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Repair Performance of Self-Healing Microcapsule/Epoxy Resin Insulating Composite to Physical Damage

Youyuan Wang [1], Yudong Li [1,*], Zhanxi Zhang [1], Haisen Zhao [2] and Yanfang Zhang [1]

[1] The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400044, China; y.wang@cqu.edu.cn (Y.W.); zhx.zhang@cqu.edu.cn (Z.Z.); 20121813107@cqu.edu.cn (Y.Z.)

[2] Jinzhong Power Supply Company of State Grid Shanxi Electric Power Company, Shanxi 030600, China; 20134209@cqu.edu.cn

* Correspondence: 20171102031t@cqu.edu.cn; Tel.: +86-1330-837-4882

Received: 3 September 2019; Accepted: 23 September 2019; Published: 1 October 2019



Abstract: Minor physical damage can reduce the insulation performance of epoxy resin, which seriously threatens the reliability of electrical equipment. In this paper, the epoxy resin insulating composite was prepared by a microcapsule system to achieve its self-healing goal. The repair performance to physical damage was analyzed by the tests of scratch, cross-section damage, electric tree, and breakdown strength. The results show that compared with pure epoxy resin, the composite has the obvious self-healing performance. For mechanical damage, the maximum repair rate of physical structure is 100%, and the breakdown strength can be restored to 83% of the original state. For electrical damage, microcapsule can not only attract the electrical tree and inhibit its propagation process, but also repair the tubules of electrical tree effectively. Moreover, the repair rate is fast, which meets the application requirements of epoxy resin insulating material. In addition, the repair behavior is dominated by capillarity and molecular diffusion on the defect surface. Furthermore, the electrical properties of repaired part are greatly affected by the characteristics of damage interface and repair product. In a word, the composite shows better repair performance to physical damage, which is conducive to improving the reliability of electrical insulating materials.

Keywords: self-healing; epoxy resin; microcapsule; insulating composite; breakdown strength; physical damage; electrical tree

1. Introduction

Epoxy resin has been widely used in the field of electrical insulating materials due to its high insulation strength, stable chemical performance, and excellent weatherability [1–4]. However, in the process of manufacture, transportation, and operation, the material can be deteriorated gradually by various factors (such as electrical, thermal, and mechanical factors). The deterioration can lead to the physical damage in material, such as micro-voids and micro-cracks [4–8]. In addition, micro defects can distort the electric field and lead to partial discharge, reducing the insulation performance of material [9–11]. Furthermore, the existing technologies are difficult to detect and repair the damaged parts. And most methods require maintenance after the power outage [11–15]. Therefore, the physical damage has a great impact on the operation of electrical power system. If the insulating material has the self-healing ability, the further deterioration of defects can be prevented in time. So, the electrical and mechanical performances of material can be restored, which can greatly reduce the impact of tiny physical damage on the power system. However, the existing research on self-healing material are mostly related to the mechanical performances of building and coating material, and rarely involve the

insulating material [16,17]. Therefore, it is necessary to develop the self-healing epoxy resin insulating composite. It can prolong the service life of insulating material fundamentally and improve the reliability of electrical power system.

Recently, the self-healing technologies are mainly divided into two types: intrinsic and extrinsic [17–21]. The repair behavior of intrinsic material is mainly realized by the reversible chemical reaction or the diffusion of macromolecules [18,19]. However, the intrinsic method has higher requirements on the properties of material, and its application range has some limitations. Compared with the intrinsic material, the extrinsic material has better weatherability, wider application range and more manufacturing process [20,21]. Moreover, among them, the microcapsule system has higher stability, better repair rate and less damage to the matrix material structure [16,17,21]. Considering the operation environment and repair requirements of insulating material, the microcapsule system was selected as the research object in this paper. For microcapsule/epoxy resin composite, the self-healing characteristic of electrical performances have not been involved yet, and the repair behavior is still lack of systematic mechanism [20–22].

At present, there are few reports about self-healing insulation material. In the aspect of simulation, the static stress distribution of the microcapsule used for epoxy resin insulating material was simulated [2]. The results confirmed that the internal stress of insulating material can lead to the rupture of the microcapsule, thereby completing the repairing behavior. However, it does not involve the repairing ability of actual insulating material. In terms of experiment, the ability of microcapsule to repair electrical tree damage in epoxy resin was studied [23]. The results showed that the microcapsules can delay the development of electrical trees. But the change rules and mechanism of repair performance are still insufficient. In addition, the migration behavior of superparamagnetic nanoparticles was used to repair the electrical tree damage in polymers [24]. However, this method requires the stimulation of an external magnetic field, which belongs to the inductive repair system. There is still a certain gap with the active self-healing target of insulating material. Therefore, the research on the self-healing epoxy resin insulating material remains to be deepened.

In this paper, based on the preparation of microcapsule/epoxy resin composite, its self-healing performance to physical damage was analyzed by the tests of scratch, cross-section, electric tree, and breakdown. Furthermore, the repair mechanism was analyzed by the capillary theory and molecular diffusion model on the defect surface. In addition, the change of alternating current (AC) breakdown strength of epoxy resin composite was studied innovatively. Combined with the reaction mechanism and the interface electric field model, the changes of composite electrical insulation performance were explained. The goal of this work is to explore the repair ability of insulating material to physical damage and prolong the service life of insulation material fundamentally. Furthermore, the work in this paper can lay an experimental foundation for the development of self-healing insulation material.

2. Materials and Methods

2.1. Materials and Preparation

In the existing research, the microcapsule system of urea-formaldehyde (UF) resin coated epoxy resin is mostly selected to achieve the self-healing behavior in epoxy resin matrix [2,17,20]. However, previous studies did not consider the application requirements of epoxy resin insulating material. Although the compatibility of the epoxy repairing agent and the epoxy matrix is good, the curing rate of epoxy repairing agent is slow. It is not suitable for the timely requirement of repair behavior in insulating material. Especially, in high electric field, the epoxy repairing agent cannot suppress the partial discharge in time. The reaction rate of dicyclopentadiene (DCPD) is faster. And the dielectric constant of its reaction product (i.e., polydicyclopentadiene (PDCPD)) are close to those of epoxy resin, which can effectively homogenize the local high field of the defect, thus reducing the impact of structural damage [23]. Therefore, the UF/DCPD microcapsule was selected in this paper.

2.1.1. Preparation of Microcapsule

In this paper, the microcapsule was prepared by the "two-step" in-situ polymerization. The two-step method is to first obtain the UF prepolymer. And then the prepolymer undergoes the polycondensation reaction in the core emulsion to form UF shell. Therefore, the two-step reaction process is stable and controllable, and the performance of the products are superior. The raw materials used are all analytical reagent (AR) level.

(1) UF prepolymer

First, the urea was dissolved in deionized water, then formaldehyde solution was added, and the pH was adjusted to 8.0~9.0. The reaction time was 1 h. at 70 °C. After the solution was cooled to room temperature, the UF prepolymer was obtained. The mass ratio of urea to formaldehyde was about 1:2.3 to ensure the sufficient content of dimethylol urea in prepolymer, which can enhance the net structure of UF product.

(2) Microcapsule

The DCPD emulsion was obtained by mixing sodium dodecyl benzene sulfonate (SDBS) emulsifier, melted DCPD and deionized water at 400 rpm for 30 min. In order to obtain the good dispersion and stability of emulsion, the dosage of SDBS was about 5% of the DCPD mass. Subsequently, the UF prepolymer, the UF curing agent ammonium chloride and the UF water resistant modifier resorcinol were added in the emulsion. The mass ratio of UF prepolymer to DCPD was about 2:1 to ensure the encapsulation effect of microcapsule. The dosage of ammonium chloride and resorcinol were about 1.5% and 2.5% of the prepolymer respectively to ensure the curing and modification effect of wall material. After that, the emulsion pH was slowly adjusted to about 3.0. The acidification time was controlled about 30 min to obtain the intact sphericity of microcapsule. Finally, the microcapsules were obtained by reaction at 60 °C for 3 h.

2.1.2. Preparation of Self-Healing Epoxy Resin Insulating Composite

The temperature factor has a great influence on the curing reaction rate of epoxy resin and material properties. Thus, the room temperature curing system of epoxy resin-low molecular weight polyamide was selected to facilitate the operation of doping microcapsule and ensure the basic properties of insulating material. The raw materials used are all AR level.

First, 80 parts of epoxy resin E-51 was diluted with 20 parts of epoxypropane butyl ether 660 as the matrix. Then 60 parts of room temperature curing agent polyamide, 3 parts of curing accelerator tri (dimethylamine methyl) phenol (DMP-30) and 10 parts of toughening agent dibutyl phthalate were added in matrix to obtain the epoxy room temperature curing system. After that, the microcapsule and the catalyst for core material (i.e., repairing agent) were mixed into the epoxy room temperature curing system to obtain the microcapsule/epoxy resin composite system. In addition, Grubbs' second-generation catalyst with better stability and catalytic efficiency was selected to improve the effect of self-healing. And the dosage of catalyst was 10% of the microcapsules mass.

The composite system was mixed for 30 min at room temperature to ensure uniform dispersion. Then the bubbles in the system were removed by ultrasonic oscillation for 1 h and vacuum treatment for 20 min. Finally, it was cured for 4 days in the room temperature (25 ± 1 °C).

According to the relevant literature [16,25] and my previous work (as shown in Table 1), the important basic properties (such as thermal stability, Young's modulus and tensile strength) of composite with about 1 wt. % microcapsule are more in line with the application requirements of epoxy resin insulating material.

Table 1. Basic performances of composite with different concentrations of microcapsule.

Basic Performances of Composite	Concentrations of Microcapsule in Composite				
	0 wt. %	0.5 wt. %	1 wt. %	5 wt. %	10 wt. %
Repair efficiency to scratch about 25 μm wide (%)	0	≥50	≥70	≥73	≥76
Thermal decomposition temperature (°C)	396.8 ± 1.5	399.1 ± 1.9	402.7 ± 2.3	400.3 ± 2.1	391.0 ± 3.9
Young's modulus (GPa)	2.67 ± 0.03	2.63 ± 0.13	2.50 ± 0.21	2.34 ± 0.17	2.11 ± 0.33
Tensile strength (MPa)	51.6 ± 2.7	50.0 ± 1.9	46.1 ± 3.1	40.3 ± 2.9	32.6 ± 3.7

As the insulating material for industrial products, the thermal and mechanical properties of epoxy resin are crucial for its application. Moreover, the composite with 1 wt. % microcapsule has the best thermal stability and better mechanical properties on the premise of higher repair efficiency. Preliminary analysis shows that the effect of microcapsule on the basic properties of polyethylene is mainly related to the introduction of interface and impurities by microcapsule.

On the one hand, the local state formed by the interface structure can anchor the macromolecular chains in the matrix material, improving the stability of matrix structure [25]. And the stable internal structure can hinder the invasion of external factors (such as thermal factor). Thus, appropriate number of interfaces can improve the properties of material (such as thermal stability). On the other hand, the excessive impurities and interface defects can increase the defect structure in the matrix material. Furthermore, the dispersion of microcapsules will be deteriorated with the increase of microcapsule concentration, affecting the properties of matrix material. Thus, higher concentration of microcapsules can reduce the properties of epoxy resin (such as mechanical properties and thermal stability). Therefore, the performances of composite are affected by the concentration of microcapsule.

Overall, when the dosage of microcapsule was about 1% of the epoxy matrix mass, the comprehensive properties of composite are better. Thus, the more appropriate concentration (1 wt. %) was selected to study the repair performance of composite to physical damage and exclude the influence of other secondary factors.

2.2. Methods

In this paper, the repair performance of composite to physical damage was verified from mechanical damage and electrical damage. Moreover, the effect of microcapsule on the tree discharge and insulation strength of epoxy resin were explored.

2.2.1. Mechanical Damage Test

The scratch damage was used to simulate the mechanical damage in epoxy resin insulating material to verify the repair behavior to physical damage. The scratches were carried out with China Tianchuang QHZ scratch tester. The morphology of scratches was observed by China Guanggu SGO-PH80 optical microscope (OM). According to the optimum polymerization temperature (about 45 °C) of repairing agent (DCPD), the curing temperature (above 60 °C) of reaction product (PDCPD) and the normal operating temperature (less than 155 °C) of epoxy resin insulating material, the temperatures of 60 °C were selected in this paper. The heating time was 30 min and 60 min, respectively.

Moreover, the alternating current (AC) breakdown strength of samples was carried out to verify the self-healing effect to mechanical damage in electrical insulation performance. The breakdown strength was tested on the platform constructed by Ningxia High Voltage Electronic Instrument Company JNC801 transformer. The cylinder-plate electrodes manufactured according to GB/T 1048-2006 standard were used as the electrodes, which are made of brass. In addition, the electrodes and samples were immersed in 25# mineral insulating oil to prevent the surface discharge. The breakdown test for each type of samples was repeated 20 times.

Furthermore, the cross-section test was carried out to further observe the reaction process of repairing agent. And the Czech Tescan MIRA3 scanning electron microscope (SEM) was used to make an intuitive comparison between the pure sample and composite.

2.2.2. Electrical Damage Test

The self-healing ability of composite to electrical damage was verified by electrical tree. The needle-plate electrode system was used to initiate electrical tree. The needle electrode was inserted into the sample during the preparation process, while the curvature radius of the needle tip was 5 μm. The plate electrode was contacted the sample through conductive adhesive, and the distance between electrodes was 3 mm. Moreover, the sample was immersed in transformer oil to prevent the surface flashover. In the experiment, using the pressure platform in Section 2.2.1, the AC voltage of 10 kV/50 Hz was applied for 60 min at room temperature. The morphological characteristic of electrical tree was observed by OM.

3. Results and Discussion

3.1. Repair Performance of Mechanical Damage

3.1.1. Structural Change of Scratch

Figure 1 shows the OM results of pure epoxy resin and its composite. Compared with the pure epoxy resin, there are obvious microcapsules in composite. And the microcapsules have excellent dispersion in the epoxy resin matrix without obvious rupture. The excellent dispersion and intact morphology of microcapsule in the matrix can ensure the better repair effect of damage based on the less influence on the basic properties of matrix material.

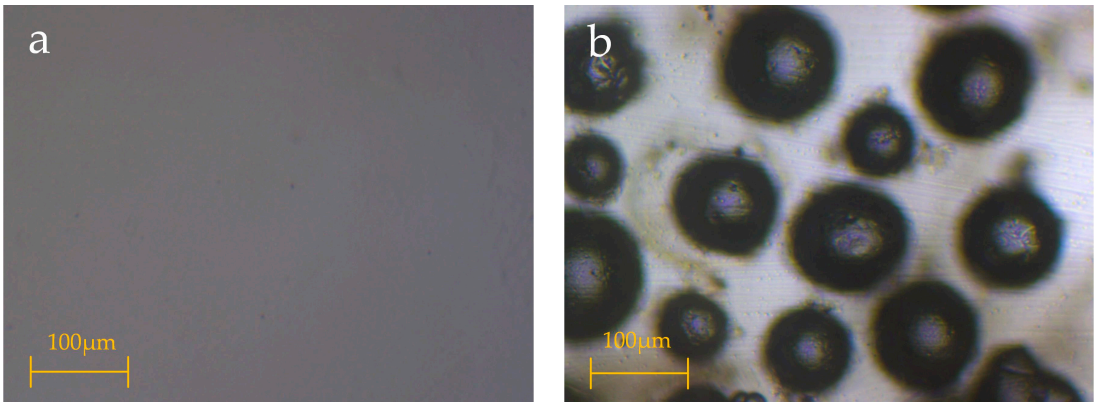


Figure 1. Morphology of epoxy resin samples. (**a**) Pure epoxy resin. (**b**) Microcapsule/epoxy resin composite.

Figure 2 is the OM results of the scratch test. The composite without catalyst was added as the contrast to verify the repair effect to scratch damage more intuitively. The scratch could cause physical structural damage to epoxy resin insulating material. And the scratch width in pure epoxy resin had no obvious change after heating. The results indicate that the original epoxy resin insulating material does not have any self-healing ability to physical damage. Moreover, the influence of heating factor on the physical damage (such as scratch) in epoxy resin material is very small, which can be ignored.

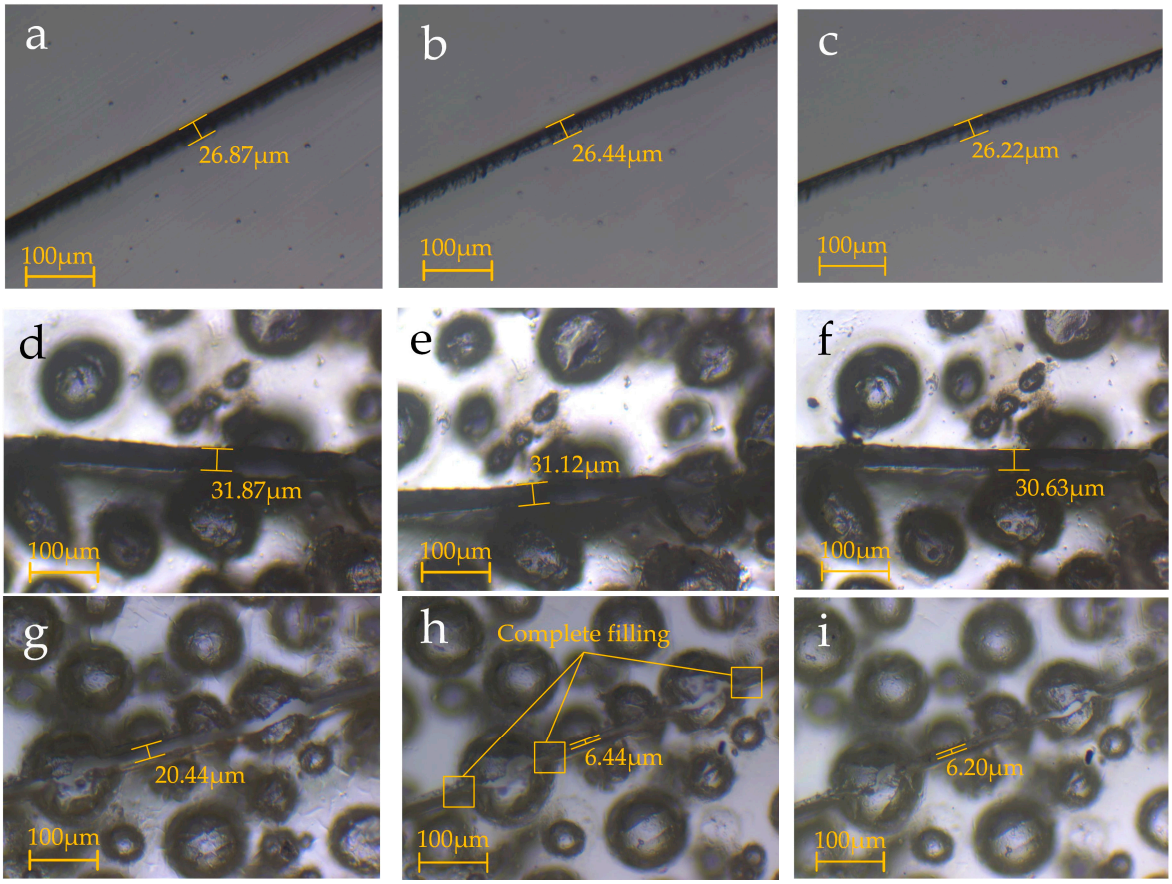


Figure 2. Morphology of the scratch: (**a**) Unheated pure LDPE epoxy resin; (**b**) Heated pure epoxy resin for 30 min; (**c**) Heated pure epoxy resin for 60 min; (**d**) Unheated composite without catalyst; (**e**) Heated composite without catalyst for 30 min; (**f**) Heated composite without catalyst for 60 min; (**g**) Unheated composite; (**h**) Heated composite for 30 min; and (**i**) Heated composite for 60 min.

The scratch can destroy the microcapsules in the sample, resulting in the rupture of wall structure. And the heating condition would cause the core material to flow out. For the composite without catalyst, the unreacted DCPD was volatilized by heating. So, the scratch of this composite had no repair effect, which is similar to the pure epoxy resin. When the composite contained catalyst, its repair behavior is shown in Figure 3. The melted repairing agent (DCPD) flowed to the damaged area, contacted with the catalyst and reacted to form solid repair product (PDPCD) at the defect area. In other words, the microcapsule can fill the damage structure. Therefore, the scratch structure was reduced dramatically. If the scratch width is taken as the criterion of the repair efficiency, the self-healing rate is 70%~100%.

Furthermore, infrared results (as shown in Figure 4) show that the filler in scratch is really the PDCPD (3050 cm^{-1} and 3003 cm^{-1} indicate = C–H, 2926 cm^{-1} and 2851 cm^{-1} indicate –CH_2–, 1701 cm^{-1} and 1633 cm^{-1} indicate C=C) [26]. In addition, the carbon-carbon double bonds are retained after the reaction, which makes the stiffness and toughness of product reach an excellent balance. Thus, the good repair effect of the damaged part is ensured.

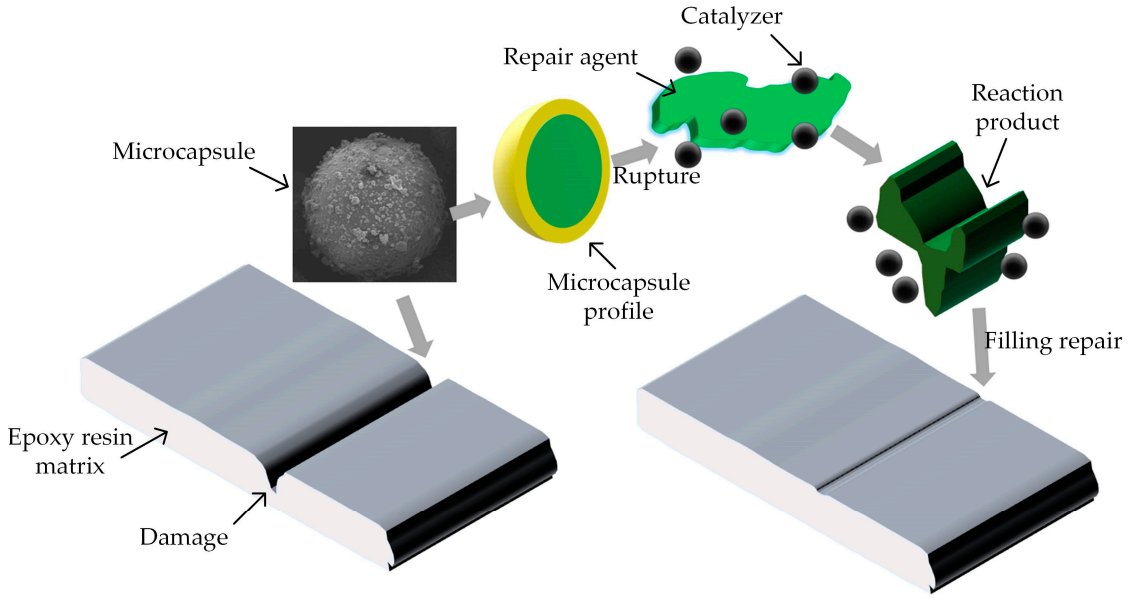


Figure 3. Repair behavior of composite.

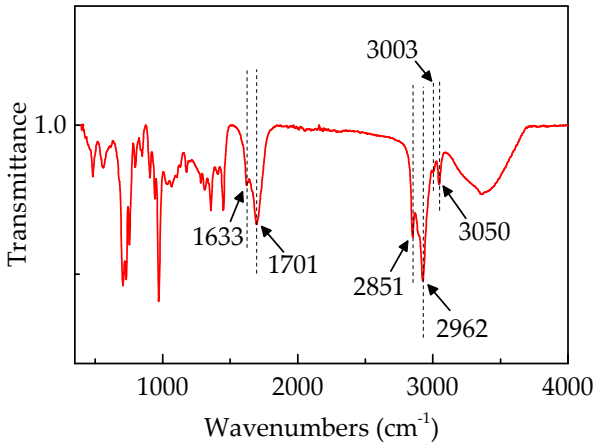


Figure 4. Infrared spectroscopy analysis of the filler in scratch.

The repair effect around the region of ruptured microcapsule is more obvious, and the scratch is almost completely repaired. The main reason is that the damage region near the microcapsule would contact a large number of core material preferentially. Moreover, the reaction rate of core material is relatively fast, leading to the repairing agent having already begun to react in the diffusion process. Furthermore, the comparison between Figure 2h,i shows that the reaction process of core material is concentrated in the first 30 min. It proves that the repair reaction speed is fast, which can better meet the timely requirement of damage treatment in insulating material. Thus, the repair ability of microcapsule can effectively and timely prevent the further deterioration of insulating material.

In short, the obvious self-healing ability of composite to physical damage can be proved by the comparison of three groups of scratch experiments. The repair performance of insulating material to physical defects is realized, thus ensuring the reliable operation of electrical equipment.

3.1.2. Structural Change of Cross-Section

The SEM results of cross-section are showed in Figure 5. From Section 3.1.1, the repair behavior was concentrated in the first 30 min. So, the samples of cross-section were heated for 30 min. Compared with the pure epoxy resin, there are obvious microcapsules in the composite. And the dispersion of microcapsules is great, which is similar to the OM results in Figure 1. Moreover, the microcapsule

has obvious core-wall structure and it can be damaged in the cross-section operation (as shown in Figure 5c). It indicates that the wall structure of microcapsule has the rupture response to the stress change of insulating material.

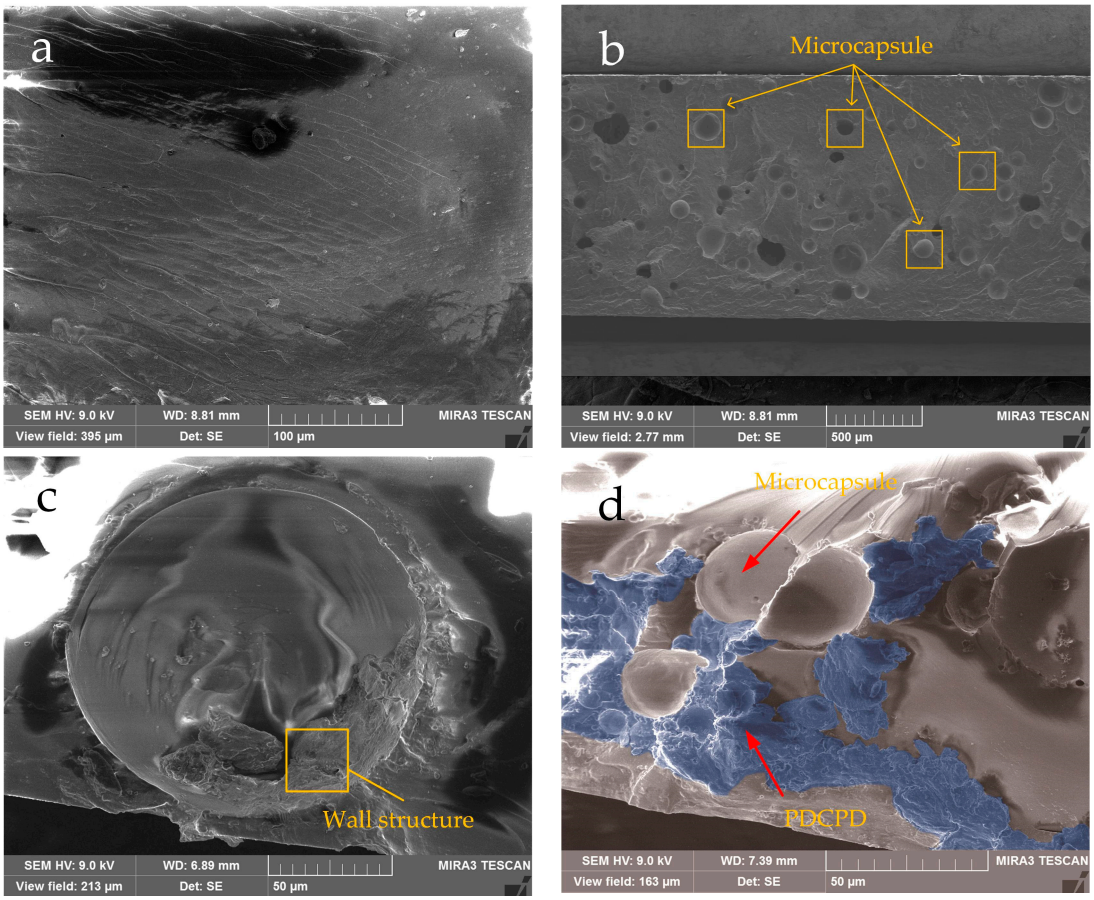


Figure 5. Cross-section characteristics of epoxy resin. (**a**) Pure epoxy resin; (**b**) and (**c**) Composites before reaction; and (**d**) Repair effect.

The reaction effect of the repairing agent is shown in Figure 5d. When the microcapsule was damaged, the core material flowed out and reacted in the damage area. And the PDCPD product appeared as the irregular flocculent material at the cross-section. The flow of DCPD due to the gravity influence is the main reason for the concentration of repair product at the section bottom. This phenomenon also proves that he fluidity of core material is well, which meets the design requirement of repair behavior.

The repair mechanism can be analyzed by combining the capillary flow theory and the molecular diffusion model on defect surface [27]. With the appearance of the minor damage in matrix, the pressure difference would be formed on both sides of the defect. And due to the DCPD is the Newtonian liquid between 32.5~172 °C, the repairing agent would continuously diffuse into the defect depth under the capillary effect. Meanwhile, the core material covers the defect interface to form the surface or body containing the repairing agent. And then the repairing agent molecules attract and react with each other. Although the molecular weight of DCPD is small, its molecular space structure is complex. So, the arrangement of molecule in the reaction process is irregular, resulting in the irregular morphology of repair product. Therefore, the core material of microcapsule can achieve the better repair effect to the physical damage, but the regularity of product is still needed to be improved.

All in all, the experimental results intuitively demonstrate that the doping effect of microcapsule in epoxy resin insulating material is excellent. The wall structure of microcapsule has timely response

to the stress change in matrix. And the fluidity and reactivity of core material is great. Therefore, it is proved that the epoxy resin insulating composite based on microcapsule system can repair the damaged parts quickly and automatically.

3.1.3. Change of Insulation Strength to Scratch Damage

Breakdown strength is one of the most important macroscopic performances of insulating material, which can be affected by damage defects. Moreover, the scratch defect can equivalent to the structural damage. Therefore, alternating current (AC) breakdown strength of damaged samples is measured. From Section 3.1.1, the damaged samples were heated for 30 min.

This experiment can reflect the influence of physical damage on the epoxy resin insulating material and the repair effect of composite on its electrical properties. Due to the breakdown data usually have great dispersion, the Weibull distribution (as shown in Formula (1)) is used to reduce the error [28].

$$F(U) = 1 - \exp\left[-\left(\frac{U}{\alpha}\right)^{\beta}\right], \quad (1)$$

where, U is the breakdown voltage value; α is the scale parameter, indicating the breakdown voltage value when the material failure probability is 63.2%; and β is the shape parameter, indicating the dispersion of data.

The AC breakdown strength is shown in Figure 6. The breakdown strengths of epoxy resin before and after doping the microcapsule are maintained at about 45 kV/mm, which indicates that the 1 wt. % microcapsule has little effect on the insulation strength of epoxy resin. On the one hand, the impurities and interface defects introduced by microcapsule will destroy the original continuous structure of matrix material. It can make the internal electric field distribution uneven, thus reducing the electrical insulation performance of matrix [29]. On the other hand, the microcapsule distributes evenly in epoxy resin, which can reduce the influence of impurities on the internal structure of matrix. In addition, the local state can be formed by the interface between microcapsule and epoxy matrix, resulting in many charge traps. The migration of carrier can be affected by charge traps. In other words, the microcapsule can shorten the average free path of carrier, which improves the insulation performance of matrix material [1]. Therefore, the breakdown strength of composite is not decreased significantly, which can meet the application requirements of epoxy resin insulating material.

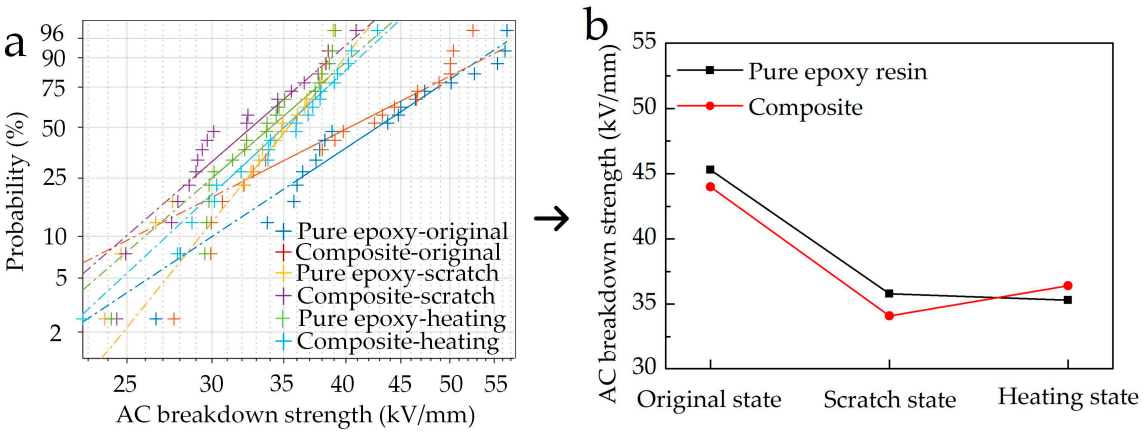


Figure 6. (**a**) Weibull probability. (**b**) Alternating current AC breakdown strength of epoxy resin.

After the scratch treatment, the breakdown strengths of the pure sample and its composite are all reduced by about 10 kV/mm. Moreover, the breakdown point occurs at the scratch site. It is proved that the physical defect (such as a scratch) can directly affect the electrical insulation performance of insulating material, threatening the safe operation of electrical equipment. And the similar decrease

amplitude of breakdown strength proves that the 1 wt. % microcapsule has little effect on the original properties of epoxy resin.

There are three main reasons for the influence of scratch on breakdown strength: (1) According to the theory of electrical-mechanical aging, the micro-defect in the material can distort the electric field and form a high field strength area at the damage site [11]. And the electric field at the scratch was more concentrated, so the breakdown strength was reduced. (2) Physical damage would directly reduce the thickness in the direction of breakdown. At the same external electric field, the field strength at the scratch was greater. Therefore, the breakdown would occur at the scratch. (3) The physical damage can be equivalent to the filling of another dielectric. In this experiment, the oil used in the test replaced the epoxy resin in the damaged parts. And the insulation strength of oil is lower than that of epoxy resin. Considering the interface charge effect, more space charge would be accumulated at the interface between oil and epoxy resin [29], which exacerbates the electric field distortion and caused the breakdown phenomenon.

After heating, the breakdown strength of pure epoxy resin is fluctuated slightly, and there is no obvious recovery. Therefore, the physical damage (such as a scratch) has a greater impact on the electrical breakdown characteristics of insulating material. And the degradation of insulation property is permanent and cannot be recovered by itself. Compared with the pure sample, the insulation strength of the composite obviously rises after heating. Moreover, the breakdown strength of composite can be restored to about 83% of its initial state.

The microcapsule can not only repair the physical structure of damage site, but also eliminate the impact of damage on the electrical insulation property of the epoxy resin. On the one hand, the thickness of the defect in the breakdown direction is increased by the filling ability of the microcapsule, improving its microstructure. In other words, the repair ability of the microcapsule can inhibit the distortion and concentration of the electric field at the damage site. On the other hand, the dielectric constant of the repair product (PDCPD) is about 2.78 which is closed to that of epoxy resin (about 3). Therefore, the repair product can effectively uniform the local high electric field and reduce the electrical-mechanical stress of the damage site [11]. Thus, the development of electrical breakdown can be effectively inhibited. In addition, the local state can be introduced by the interface area between the repair product and matrix martial. The discharge energy initially concentrated on the defect can be dispersed by the charge transport of the lower barrier around the local state [1]. Therefore, the electrical insulation property of damaged composite can be restored after repair.

Based on the self-healing mechanism, the incomplete repair phenomenon of breakdown strength in composite is explained in this paper. On the one hand, the reaction rate of repairing agent is too fast and the scope of scratch damage is relatively large. So, the reaction process of the repairing agent may have been completed when the damaged part is not completely covered by the repairing agent. In other words, a part of the physical damage gap is still retained, which is similar to the repair result in Figure 2h. Moreover, as shown in Figure 5d (i.e., the reaction result of cross-section), the surface of the product is uneven and there is a physical difference between the product and the matrix. Thus, there are still some physical defects in the damaged area after repair. So, the insulation performance of the material cannot be restored to its initial state. On the other hand, although the electrical properties of PDCPD and epoxy resin are similar, there are still some differences in the material properties. The density of PDCPD (about 1.03 g/cm^3) is less than that of epoxy resin (about 2 g/cm^3), so the local low-density area will be formed in the repair site [5]. Thus, the disorder of structure and the density of charge trap are increased, reducing the electrical insulation property. Therefore, the breakdown strength of the damaged composite can be raised after the repair, but it still cannot be restored to the initial state.

In general, the experiment results prove that the composite can do repair its electrical insulation property. Therefore, the decrease of breakdown strength caused by physical damage in insulating material can be alleviated, improving the reliability of the power system. At present, the research on self-healing insulating material is still in the exploratory stage. Although a small part of insulation

strength is sacrificed, composite can quickly restore its insulation performance after damage. Thus, the composite has good research value.

3.2. Repair Performance of Electrical Damage

In the actual operation process, the electrical tree is the main factor leading to the insulation failure of insulating material [30]. The electrical tree can cause the irreversible structural damage of micron and above, thus directly threatening the safe operation of power system [30,31]. Therefore, the self-healing performance to electrical tree can greatly improve the service life of insulating material. However, there are still few reports about it. This paper mainly studies the propagation stage of electrical tree in epoxy resin. The results are shown in Figure 7. From Section 3.1.1, the heating condition is 60 °C/30 min. This paper observes the panorama of the electrical tree by the mosaic of multiple graphs to ensure the clarity.

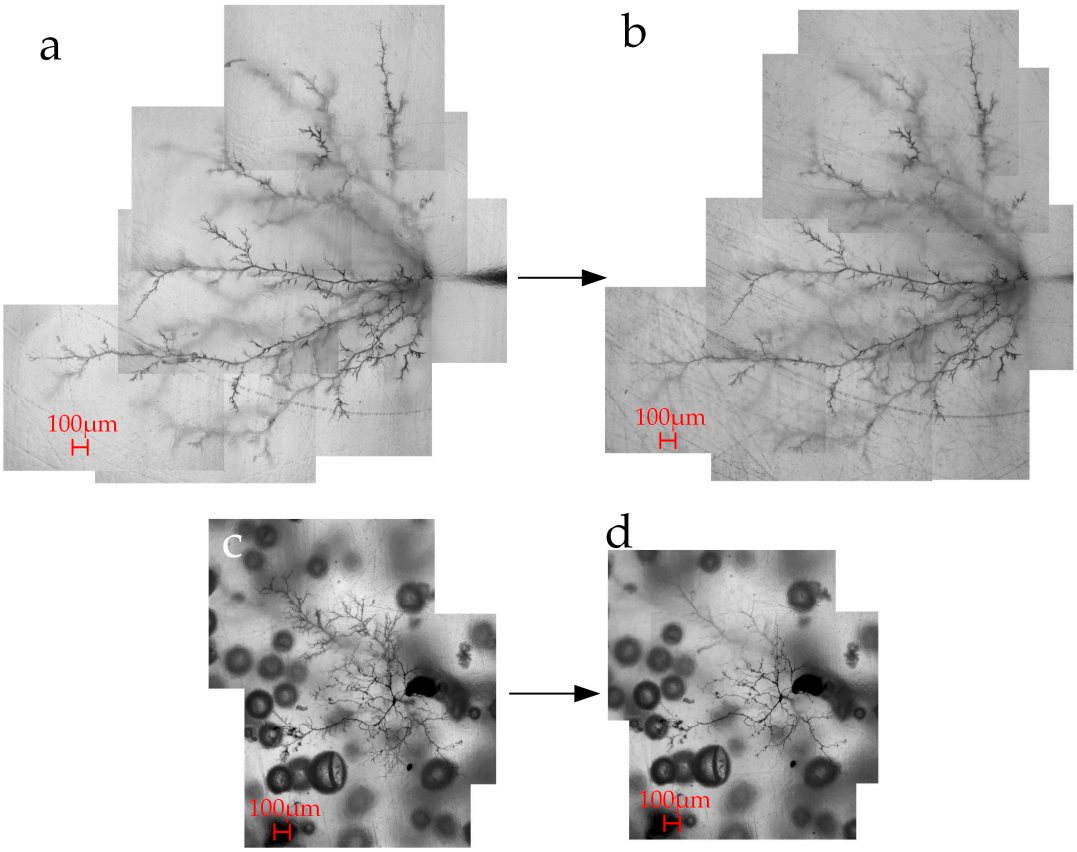


Figure 7. Morphology of the electrical tree. (**a**) Unheated pure epoxy resin. (**b**) Heated pure epoxy resin. (**c**) Unheated composite. (**d**) Heated composite.

Compared with pure epoxy resin, the size of the electrical tree in composite is decreased significantly, which is similar to the result in [23]. In addition, the electrical tree in composite tends to develop into a microcapsule and branches near the microcapsule. It can be concluded that the local electric field can be affected by the microcapsule, which attracts the propagation of the electrical tree. When the electric tree develops into the microcapsule, it can break the wall structure of the microcapsule and consume some energy. The residual energy will turn into a new branch, thus the propagation of the electric tree is inhibited. On the other hand, the continuity of the original structure in epoxy resin can be destroyed by microcapsule, thus hindering the propagation of the electrical tree. Therefore, the electrical tree in the composite tends to develop towards the microcapsule area, and its overall size is decreased.

After heating, the morphology of electrical tree in pure epoxy resin has no obvious change. In composite, except for the main branch of electric tree, the other branches disappeared after heating. Moreover, the width of the main branch in the composite is decreased after heating. Thus, the composite exhibits the obvious self-healing ability to electrical damage. The repair mechanism is similar to that described in Section 3.1, the wall structure of the microcapsule can be broken by the electrical tree, while the core material (repairing agent) can flow into the tubules of the electrical tree through the action of capillary and molecular diffusion. Thus, the partial tubules of the electric tree are filled with repaired product. In addition, due to the dielectric constant of the reaction product being close to that of the epoxy resin, the compatibility between the PDCPD and the matrix is good. Therefore, the local high electric field is weakened, which can further inhibit the development of the electric tree.

Due to the influence of the voltage condition in this paper, the size of the electrical tree is relatively large. Thus, the repairing agent cannot completely repair all the tubules of the electrical tree. However, the temperature and electric field coexisted in the actual operation of the epoxy resin insulating material. And the propagation time of the actual electrical tree is longer [23,30]. Therefore, the repairing agent in the microcapsule has a good opportunity to repair the electrical tree in its early stage. In other words, on the premise of reasonable control of the microcapsule concentration, epoxy resin insulating composite is fully capable of repairing the electrical damage.

The damage to the electrical tree has been regarded as an irreversible permanent defect [24]. In this paper, the microcapsule can not only inhibit the propagation of electrical tree, but also repair the tubules of electrical tree effectively. It has good application value in reducing the harm of electrical damage to insulating material.

4. Conclusions

In this paper, the preparation method and self-healing performance of the microcapsule/epoxy resin insulating composite were explored exploitively and creatively. Moreover, the repair performance to physical damage and the change rule of electrical insulation performance are emphatically studied. The application advantage of self-healing insulating composite is proved by linking the micro-changes with the macro-properties. The main conclusions are as follows:

(1) For the mechanical damage, the microcapsule/epoxy resin composite exhibit excellent self-healing ability. The repair efficiency of scratch width is 70%~100%, and the repair rate is relatively fast. Moreover, the core material of the microcapsule has great fluidity and reactivity. In addition, the repair process is mainly affected by the action of the capillary and molecular diffusion model on the defect surface.

(2) For the electrical damage, the repair effect of composite to the electrical tree is obvious. The microcapsule can not only attract the electrical tree and inhibit its propagation, but also repair the tubules of electrical tree effectively. It has good application value in reducing the harm of electrical damage to insulating material.

(3) Physical damage can reduce the insulation strength of material, thus threatening the stability of the power system. The composite can not only fill the structural defect caused by electrical damage (such as an electrical tree) and mechanical damage (such as a scratch), but also homogenize the local high electric field in the defect area, restoring its insulation strength. The restoration effect of electrical insulation performance is mainly affected by the reaction effect of repairing agent and the interface characteristic between the repair product and the matrix material.

In addition, the microcapsules are uniformly dispersed in epoxy resin insulating material with great morphology. It is conducive to repairing the damaged parts effectively on the premise of ensuring the basic properties of the material (such as thermal and mechanical properties).

Author Contributions: Conceptualization, Y.W. and Y.L.; Methodology, Y.L.; Validation, Y.W., Y.L., and Z.Z.; Data curation, Y.Z., Z.Z., and H.Z.; Formal analysis, Y.W. and Y.L.; Writing—Original draft preparation, Y.L.; Writing—Review and editing, Y.W.; Visualization, Y.L. and Y.W.; Project administration, Y.W.

Funding: This research was funded by National Natural Science Foundation of China (51777018), Fundamental Research Funds for the Central Universities (2019CDXYDQ0010) and the Science and Technology Project of SGCC under Grant (SGTYHT/14-JS-188).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, C.; Zheng, X.; Bie, C. Research of Preparation and Non-Linear Conductivity Modification of Doped ZnO/Epoxide Resin Material. *Trans. Chin. Electrotech. Soc.* **2016**, *31*, 24–30.
2. Zhang, X.; Wu, Y.; Wen, H.; Chen, X.; Xiao, S. Study on Microcapsules for Self-healing System of Insulating Epoxy Resins. *Proc. CSEE* **2018**, *38*, 2808–2814.
3. Wang, Y.; Liu, H.; Li, W.; Ding, R. An Investigation of Surface Tracking Characteristics and Factors Influencing Epoxy Resin Pouring Insulation for Dry-type Reactors. *Macromol. Res.* **2018**, *27*, 310–320. [CrossRef]
4. Liang, M.; Wong, K. Improving the long-term performance of composite insulators use nanocomposite: A review. *Energy Procedia* **2017**, *110*, 168–173. [CrossRef]
5. Wang, Y.; Liu, Y.; Wang, S.; Xu, H. The Effect of Electrothermal Aging on the Properties of Epoxy Resin in Dry-Type Transformer. *Trans. Chin. Electrotech. Soc.* **2018**, *33*, 250–260.
6. Arronche, L.; Saponara, V.; Yesil, S. Impact damage sensing of multiscale composites through epoxy matrix containing carbon nanotubes. *J. Appl. Polym. Sci.* **2013**, *128*, 2797–2806. [CrossRef]
7. Saurín, N.; Sanes, J.; Bermúdez, M. Self-Healing of Abrasion Damage in Epoxy Resin–Ionic Liquid Nanocomposites. *Tribol. Lett.* **2015**, *58*, 4. [CrossRef]
8. Hu, P.; Li, C.; Chen, D. Cause Analysis and Countermeasure Study of Cracking Accident of Cable GIS Terminal Epoxy Casing. *Electr. Power Eng. Technol.* **2017**, *36*, 102–105.
9. Wang, Y.; Liu, Y.; Xiao, K. The effect of hygrothermal aging on the properties of epoxy resin. *J. Electr. Eng. Technol.* **2018**, *13*, 892–901.
10. Chen, L.; Tsao, T.; Lin, Y. New diagnosis approach to epoxy resin transformer partial discharge using acoustic technology. *IEEE Trans. Power Deliv.* **2005**, *20*, 2501–2508. [CrossRef]
11. Huang, M.; Zhou, K.; Yang, D.; Yang, M. Effect of On-Line Rejuvenation on Water Tree Propagation in XLPE Cables. *Trans. Chin. Electrotech. Soc.* **2016**, *31*, 176–182.
12. Brown, E.N.; White, S.R.; Sottos, N.R. Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part II: In situ self-healing. *Compos. Sci. Technol.* **2005**, *65*, 2474–2480. [CrossRef]
13. Yang, M.; Zhou, K.; Wu, K.; Tao, W.; Yang, D. A New Rejuvenation Technology Based on Formation of Nano-SiO_2 Composite Fillers for Water Tree Aged XLPE Cables. *Trans. Chin. Electrotech. Soc.* **2015**, *30*, 481–487.
14. Wei, G.; Tang, J.; Zhang, X.; Lin, J. Gray intensity image feature extraction of partial discharge in high-voltage cross-linked polyethylene power cable joint. *Int. Trans. Electr. Energy Syst.* **2014**, *24*, 215–226. [CrossRef]
15. Xu, T.; Dong, X.; Li, R.; Liu, G.; Xia, H.; Xia, Z. Ultrasonic Phased Array Detection of Composite Insulator Internal Defects. *Electr. Power Eng. Technol.* **2018**, *37*, 75–79.
16. White, S.R.; Sottos, N.R.; Geubelle, P.H.; Moore, J.S.; Kessler, M.R.; Sriram, S.R. Autonomic healing of polymer composites. *Nature* **2001**, *409*, 794–797. [CrossRef] [PubMed]
17. Bekas, D.G.; Tsirka, K.; Baltzis, D.; Paipetis, A.S. Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques. *Compos. Part. B Eng.* **2016**, *87*, 92–119. [CrossRef]
18. Kang, J.; Tok, J.B.-H.; Bao, Z. Self-Healing Soft Electronics. *Nat. Electron.* **2019**, *2*, 144–150. [CrossRef]
19. Li, W.; Dong, B.; Yang, Z.; Xu, J.; Chen, Q.; Li, H.; Xing, F.; Jiang, Z. Recent Advances in Intrinsic Self-Healing Cementitious Materials. *Adv. Mater.* **2018**, *30*, 1705679. [CrossRef]
20. Murphy, E.B.; Wudl, F. The world of smart healable materials. *Prog. Polym. Sci.* **2010**, *35*, 223–251. [CrossRef]
21. An, S.; Lee, M.W.; Yarin, A.L.; Yoon, S.S. A Review on Corrosion-Protective Extrinsic Self-Healing: Comparison of Microcapsule-Based Systems and Those Based on Core-Shell Vascular Networks. *Chem. Eng. J.* **2018**, *344*, 206–220. [CrossRef]
22. Zhang, X.; Ji, H.; Qiao, Z. Residual stress in self-healing microcapsule-loaded epoxy. *Mater. Lett.* **2014**, *137*, 9–12. [CrossRef]

23. Lesaint, C.; Risinggard, V.; Hølto, J.; Saeternes, H.H.; Hestad, Ø.; Hvidsten, S. Self-healing high voltage electrical insulation materials. In *2014 IEEE Electrical Insulation Conference (EIC)*; IEEE: Piscataway, NJ, USA, 2014; pp. 241–244.
24. Yang, Y.; He, J.; Li, Q.; Gao, L.; Hu, J.; Zeng, R.; Qin, J.; Wang, S.; Wang, Q. Self-healing of electrical damage in polymers using superparamagnetic nanoparticles. *Nat. Nanotechnol.* **2019**, *14*, 151. [CrossRef] [PubMed]
25. Wang, Y.; Li, Y.; Zhang, Z.; Zhang, Y. Effect of Doping Microcapsules on Typical Electrical Performances of Self-Healing Polyethylene Insulating Composite. *Appl. Sci.* **2019**, *9*, 3039. [CrossRef]
26. Schaubroeck, D.; Brughmans, S.; Vercaemst, C.; Scheaubroeck, J.; Verpoort, F. Qualitative FT-Raman investigation of the ring opening metathesis polymerization of dicyclopentadiene. *J. Mol. Catal. A Chem.* **2006**, *254*, 180–185. [CrossRef]
27. Álvaro, G. Self-healing of open cracks in asphalt mastic. *Fuel* **2011**, *93*, 264–272.
28. Wang, Y.; Wang, S.; Lu, G.; Huang, Y.; Yi, L. Influence of Nano-Al N Modification on the Insulation Properties of Epoxy Resin of Dry-Type. *Trans. Chin. Electrotech. Soc.* **2017**, *32*, 174–180.
29. Wu, Z.; Wang, C.; Zhang, M.; Pei, X.; Jiang, P. Interface of Epoxy Resin Composites, and Its Influence on Electrical Performance. *Trans. Chin. Electrotech. Soc.* **2018**, *33*, 241–249.
30. Chen, Y.; Meng, G.; Dong, C. Review on the Breakdown Characteristics and Discharge Behaviors at the Micro & Nano Scale. *Trans. Chin. Electrotech. Soc.* **2017**, *32*, 13–23.
31. Rohde, B.J.; Le, K.M.; Krishnamoorti, R.; Robertson, M.L. Thermoset Blends of an Epoxy Resin and Polydicyclopentadiene. *Macromolecules* **2016**, *49*, 8960–8970. [CrossRef]



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