroelectric polymers. *Nat. Mater.* **19**, 1169-1174 (2020).

R2 Chen, X. *et al.* Interfacial origin of dielectric constant enhancement in high-temperature polymer dilute nanocomposites. *Appl. Phys. Lett.* **122**, 212901 (2023).

R3 Zhu, L. *et al.* Crosslinked polyetherimide nanocomposites with superior energy storage achieved via trace Al2O3 nanoparticles. *Compos. Sci. Technol.* **223**, 109421 (2022).

R4 Zhu, W. *et al.* AFM-IR study of interfacial nanostructures in high-temperature dilute nanocomposites. *Appl. Phys. Lett.* **124**, 162901 (2024).

R5 Ajayan, P. M., Schadler, L. S. & Braun, P. V. *Nanocomposite Science and Technology*, (Wiley-VCH GmbH & Co. KGaA, 2004).

R6 Li, H. *et al.* Dielectric polymers for high-temperature capacitive energy storage. *Chem. Soc. Rev.* **50**, 6369-6400 (2021).

R7 Tan, D., Zhang, L., Chen, Q. & Irwin, P. High-Temperature Capacitor Polymer Films. *J. Electron. Mater.* **43**, 4569-4575 (2014).

R8 Tanaka, T., Kozako, M., Fuse, N. & Ohki, Y. Proposal of a multi-core model for polymer nanocomposite dielectrics. *IEEE Trans. Dielectr. Electr. Insul.* **12**, 669-681 (2005).

R9 Lewis, T. J. Interfaces are the dominant feature of dielectrics at the nanometric level. *IEEE Trans. Dielectr. Electr. Insul.* **11**, 739-753 (2004).

R10 Rahimabady, M., Mirshekarloo, M. S., Yao, K. & Lu, L. Dielectric behaviors and high energy storage density of nanocomposites with core–shell BaTiO3@TiO2 in poly(vinylidene fluoride-hexafluoropropylene). *Phys. Chem. Chem. Phys.* **15**, 16242-16248 (2013).

R11 Yang, J. *et al.* Achieving excellent dielectric performance in polymer composites with ultralow filler loadings via constructing hollow-structured filler frameworks. *Compos. Part A Appl. Sci. Manuf.* **131**, 105814 (2020).

R12 Zhang, Y. *et al.* Excellent dielectric properties of anisotropic polymer composites filled with parallel aligned zinc flakes. *Appl. Phys. Lett.* **101**, 192904 (2012).

R13 Vella, N. & Toureille, A. Space charge behaviour of different PEI observed by the coupling of thermal step method and TSDC method. *IEEE Conference on Electrical Insulation and Dielectric Phenomena* **1**, 84-87 (1997).

R14 Ren, L. *et al.* High-Temperature High-Energy-Density Dielectric Polymer Nanocomposites Utilizing Inorganic Core-Shell Nanostructured Nanofillers. *Adv. Energy Mater.* **11**, 2101297 (2021).

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REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed my concerns point-by-point in the response letter, and this paper is well organized and logical now. So it is suitable to be published in your magazine.

Reviewer #3 (Remarks to the Author):

The authors have thoroughly addressed my comments, questions, and suggestions, and the manuscript, in its revised version, has improved notably. Thus, I would consider the present work acceptable for publication. Congratulations to the authors for their outstanding work.