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Thermal Decomposition and Moisture Absorption Kinetic Analysis of Spaceflight Cork Board

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Abstract: *The thermal properties of aerospace cork board were studied by thermogravimetric analyzer at room temperature to 1000 ℃. The hygroscopic characteristics of aerospace cork board were studied by constant temperature hygroscopic method in the range of 20 ℃ to 40 ℃. The results show that the pyrolysis process of cork board is similar to that of cork (particle), and the remaining products are mainly adhesives. The initial hygroscopicity of cork board meets Fick's second law, and the wet diffusivity and activation energy increase with the increase of temperature. According to the C-R model of thermal decomposition and water diffusion formula, the kinetics of pyrolysis and moisture absorption of cork boards were described, and the related kinetic parameters were calculated, which provided a reference for the aging research of cork board.*

Keywords: *cork board, kinetic analysis, thermal decomposition, moisture absorption*

1. Introduction

Cork is the existence in nature of a kind of porosity is high, density is small, the material that can have screen effect to heat, its product also has low heat conduction, heat resisting and chemical stability good wait for numerous advantages [1]. Cork and the performance of its products in production, manufacture and use process can be affected by temperature and moisture, because this is more to cork pyrolytic and hygroscopic characteristics.

The DSC-TGA method is widely used in pyrolysis studies of cork at home and abroad, and it is found that the pyrolysis of cork (particle) mainly takes place in the range of 150℃ to 550℃. Among the main components, hemicellulose is decomposed first, followed by cellulose and lignin, followed by extract and suberin [2-3].Ali Sen et al.[4] also found the thermal resistance effect of suberin and extract and the possible catalytic effect of inorganic substances through research.Yanming Ding et al. [5] analyzed the reaction mechanism of cork by using the Coats-Redfern method. By comparing the activation energy calculated by the Flynn-Wall-Ozawa method, they found that the activation energy based on diffusion mechanism was the best when the conversion rate was lower than the limit value.

A. M. Gil et al. [6] found that cork is a hydrophobic material, and suberin is the key component that determines the water resistance of cork. Rosa M et al. [7] found that the radial water diffusion rate of cork was fast and the anisotropy was small under the water immersion conditions of room temperature (20℃) and 90-100℃. The diffusion coefficient at 90℃ was two orders of magnitude larger than that at room temperature. Lequin Sonia et al. [8] found by thermogravimetric analysis that the adsorpt-desorption process of cork was irreversible and only a physical process, and obtained a two-step adsorption process in which water formed cluster adsorption on the surface and water diffused to the cell wall.

At present, cork particles and natural cork are mainly used to study their pyrolysis at high temperature and their hygroscopic characteristics mainly by cooking. However, there are few researches on pyrolysis and hygroscopicity of cork products, and the pyrolysis curve and hygroscopicity of cork wood at relatively low temperature are not known.

In this paper, the TG-DTG curve and hygroscopic characteristic curve of the aerospace cork board were obtained through thermogravimetric and hygroscopic experiments. The decomposition and hygroscopic process of the cork board were described by using the kinetic equation and microscopic properties characterization, which provided a reference for the follow-up study on the hygroscopic aging performance of the cork board.

2. The Experiment Part

2.1. The Experiment Material

The selected sample for this experiment is cork for aerospace, provided by the Fourth Institute of Science and Industry. The cork board is composed of high-quality cork particles and butanitrile phenolic adhesive, the diameter of cork particles is 0.3-0.45mm, the mass fraction of cork particles and adhesive is about 78% and 22% respectively. The cork board sample will be stored in a drying box at 80℃ for 2h before the experiment, and then stored in the drying box at room temperature.

2.2. Pyrolysis Experiment

The thermogravimetric analysis experiment was carried out by using SDT-Q600 thermogravimetric differential thermal analyzer manufactured by TA Company, and the TGA signal of the sample was measured at the same time. The sample in the drying oven was cut 5-10mg and put into the ceramic crucible. The initial temperature was set at room temperature, the termination temperature was set at 1000℃, the purge gas was N_2, the flow rate was set at 20 ml/min, and the sample heating rate was 20℃ /min.

2.3. Moisture Absorption Experiment

A digital display constant temperature water bath was used to conduct the moisture absorption experiment of the cork board. In the process of moisture absorption, a high precision electronic balance (accuracy is 0.0001g) was used to measure the quality change of the sample. In the experiment, the hygroscopic temperature of distilled water was set at 20℃, 25℃, 30℃, 35℃ and 40℃. Three parallel samples were taken from each group, and the average hygroscopic rate of the samples was taken. According to ISO 7322-2014 composite cork test method, the size of cork board hygroscopic sample is 50 mm×50 mm.

2.4. Microstructure Characterization

Through fourier transform infrared spectrometer, the functional groups of the cork board sample before and after hygroscopic were analyzed and tested. According to the position, shape and strength of the absorption peak of the functional group, the chemical changes of the cork board sample before and after hygroscopic were speculated.

3. Kinetic Theory

3.1. Pyrolysis Kinetics Equation

Assuming that the pyrolysis process of cork board is combined with a simple kinetic equation, $f(\alpha)=(1-\alpha)^n$ is selected as the reaction mechanism function of cork board, then:

$$\frac{d\alpha}{dt}=k\left(1-\alpha\right)^{n} \tag{1}$$

α is pyrolysis rate:

$$\alpha=\frac{w_0-w_t}{w_0-w_f}\times 100\% \tag{2}$$

w_0 is the initial mass of the sample, w_f is the final mass of the sample, w_t is the instantaneous mass of the sample. A single scanning rate was adopted in the experiment, and β was the experimental heating rate:

$$\beta=\frac{dT}{dt}=20℃/\min \tag{3}$$

The Arrhenius and pyrolysis kinetic reaction equation were combined to obtain:

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$$\frac{d\alpha}{dT}=\frac{A}{\beta}\times\exp(-\frac{E}{RT})\times\left(1-\alpha\right)^{n} \tag{4}$$

After finishing the integral:

$$\int_0^{\alpha}\frac{d\alpha}{\left(1-\alpha\right)^{n}}=\int_{T_0}^{T}\frac{A}{\beta}\times\exp(-\frac{E}{RT})dT \tag{5}$$

Cork pyrolysis reaction can be regarded as first-order reaction, so formula (5) can be expressed as:

$$\int_0^{\alpha}\frac{d\alpha}{1-\alpha}=\int_{T_0}^{T}\frac{A}{\beta}\times\exp(-\frac{E}{RT})dT \tag{6}$$

Formula (6) has no exact analytical solution. After obtaining the thermogravimetric analysis data, there are two mathematical methods to solve it, model method and non-model method. Coats-Redfern model is a commonly used method for solving kinetic parameters and is considered suitable for computing the frequency factor, apparent reaction order and activation energy. Therefore, Coats-Redfern model is applied in this paper and asymptotic series expansion is used to approximate the exponential integral of the above formula [9].

$$In\left[-\frac{In\left(1-\alpha\right)}{T^{2}}\right]=In\left[\frac{AR}{\beta E}\times\left(1-\frac{2RT}{E}\right)\right]-\left(\frac{E}{2.303RT}\right),n=1 \tag{7}$$

$$In\left[\frac{1-(1-\alpha)^{1-n}}{T^{2}(1-n)}\right]=In\left[\frac{AR}{\beta E}\times\left(1-\frac{2RT}{E}\right)\right]-\left(\frac{E}{2.303RT}\right),n\neq 1 \tag{8}$$

2RT/E can be considered much smaller than 1 and therefore negligible. Under this assumption:

$$In\left[-\frac{In\left(1-\alpha\right)}{T^{2}}\right]=In\left(\frac{AR}{\beta E}\right)-\left(\frac{E}{2.303RT}\right),n=1 \tag{9}$$

$$In\left[\frac{1-(1-\alpha)^{1-n}}{T^{2}(1-n)}\right]=In(\frac{AR}{\beta E})-\left(\frac{E}{2.303RT}\right),n\neq 1 \tag{10}$$

According to formulas (9) and (10), the logarithmic term on the left corresponds to A straight line with slope *-E/2.303R* and intercept *In(AR/βE)*, from which the values of E and A can be obtained.

3.2. Hygroscopic Kinetic Equation

Studies have shown that the diffusion of water in the cork board conforms to Fick's law, and Fick's second law can be used to describe the moisture absorption behavior of the cork board in the initial stage [10]:

$$\frac{\partial M}{\partial t}=D\times\frac{\partial^{2}M}{\partial^{2}z} \tag{11}$$

Where D is the diffusion coefficient, in mm^2/h; M is moisture absorption rate; T is the hygroscopic time, in unit of h; Z is the direction of sample thickness. The separation of variables is as follows:

$$\frac{M_t-M_0}{M_\infty-M_0}=4\sqrt{\frac{Dt}{\pi h^{2}}} \tag{12}$$

Where M_0 is the initial moisture absorption rate, which can be regarded as 0; M_∞ is the equilibrium moisture absorption rate; H is the thickness of the sample, and the size is 3mm.

$$M_t=\frac{4M_\infty}{h\pi^{0.5}}\sqrt{Dt} \tag{13}$$

According to the linear part of the hygroscopic curve, the diffusion coefficient D can be obtained:

$$D=\pi\left(\frac{h}{4M_\infty}\right)^{2}\left(\frac{M_{t2}-M_{t1}}{\sqrt{t_2}-\sqrt{t_1}}\right)^{2} \tag{14}$$

Where M_{t1} is the hygroscopicity of the sample at t_1; M_{t2} is the hygroscopicity of t_2 time pattern. Reason:

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$$k = \frac{M_{t_2} - M_{t_1}}{\sqrt{t_2} - \sqrt{t_1}} \tag{15}$$

K is the slope of the initial section of M_t-$T^{0.5}$ curve:

$$D = \pi \left(\frac{h}{4M_\infty} \right)^2 k^2 \tag{16}$$

Studies have shown that many physical and chemical reaction processes related to temperature can be corresponding to Arrhenius Formula, and the diffusion of water in composite materials can be regarded as a process of thermal activation energy [10].Therefore, the Arrhenius formula can be used to describe the relationship between wet diffusion coefficient D and temperature T at the initial stage of cork board moisture absorption:

$$D = Ae^{-\frac{E}{RT}} \tag{17}$$

A is the hygroscopic frequency factor, in mm^2/h; E is the hygroscopic activation energy, expressed in *kJ/mol*; R is the gas constant in *kJ/(mol K)*. The logarithm of both sides of formula (17) can be obtained:

$$InD = InA - \frac{E}{RT} \tag{18}$$

The slope of *InD* versus 1/T is -*E/R*, and the intercept is *InA*.

4. Results and Discussion

4.1. Thermogravimetric curve of cork board

As can be seen from the curve in Fig.1, the pyrolysis process of cork board is roughly the same as that of other cork (particles), which can be divided into four stages. The first stage is the drying stage (room temperature ~140℃), and the mass loss rate of samples is 4.79%. The mass loss rate reaches the highest value at 85℃, which can be inferred that this stage is mainly the evaporation of water and the melting of wax components. The second stage is the heating stage (140℃~231℃), and the mass loss rate of the sample is only 1.16%. In this stage, the pyrolysis of some unstable substances begins. The third stage is the pyrolysis stage (231℃~542℃), and the mass loss rate of samples is as high as 62.54%. At this stage, stable substances such as lipids, lignin and cellulose begin to react violently. According to DTG curves and their mass fractions, cellulose began to decompose first, followed by lignin and suberin. The fourth stage is the combustion stage (above 542℃), in which the pyrolysis of cork particles is basically completed, and the reaction rate is gradually smaller and gentle. The mass fraction of the cork board sample is about 20% at about 1000℃. By analyzing the composition of the cork board, it can be found that the mass fraction of the phenolic resin is about 22%, and its melting point is as high as about 1 500 ℃. Therefore, it can be inferred that the remaining undecomposed part of the cork board is mainly phenolic resin.

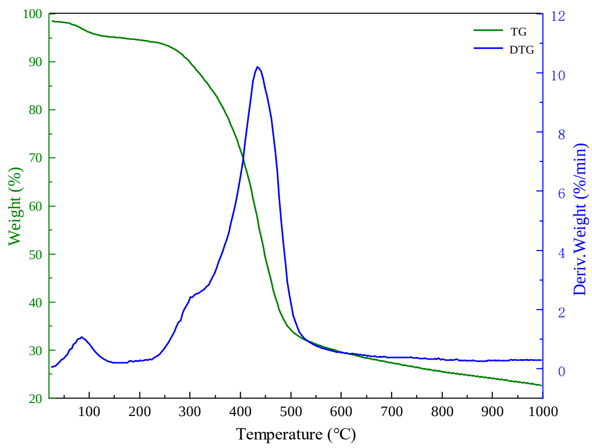

Figure 1: TG-DTG curves of cork board samples

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The pyrolysis rate and temperature of cork boards at each stage in Fig.1 were substituted into the C-R model for high-quality linear regression. The reaction order n of the C-R model could be 0.5, 1, 1.5 and 2. Table 1 shows the calculated pyrolysis activation energy E of the cork board at each stage.

Table 1: Pyrolysis activation energy of cork board at different stages.

Stage	Activation Energy	R^2
First stage	30.1	0.94
Second stage	6.5	0.93
Third stage	127	0.95
Fourth stage	52.7	0.945

The activation energy of cork board is different in each stage of pyrolysis, which may be related to the pyrolysis and volatilization characteristics of suberin, lignin, cellulose, water and other substances. The activation energy of the third stage samples is the highest, indicating that the pyrolysis reaction of materials in this stage is much more difficult than other stages.

4.2. Hygroscopic characteristic curve of cork board

It can be seen from Fig.2 that the diffusion rate of water molecules in the cork board is very fast at the initial stage of moisture absorption, and the moisture absorption rate M_{rt} is in a linear relationship with $T^{0.5}$.

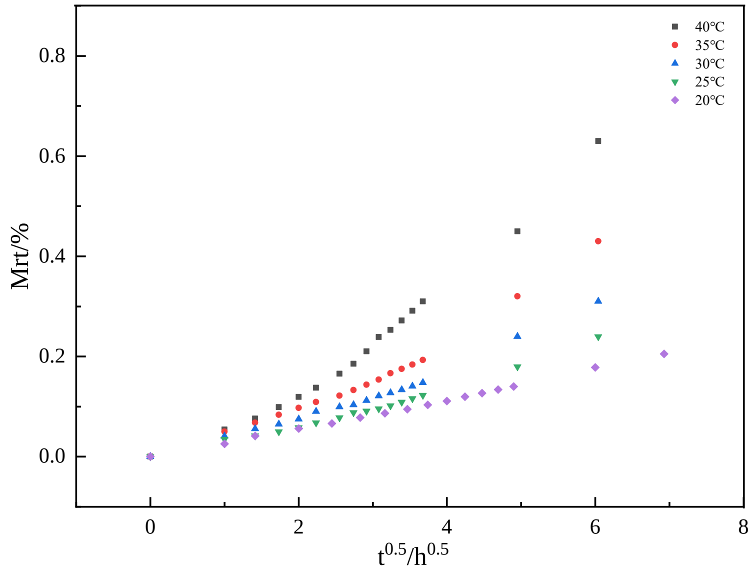

Figure 2: Initial hygroscopic characteristic curve of cork board

Through experiments, the saturated hygroscopicity of cork board samples at 20℃~40℃ are 90%, 93%, 98%, 103% and 106%, respectively. According to the hygroscopicity data of formula (16), (17) and the initial stage, the equilibrium hygroscopicity and wet diffusion coefficient of cork board at different soaking temperatures can be calculated. The calculation results are shown in Table 2.

Table 2: Moisture diffusivity of cork board at different immersion temperature.

Temperature/℃	k	$D\times10^{-3}/(mm^2\ h^{-1})$
20	0.0276	1.661902
25	0.0339	2.348042
30	0.0395	2.870876
35	0.0504	4.231156
40	0.0744	8.703417

According to formula (8), the hygroscopic activation energy E is *59.23kJ/mol*, and the hygroscopic frequency factor A is $3.3\times10^{9}min^{-1}$.

4.3. Fourier infrared Spectroscopy

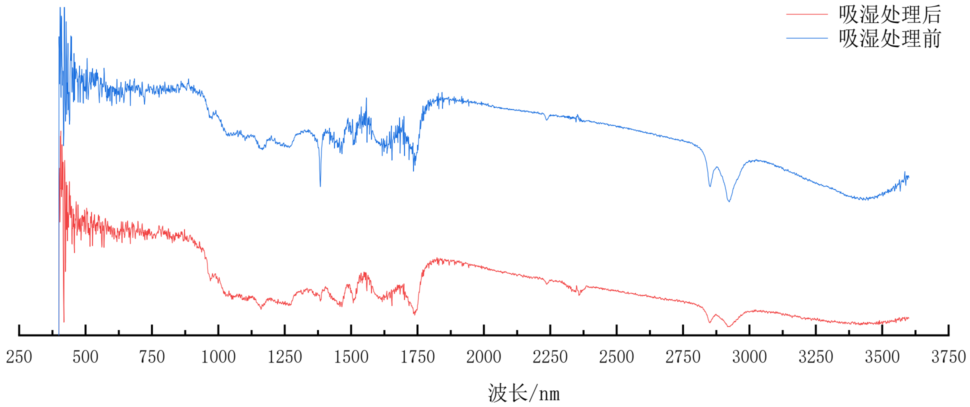

Figure 3: Infrared spectrum analysis of cork board before and after hygroscopic

Fig.3 shows the original spectra of the infrared spectrum analysis of the cork board and the spectra after smooth filtering. No new spectral peak was generated in the infrared spectrum analysis of the cork board after hygroscopic treatment compared with that before hygroscopic treatment. It can be seen that no new substances were generated in the cork board after hygroscopic treatment.

5. Conclusions

(1) The cork pyrolysis under 1000℃ is mainly cork (particles) of pyrolysis, mixed with various physical and chemical reaction, pyrolysis reaction process can be broadly divided into four stages, one of the third phase reaction, activation energy of reactant molecules the *127 kJ/mol*, but compared to other cork (particles) are more likely to happen pyrolysis; Cork board has a high melting point and is the main residual reactant after pyrolysis at 1000℃.

(2) The initial hygroscopicity of the cork board conforms to Arrhenius formula and Fick's law under the wet and hot condition of 20℃ to 40℃. Fick's second diffusion law only applies to the linear hygroscopicity stage. The higher the soaking temperature is, the greater the equilibrium hygroscopicity and wet diffusion coefficient of the cork board are.

(3) It can be seen from the infrared spectrum analysis that there is no significant change in the infrared spectrum peak of particles after 40℃ water soaking and hygroscoping, so it can be inferred that no new substances are produced after the hygroscoping treatment of cork board.

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