Hydroxypropyl Methyl Cellulose의 자연발화온도와 활성화 에너지에 관한 연구

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A Study on Spontaneous Ignition Temperature and Activation Energy of Hydroxypropyl Methyl Cellulose

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Abstract : This study is conducted on spontaneous ignition temperature and activation energy of Hydroxypropyl Methyl Cellulose(HMC) powder. HMC is a kind of cellulose derivative and used as additives for building material, surface coating, printing ink, adhesives, cosmetics and medical supplies. So this material has been widely used as important additive in the chemical industry fields and a mount of production has increased year by year. Therefore, it is very important to find out the thermal ignition characteristics of its danger and the critical ignition temperature. This study was performed by the Spontaneous Ignition Tester(SIT) and so on. Based on the data of the SIT-II, the critical ignition point of HMC is about 186℃ which is slightly lower than normal cellulose.

요 약 : 식물류에 다량으로 함유되어 있는 Cellulose는 인체에 무해할 뿐 아니라 연소시에 발생하는 유해가스가 적어서 친환경적인 에너지 자원으로 대두되고 있다. 특히 Cellulose의 유도체 중 하나인 Hydroxypropyl Methyl Cellulose (HMC)는 의약품의 코팅재료를 비롯하여, 고급용 건축자재, 염료, 화장품 등의 첨가제로 사용되면서, 사용량이 계속해서 증가하고 있다. 따라서 여러 가지 위험에 노출될 수 있으며, 열적 위험특성을 알기 위한 방법으로 일본에서 많이 사용되고 있는 단열자기발열실험장치(SIT-II)를 이용하여 HMC의 한계발화온도와 겉보기활성화에너지를 구하였다. 또한 국제적으로 널리 알려진 Frank-Kamenetskii의 무한평판을 기준으로 한 자연발화실험(IF-SIT)자료를 이용하여 자연발화온도와 활성화 에너지 값을 비교 하였다. HMC의 자연발화온도와 겉보기 활성화 에너지는 SIT-II의 경우 186℃의 한계발화온도와 104.5kJ/mol의 활성화 에너지를 구하였다. 기존에 구하여진 IF-SIT 결과 값과 비교하였을 때 무한평판의 두께 3cm, 5cm, 7cm에 대해 각각 한계발화온도가 199.5℃, 188.5℃, 180.5℃이고, 167.4kJ/mol의 활성화 에너지 값을 지니므로, SIT-II로 구하여진 겉보기 활성화 에너지는 IF-SIT로 구하여진 값 보다 낮게 나타났으며, 이 값은 일반 Cellulose의 활성화 에너지 값 보다 도 더 낮은 것으로 나타났다.
Key Words : hydroxypropyl methyl cellulose(HMC), spontaneous ignition, critical temperature, activation energy, frank-kamenetskii

1. INTRODUCTION

One of the goals of material research is to create and develop new materials tailored to a particular application and to understand the physical mechanisms that determine their properties[1]. However, their dangerous characteristics might not be understood well as far as not being scrutinized. Therefore, most accidents happen in the process of producing new materials or changing their processes carelessly[2].

It is important to find out the spontaneous ignition temperature and activation energy to estimate the danger of chemical material, because the spontaneous ignition is characterized by causing combustion in the

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low temperature without ignition source. If not finding out the thermal characteristics of materials, it is frequent that causes of fires could not be found.

Therefore, hazard level of spontaneous ignition material should be estimated by closely studying its thermal characteristic of spontaneous ignition materials and gaining its critical ignition temperature and calculating its activation energy.

In the study of spontaneous ignition concerned with thermal characteristic of dust, Lu[3] studied about index gas of the coal spontaneous at low temperature and Schmidt[4] studied spontaneous ignition phenomenon of dust followed by volume decrease under oxygen atmosphere. And Lebecki[5] and Krause[6] studied influence on spontaneous ignition temperature according to several kinds and deposit states.

This study performed about thermal characteristics of Hydroxypropyl Methyl Cellulose(HMC), which is widely used in the industry of cosmetics and medicine fields all over the world. First, after observing the fundamental action of its thermal change, apparent activation energy was calculated and compared using two kinds of spontaneous ignition test. One of the spontaneous ignition test type is an adiabatic self-heating process recorder type tester(SIT-II) which is recently developed equipment in Japan[7]. Other type is infinite slab by theory of Frank-Kamenetskii(IF-SIT) which is using widely in the study[8].

SIT-II has not only good reproducibility but also safety of combustion sustaining a certain degree for a long time whereas it is not beyond reality because of measuring spontaneous ignition temperature using less amount of sample.

IF-SIT can be almost actually tested using relatively much more amount of sample but the larger a sample container is, the more higher the danger of fire is. And temperature control in longer experiment is likely to wrong because of the nature of experiment. Therefore, whether IF-SIT could be spontaneously ignited or not should be estimated within 24hours.

Studies of spontaneous ignition temperature using SIT-II are very popular abroad[9-11] these days except home but studies of IF-SIT have been much under way in Korea[12,13]. So this study shows a comparison each.

Also, based on the data of the critical spontaneous ignition temperature, activation energy will be very useful for fire prevention against HMC.

2. THEORY

The procedure of this study is focused on the Frank-Kamenetskii theory which was the one that was made by compounding the Fourier's heat transfer equation of the Arrhenius' reaction equation. In order to make the Arrhenius type equation briefly arranged, it can be shown a function of time and temperature as follow equation (1)[14]. And it can be represented by the way of the Frank-Kamenetskii's parameter(δ_c) as follow equation (2), but since it can not be solved by numerical analysis, it should be transformed into a linear equation(3) as followings[8].

$$\Delta t = t_0 \times \exp(E/RT) \tag{1}$$

$$\delta = \frac{QEa^2 A \exp(-E/RT_c)}{kRT_c^2} \tag{2}$$

$$\ln\frac{\delta_c T_c^2}{a^2} = -\frac{E}{R}\frac{1}{T_c} + \ln\frac{QEA}{kR} \tag{3}$$

Where Δt; ignition induction time(min), t_0; constant factor(-), E; apparent activation energy(J/mol), R; ideal gas constant(J/mol K), T; initial temperature (K), Q; heat of reaction(J/g), a; sample thickness(cm), A; apparent frequency factor(1/min), k; thermal conductivity(J/sec m K) and Tc; critical temperature(K).

The value of δc at the critical conditions for a pile in the shape of an infinite slab is 0.878.

3. SAMPLE, APPARATUS AND METHOD

3.1. Sample

Hydroxypropyl Methyl Cellulose(HMC) sample was used in this study. And according to the dust classification method of ASTM E11 standard sieve mesh, dust particle was divided under -325mesh.

SEM picture of HMC is shown in Fig. 1, and its molecule structure is shown in Fig. 2. Because of its chemical structure, and combination of one Hydroxy-

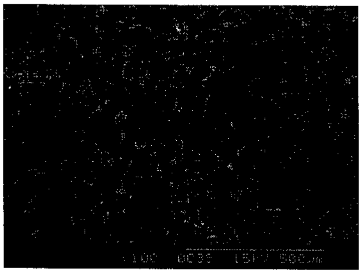
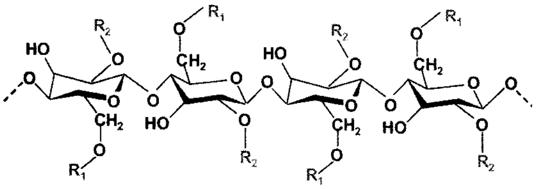
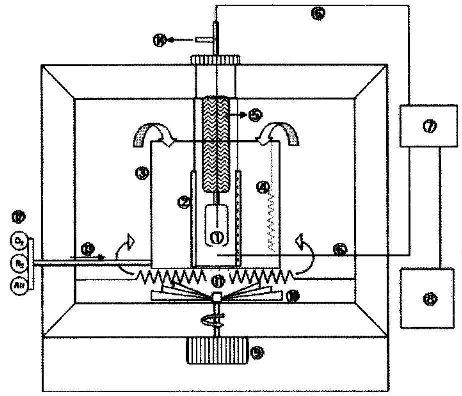


Fig. 1. SEM picture of HMC.



R1 = -CH2CHOHCH3 R2 = -CH3

Fig. 2. Molecule structure of HMC.



① sample cell
② adiabatic jacket
③ air bath
④ resistance thermometer
⑤ glass wool
⑥ thermocouples
⑦ temperature recorder
⑧ temperature controller
⑨ fan motor
⑩ fan
⑪ heaters
⑫ gas bombes
⑬ gas in
⑭ gas out

Fig. 3. Cross section of the adiabatic self-heating process recorder type SIT.

propyl with one Methyl on basic structure of Cellulose, it can be solved well in cold water but not well in hot water. Having good solubility and moisturizing, it has a property of increasing the bond between an organic and an inorganic material as a surface active agent.

3.2. Adiabatic self-heating process type (SIT-II)

An adiabatic self-heating process recorder(SIT-II) is the new type analysis equipment, which can measure the critical spontaneous ignition temperature with small amount of sample.

And sample cell is draft type which is made of quartz and the base side of this cell is empty as ① in Fig. 3, which side is blocked by wire mesh and prohibits powder of HMC from flowing down using glass fiber that is incombustible. And air is supposed to pass through the base of the cell and enter the inside of the cell and release ⑭.

Air entering sample cell enters adiabatic jacket and passes through the inside of sample cell consistently under 2mL/min in the air flux.

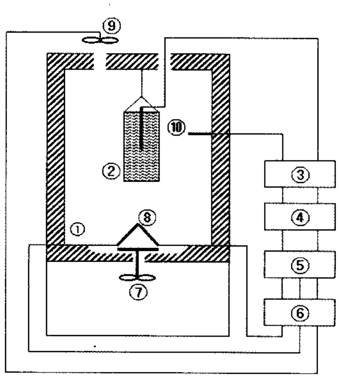
Until reaching from the room temperature to the established temperature, N_2 was sent to prevent the decrease of material of cell inside. After arriving the regular temperature, this test was begun by sending air to the inside of sample cell. Also, the amount of sample for each test was about 570mg, which was standardized in the test of adiabatic self-heating process recorder.

3.3. Frank-Kamenetskii's infinite slab type (IF-SIT)

This test supposed that spontaneous ignition test unit shown in Fig. 4 was infinite slab by theory of Frank-Kamenetskii[8](IF-SIT) which consists of furnace, thermocouple, temperature recorder, temperature control and sample cell. The furnace is operated by hot wind circulation process, which is 27L(30cm×30cm×30cm) volume.

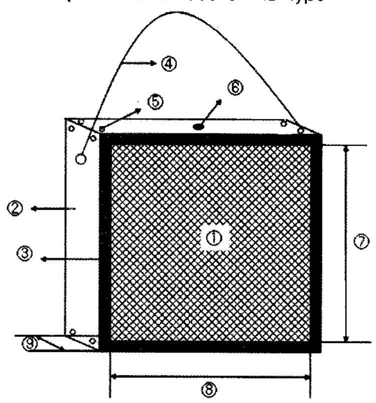
Thermocouple is two Chromel-Alumels that are 0.35mm diameter each, which was for the control of the surrounding temperature and the measurement of the sample temperature. Temperature control process is PID type controller for the accuracy of temperature changes. And the temperature recorder is Yokogawa, model 4151, pen type recorder, which recorded consecutive temperature changes.

Sample cells are three kinds that are 20cm wide, 20cm long, and 3cm, 5cm, 7cm deep each size. Also, they are rectangular, only two side of which are stainless wire mesh and the rest of which are insulated by asbestos plate 1cm thickness.



① electric furnace
② sample cell
③ cold junction
④ program controller
⑤ temperature recorder
⑥ relay switch
⑦ sirocco fan
⑧ heater
⑨ fan
⑩ chromel-alumel TC

A. Electric furnace of PID type



① wire mesh
② steel plate
③ adiabatic material
④ hanger
⑤ pin
⑥ thermocouple hole
⑦ height (20cm)
⑧ width (20cm)
⑨ sample thickness (each 3, 5, 7 cm)

B. Four side adiabatic sample cell.

Fig. 4. Schematic diagrams of Frank-Kamenetskii's infinite slab type SIT.

The orders of the test are followings; In established temperature of electronic furnace, sample cell should be hung on the center of furnace and then inserting thermocouple inside of sample cell, temperature changes of the inside of sample and thermostat were recorded.

4. RESULTS AND DISCUSSION

4.1. SIT-II

SIT-II whose spontaneous ignition temperature can be measured by using 570mg sample is much safer because of a little amount of sample and very excellent reproducibility. But spontaneous ignition temperature, which can be seriously effected by the volume of sample, causes a few problems in the reality of the critical ignition temperature.

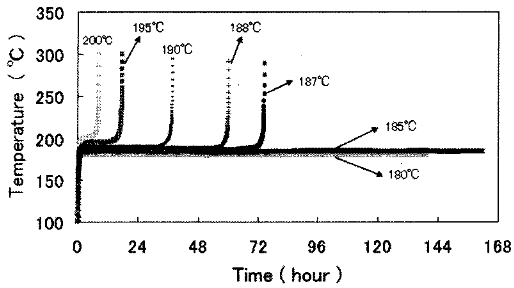


Fig. 5. Result of adiabatic self-heating process recorder type.

Fig. 5 shows the result of the experiment obtained by using SIT-II. At 195℃ and 200℃, ignition happened within 24hours. At 190℃, ignition happened after 30 hours. Also, at 187℃ and 188℃, ignition happened within 3 days but below 185℃, no ignition happened though over five days passed.

The reason that ignition does not occur below 185℃ during 5 days, a relatively long time, is that heat accumulation does not occur below this temperature. But when the amount of sample is larger for some degree, ignition can happen below this temperature. Therefore, this temperature can not said absolutely critical ignition temperature.

Table 1 shows the time to ignite, which was taken from air input time to ignition at established temperature, and the ignition temperature.

Fig. 6 described the relation to ignition delay time and ignition temperature by using Table 1, it's the Arrhenius' equation[9]. Here, the value of apparent activation energy was obtained 104.54kJ/mol, which is judged quite considerable value. With data of ignition

Table 1. Relation between spontaneous ignition temper-ature and ignition delay time

Temp. (℃)	I.T.(min)	1000/T (1/K)	ln △T
200	185.3	2.11	5.22
195	659.2	2.14	6.49
190	1926	2.16	7.56
188	3591	2.17	8.19
187	4358	2.17	8.38

Where Temp.; temperature of setting point (℃), I.T.; ignition delay time (min).

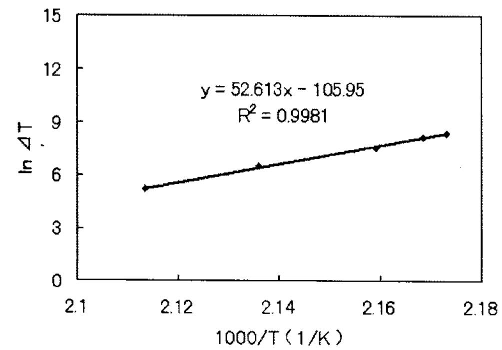


Fig. 6. Estimation of activation energy.

within 24 hours, the result value of apparent activation energy is 111.73kJ/mol which is slightly higher than 104.54kJ/ mol. Of course, the reason that more time than regulation of experiment time 24 hours was taken is to find out how much lower ignition temperature is and to observe the changes of activation energy.

The results of these two observations are that if the time of storage is longer, the possibility of ignition is higher at low temperature and that much storage time is needed in lowering ignition time after 24 hours. For example in SIT-II results, when the ignition temperature at 200℃, this experiment of ignition delay time was about 3 hours. But the ignition temperature was 195℃, 190℃, 188℃ and 187℃, the ignition delay time was about 11 hours, 32 hours, 60 hours and 73 hours each.

And as the result of calculating activation energy, it is concluded that a little difference exists according to the change of time but no much bigger difference exists.

Also, the activation energy of HMC is slightly lower than normal cellulose, because the activation energy of Cellulose is 150-220kJ/mol[15].

4.2. IF-SIT

The result of this experiment shows how ignition temperature changes according to the thickness of samples filed, when HMC files on the floor of workplace or storages.

At the 3cm thickness sample was experimented under 199℃, inner temperatures of electric furnace and sample cell did not change. But an experiment at 200℃, inner temperatures of sample cell was change after 10 hours and then ignition happened as the inside of sample temperature sharply increased.

Also, experiment results of non-ignition and ignition when 5cm and 7cm thick sample. Non-ignition was under 188℃ and 180℃ each. Ignition was happened at 189℃ and 181℃. Therefore, the thicker samples file has the lower the temperature of ignition.

Comparing this result with the critical ignition temperature 186℃, the amount of IF-SIT sample was much larger than that of SIT-II in case of 3cm and 5cm sample in thickness but IF-SIT of the critical ignition temperature was rather much higher. The reason was that SIT-II made heat accumulation much easier despite the small amount of SIT-II having better insulation condition. And IF-SIT which is 7cm thick has the low critical ignition temperature 180℃. It is estimated that the theory of spontaneous ignition that according to increasing sample volume[12,13], heat accumulation is easier to occur was accurately applied.

Table 2 shows calculations of functions of Frank-Kamenetskii's equation[8] and shows the thickness of sample. In this experiment, since hear transfer was performed in two side, the value of a half thickness of sample comes under the value of heat transfer length.

And Tc shows critical temperature, which is the value of ignition and non-ignition. δ_c has the value 0.878 in case of infinite slab as Frank-Kamenetskii's invariable.

Therefore, to calculate apparent activation energy from Fig. 7, the result was E = 167.4kJ/mol. This activation energy values was higher than normal cellulose and SIT-II tester results.

The reason is that the way of measuring and calculating activation energy is rather different. That is to say, when measuring activation energy, the critical ignition temperature is used according to the

Table 2. Relation between critical spontaneous ignition temperature and thickness of sample

$a\times10^{-2}$ (m)	T_c (℃)	δ_c	ln $(\delta_c T_c^2/a^2)$	$1/T_c\times10^3$
1.5	199.5		20.58	2.12
2.5	188.5	0.878	19.52	2.17
3.5	180.5		18.81	2.20

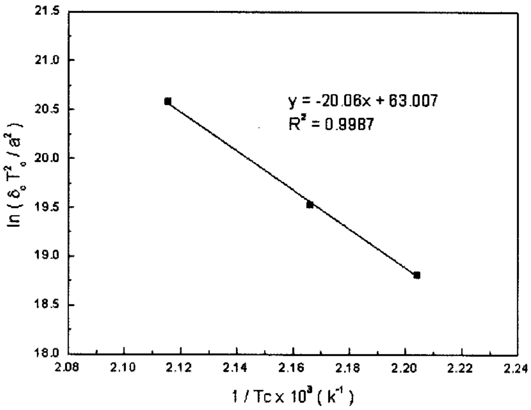


Fig. 7. Determination of activation energy.

thickness of sample. In this case, because spontaneous ignition temperature is decided as an ignition temperature experimented for 24 hours. the thicker sample is, the lower the speed of heat delivery is. Therefore since the time that it takes for heat to be accumulated becomes longer, much more activation energy is required. On the contrary, since SIT-II using small amount of sample is experimented under the state of insulation, it needs less activation energy than IF-SIT.

Also, SIT-II is possible to experiment for a long time but spontaneous ignition temperature can be acquired at lower temperature. At this time, lower temperature has an effect on the calculation of activation energy value. Therefore, it is estimated that SIT-II has lower activation energy than IF-SIT in this study.

5. CONCLUSION

In the spontaneous ignition tester, the adiabatic self-heating process recorder(SIT-II), the critical ignition temperature was about 186℃ and apparent activation energy was 104.5kJ/mol. In the Frank- Kamenetskii's infinite slab test, 3cm, 5cm, 7cm thickness samples had the limit ignition temperature 199.5℃, 188.5℃, 180.5℃ each and the thicker samples were, the lower limit ignition temperature was. Apparent activation energy was 167.4kJ/mol, which was somewhat higher than expected. By the way, the activation energy of HMC was slightly lower than normal cellulose.

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