



Dust Explosion Characteristics of Cellulose Acetates with Different Degrees of Acetylation

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Abstract

In this work, the relation between various degrees of acetylation (CAs) of Cellulose acetate (CA) to dust explosion characteristics as minimum explosible concentration (MEC) and minimum ignition energy (MIE) have been studied.

Also, we attempt to clarify the relative of moisture content and water adsorption to cellulose, cellulose ester as CA and cellulose ether as Methyl cellulose (MC), Ethyl cellulose (EC), Hydroxyethyl cellulose (HEC), Hydroxypropyl cellulose (HPC), and sodium carboxymethyl cellulose (CMC) to MEC and MIE have been studied.

We found that the chemical derivatives have significant on thermal behavior of cellulose which T_d of CA shifted to higher temperature because of acetate derivative effect. Meanwhile, T_d of cellulose ethers as MC, EC, HEC, HEC and CMC were shifted to lower temperature. Moreover, CAs was not evident effect to T_d of CA.

Moisture content of cellulose powder had not significant on MEC of both air dry and absolute dry powder were 55 g/m³. But, we found MEC was relative to its moisture content of CA which absolute dry was more sensitive on explosion than dry CA powder. However, MEC was consistent with the hydrophilicity index at 75%RH of dry and absolute dry of cellulose, cellulose acetate and cellulose ethers in present work.

MIE was not corresponding to moisture content of cellulose ether and cellulose ester but it was

relative to cellulose.

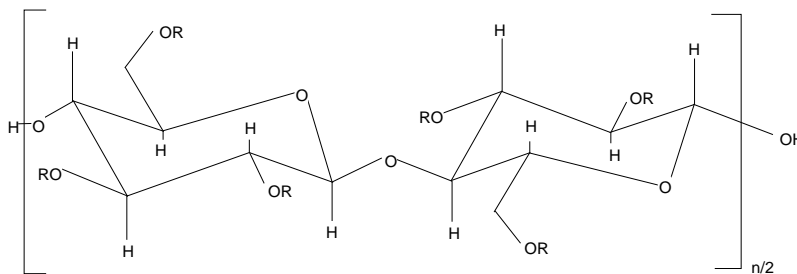
The results from our experiments, comparing with CAs, chemical derivatives have more significant on moisture adsorption, thermal stability and dust explosion characteristics of cellulose.

Introduction

As well known, there are several tons of powders are being handled in the processes of transportation, storage, filtration, etc. in powder handling industries. However, these powder handling industries are facing troubles and accidents such as fire and explosion in many situation. During 1952-1995 years number of fire and explosion accidents in Japan which occurred more than 20 times are metals, intermediate additives, food and feed, chemical synthetic, inorganic and cellulosic materials, respectively [1]. Also, most of accidents occurred during winter months when the atmosphere has the lowest humidity content [2].

However, there are not available for the inherent safety as hazard or risk assessment on the relationship during dust explosivity, water adsorption and chemical nature of the particles of cellulosic materials powders [3].

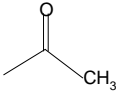
Cellulose is the primary constituent of wood, paper, and cotton. It is a carbohydrate made up of glucose units. These have an empirical formula, $(C_6H_{12}O_6)_n$ and can be given a cyclic structure



as shown in Figure 1.

Figure 1. Cellulose structure

Table1. Summary of present cellulosic materials in this present work

Cellulosic materials	Derivatives	R groups
Cellulose ester	Cellulose acetate (CA)	H, 
Cellulose ether	Methyl Cellulose (MC)	H, CH ₃
	Ethyl Cellulose (EC)	H, CH ₂ CH ₃
	Hydroxyethyl Cellulose (HEC)	H, CH ₂ CH ₂ OH
	Hydroxypropyl Cellulose (HPC)	H, [CH ₂ CH(CCH ₃)O] _n H
	Sodium Carboxymethyl Cellulose (CMC)	H, CH ₂ COONa

Cellulose ester and cellulose ether are two main groups of cellulosic materials of cellulose [4]. Examples of mostly used cellulose ethers are: Methyl cellulose (MC), Ethyl cellulose (EC), Hydroxyethyl cellulose (HEC), Hydroxypropyl cellulose (HPC), and sodium carboxymethyl cellulose (CMC). And mostly used cellulose esters are: cellulose acetate (CA), cellulose acetate phthalate (CAP), Cellulose acetate butyrate (CAB), Cellulose acetate trimelitate (CAT), hydroxupropylmethyl cellulose phthalate (HPMCP). The applications of each cellulosic materials in this study are shown in Table 2.

In this work, the relation between various CAs of CA to MEC and MIE have been studied. Also, we attempt to clarify the relative of moisture content and water adsorption to cellulose, CA and cellulose ether as MC, EC, HEC, HPC, and CMC to MEC and MIE have been studied.

Table2. The applications of the present cellulosic materials

Cellulosic materials	Derivatives	Industrial sector	Applications
Cellulose ester	CA	Packing, Textile, Plastic, Photo, Surface coating, Tobacco	Packaging film, Fiber, Molding, Film, Lacquer, Filter
Cellulose ether	MC	Medicine, Cosmetics, Pottery, Skin, Leather	Court of enteric, Emulsion stabilizer, Binder, Processing agent
	EC	Plastic, Surface coating, Paper making, Print	Molding, Lacquer, Painting, Coating agent, Ink stabilizer
	HEC	Textile, Surface coating, Cosmetics, Chemical	Binder of non-woven fabric, Paint, Emulsion stabilizer, Cement additive, Emulsion polymerization agent
	HPC	Food, Medicine, Cosmetics	Emulsion stabilizer, Coating agent, Increase granules, Emulsion stabilizer
	CMC	Textile, Surface coating, Dispersant, Food, Medicine, Oil	Sizing, Painting, Pesticide, Emulsion stabilizer, Laxative, Emulsion stabilizer, Oil

Experimental

Material

Samples used in the research were commercial grade except cellulose acetates with three kinds of degree of acetylation. Cellulose was purchased from Sigma-Aldrich, Japan. Cellulose acetate with three kinds of degree of acetylation (CA_C) as 61.7, 55.8 and 51.6 (wt.%) were kindly provided by Daicel, Japan. Commercial grade of methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and sodium carboxymethyl cellulose (NaCMC) were purchased from WAKO, Japan.

Sample preparation

The preparation of samples included grinding and sieving the samples. After grinding process with grinder, the samples would be sieved to get the particle sized to be lower than 75 μ m. After that, the sample would be stored in a tight container to minimize the loss of moisture. Upon the explosion test for absolute dry case of sample, the samples would be dried as empty glass crucible (diameter of 6 cm) was weighted. Then, approximately 1 \pm 0.1 g of the sample was added to the crucible. The new weight of the crucible and the sample was recorded. The crucible and contents were placed in the samples would be dried in a depressurization 15 hours as a drying process. The crucible was then cooled in a desiccator and reweighed. The amount of moisture in the sample was then calculated using Eg.1

$$\% \text{moisture} = \frac{\text{Mass of water removed (g)}}{\text{Mass of absolute dry sample (g)}} \quad (1)$$

Each sample’s particle size and samples suppliers in this work was summarized in Table 3.

Table3. Summary of the present cellulosic material and suppliers

Water vapor adsorbtion test in cellulosic materials

Based on JIS B 7920, to investigate the effect of absorbed water (hydrophilic index) on Cellulosic, Cellulose ether as MC, EC, HEC, HPC, and CMC, and Cellulose ester as CA to MEC and MIE was performed. Air dry and absolute dry of cellulosic materials were weighed then these samples were placed into the container which maintained constant 75.3%RH and 25 °C for 72 hours [5].

Characteristic	Cellulose	CA			MC	EC	HEC	HPC	CMC
		CA _c : 61.7	CA _c : 55.8	CA _c : 51.6					
Supplier	Sigma-aldrich	Daicel			Wako				
Particle (size)	75 μ m								

Thermal behavior

A thermogravimetric/differentialthermal (TG/DTA) analysis system (TG/DTA7220 HITACHI) was used to examine the thermal behavior of Cellulose Ethers as MC, EC, HEC, HPC, and CMC, and Cellulose Ester as CA. TG/DTA was carried out in aluminum sample holder at a heating rate of 10 K min⁻¹ from 30 to 1000 °C under steady-state air flow using an almost constant sample mass of 3.0 mg.

Evaluation of dust explosion hazards

During this work, both the MEC and MIE values were determined by 1.2-L Hartmann tube apparatus (Seishin Enterprises, PIE-1200). The MEC measurement conditions consisted of: electrode gap of 5 mm, compressed air at 0.075 MPa, charging voltage of 1000 V, and ignition delay time of 0.1 s. Using these test parameters, the MEC of a standard reference material composed of Lycopodium was found to be 40 ± 5 g m⁻³. During MIE measurements, the discharge energy was obtained by adjusting the ohmic value of the circuit with discharge time.

Explosion hazards may be placed into three levels based on the MEC value: high (<40 g m⁻³), moderate (40–100 g m⁻³), and low (>100 g m⁻³). Similarly, there are three levels based on MIE value: high (1–10 mJ), moderate (10–100 mJ), and low (100–1000 mJ). Energy value calculations were performed using the following equation, according to the EN 13821 standard.

$$E_s = 10^{(\log E_2 - \frac{I[E_2](\log E_2 - \log E_1)}{(NI+I)[E_2]+1})} \quad (2)$$

Here, E_1 is the highest energy at which ignition does not occur, E_2 is the lowest energy at which ignition is observed, NI is the number of non-ignitions observed at E_2 , and I is the number of ignitions observed at E_2 .

Result and Discussion

Thermal behavior

Thermal gravimetric (TG) and differential thermal gravimetric (DTG) profiles depicting the combustion process of Cellulose, Cellulose esters and Cellulose ethers are presented in Figure 2 to Figure 5.

From figure 2 shown TG of cellulose and 61.7, 55.8 and 51.6 (wt.%) CAs of CA. These results

shown initial temperature (T_d) of cellulose was 297 °C meanwhile T_d of 61.7, 55.8 and 51.6 (wt.%) CAs of CA were 317, 314 and 311 °C, respectively. It can be considered that T_d of cellulose was shifted to higher temperature or it has been referred to more thermal stability because of acetate derivative. However, the different CAs was not significant evident effect to CA.

Moreover, figure 3 shown DTG of cellulose and 61.7, 55.8 and 51.6 (wt.%) CAs of CA. The combustion profiles of the cellulose took place in only one visible stage, which its ranging from 280 to 390 °C. The maximum weight loss of this stage occurred around 297°C then it can be attributed to the degradation of the cellulose [6].

Furthermore, the combustion of CA took place in two visible stages, the first stage ranging from 280 to 390 °C corresponded to the loss of the cellulose molecule. The second one of visible stage ranging from 400 to 530 °C. It can be considered that these stage could be attributed to the evolution of the volatile compounds generated by acetate derivatives. However, the degree of acetate does not affect during this the combustion stage. The devolatilization generated a mass loss of three kinds of CAc were more than 90 wt%.

In case of cellulose esters, figure 4 shown TG of cellulose and cellulose ether as MC, EC, HEC, HPC and CMC. Comparing to cellulose, T_d of all cellulose ethers in this work were shifted to lower temperature. Cellulose with hydroxyethyl derivative was shifted from 297 °C to 206 °C which it shifted more than other derivatives of the presented cellulose ether. Also, cellulose with hydroxypropy derivative was shift less than others which shifted from 297 °C to 270 °C .

Figure 5 shown DTG of MC, EC, HEC, HPC and CMC. The combustion of these samples also took place in two visible stages, all of them shown the first stage ranging nearby 220 to 390 °C corresponded to the loss of the cellulose molecule. However, the second one of visible stage could separate in two groups; the first group as MC, EC and HEC which the second visible stage ranging from 420 to 530 °C and the other as HPC and CMC which the second visible stage ranging over than 600 °C. The devolatilization generated weight loss of these group were more than 90 wt.%.

However, it can be considered that these second stage could be attributed to the evolution of the volatile compounds generated by each derivatives.

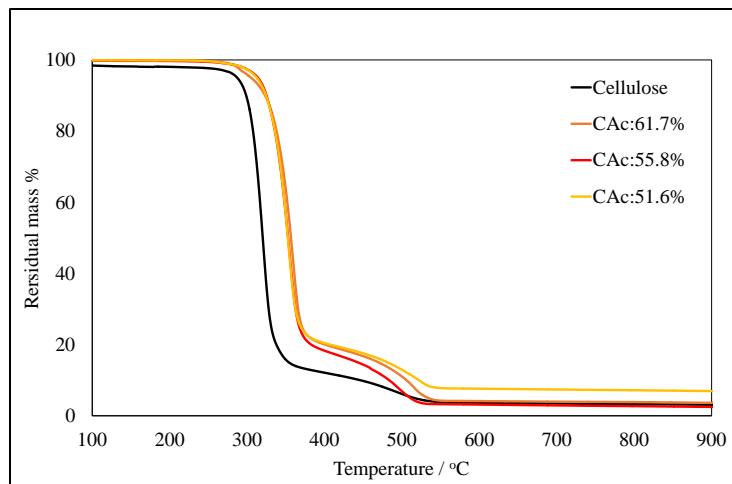


Figure 2 TG curves of cellulose and three kinds of CAs of CA; 61.7%, 55.8% and 51.6%

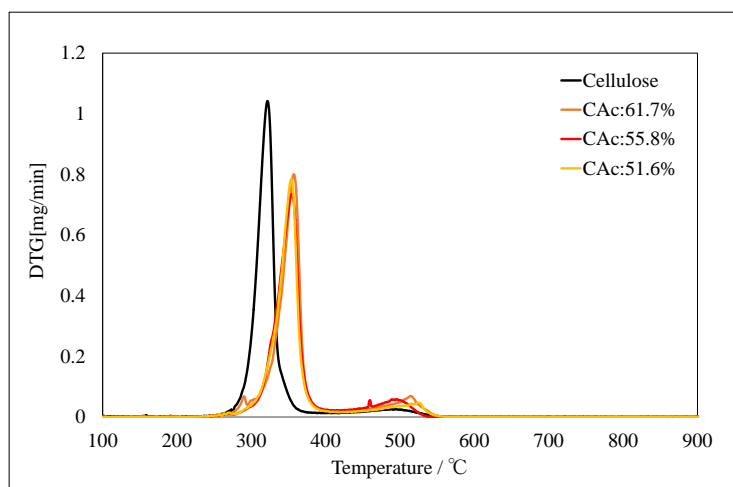


Figure 3 DTG curves of cellulose and three kinds of CAs of CA; 61.7%, 55.8% and 51.6%

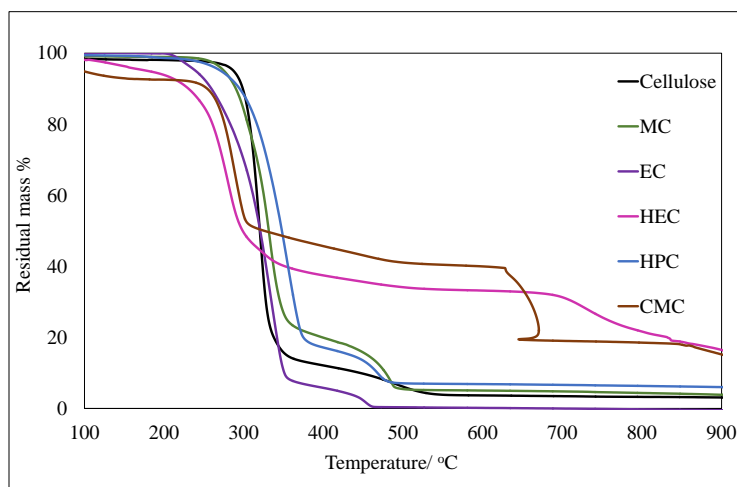


Figure 4 TG curves of cellulose and each cellulose ether

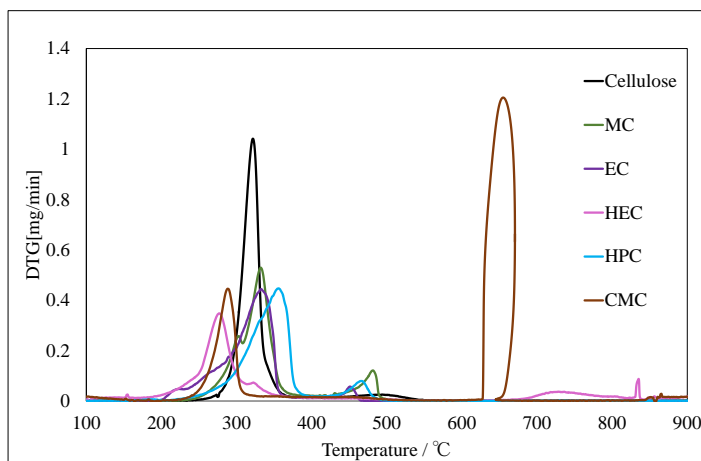


Figure 5 DTG curves of cellulose and each cellulose ether

Table4. Summary of initial temperature and weigh loss of each present cellulosic material

Cellulosic materials	Derivatives	Initial Temperature / °C	Weight loss (%)	
Cellulose	-	297	97	
Cellulose ester	Cellulose acetate (CA)	CAC:61.7	317	97
		CAC :55.8	314	98
		CAC :51.6	311	93
Cellulose ether	MC	260	97	
	EC	221	100	
	HEC	206	89	
	HPC	270	95	
	CMC	250	91	

Table 5. Summary of moisture content, and hydrophilicity index, MEC and MIE of each present cellulosic material

	Derivatives		Moisture content (wt.%)	Hydrophilicity Index at 75%RH	MEC [g/m ³]		MIE [mJ]	
					Dry	Abs. Dry	Dry	Abs. Dry
Cellulose	-		4.50	4.65	55	55	38.17	7.86
Cellulose ester	CA	CAC:61.7	2.22	3.65	55	40	1.3	1.73
		CAC :55.8	2.39	4.68	50	40	1.2	1.99
		CAC :51.6	2.80	5.98	55	50	1.4	1.51
Cellulose ether	MC		3.97	8.46	50	40	2.41	6.18
	EC		0.87	1.70	25	25	>1	>1
	HEC		9.13	40.6	Non-exploded	Non-exploded	N.E.	N.E.
	HPC		2.97	7.47	45	45	>1	>1
	CMC		7.54	17.62	Non-exploded	Non-exploded	N.E.	N.E.

N.E. = Experiment did not carry out.

Evaluation of dust explosion hazards

Table 4 shown MEC measurement results of the different cellulose, cellulose esters and cellulose ethers. We observed that there was not different on MEC values for both air dry (4.5% moisture content) and abs. dry cellulose powders which existed for both conditions powders were 55 g/m³.

In case of CA, it shown evident difference on MEC results. MEC of three kinds of CAC as 61.7, 55.8 and 51.6 of air dry and abs. dry CA were during 50~55 g/m³ and 40~50 g/m³. Then, it can be concluded that MEC was relative of moisture content of CA which abs. dry shown more hazard on explosion than dry powders.

Moreover, in case of cellulose ethers, it can be categorized in three groups, (1) Non-exploded

as HEC and CME, (2) Exploded at below than 40 g/m^3 (corresponding to high risk level) as ME

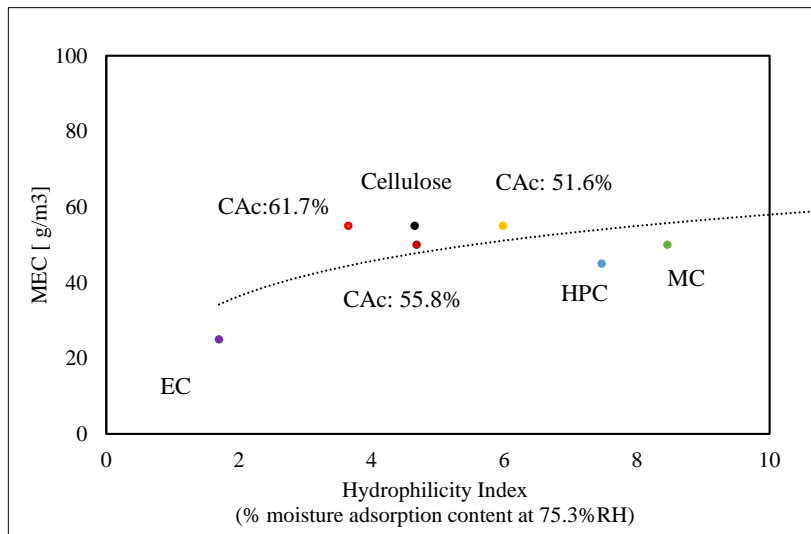


Figure 6. MEC of dry cellulose and cellulosic material powders relative to hydrophilicity index

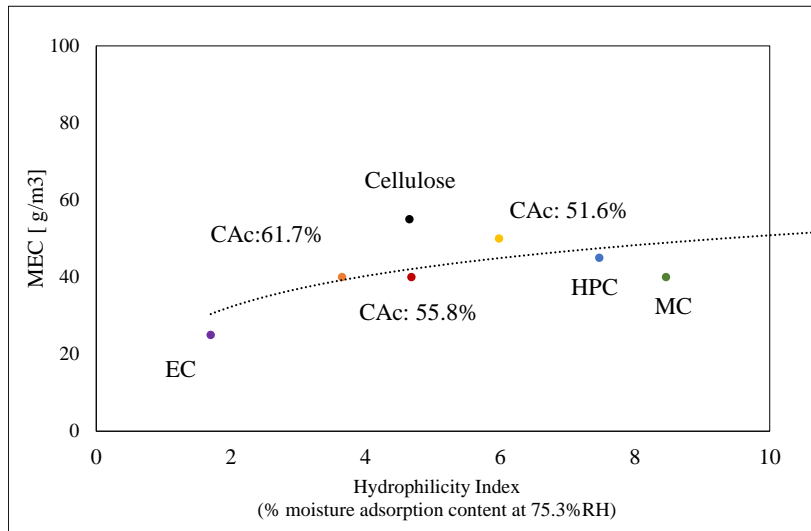


Figure 7. MEC of abs.dry cellulose and cellulosic material powders relative to hydrophilicity index

and HPC, (3) Exploded at more than 40 g/m^3 (corresponding to moderate risk level) as EC. However, there were not different on MEC value on both air dry and abs.dry cellulose ethers powders. Then, based on these results, MIE of cellulose ethers were not relative with moisture

content.

In this work, the relative of the moisture adsorption of cellulosic materials to MEC was considered. Fig.6 and 7 shown the relationship during hydrophilicity index at 75%RH and MEC. We observed that MEC was consistent with the hydrophilicity index at 75%RH of air dry and abs.dry of cellulose, cellulose acetate and cellulose ethers in present work.

On the other hand, MIE of cellulose was shown in table 4, three kinds of cellulose acetate and cellulose ethers. MIE of air dry (4.5wt.% moisture content) and abs. dry cellulose powder were 38.17 mJ and 7.86 mJ, respectively. It can be considered that moisture content of cellulose was significant effect to its MIE values. Comparing to cellulose, MIE of CA and cellulose ethers of both air dry and abs.dry were increased. Especially in case of air dry powders which were below than air dry cellulose around 20 mJ.

It can concluded that MIE was not corresponding to moisture content of cellulose ether and cellulose ester but it was relative to cellulose.

Conclusions

The aim of this study is to investigate the relative of water adsorption on hydrophilic cellulosic materials and CAs of CA to MEC and MIE.

The main conclusions of the present study summarized below

- The chemical derivatives have significant on thermal stability of Cellulose which T_d of cellulose esters as cellulose acetate shifted to higher temperature because of acetate derivative effect. Meanwhile, T_d of cellulose ethers as MC, EC, HEC, HEC and CMC in this work were shifted to lower temperature.
- CAs was not evident effect to T_d of CA.
- Moisture content of cellulose powder had not significant on MEC value. Both air dry and abs. dry powder was 55 g/m³. But in case of CA, MEC was relative to its moisture content MEC of CA which abs. dry shown more hazard on explosion than air dry powders.
- MEC was consistent with the hydrophilicity index at 75%RH of air dry and abs.dry of cellulose, cellulose acetate and cellulose ethers in present work.
- MIE was not corresponding to moisture content of cellulose ether and cellulose ester but it was relative to cellulose.

The results from our experiments, chemical derivatives have significant on thermal stability and dust explosion characteristics of cellulose.

References

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