

Dielectric and Breakdown Properties of MWCNTand OMMT-Reinforced Epoxy Composites

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Development of the power industry, especially in the field of high-power electricity, is limited by the insulating materials. The main problem of power generation equipment, especially ultra-high-voltage and high-power equipment, is the ability of insulating materials to withstanding voltage. Epoxy resin (EP) is widely used in the power industry. Therefore, it is necessary to improve the performance of EP and demonstrate an energy model of material electrical breakdown. EP has excellent insulation properties, yet poor toughness. By doping with nanomaterials, the toughness of the matrix can be improved on the premise of having little influence on insulation performance. In this paper, two kinds of nanomaterials were added into the matrix, namely multi-walled carbon nanotubes (MWCNTs) and organically modified montmorillonite (OMMT). MWCNTs are conductive, and the insulation properties of EP will be adversely affected if doped in large quantities. OMMT is a nanomaterial with lamellar structure. The toughness of EP can be improved by being doped with OMMT without adverse effect on the insulation performance. Various factors affecting the electric field strength and dielectric properties are analyzed, and models of electric and thermal breakdown are established. In addition, by observing the phenomena of material after breakdown, the energy relation equation of breakdown is re-established.

Key words: Epoxy resin, MWCNTs, OMMT, dielectric properties, breakdown

INTRODUCTION

The electric power industry, especially the ultrahigh-voltage power transmission and transformation industry, has developed rapidly in recent years. In order to reduce transmission loss, it is necessary to continuously improve the voltage level. However, the toughness and heat resistance of traditional insulation materials are very poor, which limits the development of ultra-high-voltage power equipment.^{1,2}

Multi-walled carbon nanotubes (MWCNTs) have excellent electrical conductivity, thermal conductivity and high modulus of elasticity.^{3–5} Carbon nanotubes (CNTs) have a significant effect on the electrical properties of most polymers such that the electrical conductivity of the composites changes evidently as the content of CNTs reaches approximately 1 vol.%.⁶ Meanwhile, CNTs improve the mechanical properties of polymers, yet not the excellent insulation properties.^{7,8} Layered silicates, which could improve the mechanical properties of

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polymers, do not possess the same conductivity as CNTs.⁹ Montmorillonite (MMT), a kind of layered silicate material, is often toughened by polymer. But, on the other hand, when doped with this material, the effect of CNTs on the insulation properties of polymer matrix is reduced to some extent.⁸ Maria et al.¹⁰ found that a very low impurity content of CNTs in a CNT/epoxy resin (EP) mixture could achieve excellent electrical conductivity without decreasing mechanical properties. For most polymers (e.g. EP), improving the dielectric properties is the key to expanding the fields of application. In addition to doped nanofillers, temperature and electric field frequency have great influence on the dielectric properties of polymers.^{11,12} At low temperature, the volume resistance and electrical breakdown strength of many polymers show an upward trend, yet dielectric loss shows a downward trend.^{13–17} Wang et al.¹⁸ discovered that EP matrix composites still possess excellent dielectric properties at low tem-peratures. The research of Tang et al.¹⁹ indicates that a certain amount of CNTs may show an upward trend for the dielectric constant of composites. As the electric field frequency increases to a certain extent, the dipole polarization could not be established in time, which results in the decrease of dielectric constant of almost all polymers.^{20,21} Many nano-fillers, mainly CNTs, have been widely used to modify the dielectric properties of polymers.²

In this paper, MWCNTs after acidification treatment and MMT after simultaneous organic treatment are better dispersed in EP matrix. The dielectric and breakdown properties of EP composites were studied by doping with MWCNTs and OMMT nanoparticles. Meanwhile, the model of minimizing the degree of electrical breakdown damage is found through further study of the breakdown mechanism.

EXPERIMENTAL SECTION

Materials

Industrial-grade bisphenol A EP (E-44) was purchased from Wuxi Resin Phoenix Co., Ltd., China. Methyl hexahydrophthalic anhydride obtained from Anagel Chemical Co., Ltd., China (purity: > 99%) was used as a curing agent. Pyriodine obtained from Tianjin No. 6 Chemical Reagent Factory (purity: > 99%) was used as accelerator. Primordial multiwalled carbon nanotubes (MWCNTs) of length 5-15 μ m, diameter 40–60 nm and purity > 97% were purchased from Shenzhen Nanotech Port Co., Ltd. Primitive montmorillonite (MMT) was purchased from Xi'an Comprehensive Test Center Rock Mineral Chemical Institute, China. Octadecyl trimethyl ammonium chloride, used as an organic modification reagent, was supplied by China Pharmaceutical Group Chemical Reagents Co., Ltd.

Preparation of Acidified Multi-Walled Carbon Nanotubes

Primitive MWCNTs with a mass of 2.5 g, which are doped with concentrated sulfuric acid (98%) and nitric acid (68%) with a volume ratio of about 3:1, are placed in flasks at 80° C for 6 h under the condition of ultrasonication. Then, the mixture is poured into distilled water and filtered by a suction device, and distilled water is continuously poured to dilute the mixture until the PH value of MWCNTs is closely neutral. For further filtration to ensure that the distilled water is completely removed, the acetone is poured into the suction device. The treated MWCNTs nanoparticles are dissolved in acetone reagent for preservation.

Preparation of Organically Treated Montmorillonite

Primitive montmorillonite with a mass of about 20 g and a certain amount of distilled water were placed into a three-necked flask and stirred for 30 min in a water bath at 80°C. Octadecyl quaternary ammonium salt with a mass of 5.6 g was dissolved in distilled water and slowly poured into the three-necked flask to prevent the emergence of a large number of bubbles. The mixture, which was mechanically stirred in a water bath pot at 80°C for 2 h, was filtered by a suction device, while the presence of chloride ions was not detected with silver nitrate solution by continuously pouring distilled water. The final organically treated montmorillonite (OMMT) was dried and preserved.

Preparation of MWCNTs and OMMT/EP composites

The preparation of OMMT (2 wt.%)/MWCNTs (0.1 wt.%))/EP composites is used as an example. EP (100 g) placed in a three-necked flask was sufficiently dissolved in acetone solution. Subsequently, OMMT (2 g) and MWCNTs (0.1 g) were doped with the epoxy matrix and stirred for 24 h in a water bath at 80°C. Simultaneously, the residual acetone and bubbles were removed by vacuum evacuation to avoid affecting the properties of the composites. After that, the curing agent (methyl hexahydrophthalic anhydride) with a mass of 74 g was poured into the mixture and stirred for about 30 min to achieve uniform mixing. Then, the accelerator (pyridine) with a mass of 0.5 g was poured into the mixture. The mixture was poured into a special mold coated with demolding agent, then cured by a certain heating procedure. Finally, the obtained nanocomposites were cooled.

Characterization

The electrical breakdown morphology and fracture surface morphology of composites were observed by scanning electron microscopy (SEM). An Alpha-A dielectric constant and dielectric loss analyzer was purchased from Novocontrol Technologies Co., Ltd.. Samples were processed into circular slices with a diameter of 30 mm and a thickness of 1 mm, and aluminum electrodes were then coated on both layers, simultaneously. The equipment used in the electrical breakdown test was an alternating current (AC) voltage withstand test transformer.

RESULTS AND DISCUSSION

Acidification Mechanism of MWCNTs

CNTs contain amorphous carbon impurities such as amorphous carbon and metal catalysts, which should be functionalized.²⁸ For example, carboxyl groups and hydroxyl groups should be attached to the defects of CNTs.²⁹ Figure 1a is a CNT model with carboxyl functional groups on the surface, which will react with epoxy groups to form chemical bonds as shown in Fig. 1b. Covalent bonds are formed between CNTs and EP, which enhance the interfacial bonding and play a toughening role. Covalent modification is achieved by chemical reaction on the surface of CNTs. In the process of experimental research, covalent modification has been applied widely. The surface of CNTs is bonded with organic groups through chemical reaction, and the organic groups react with organic matrix to improve the dispersion of CNTs and reduce the agglomeration and interface effect.^{30,31} The method applied in this paper was mixing acid acidification of sulfuric acid and nitric acid to make the carbon fivemembered ring structure of fullerene-shaped CNTs. Carboxyl and hydroxyl groups were formed on the surface of the CNTs after strong acid oxidation. Meanwhile, carboxyl and hydroxyl groups were easily formed on CNTs due to the existence of large functional groups and unstable carbon rings, such as five-membered rings and seven-membered rings.

Organization Mechanism of MMT

As a layered silicate crystal, MMT is composed of silica tetrahedron and alumina octahedron in a ratio of 2:1.³² The silicon in silica tetrahedron is replaced by aluminum to decrease the cation concentration among layers; meanwhile, the aluminum in alumina octahedron is replaced by magnesium.³³ The layers of the MMT must be negatively charged for hydrated cations (Na⁺, K⁺, Mg²⁺) to enter the layers



Fig. 1. Model diagram of acidified CNTs (a) and reaction between acidified CNTs and EP (b).



Fig. 2. Model diagram of the MMT layer structure cell (a) and SEM image of MMT (b).

to make the MMT neutral, as shown in Fig. 2a. Nevertheless, the two adjacent layers in MMT are connected by oxygen atoms, with only a weak van der Waals force existing. The layers can slip and rotate, and the cations between the layers can be exchanged.³⁴ There are a lot of hydrophilic and oilthinning inorganic ions among the layers of MMT, which will affect the dispersion in organic matter and the insulation performance of EP.³⁵ Therefore, organized treatment of MMT can change the hydrophilicity of MMT into oil affinity and MMT hydrophilic, which is extremely necessary. In pace with the increase of lamellar spacing, the organic long chain of macromolecules can enter and play a role in the modification of MMT. After modification of organic quaternary ammonum salt cations, the organic part of the long-chain molecule exists among layers, which enlarges the interval between layers to change the hydrophilicity of MMT. The morphology of MMT is shown in Fig. 2b.

Dielectric Constant and Dielectric Loss

The curing temperature has a great influence on the formation of the spatial network structure in EP, which is mainly reflected by the degree of crosslinking and the length of molecular chains among adjacent crosslinking points. The increase of curing temperature leads to the enlargement of crosslinking degree; nevertheless, the length of the molecular chain between adjacent crosslinking points decreases. Under the condition of applied electric field, a larger degree of crosslinking and smaller molecular chain length among adjacent crosslinking points make it more difficult to establish dipole polarization. In Fig. 3a, the relative dielectric constants of pure EP with two curing gradients were measured. In pace with the increase of electric field frequency, the relative dielectric constant decreases gradually. As the electric field frequency increases to a certain extent, the relative dielectric constant tends to be constant. Meanwhile, the accelerated electron oscillation in the material and the dipole are unable to rotate, resulting in the decrease of the relative dielectric constant. Figure 3b shows the trend of dielectric loss of pure EP with the increase of electric field frequency. In pace with the increase of electric field frequency, the dielectric loss of the materials with different curing temperature gradients tends to increase rapidly at first and then reaches a fixed value; simultaneously, the vibration frequency of electrons also rises rapidly. Additionally, the loss becomes greater as the electric field frequency grows. Nevertheless, as the electric field frequency rises to a certain extent, the oscillation speed of electrons is unable to keep up with the change of electric field frequency, resulting in the loss tending to be fixed.

For EP/MWCNT composites, MWCNTs and EP can be regarded as many tiny capacitors. Under the condition of an external alternating electric field,



Fig. 3. The frequency as a function of dielectric constant (a) and dielectric loss (b) under the condition of different curing temperature gradients.

many electrons are captured by the interface between MWCNTs and EP, resulting in the local accumulation of space charge, the non-uniform distribution of free charge in the medium and the polarization of space charge with macroscopic dipole moment.

This occurs according to the equation:

$$tg\delta = \frac{\omega\tau k}{1+\omega^2\tau^2+k} \tag{1}$$

$$k = \frac{\left(R_2 C_2 - R_1 C_1\right)^2}{C_1 C_2 \left(R_1 + R_2\right)^2} \tag{2}$$

where τ is the relaxation time; ω is the angular frequency of applied electric field; R_1 is the resistance of MWCNTs; R_2 is the resistance of EP; C_1 is the capacitance of MWCNTs; and C_2 is the capacitance of EP.

It can be seen from Eq. 1 that dielectric loss $(tg\delta)$ is determined by electric field frequency, resistance, capacitance and relaxation time of the two materials. As shown in Fig. 4a, the dielectric constant of MWCNT composites with different contents changes in pace with frequency increasing. With improvement of the applied electric field frequency, the relative dielectric constant of the composite decreases rapidly at first and tends to be fixed eventually. As shown in Fig. 4b, the dielectric loss of MWCNT composites with different contents



Fig. 4. The frequency and MWCNT content as a function of dielectric constant (a) and dielectric loss (b).

changes in pace with frequency increasing. According to Eq. 1, as $\omega = 0$, particular material

 $tg\delta = 0$, and as $\omega \to \infty$, $tg\delta = 0$; obviously, there is a maximum for $tg\delta$ at a certain frequency. At a certain temperature, the frequency at which the corresponding $tg\delta$ is maximum can be found, due to $\frac{dtg\delta}{d\omega} = 0$:

$$\omega_m = \frac{\sqrt{1+k}}{\tau} \tag{3}$$

When $\omega = \omega_m$,

$$tg\delta_{\max} = \frac{k}{2\sqrt{1+k}} \tag{4}$$

 $tg \delta_{max}$ usually appears at power or audio frequency. As shown in Fig. 4b, the electric field frequencies corresponding to the highest dielectric loss endpoints are identical, which should be power frequency and audio frequency. The polar dielectrics with EP as an example all conform to such characteristics. The polarizability of the medium, depending on molecular polarizability, includes electron displacement polarization, ion displacement polarization, steering polarization and thermionic polarization. Nevertheless, electron displacement polarization and steering polarization mainly have a function for EP/MWCNT/OMMT composite. Electron displacement polarization, which exists in various dielectrics and has a short establishment and disappearance time (about 10^{-15} – 10^{-16} s), is a phenomenon about induced dipole moment, caused by the elastic displacement of the peripheral electron cloud that is relative to the nucleus. In addition, the electron polarizability is determined by the distribution of electrons in the atom but not temperature. On the other hand, the establishment of steering polarization, which takes a long time $(10^{-6}-10^{-2} \text{ s})$, is unable to keep pace with quickly changing frequency. Therefore, the dielectric constant finally tends to be fixed, as the frequency of the alternating electric field increases to a certain degree; the situation is shown evidently in Fig. 5. The different content of OMMT nanomaterial has a great influence on the polarizability and leads to various trends of the dielectric constant. The dielectric constant increases with improvement of OMMT content due to the interfacial polarization. On the other hand, excessive OMMT is unable to be well dispersed in the epoxy matrix, resulting in defects and free charge accumulation. Nevertheless, the existence of OMMT nanomaterial causes the free charge movement on MWCNTs to be blocked, thus inhibiting the formation of the conducive network. On the other hand, the variety of alternating voltage frequency has a great influence on the dielectric loss of composite. In Fig. 6, the results show that the dielectric loss of the composites varies with the frequency of alternating voltage, under the condition of different OMMT contents (2 wt.%, 4 wt.%, 8 wt.%). In the process of increasing frequency, the dielectric loss $(tg\delta)$ rises rapidly at first. As the electric field frequency reaches a certain value, $tg\delta$ tends to be stable because of the relaxation polarization not being established. Nevertheless, the dielectric loss is much greater than others occurring at low electric field frequency, as presented in Fig. 6, which shows that the maximum dielectric loss could satisfy Eq. 4. On the other hand, the influence of nanomaterials on polarization time makes the epoxy matrix produce the maximum dielectric loss in the case of different alternating electric field frequency. The model can be used to determine the conditions of minimum dielectric loss, to reduce the loss and the electrical aging speed of insulating materials and to prolong the service life time of power equipment.

Voltage Breakdown

Figure 7 is a schematic diagram of the powerfrequency AC voltage withstanding test of the sample. Because the area of the electrode is larger than the area of the sample, the voltage withstanding test should be carried out in the insulating oil to prevent flashover discharge at the edge.



Fig. 5. The frequency and MWCNT content as a function of dielectric constant when the OMMT content is 2 wt.% (a), 4 wt.% (b) and 8 wt.% (c), respectively.

The sample of AC voltage breakdown is regarded as the result of the continuous oscillation of electrons under an electric field, resulting in impact on materials, as shown in Fig. 8a. After the material is broken down, besides the breakdown hole, the carbonization and the crack area are also generated,



Fig. 6. The frequency and MWCNT content as a function of dielectric loss when the OMMT content is 2 wt.% (a), 4 wt.% (b) and 8 wt.% (c), respectively.

as shown in Fig. 8b. The formation of carbonization area is due to the heat loss caused by the repeated oscillation of electrons, which leads to the higher temperature in the relevant area and carbonization. In addition to the energy of carbonization and breakdown, some of the energy generated by the



Fig. 7. Model diagram of sample applied voltage.



Fig. 8. Voltage breakdown diagrams.

applied electric field needs to be absorbed in the form of strain energy of the material, which results in cracks.

Electrical breakdown damage is an irreversible process of change, which goes through the process of origin, development, instability and destruction. Failure of materials will result in irreversible deformation, such as a carbide zone and permanent fracture. In the actual experiment, it is difficult to observe the origin and development of material electrical breakdown from the randomness of electrical breakdown due to the short time. Nevertheless, the channels formed after material breakdown can be obtained by scanning electron microscopy (SEM). Figure 9 shows the voltage breakdown SEM of composites with different components of MWCNTs and OMMT. The degree of carbonization in the breakdown diagram of pure EP is very low, yet the cracking is serious. This phenomenon shows that the toughness of EP is enhanced by the addition of nanomaterials; nevertheless, the breakdown energy produced by the applied electric field is released by carbonizing the material. Compared with Fig. 9d, e and f, the longer the length of MWCNTs, the more serious the carbonization occurs, and the larger the diameter of the perforation. In pace with the increase of the length of CNTs, the higher the surface energy is, and the easier the agglomeration is, the greater the influence on dielectric properties is. After OMMT nanoparticles were phenomenon doped. the carbonization was reduced, which indicated that the addition of OMMT improved the adverse effects caused by MWCNTs. For further information, refer to Supplementary Fig. S1. Figure 10 shows the breakdown strength of the composites with different content of OMMT as the content of MWCNTs is 0.5 wt.%. The breakdown strength of pure EP is 26.5 kV/mm by testing. Comparing with the data in Fig. 10, the breakdown strength of composites with OMMT content of 4 wt.% is slightly higher than that of pure EP, yet the breakdown strength of composites with other components is slightly lower than that of pure EP, which shows that the addition of MWCNTs and OMMT nanoparticles has a negative effect on the breakdown strength of EP.

Wagner first tried to quantitatively determine the thermal breakdown voltage of solid dielectrics by mathematical method. According to the analysis of Wagner's thermal breakdown theory, the research on thermal breakdown can be attributed to the establishment of a thermal equilibrium equation under an electric field, for solving the problem of thermal breakdown voltage. The effective resistivity of dielectrics under alternating voltage is smaller than that of direct current (DC); hence, the AC thermal breakdown voltage is usually lower than that of DC thermal breakdown voltage. The AC thermal breakdown voltage is proportional to the square root of the dielectric effective resistivity, and the effective resistivity is inversely proportional to the dielectric constant, loss angle tangent and voltage frequency. Consequently, the thermal breakdown field strength of dielectrics can be expressed as follows:³⁶



Fig. 9. SEM images of voltage breakdown of composites: (a) pure EP, (b) MWCNTs(0.9 wt.%)/OMMT(2 wt.%), (c) MWCNTs(0.7 wt.%)/OMMT(6 wt.%), (d) 0.5 wt.%MWCNTs (5–15 μ m), (e) 0.5 wt.% raw MWCNTs, (f) 0.5 wt.% MWCNTs (< 2 μ m), (g) MWCNTs(0.5 wt.%)/OMMT(4 wt.%).



Fig. 10. Breakdown voltage of EP/MWCNT/OMMT composite.

$$E_{0c} = \frac{B}{\sqrt{\varepsilon_r f t g \delta}} \tag{5}$$

where *B* is a constant, *f* is the electric field frequency, ε_r is the relative dielectric constant, and $tg\delta$ is the dielectric loss.

The thermal breakdown field strength decreases in pace with the increase of frequency, because the dielectric loss increasing in the wake of the rise of frequency. With a constant applied voltage, the heating of dielectric increases with frequency rising, resulting in the decrease of thermal breakdown field strength.

Yixuan et al. established a model for predicting the critical breakdown electric field strength of materials under electrostatic field.^{37,38} The energy at the channel is composed of electrostatic energy 7278

and electromechanical energy. In pace with the rise of the applied electric field, the crack propagates, and the surface energy of the channel is overcome. When the external electrostatic and electromechanical energy is higher than the surface energy of the channel crack, the dielectrics are broken down.³⁹ The energy required for crack passage propagation during electric shock can be regarded as the energy required for crack propagation in fracture mechanics. The expression of critical electric field strength for breakdown is as follows:

$$E_c = \left[\frac{2}{r\varepsilon_0\varepsilon_r} \left(\sqrt{r^2Y^2 + 4G_crY} - rY\right)\right]^{\frac{1}{2}}$$
(6)

where r is the cylindrical channel with radius, Y is Young modulus, and G_c is the mechanical energy release rate of materials.

The thermal and electrical breakdown theories cited in the previous paper are compared and analyzed. The steady thermal breakdown voltage is lower than the electric breakdown voltage; otherwise, the electric breakdown should occur instead of the thermal breakdown:

$$\left[\frac{2}{r\varepsilon_0\varepsilon_r}\left(\sqrt{r^2Y^2 + 4G_crY} - rY\right)\right]^{\frac{1}{2}} > \frac{B}{\sqrt{\varepsilon_r ftg\delta}}$$
(7)

$$r\frac{16f^2tg^2\delta G_c Y}{4B^2Y\varepsilon_0 ftg\delta + B^4\varepsilon_0^2} = r_c \tag{8}$$

For a particular material, *Y*, G_c , *B* and ε_0 are all the constants.

$$tg\delta = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty\omega^2\tau^2} \tag{9}$$

where ε_{∞} is the relative dielectric constant of the optical frequency and ε_s is the static relative dielectric constant.

So r_c is a function of f. According to $\frac{dr_c}{df} = 0$, the following conclusions can be drawn:

$$f = \sqrt{\frac{\varepsilon_s}{2\pi\tau(\varepsilon_s - \varepsilon_\infty) - 4\pi^2\tau^2\varepsilon_\infty}}$$
(10)

Under the condition that Eq. 10 is satisfied, the minimum value of r_c is obtained, which shows the radius of a specific material's breakdown hole is minimized at a specific electric field frequency. The relationship between electric field frequency and relaxation polarization time of EP at different curing temperatures and composites with different contents of OMMT and MWCNTs is shown in Fig. 11. In pace with the relaxation polarization time increasing, the electric field frequency decreases. As the relaxation polarization time increases to a certain extent, the electric field frequency of the electric field increases to a certain extent, the fast change of alternating electric field leads to the

inability to establish relaxation polarization. The correctness of Eq. 10 can be seen from the curve trend shown in Fig. 11. The relationship between relaxation polarization time and electric field frequency of pure EP at three different curing temperatures is shown in Fig. 11a, and it can be seen that curing temperature has little influence on the relationship between relaxation polarization time and electric field frequency due to the three curves having little difference. The relationship between the relaxation polarization time and the electric field frequency of EP/MWCNTs is shown in Fig. 11b. In pace with the increase of MWCNT content, the relaxation polarization time decreases at the same electric field frequency, which indicates that doping with a certain amount of MWCNT is beneficial to the establishment of relaxation polarization of composites. Figure 11c shows that OMMT with 2 wt.% content has little effect on the relationship between electric field frequency and relaxation polarization time. As shown in Fig. 11d, e and f, the relationship between electric field frequency and relaxation polarization time of the composites is obviously affected by OMMT content of 4 wt.%, 6 wt.% and 8 wt.%, which indicates that the relaxation polarization of the composites will be significantly affected as OMMT content reaches a certain level. For power equipment, minimizing the size of breakdown holes, generated by an electric field, can reduce the degree of damage and the difficulty of repairing the damaged parts.

The energy applied on the sample is as follows:

$$W_{_{0}} = U^{2}\omega Ct = U^{2}\omega \frac{\varepsilon_{r}S_{1}}{4\pi kd}t \qquad (11)$$

where S_1 is the electrode surface area, d is the specimen thickness and k is the electrostatic force constant (9 × 10⁹ N m²/C²).

If the energy applied is electrostatic and electromechanical, Eq. 11 should be changed to

$$W_{_{0}} = U^{2}\omega Ct = U^{2}\omega \frac{\varepsilon_{r}S_{1}}{4\pi kd}t = \frac{1}{2}\varepsilon E^{2}dV + \frac{1}{2}\sigma\gamma dV$$
(12)

Taking pure EP as an example, $t = 6.1979 \times 10^{-9}$ s in the equation is obtained.

The actual electric shock penetration process does not take place in such a short time; consequently, the excess energy is used to generate cracks and carbonization on the surface of the sample. Nevertheless, the toughness of EP is improved by doping with nanoparticles (MWCNTs and OMMT), and the critical surface energy release rate of surface cracking becomes larger. Hence, excess energy must be released in the form of carbonization of materials, which leads to the aggravation of carbonization. Equation 12 is unable to express the energy relationship. The energy equation should be modified as follows:



Fig. 11. The relationship between relaxation polarization time and electric field frequency: (a) different curing temperatures (pure EP), (b) EP/ MWCNTs composite, (c) EP/MWCNTs/OMMT (2 wt.% OMMT), (d) EP/MWCNTs/OMMT (4 wt.% OMMT), (e) EP/MWCNTs/OMMT (6 wt.% OMMT), (f) EP/MWCNTs/OMMT (8 wt.% OMMT).

where W_c is the carbonization energy.

The modified expression can more accurately reflect the real energy composition when the breakdown occurs.

When nanoparticles are doped with EP, the fracture section also shows the difference between brittle fracture and ductile fracture, and relevant pictures can be seen in supplementary Figs. S2 and S3. The effect of nanoparticles on the toughness of EP was confirmed by impact tests of composites with different content of nanoparticles.

CONCLUSION

In this paper, the mechanical and dielectric properties of EP reinforced by MWCNTs and OMMT nanoparticles are analyzed. The dielectric properties of the composites are mainly measured and analyzed in terms of frequency conversion dielectric constant, frequency conversion dielectric loss and breakdown voltage. In pace with the increase of electric field frequency, the dielectric constant of the composites decreases rapidly and tends to a fixed value; meanwhile, the dielectric loss of the composites reaches a maximum when the frequency of the electric field reaches a certain value. Referring to the electric field breakdown images, we find that there are carbonization and cracks in the morphology after breakdown, and the breakdown phenomena on composites are discrepant with varying content of nanoparticles. According to the theory of thermal breakdown and electrical breakdown, the model of thermal breakdown voltage less than electrical breakdown voltage is modified. On the other hand, as the electric field frequency and relaxation polarization time reach a certain functional relationship, the smallest breakdown size and breakdown damage can be achieved.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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