Experimental study on temperature-domain dielectric spectroscopy of spontaneous combustion propensity coal

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Abstract
To investigate the effects of spontaneous combustion coal on the measurements of temperature-domain dielectric characteristics in heating process, low-frequency dielectric characteristics experiment was performed by the Hioki 3532-50 LCR tester and self-developed and programmed temperature dielectric clamping device. Three different thicknesses of dried coal samples were collected and their dielectric properties were studied at different temperatures, frequencies and voltages. The results show that the thickness of coal samples would bring error to the measurement, the different voltage does not substantially affect the results in the test voltage range of AC 1-5V, and the relative dielectric constant gradually increased under different test frequencies from 30 ℃ to 110 ℃ and then sharply decreases from 180 ℃, following a stabilized value. The relative dielectric loss was slowly increasing from 30 ℃ to 200 ℃. It was concluded that the relative dielectric constant and dielectric loss of spontaneous combustion coal heated up to 200 ℃ were significantly lower than the value of the initial room temperature.
Keywords: SPONTANEOUS COMBUSTION COAL, TEMPERATURE-PROGRAMMED, DIELECTRIC CHARACTERISTICS, LOW FREQUENCY

1. Introduction

Coal is one of the important raw material and strategic resources for iron and steel industries [1-4]. Like other fossil fuels, coal is non-renewable energy resource[5]. However, coal spontaneous combustion occurred in the coal outcrop, ground coal storage pile, gob and the pillar, not only burn a lot of coal resources, emit large amounts of harmful gases and pollute atmosphere, but also cause secondary disasters. In China, there is a high percentage and wide coverage of coal seams, coal piles and coal mines with the risk of spontaneous combustion, and annual economic losses caused by spontaneous combustion cost billions of dollars[6]. Many researchers [6-10] from home and abroad have carried out research on localization of high-temperature zone of coal spontaneous combustion fire and made many achievements in research. Studying the dielectric properties of coal spontaneous combustion of coal body with temperature change is an important means of location the of high temperature source. But there are still no comprehensive study on its mechanism so far. In view of this, to carry out experiments on spontaneous combustion of coal dielectric properties changes in physical characteristics and localization of coal fire will be of great scientific significance, and has important social and economic significance for protection of resources and environment.

In natural occurrence state, coal show some dielectric properties in alternative electric field, which can be explained by micro and macro mechanisms. Looking from microcosmic level, condensed aromatic structures of coals contain a certain amount of polar oxygenic functional groups (such as -COOH and -OH, etc.). As the key moment vector sum of these polar functional groups is generally not zero, and the sum of segment dipole moment and molecular dipole moment is not zero, they showed significant polarization properties. From the macro level, coal is a complex mixture of compounds, and contain developed pore structure, inorganic mineral components (such as sulfur grading), and pore water (higher dielectric constant value) which contributed greatly to the dielectric properties of the coal.

Dielectric characteristics of coal usually is characterized by dielectric constant (real part) and dielectric loss (imaginary part) when the additional power supply is an AC electric field. The expression of dielectric constant:

$$\varepsilon = \varepsilon' - i \cdot \varepsilon'' = \varepsilon_0 (\varepsilon_r - i \cdot \varepsilon_i) \quad (1)$$

ε' is the dielectric constant, F/m; ε'' is the dielectric loss, F/m; i equals $\sqrt{-1}$; ε_0 is the vacuum dielectric constant, equals 8.85×10^{-12} F/m; ε_r is the relative dielectric constant; ε_i is the relative dielectric loss.

At low frequencies (1 KHz ~ 20 MHz), the parallel plate capacitor method combined with digital bridge is usually adopted to measure the dielectric of coal samples[11], and dielectric loss tangent capacitor can be directly read in digital bridge. Coal is larger dielectric-loss medium, which the external electric field energy will cause a larger loss under the polarization of external electric field impact, and dielectric loss of such a medium should be studied by series equivalent circuit. Therefore, parallel plate capacitor can be equivalent to the resistor *Rs* and capacitor *Cs* connected in series. The series equivalent circuit as shown in Fig.1. Coal's dielectric constant and dielectric loss can be calculated by the following formula:

$$\varepsilon' = \frac{tC}{\pi (d/2)^2} \quad (2)$$

$$\varepsilon_r = \varepsilon' / \varepsilon_0 \quad (3)$$

$$\varepsilon'' = \varepsilon' D = \varepsilon' \tan\delta \quad (4)$$

$$\varepsilon_i = \varepsilon'' / \varepsilon_0 \quad (5)$$

C is parallel plate capacitor (F); *t* is the thickness of coal sample (m); *d* is the diameter of the electrode plate (m); Ratio of the real and imaginary part called dielectric loss tangent is represented by *D*.

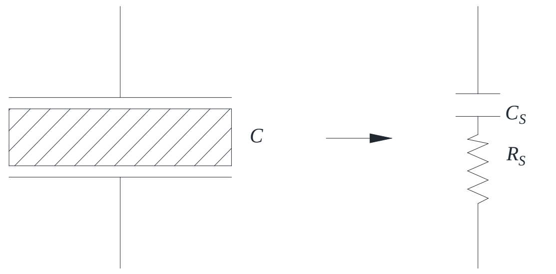


Figure 1. Series equivalent circuit model of coal sample

Formerly, several researchers have achieve some preliminary findings on dielectric characteristics of coals in high-temperature environment. Wan [12]studied the temperature dependence of dielectric properties of eight kinds of different rank coal samples between room temperature and 120℃ and the findings revealed that the increase in temperature produces a reduction in the dielectric constant. Xu [13]used a high frequency Q meter in 1 MHz and 160 MHz frequency to study the dielectric characteristics of a plurality of coal sample heated to 120 ℃ and the study results show that relative dielectric constant of different degrees of metamorphism of coals have reduced to varying degrees with increasing temperature. Marland [14] studied the dielectric properties of different rank of Britain coals at different temperatures by circular cavity method and the study results showed that a substantial decrease in the dielectric constant is evident between 80 and 180 ℃, and the dielectric constant remains relatively constant during the cooling cycle in (0.615, 1.413, 2.216 GHz)frequency selected. Zubkova et al. [15] studied the mechanism of the dielectric changes of three Australian coals in pyrolysis process, and established the relationship between coal pyrolysis process variation and dielectric properties of the coke quality.

In all these studies, the experiment parameters were limited in high-frequency range, low temperature stage of 25-100℃, and milled shape of coal samples which after a polished, especially for coal dielectric properties easily from less coal. Therefore, we study the dielectric properties at low frequency sweep conditions on spontaneous combustion coal, which could provide a theoretical basis for the use of electromagnetic prospecting method for detecting the coal spontaneous combustion fire area of coal outcrop, ground coal storage pile, gob and the pillar.

2. Experimental

2.1 Analysis and preparation of coal samples

The test coal samples are gas coal from #12 spontaneous combustion seam of Linnancang coal mine, of which the tendency of spontaneous combustion is class Ⅱ, spontaneous combustion, combustion period is two months. The proximate analysis experiments were accordant with the standard (GB/T212—2001), and analyze the coal samples by GF-A6 automatic proximate analyzer. The ultimate analysis experiment using Germany Elementar vario Macro CNS(with Oxygen Kit) ultimate analyzer. Proximate and ultimate analysis results are shown in Table 1.

Preparation of coal samples were conducted in the following manner. The big lump coal samples collected from underground with seal preservation treatment. Then, they were cored and cut by machine and manual polishing. After that, the samples were made in the form of cylindrical shape which the diameter was Φ50 mm, height was 10 mm, 20 mm or 30 mm and the flatness of the end face of the specimen were controlled within 0.5 mm. To eliminate the influence of external moisture on the experimental results, the coal sample was dried in a vacuum drying oven (DZF-6050D). To avoid damage of coal structure due to high temperature drying, the heating temperature kept at 50 ℃ and lasting for 24 h. Finally, taking out the coal samples that were cooled down to room temperature, and sealed in a glass bottle filled with dry N_2 for following use.

Table 1. Proximate and ultimate analysis of the coal samples used in this study

Proximate analysis (%)					Ultimate analysis (%)				
M_{ad}	A_{ad}	V_{ad}	FC_{ad}		C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}
2.06	5.49	38.06	54.39		75.33	5.99	11.01	1.74	0.55

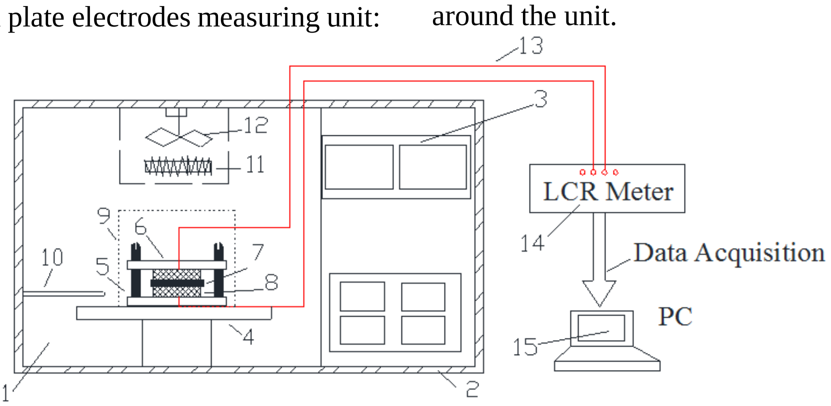
2.2 Dielectric test system

Coal dielectric measurements experimental system is shown in figure 2. The apparatus comprises four units: (a) programmed temperature control and display unit; (b)parallel plate electrodes measuring unit; (c) specimen holding unit, data acquisition and recording unit. Instructions of each unit are shown below:

(1) Programmed temperature control and display unit: Stainless steel liner, and the interior is filled with asbestos insulation materials, which can achieve 0.1 ℃ accuracy temperature control in the temperature range of 30 to 250 ℃. The temperature-control chamber and sample temperature can be displayed on the digital meter timely.

(2) Parallel plate electrodes measuring unit: Three-electrode system, and the electrode materials are stainless steel (309S) with good conductive properties, high temperature resistance and anti-oxidation. Measuring electrode and the counter electrode are 35 mm, 42 mm diameter disc with the guard electrode adopted concentric ring structure which the inner diameter is 37 mm, and outer diameter is 42 mm.

(3) Specimen holding unit: Using high temperature resistance stainless steel sheet (309S) and bolts to hold the samples. By use of high temperature resistance quartz glass to insulate treatment between the stainless steel sheet and the measuring electrode, and shielded copper net to prevent external electromagnetic interference around the unit.



(1)temperature-programmed furnace; (2) insulation; (3) temperature controlling system; (4) steel scaffold; (5) test fixture; (6) quartz glass; (7) coal sample; (8) stainless steel electrode; (9)—shielding net; (10) thermocouple; (11)

heater; (12) fan; (13) shielded wire; (14) LCR meter; (15) PC.

Figure 2. Schematic diagram of dielectric parameters measurement system

2.3 Experimental Methods

According to dielectric parameter measuring system diagram shown in Fig.2, each of units the system were completely assembled, and then the different thickness of coal samples were put into the specimen holding apparatus and adjusted the bolt so that no gap between the coal sample and the electrode plate. Setup temperature of the oven in the range of 30-200 ℃ with heating rate of 1 ℃/min. Select 1 kHz, 10 kHz, 20 kHz, 50 kHz, 100 kHz frequency, and 1 V, 2 V, 3 V, 4 V, 5 V voltage values. Open and short calibration was carried out before measurement. Then record dielectric data of the coal samples when the values of LCR meter were stable.

3 Results and Discussion

3.1 Effects of sample thickness and test voltage

Since the thickness of coal samples may affect the homogeneity of heating, and the electric field edge distortion of parallel plate electrodes. We studied the dielectric properties（ε', ε''）from different thickness of coal samples, so as to select the right type of sample suit for experimental heating conditions. As shown in figure 3, under the 100 KHz frequency and 2 V voltage condition, the dielectric constant of the 10 mm and 20 mm thickness of coal samples were in the same trend with increasing temperature, but the dielectric loss of the 30 mm thickness of coal sample was negative value in many measured point. So the 30 mm thickness of sample is not suitable for measurement in this test conditions. From figure 3, with the increase in the thickness of the coal sample, the initial dielectric constant was small, but as the temperature was raised to 180 ℃, the dielectric constant of the both samples became to converged.

At the 100 KHz frequency and different voltages, the 10 mm thickness of coal sample was selected to do dielectric measurements. From the experimental results, a slight (1-5 V) of the sinusoidal AC voltage has little effect on the dielectric properties of coal sample, as shown in figure 4.

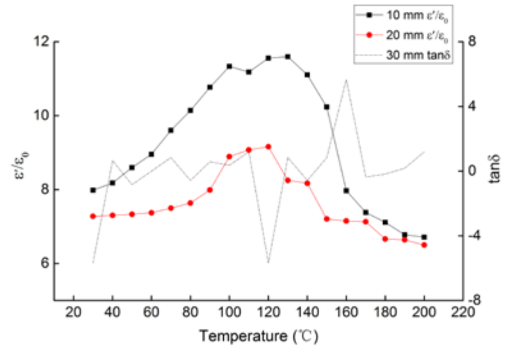


Figure 3. Relative dielectric constant and loss tangent of the different thickness coal samples

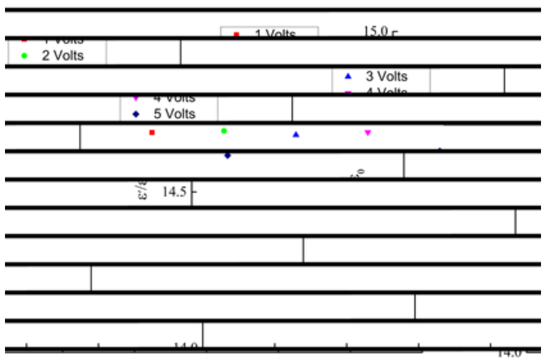


Figure 4. Relative dielectric constant of coal samples at different voltages

3.2 Effect of the test frequency on the dielectric constant during the heating process

Figure 5 represents the relative dielectric constant curve of a 10mm of coal samples at 2 V voltages and different frequency with changing temperature. The experimental results show that the temperature dielectric constant curve of each frequency showed a similar regularity: in the temperature-rising process of 30 ℃ to 110 ℃, the relative dielectric constant was slowly increasing and reached the maximum value at 110 ℃; In the temperature-rising process of 110 ℃ to 180 ℃, the relative dielectric constant began to decrease rapidly, showing a linearly decreasing trend; However, over the 180 ℃，the relative dielectric constant was stable, and reduced by 18%～40% than in the initial temperature. The reason for this phenomenon is that the coal sample simply removed external water at low-temperature drying (50 ℃), meanwhile a portion of intrinsic water and bound water was left in the pores. The orientation polarization of water was the main contribution of the dielectric constant. The lower the frequency, the more obvious of the orientation polarization, and the dispersion phenomenon was more obvious. The pore water of coal was completely evaporated when the temperature was higher than 110 °C. Electronic polarization was the main role of the dielectric constant. The increased polar oxygen-containing functional groups in coal lead to orientation polarization interference, which reduce the degree of polarization and result in a low dielectric constant values.

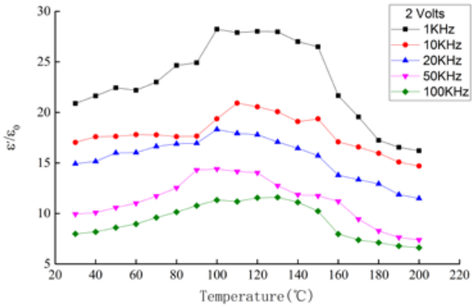


Figure 5. Effect of temperature on relative dielectric constant

In addition, the dielectric constant is smaller with the higher frequency at the same temperature of environment, it means that dispersion of the coal samples is similar in some degree. For instance, the dielectric constant is 20.89 in 1 KHz frequency and at 30°C, which is higher than 7.98 under test frequency of 100 KHz. Experimental results show a high coherence with that of [14] in the same temperature range.

The relationship of temperature and relative dielectric constant can be expressed with polynomial function and linear function as follows:

$$\varepsilon'/\varepsilon_0 = \begin{cases} aT^2 + bT + c & (30 \le T < 110) \\ aT + bT & (110 \le T \le 180) \end{cases} \quad (6)$$

Where T is the temperature of environment and a, b and c are functional relationship.

Coefficients of fitting equation and correlation coefficients under different frequency have been showed in Table 2. Fitting result shows that relative dielectric constant and temperature of environment have significantly linear relationship when the temperature over 110 °C.

Table 2. Fitting relationship of relative dielectric constant and temperature

Temperature (℃)	Frequency （KHz）	*a*	*b*	*c*	Correlation R^2
$30 \le T < 110$	1	1.37E-03	-0.08863	22.74615	0.92171
	10	3.85E-04	-0.03038	17.95289	0.82585
	20	1.70E-04	0.02069	14.20911	0.91131
	50	6.90E-04	-0.01975	9.82871	0.9613
	100	0.00971	0.00971	7.35633	0.99644
$110 \le T \le 180$	1	-0.16229	48.01506	—	0.81622
	10	-0.07537	29.6323	—	0.92569
	20	-0.08071	27.33271	—	0.94911
	50	-0.08196	23.56443	—	0.94345
	100	-0.07275	20.31577	—	0.81065

3.3 Effect of frequency on the dielectric loss during the heating process

Figure 6 shows the curve of 10mm thick coal samples were tested in different frequency and in different temperatures. The dielectric loss have major difference in different frequency and have higher value. Obvious loss peaks were found when the frequency of applied AC are 1 KHz and 10 KHz. It is because that water in porosity of coal cause interfacial polarization when testing frequency is low. The dielectric loss of 20 KHz,50 KHz and 100 KHz will increase slowly with the temperature increment before 110 °C. When coal is at stage of low temperature and oxidation, inrush of oxygen makes side-chain of aliphatic hydrocarbon be attacked more easily. That leads to that -OH and -COOH gradually increase with the increase of temperature. The speed of turning-direction polarization of polar functional groups lag the turning rate of electric field, which lead to the loss of electric energy which is used to overcome viscosity resistance of medium. When the increase of temperature and oxidation keep going, carbonyl is generated from hydroxyl oxidation, and carbonyl falls off and resolves under high temperature. CO and CO_2 will be generated and overflow from coal, which leads to the decrease of polar oxygen-containing functional groups. Turning-direction polarization of polar oxygen-containing functional groups remained can't keep up with the change of electric field and decreases gradually, then dielectric loss becomes small.

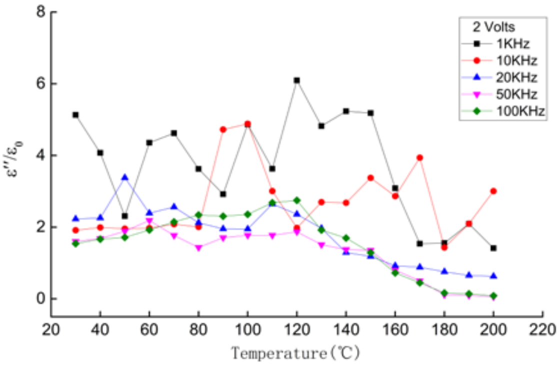


Figure 6. Effect of temperature on relative dielectric loss

4. Conclusion

We conduct a series of experiments on the dielectric characteristic of spontaneous combustion propensity coal samples at low frequency in the experimental platform. The characteristics of dielectric constant and dielectric loss are analyzed in detail, and then main conclusion as following:

(1) To ensure reliability of experimental results, experimental conditions are revised in advance. It is found that the thickness of coal sample have effect in the result of experiment, so we recommend its' thickness should be less than 10mm. In addition, testing sinusoidal voltage have little effect in experimental result.

(2) Dielectric characteristic of coal samples in different testing frequency and temperature is determined by LCR digital bridge. Relative dielectric constants $\varepsilon'/\varepsilon_0$ in those cures showed similar disciplinarian. The relative dielectric constant increase slowly in the range of 30 ℃ to 110 ℃, but show a rapid linear reduction until 180 ℃, and reach a stable value finally. At the same time, the fitting result of experimental data prove this trend.

(3) Because of the conduction loss of water and interfacial polarization, relative dielectric constant $\varepsilon'/\varepsilon_0$ have obvious dispersion phenomenon at low frequency(1 KHz and 10 KHz) when in heating. The dielectric loss of other three frequency do not change sharply in the range of 30 ℃ to 200℃, but only increase at first and then decrease slowly.

(4) When the temperature of coal samples over 200 ℃, the relative dielectric constant and the dielectric loss are both lower than that of initial temperature significantly.

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