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High strength, stable and self-healing copolyimide for defects induced by mechanical and electrical damages

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Self-healing of damage is a common phenomenon in organisms but is hardly ever encountered in rigid polymer materials. For next-generation electricals and electronics, it is crucial to accurately mimic organisms to detect and heal mechanical/electrical damage. Herein, disulfide bond exchange is designed to introduce the self-healing ability in a copolymerized polyimide (copolyimide). A copolyimide insulation film with two diamine monomers is successfully prepared, which also possesses good self-healing ability after being mechanical/electrical damaged. Furthermore, the self-healing copolyimide film still maintains its good Young's modulus (*E*) >4 GPa, high thermal stability with glass transition temperature (*Tg*) >190 oC, and excellent insulation property with breakdown strength (*Eb*) >300 kVmm−1. The combination of the simple copolymerization and unique self-healing ability is suitable for high *Tg* polyimide to make this ideal method for insulation field.

**Keywords:** disulfide bond, self-healing, mechanical/electrical damage, polyimide

Introduction

The polyimide with high thermal stability, stable chemical resistance, and excellent insulation properties has been widely applied in coatings, adhesives, insulation and packaging materials for electrical appliances, etc.1-5 Under the effect of long-term external stimulation such as mechanical, electrical and thermal stresses, fatigue defects may gradually develop inside the polyimide, such as mechanical cracks or electrical trees.6-9 Moreover, these defects will develop into holes and cracks on the surface of polyimide, and eventually lead to catastrophic failure and serious accidents of the equipment.10-12 However, this type of defect damage is often unavoidable during the operation of mechanical devices. Hence, it is challenging to circumvent this issue. Self-healing polyimides can solve the problems caused by mechanical/electrical damage. Meanwhile, it can also improve the reliability and service life of materials. Therefore, the field of self-healing has aroused the extensive research interest of researchers in past few years. Nevertheless, it is extremely difficult to realize the self-healing of the thermosetting polyimide due to its high thermal stability and chemical resistance.

Most current self-healing polymers mainly target soft materials after mechanical damage, such as hydrogel and elastomer.13-17 Wang et al.18 have developed a polyacylsemicarbazide elastomer covalently cross-linked by a novel type of dynamic. The elastomer exhibits a high modulus and self-healing/recycling capability due to the reversible properties of the dynamic acylsemicarbazide groups. The different groups composed of different dihydrazides are introduced into the polymer can dramatically tune the mechanical, self-healing and reprocessing properties. However, the self-healing of thermosetting polymers (polyimide, epoxy resin and poly aryl ether ketone, etc.) after mechanical and electrical damage is much less investigated. In order to solve the self-healing problem of resin after electrical damage as much as possible, He et al.19 studied that the self-healing of electrical damage in thermosetting polymers (i.e., epoxy resins) is realized by microcapsule method based on anionic polymerization. The epoxy group was modified by 2-ethyl-4-methylimidazole to initiate the anionic polymerization of healing agent, so as to repair the electrical tree channel. The results show that the electrical tree channel in the self-healing epoxy resin can be reconstructed after contacting and breaking with the microcapsule, and its dielectric properties are completely restored. However, the process of self-healing by relying on external substances is complex, which is difficult to achieve in the polyimide system with higher thermal stability.

Moreover, aiming at the self-healing problem of polyimide-polymer after mechanical damage. Lee et al.20 blended traditional polyurethane with functional polyimide to prepare a self-healing polymer system with high mechanical properties. The outstanding self-healing and mechanical properties are attributed to the unique intermolecular networks, which is resulted from the strong supramolecular interactions between urethane groups in polyurethane and imide groups in polyimide. Sometimes, this blending technology can solve the problem of the decline of mechanical properties of soft materials and the problem of the inability of thermosetting polymers to self-healing under certain conditions. However, there are great characteristic differences among the selected blend monomers, which will greatly reduce the comprehensive properties of the prepared materials. Therefore, it is extremely significant to design and synthesize polyimide materials with self-healing ability in the intrinsic structure. Just recently, Han and Jung et al.21 developed a CPI with self-healing function based on the simple process of copolymerization, which can quickly and easily restore transparency and any damage caused by external stress. A little unfortunately, the glass transition temperature of the film was reduced so much that it cannot adapt to the conditions of high temperature and high electric field in the field of insulation.

In this work, we report the contrast between monomer containing a fully reversible group and a partially reversible group molecular state in high thermal stability and mechanically robust polyimide for the self-healing of internal and external defects. Meanwhile, a copolyimide film with excellent insulation, mechanical and self-healing properties was synthesized, which is enabled by the coexistence of reversible groups and flexible chain segments in the molecular structure. Different from traditional polyimide, diamines with dynamic covalent disulfide bond and ether bond are selected to copolymerize with dianhydride to prepare insulating film. The reversibility of dynamic covalent disulfide bond promotes the self-healing of thin films after mechanical and electrical damage. Causally, the damages can be self-healed through the reaction of disulfide bonds in the dynamic chain with the molecular chain disulfide bond radicals generated during the damage at a certain pressure and temperature. The flexible chain segment in the diamine monomer provides the flexibility of the film and adjusts the mechanical and insulating properties. We anticipate that this self-healing method by using the copolymerization of simple disulfide bonds and flexible chain segments can be extended to a broad spectrum of commercial polyimides.

Results and Discussion

Structure and characteristics of disulfide bond and CPI film

Generally, self-healing ability is contradictory to mechanical robustness and high insulation strength.22,23 Since the self-healing process requires the material to have high molecular chain mobility and large free volume, which reduces the mechanical properties and insulation strength in turn.24,25 This study started from the search of monomers containing special functional groups, including disulfide bonds, flexible molecular segments and polyphenyl ring structures, which can provide CPI good healing and high comprehensive properties. As shown in Fig. 1a, the 4-Aminophenyl disulfide (APD) containing disulfide bond was selected and polymerized with 4,4'-(4,4'-isopropylidenediphenoxy) diphthalic anhydride (BPADA) to prepare polyimide film. Fig. S1 (ESI) shows the synthetic process and reaction conditions of PI precursor and PI. Moreover, the film can self-healing after mechanical/electrical damage, because the disulfide bonds can convert each other under a certain pressure and temperature (about 20 kPa and 200 oC). In the early stage of the experiment, the films (APD+BPADA) could not heal well under simple self-healing conditions (Only heated to *Tg*+30 oC),26 as shown in Fig. S2a (ESI). Moreover, try to apply a pressure of 40 kPa to the films at this temperature,27 and there was weak melting on the film surface (Fig. S2b, ESI). Therefore, this self-healing condition has been determined in order to improve the self-healing efficiency of the film on the basis of ensuring the good morphology. However, the introduction of dynamic bond leads to the decline of thermal and insulating properties of the film. In order to obtain concurrently decent mechanical robustness, insulation property and healing ability, a self-healing copolyimide with disulfide bond exchange function is designed, as shown in Fig. 1b, the 1,3-bis(4'-Aminophenoxyl) benzene (BAPB) was introduced into the system to prepare copolyimide films (Fig. S3, ESI). Moreover, the synthesis process and conditions of PI and CPI films are shown in Fig. S4 (ESI). As a result of the BAPB has more benzene ring structure, it is easy to form mutual π-π conjugate structure when the molecular chains are stacked with each other. Moreover, the structure is more conducive to the overall improvement of mechanical robustness and insulation property of the CPI film. During this period, two functional diamine monomers are the key to realize the self-healing of CPI film, and the exchange of disulfide bonds is triggered by pressure and heat.

In order to research the appropriate proportion of two diamine monomers to meet the requirement of ensuring good self-healing ability and high insulation strength simultaneously. The ratio of APD to BAPB is regulated in a wide range in the synthesis of CPI. The specific composition details are shown in Table S1 (ESI). Fig. S5a (ESI) shows the FT-IR spectra of the CPI film with diamine monomers in different proportions. The FT-IR of CPI films exhibit similar patterns. For example, the asymmetric and symmetric vibrations of −C=O groups at 1779, 1723 cm−1 and the stretching vibration band of −C−N−C at 1370 cm−1, respectively, which indicates that the CPI films are prepared successfully and retain the same chemical structure. Moreover, the thermal stability and mechanical properties of the CPI films are assessed by *Tg* and tensile strength (*σt*) as exhibited in Fig. S5b-S5c (ESI). Fig. S5b (ESI) clearly reveals that the different CPI films have high *Tg* ~190 oC. Furthermore, the *Tg* of the CPI decreases slightly with the increase of BAPB ratio in the process of synthesizing the film. The introduction of BAPB increases the flexibility of polymer segments, which makes the molecular chain of CPI easier to rotate. Moreover, the easily rotating molecular chain will cause the decrease of *Tg*.28,29 However, it can be seen from Fig. S5c (ESI) that the mechanical properties of the CPI film are improved with the increase of BAPB ratio. During the experiment, the breakdown strength of the film was also verified and found to have the same variation law (Fig. S6, ESI). As a result of the flexibility of BAPB itself and the π-π conjugate structure formed by accumulation contribute to energy dissipation.30 In addition, the different CPI films are self-healed and bonded by malposition after thermal imidization. Fig. S7 (ESI) illustrates digital photos of CPI precursor solutions with different colours and repaired CPI films. The analysis shows that the film has no self-healing ability, when the ratio of APD to BAPB is less than 7:3. In this regard, the proportion of APD and BAPB has been further refined to carry out the remaining research content in the



Fig. 1. (a) Schematic diagram of disulfide bond exchange process. (b) Molecular composition and schematic diagram of PI and CPI.

experimental process. The ratio between APD and BAPB was redesigned in the experimental process. The specific composition details are shown in Table S1 (ESI). Fig. 2a shows the FT-IR spectra of the different CPI films. It is the same as the characteristic functional groups of the above films, such as the asymmetric and symmetric vibrations of −C=O groups at 1779, 1723 cm−1 and the stretching vibration band of −C−N−C at 1370 cm−1, respectively. Moreover, all films have almost the same *Tg* ~190 oC, as shown in Fig. 2b. The copolymerization doping of small proportion BAPB cannot significantly affect the *Tg* of CPI films, which will contribute to the preparation of CPI with high thermal stability, excellent insulation property and good self-healing ability. However, the thermal stability of *Td5%* are slightly decreased, which may be attributed to that the higher oxygen content in BAPB promotes the thermal decomposition as illustrated in Fig. 2c.31 The tensile strength (*σt*), toughness and Young's modulus (*E*) of different CPI films are also analysed as shown in Fig. 2d-2f. Fig. 2d reveals that the mechanical properties of the CPI films are improved with the increase of BAPB ratio. Moreover, the toughness of the CPI film decreases gradually with the decrease of BAPB copolymerization content (Fig. 2e), which may be attributed to flexibility of BAPB itself. Nonetheless, the CPI films still have high Young's modulus (*E*) >4 GPa values (see Fig. 2f). In addition, the CPI films with all proportions have been tested for malposition self-healing and bonding, and the results are shown in Fig. S8 (ESI). It is researching that the weak self-healing ability of the CPI film cannot meet the self-healing of the film after mechanical damage, when the copolymerization ratio of APD and BAPB is less than 9:1. Furthermore, the videos of the tensile test of the CPI films after being self-healed by malposition are included in the supplementary information. It can be seen from Fig. S8 (ESI) and the videos that the original self-healed position is separated during the CPI film (copolymerization ratio of APD and BAPB is 8:2, video 1, ESI) being stretched, but the CPI film (copolymerization ratio of APD and BAPB is 9:1, video 2, ESI) has another new destruction position. In this regard, the CPI films with copolymerization ratios of 10:0 and 9:1 are selected to study self-healing ability after mechanical and electrical damage. Next, the two polyimide films studied are defined as: CPI-100 is a CPI film with APD and BAPB ratio of 10:0 and CPI-91 is a CPI film with APD and BAPB ratio of 9:1.



Fig. 2. (a) FT-IR patterns, (b) DSC curves, (c) TGA curves, (d) stress-strain curves, (e) toughness histogram, and (f) Young’s modulus and tensile strength histograms of the different proportion CPI films.

Self-healing of CPI film after mechanical damage

Usually, self-healing of polymers is realized by repeated dissociation and polymerization of dynamic covalent bonds or dynamic reversible reactions.32-36 Fig. 3a shows the optical microscope images of a scratched CPI-100 film by a scalpel. The scratch of film is self-healed as illustrated in Fig. 3b, after hot pressing at 20 kPa and 200 oC. Similar to the above mechanical damaged film, the surface cracks of the remaining proportion (8:2, 7:3, 6:4) of the CPI films cannot be healed under this condition as shown in Fig. S9 (ESI). To highlight the self-healing effect, the CPI-100 film is simply repaired by a malposition method as shown in Fig. 3c-3d. Briefly, a rectangular strip (LxW = 50x10 mm2) of the CPI-100 film is cut into two pieces with a doctor blade, which then overlap each other by 5 mm. Next, putting the overlapped films on the hot press for hot pressing at 20 kPa and 200 oC. Tension test (see Fig. 3c) is then conducted on the self-healed film, and the stress-strain curve obtained is compared to that of the origin CPI-100 film as shown in Fig. 3d. Clearly, there is difference between the CPI-100 film and the self-healed film by hot pressing. The CPI-100 film healed by hot pressing has high tensile strength, which is due to a large number of disulfide bonds converged and exchanged with each other in the overlapping part. The exchange of more disulfide bonds will provide greater energy diffusion and flexibility to the film. A schematic diagram of the process is given in Fig. 3e. The molecular chain with disulfide bond will be free around the scratch, when the surface of the film is damaged. Moreover, the disulfide bonds will exchange with each other to form new molecular segments to achieve the self-healing objective under certain pressure and temperature. The CPI-91 has also been studied on self-healing after mechanical damage under the same technology and principle as shown in Fig. 3f-3i. Fig. 3f illustrates the optical microscope images of a scratched CPI-91 film by a scalpel. However, the scratch is not completely self-healed as illustrated in Fig. 3g, after hot pressing at 20 kPa and 200 oC. Similarly, the tensile test of CPI-91 film is carried out after self-healing by a malposition method (Fig. 3h), and the results are shown in Fig. 3i. There is little difference between the origin CPI-91 film and the self-healed film by hot pressing. These are attributed to the fact that the copolymerization of BAPB reduces the content of disulfide bonds and affects the exchange between disulfide bonds at high temperature.37 In order to effectively describe the self-healing effect of CPI film, the self-healing efficiency is defined with the literature and material characteristics, such as the 4th part of the supporting information and Fig. S10 (ESI). As shown in Fig. S11 (ESI), the analysis shows that the self-healing efficiency of CPI-100 and CPI-91 are 92% and 84%, respectively. Furthermore, in order to evaluate the self-healing effect of the system, some recent data on the self-healing efficiency of thermosetting resin are provided for comparison (Fig. 3j). Clearly, the CPI films has relatively high repair efficiency, especially the self-healing efficiency of CPI-100 is as high as 92%.



Fig. 3. Optical microscope images of the (a) CPI-100 film scratched by a scalpel and (b) CPI-100 film repaired by hot pressing. (c) Mechanical testing of the healed CPI-100 films. (d) Stress-strain curves of CPI-100 films before and after self-healing. (e) Schematic diagram of CPI films during self-healing. Optical microscope images of the (f) CPI-91 film scratched by a scalpel and (g) CPI-91 film repaired by hot pressing. (h) Mechanical testing of the healed CPI-91 films. (i) Stress-strain curves of CPI-91 films before and after self-healing. (j) Histogram of self-healing efficiency comparison.

Self-healing influence mechanism

Just like the self-healing standard of other soft materials, hard CPI films need to meet at least two conditions to self-healing after damage. Firstly, the damage sites of the film need to contact each other, which is also the reason for the pressure in the self-healing process. The second is need to ensure the movement of CPI molecular chain, which is the reason for the temperature in the self-healing process.21,38 Therefore, both pressure and temperature are satisfied to provide the conditions for the exchange of disulfide bonds (S-S) in this work.

Disulfide bond is a reversible dynamic covalent bond, which will form free radicals after being damaged. Moreover, these free radicals will recombine and connect to achieve the purpose of self-healing under certain conditions.39,40 Exactly as described by Han and Jung et al.21, take CPI-100 as an example, XPS tests were carried out on the surface of the original, damaged and self-healing CPI films in order to determine the mechanism of disulfide bond self-healing, respectively (Fig. 4a). As shown in Fig. 4b, there are new C-S and S-S peaks in the test results of the scratched film due to the different binding energies.41 The emergence of these new results stems from the free C-S and S-S peaks in the process of damage, as shown in Fig.4c. However, the original and self-healing films did not show new peaks during the test, and also had similar C-S and S-S ratios. Furthermore, it can be observed from the SEM image and mapping in Fig. S12 (ESI) that the S content on the damaged and self-healing film surfaces is the same, which indicates that there is no loss in the self-healing process. The above results show that the mutual conversion of disulfide bonds leads to the self-healing of the CPI films.



Fig. 4. (a) Schematic diagram, (b) XPS and (C) schematic diagram of disulfide bond structure of original, damaged and self-healed CPI-100 film.

Self-healing of CPI film after electrical damage

Based on the mechanical damage and self-healing mechanism of the above research, the more important electrical damage and self-healing process should be started. Self-healing of thermosetting polymers is considered to be exceedingly difficult after electrical damage. However, the CPI-100 and CPI-91 films can realize good self-healing after electrical damage. In this case, it refers to corona damage. Fig. 5a gives a schematic of the self-healing process of CPI-100 and CPI-91 films after corona damage. Furthermore, the specific corona phenomenon with blue violet is shown in Fig. 5a-I. The rough cracked surface of the corona damaged CPI-100 film is hot pressed at 20 kPa and 200 oC. Pleasantly, the surface of the film is healed smoothly due to the exchange of disulfide bonds under such pressure and temperature. In order to measure the self-healing ability of the films after corona damage, the breakdown strength of the films is introduced.42 Fig. 5b illustrates the SEM image of CPI-100 film without any damage, and the optical microscope image embedded in it are also displayed. Similarly, the surface of CPI-91 film is shown in Fig. 5c, which is little different from CPI-100 film. More noteworthy, the breakdown strength of the CPI films in different proportions is shown in Fig. 5d. The breakdown strength of the CPI film is improved with the increase of BAPB ratio. Causally, the larger π-π conjugated structure of CPI films consisting of more and more BAPB with the multi benzene ring hinders the growth of the electrical damage path, resulting in an extremely high *Eb* (~420 kVmm−1) of the CPI film with copolymerization ratio of APD and BAPB of 6:4 relative to CPI film with ratio of APD and BAPB of 10:0 (minimum ~300 kVmm−1).43,44 Fig. 5e displays the SEM image and optical microscope image of CPI-100 film damaged by corona. The surface of the film is rough and cracked. Moreover, Fig. 5f shows that the damaged surface is healed after hot pressing at 20 kPa and 200 oC, which is similar to the self-healing process of mechanical damage. The breakdown strengths of the damaged and healed CPI-100 films are performed and the obtained results reveal that the breakdown strength of the healed CPI-100 film increase after self-healing as shown in Fig. 5g, which may be attributed to the exchange of disulfide bonds have been repaired the surface defects after hot pressing. Similarly, the CPI-91 film has also been studied. Fig. 5h illustrates the SEM image and optical microscope image of CPI-91 films damaged by corona. The images of healed film are shown in Fig. 5i. Noteworthy, the breakdown strength of the healed CPI-91 film also increase after self-healing as shown in Fig. 5j. Furthermore, the inherent breakdown strength of the CPI-91 film is higher than that of CPI-100 film, but the recovery degree of the breakdown strength of the healed film is lower than that of CPI-100 film. These are attributed to the fact that the copolymerization of BAPB reduces the content of disulfide bonds and affects the exchange between disulfide bonds at high temperature.



Fig. 5. (a) Schematic illustration of self-healing process of CPI films after corona damage, (a-I) the digital photo of corona phenomenon. SEM and optical microscope image of the (b) CPI-100 and (c) CPI-91 films without any damages. (d) Weibull distributions of breakdown strengths of CPI films. SEM and optical microscope image of the CPI-100 films (e) after corona damage and (f) after self-healing. (g) Weibull distributions of breakdown strengths of CPI-100 films: original, corona-damaged and after self-healing. SEM and optical microscope image of the CPI-91 films (h) after corona damage and (i) after self-healing. (j) Weibull distributions of breakdown strengths of CPI-91 films: original, corona-damaged and after self-healing.

Conclusion

In summary, this work reported the self-healing ability of polyimides with high thermal property and insulating strength in mechanical/electrical damage. A self-healing polyimide insulating film is designed and prepared using a preparation process of copolymerization. The synthesized CPI films have good self-healing ability as compared to common polyimide due to the presence of the mutual exchange between disulfide bonds. Also, it has good thermal property (*Tg* >190 oC) and excellent insulation breakdown strength (*Eb* >300 kVmm−1). Furthermore, the CPI-100 and CPI-91 films exhibit good self-healing ability and insulation property recovery capabilities after mechanical/electrical damage, in which CPI-91 is the most ideal CPI film. The exchange of disulfide bonds can form new molecular segments to achieve the self-healing objective under certain pressure and temperature. Self-healing of high *Tg* polymer on the intrinsic conditions is a feasible and effective strategy, which endows this approach have great potential for industrial applications.

Experimental Section

Materials

4-Aminophenyl disulfide (APD, >98%), 1,3-bis(4'-aminophenoxyl) benzene (BAPB, >98%), 4,4'-(4,4'-isopropylidenediphenoxy) diphthalic anhydride (BPADA, >98%) and n, n-dimethylacetamide (DMAC, >99.8%) were supplied from Aladdin Shanghai company in China. Moreover, ethanol (AR) was obtained from Peking Reagent Beijing in China.

Characterizations

The morphology, mapping (C, S elements) and corona damaged structure of the films were displayed by field emission scanning electron microscope (FESEM-SU8010; Hitachi, Japan) and optical microscope (LV100DA-U; Nikon, Japan), respectively. Fourier transform infrared (FTIR) spectra of CPI film were performed by using an infrared tester (Nicolet-6700; Thermo Scientific, USA). The thermal properties of CPI film were analysed by a DSC analyser (DSC-60; SHIMADZU, Japan) and a thermal gravimetric analyser (TGA-55; TA, USA). Furthermore, the tensile properties of the CPI film were measured by MARK-10 from MARK Company, USA. Moreover, the Xray photoelectron spectroscopy (Thermo ESCALAB 250XI, Thermo Kalpha, USA) evaluates the surface properties of the CPI-100 film in the original, damaged, and healed states. The electrical breakdown and corona damage were performed on a voltage withstand testing device (RK2674-A; MEIRUIKE, China) and a corona resistance testing system using a needle plate electrode (HYJH-4; HUIYUAN, China), respectively. Herein, the parameters of the common needle tip corona discharge damage were fixed at 6.5 kV/0.24 mA/20 min.

Synthesis of pure polyimide (PI) precursor

Fig, S1 (ESI) shows the synthetic process and reaction conditions of PI precursor and PI, which is conveniently synthesized from commercially available APD and BPADA. Briefly, the 3 mmol APD was dissolved in DMAC with nitrogen gas and stirred at 25 oC for 30 min. The 3 mmol BPADA was then added into the mixture to form a precursor solution under nitrogen atmosphere at 25 oC for 8 h.

Synthesis of copolyimide (CPI) precursor

Two diamine monomers were selected to prepare copolyimide precursor. Furthermore, two serial components of polyimides were synthesized. The specific composition details are shown in Table S1 (ESI). The copolymerization process of representative molar ratios of APD to BAPB (9:1) are shown in Fig. S3 (ESI). Smoothly, the 2.7 mmol APD and 0.3 mmol BAPB were dissolved in DMAC and stirred at 25 oC for 30 min. Next, the 3 mmol BPADA was added into the mixture to form a precursor solution under nitrogen atmosphere at 25 oC for 8 h.

Fabrication of polyimide and copolyimide films

The polymerization of the PI or CPI is shown in Fig. S4 (ESI). A flow-coating technique was employed to prepare PI or CPI films in this study. All the solutions were homogeneously mixed and degassed using a vacuum drying oven before coating. To prepare PI, the resulting mixed solution was coated onto glass plate and heated using a drying box at 80 oC for 2 h, 100 oC for 1 h, 150 oC for 1 h, 200 oC for 1 h and 250 oC for 1 h, respectively. To prepare CPI, the resulting mixed solution was different but the process of heating film formation is the same.

Author Contributions

**Baoquan Wan**: Writing–Original draft. **Xiaodi Dong**: Investigation. **Xing Yang**: Investigation. **Ming-Sheng Zheng**: Verification. **George Chen**: Resources. **Jun-Wei Zha**: Writing–Check, edit.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**

1. D. Ai, H. Li, Y. Zhou, L. L. Ren, Z. B. Han, B. Yao, W. Zhou, L. Zhao, J. M. Xu, Q. Wang, Adv. Energy Mater. 2020, 10, 1903881.
2. H. Y. Duan, K. Li, M. Xie, J. M. Chen, H. G. Zhou, X. F. Wu, G. H. Ning, A. I. Cooper, D. Li, J. Am. Chem. Soc. 2021, 143, 19446−19453.
3. O. A. Tafreshi, S. Ghaffari-Mosanenzadeh, S. Karamikamkar, Z. Saadatnia, So. Kiddell, C. B. Park, H. E. Naguib, J. Mater. Chem. C 2022,10, 5088-5108.
4. Y. Cheng, X. Zhang, Y. X. Qin, P. Dong, W. Yao, J. Matz, P. M. Ajayan, J. F. Shen, M. X. Ye, Nat. Commun. 2021, 12, 1−12.
5. X. J. Liu, M. S. Zheng, G. Chen, Z. M. Dang, J. W. Zha, Energy Environ. Sci. 2022, 15, 56-81.
6. L. Papargyri, M. Theristis, B. Kubicek, T. Krametz, C. Mayr, P. Papanastasiou, G. E. Georghiou, Renewable Energy 2020, 145, 2387–2408.
7. N. Shimizu, C. Laurent, IEEE Trans. Dielectr. Electr. Insul. 1998, 5, 651–659.
8. B. Q. Wan, H. Y. Li, Y. H. Xiao, S. S. Yue, Y. Y. Liu, Q. W. Zhang, Appl. Surf. Sci. 2020, 501, 144243.
9. J. W. Zha, Q. Liu, Z. M. Dang, G. Chen, IEEE Trans. Dielectr. Electr. Insul. 2016, 23, 113–120.
10. M. Ieda, IEEE Trans. Electr. Insul. 1980, EI-15, 206–224.
11. Y. Zhao, L. J. Yin, S. L. Zhong, J. W. Zha, Z. M. Dang, IET Nanodielectrics, 2020, 3, 99-106.
12. J. K. Ali, C. M. Chabib, M. A. Jaoude, E. Alhseinat, S. Teotia, S. Patole, D. H. Anjum, I. Qattan, Chem. Eng. J. 2021, 408, 128017.
13. J.-D. Liu, X.-Y. Du, C.-F. Wang, Q. Li, S. Chen, J. Mater. Chem. C 2020,8, 14083-14091.
14. N. Zheng, Y. Xu, Q. Zhao, T. Xie, Chem. Rev. 2021, 121, 1716−1745.
15. H. T. Yu, Y. Y. Feng, C. Chen, Z. X. Zhang, Y. Cai, M. M. Qin, W. Feng, Carbon 2021, 179, 348−357.
16. J. Y. Xie, L. Gao, J. Hu, Q. Li, J. L. He, J. Mater. Chem. C 2020,8, 6025-6033.
17. X. P. Li, R. Yu, Y. Y. He, Y. Zhang, X. Yang, X. J. Zhao, W. Huang, ACS Macro Lett. 2019, 8, 1511−1516.
18. S. Wang, D. H. Fu, X. R. Wang, W. L. Pu, A. Martone, X. L. Lu, M. Lavorgna, Z. H. Wang, E. Amendola, H. S. Xia, J. Mater. Chem. A 2021, 9, 4055–4065.
19. J. Y. Xie, L. Gao, J. Hu, Q. Li, J. L. He, J. Mater. Chem. C 2020, 8, 6025-6033.
20. S. Y. Lee, P. H. Hong, J. Kim, K. Choi, G. M. Moon, J. S. Kang, S. L. Lee, J. B. Ahn, W. Eom, M. J. Ko, S. W. Hong, Macromolecules 2020, 53, 2279–2286.
21. Y. N. Kim, J. Lee, Y.-O. Kim, J. Kim, H. Han, Y. C. Jung, Appl. Mater. Today 2021, 25, 101226.
22. S. Wang, M. W. Urban, Nat. Rev. Mater. 2020, 5, 562–583.
23. S. Wang, S. Q. Ma, Q. Li, X. W. Xu, B. B. Wang, K. F. Huang, Y. L. liu, J. Zhu, Macromolecules 2020, 53, 2919–2931.
24. J. F. Patrick, M. J. Robb, N. R. Sottos, J. S. Moore, S. R. White, Nature 2016, 540, 363–370.
25. Y. Hou, G. D. Zhu, J. Cui, N. N. Wu, B. T. Zhao, J. Xu, N. Zhao, J. Am. Chem. Soc. 2022, 144, 1, 436–445.
26. W. B. Li, L. H. Xiao, Y. G. Wang, J. Chen, X. A. Nie, Polymer 2021, 229, 123967.
27. S. Huang, Y. K. Shen, H. K. Bisoyi, Y. Tao, Z. C. Liu, M. Wang, H. Yang, Q. Li, J. Am. Chem. Soc. 2021, 143, 12543–12551.
28. D. D. Li, C. Y. Wang, X. Y. Yan, S. Q. Ma, R. Lu, C. H. Chen, G. T. Qian, H. W. Zhou, RSC Adv. 2022, 12, 4234–4239.
29. D. Liu, J. W. Wang, W. H. Peng, X. Z. Wang, H. Ren, D. W. Kirk, React. Funct. Polym. 2022, 170, 105139.
30. Z. C. Ding, D. L. Liu, K. Zhao, Y. C. Han, Macromolecules 2021, 54, 3907−3926.
31. M. Wa˛drzyk, R. Janus, M. Lewandowski, A. Magdziarz, Renewable Energy 2021,177, 942–952.
32. Y. H. Zhang, L. Zhang, G. T. Yang, Y. L. Yao, X. Wei, T. C. Pan, J. T. Wu, M. F. Tian, P. G. Yin, J. Mater. Sci. Technol. 2021, 92, 75–87.
33. P. Shieh, W. X. Zhang, K. E. L. Husted, S. L. Kristufek, B. Y. Xiong, D. J. Lundberg, J. Lem, D. Veysset, Y. C. Sun, K. A. Nelson, D. L. Plata, J. A. Johnson, Nature 2020, 583, 542–547.
34. Y. F. Guo, S. Chen, L. J. Sun, L. Yang, L. Z. Zhang, J. M. Lou, Z. W. You, Adv. Funct. Mater. 2021, 31, 2009799.
35. M. Pepels, I. Filot, B. Klumperman, H. Goossens, Polym. Chem. 2013, 4, 4955–4965.
36. Y. Yanagisawa, Y. L. Nan, K. Okuro, T. Aida, Science 2018, 359, 72–76.
37. C. M. Yeh, C. H. Lin, T. Y. Han, Y. T. Xiao, Y. A. Chen, H. H. Chou, J. Mater. Chem. A 2021, 9, 6109–6116.
38. W. P. Zang, X. Y. Liu, J. J. Li, Y. J. Jiang, B. Yu, H. Zou, N. Y. Ning, M. Tian, L. Q. Zhang, Chem. Eng. J. 2022, 429, 132258.
39. A.R. de Luzuriaga, J.M. Matxain, F. Ruipérez, R. Martin, J.M. Asua, G. Cabañero, I. Odriozola, J. Mater. Chem. C 2016, 4, 6220–6223.
40. A. Rekondo, R. Martin, A.R. de Luzuriaga, G. Cabañero, H.J. Grande, I. Odriozola, Mater. Horiz. 2014, 1, 237–240.
41. D. Merki, S. Fierro, H. Vrubel, X. Hu, Chem. Sci. 2011, 2, 1262–1267.
42. S. Y. Chen, G. D. Meng, B. Kong, B. Xiao, Z. D. Wang, Z. Jing, Y. S. Gao, G. L. Wu, H. Wang, Y. H. Cheng, Chem. Eng. J. 2020, 387, 123662.
43. X. J. Liao, Y. C. Ding, L. L. Chen, W. Ye, J. Zhu, H. Fang, H. Q. Hou, Chem. Commun. 2015, 51, 10127–10130.
44. Y. L. Qiao, M. S. Islam, K. Han, E. Leonhardt, J. Y. Zhang, Q. Wang, H. J. Ploehn, C. B. Tang, Adv. Funct. Mater. 2013, 5, 5638–5646.