The reaction of potassium bromate with cornstarch

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The thermal reactivity and the combustion reactivity of potassium bromate/starch binary mixtures as the one of the concrete break agents were studied by thermal analysis, the heat of reaction, the burning temperature and the burning rate.

The binary mixtures reacted vigorously just after melting of potassium bromate. As the heat of reaction, the burning temperature and the burning rate had a maximum at the stoichiometric composition in eq.(1), it became clear that the reaction proceeds mainly according to eq.(1).

1. Introduction

The break agent[1], which used the bromate and an organic compound, has been used as the one of the main agents of a concrete breaker. However, the organic compounds, such as dinitrotoluene,which is currently being used, is expensive and has the problem of treatment during production. In this report, the thermal reactivity and the combustion reactivity of potassium bromate ($KBrO_3$) and cornstarch (starch) instead of the organic compounds were studied in order to solve these problems.

2. Experimental

2.1 Reagents

Wako pure chemical reagent grade potassium bromate purified from water was screened to under 63 μm. Starch from the Japan Cornstarch Corporation was used after vacuum drying for a week at ordinary temperature. Its water content was 1.5wt.% and mean particle size was about 12～15μm.

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Table 1 Composition of mixtures

No	Starch/$KBrO_3$ (g/100g)	Weight fraction (Wt./Wt.)	Oxygen balance of starch
1	33/67	0.327	−19.4
2	24/76	0.244	− 7.2
3	20/80	0.195	− 0
4	16/84	0.162	+ 4.9
5	14/86	0.139	+ 8.2

Five kinds of samples were prepared by mixing $KBrO_3$ and starch according to eq.(1) for sixty minutes using a V-type mixer. Their compositions are shown in Table 1.

$$1/n-[C_6H_{10}O_6]n + 4KBrO_3 \rightarrow 4KBr + 6CO_2 + 5H_2O \quad (1)$$

2.2 Apparatus and method

Thermal analysis was carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was a hermetically sealed aluminum crucible which had pinholes in the center of its cover. The heating rate was 20k/min. The atmosphere was air for the $KBrO_3$ or starch, and argon when using their mixtures.

The heat of reaction was measured using a Shimadzu CA-4 Type Automatic Bomb calorimeter under argon.

Burning experiments were carried out under nor-

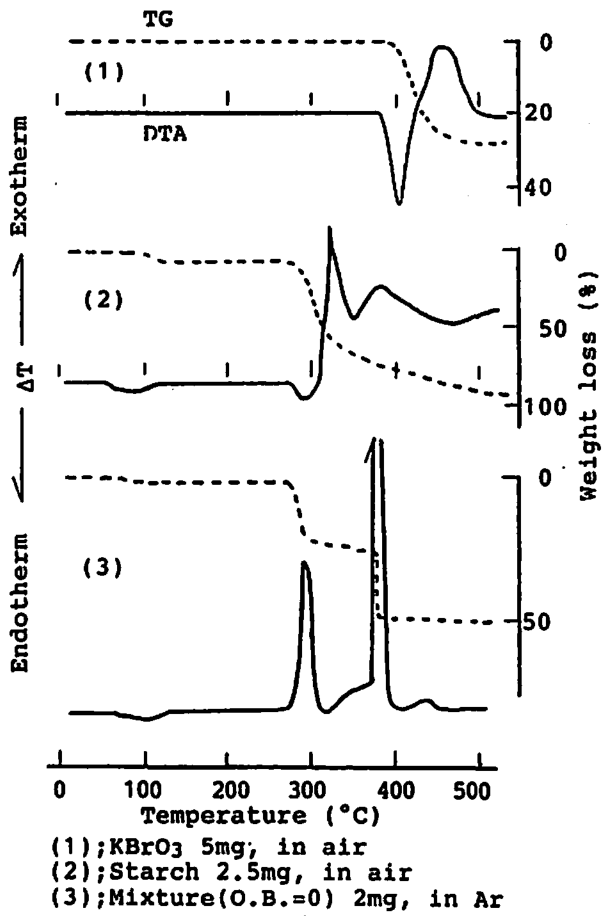

Fig. 1 DTA and TG curves of $KBrO_3$, cornstarch and their mixtures

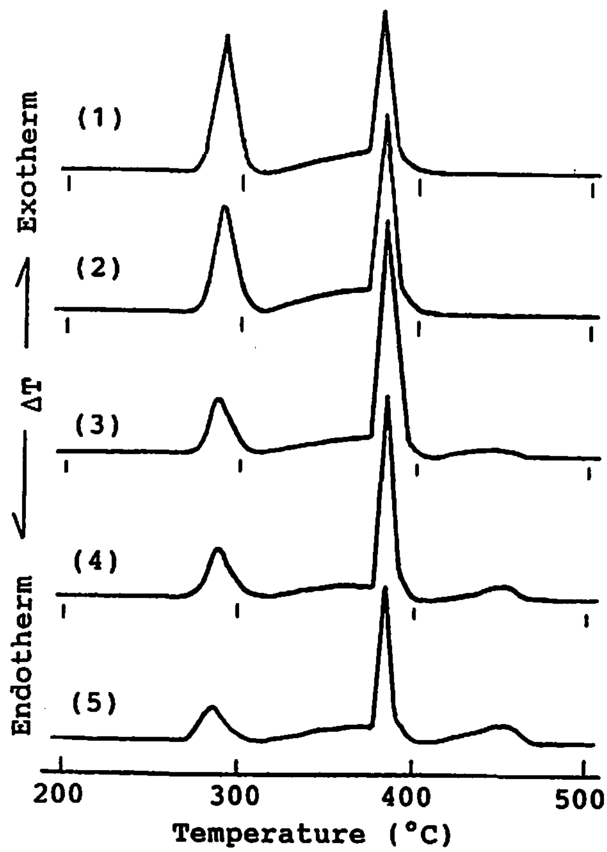

Fig. 2 DTA curves of $KBrO_3$/cornstarch mixtures

mal or pressurized conditions with argon. Samples were loaded in the aluminum cylinder at 60% of theoretical maximum density. The burning rate was determined by the time that was needed for the combustion wave to proceed 10㎜.

3. Results and Discussion

3.1 Thermal analysis

Fig. 1 shows the results of the thermal analysis for $KBrO_3$, starch and the stoichiometric mixture in eq.(1).

The decomposition of $KBrO_3$, as has been shown by many workers[2], takes place soon after melting at 390℃ producing oxygen and KBr. The weight loss in this reaction was 29% compared with the theoretical value of 28.7%.

Starch released the water contained at about 100℃ and caused the exothermic reaction just after melting at 280℃. The complicated shape of the exothermic peak shows that the main reaction of the oxidation of starch accompanies the decomposition such as the cleavage of the main chain. However, the oxidation proceeds completely showing a weight loss of about 100%.

The mixture shows an exothermic reaction at 280℃ and 375℃. These are identical with the melting temperature of starch and $KBrO_3$, respectively. So, the former peak shows the partial reaction of starch with solid $KBrO_3$ due to the melting of starch. The latter peak, on the other hand, was ascribed to the complete reaction of dissolved starch and $KBrO_3$. The weight loss exceeded the theoretical value of 43% based on eq.(1) because of sample scattering due to the vigorous exothermic reaction.

Fig. 2 shows the DTA curves for the mixtures of various compositions. There was no difference in the temperature at which the two exothermic peaks started. Though it was supposed the reaction described above took place, there was a difference in the peak area. The peak at 280℃ became large as the content ofstarch increased. In addition to this, the peak at 375℃ had a maximum in the mixture which had an oxygen balance that was equal to zero. In excess $KBrO_3$, another exothermic peak was noticed at 450℃ which was caused by the thermal decomposition of excess

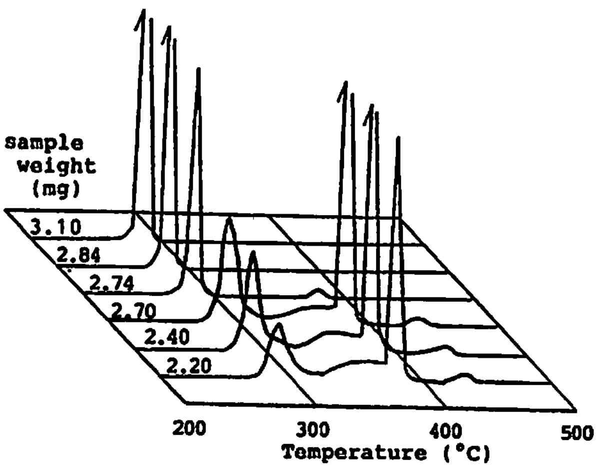

Fig. 3 Effects of sample weight on DTA curves of $KBrO_3$/cornstarch mixtures

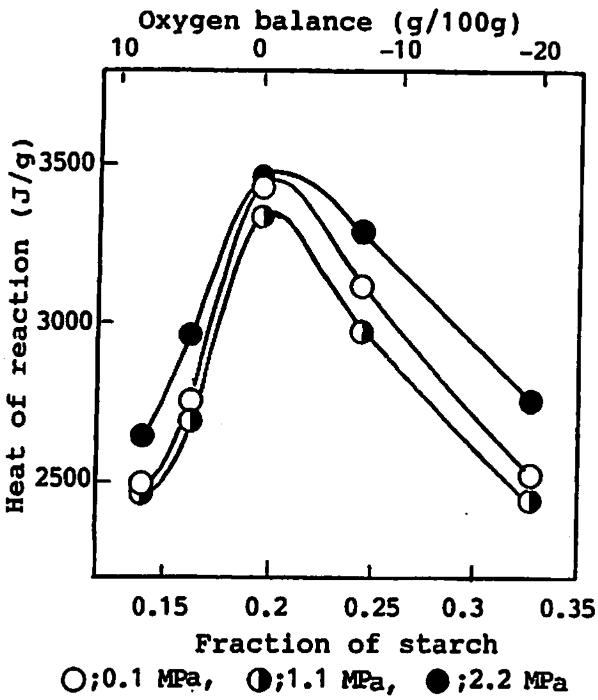

Fig. 4 Heat of combution of $KBrO_3$/cornstarch mixtures

$KBrO_3$.

The binary mixtures caused a vigorous exothermic reaction with increasing sample weight. Fig. 3 shows the DTA curves for various amounts of sample. When the amount of sample exceed 2.7mg, the reaction finished only in one step instead of in two steps. The amount that caused this one step reaction changed with the composition showing the greater the starch content, the smaller the sample weight. Consequently, it is concluded that the vigorous reaction of starch with $KBrO_3$ occurred due to melting of the $KBrO_3$ caused by the heat produced in the former reaction.

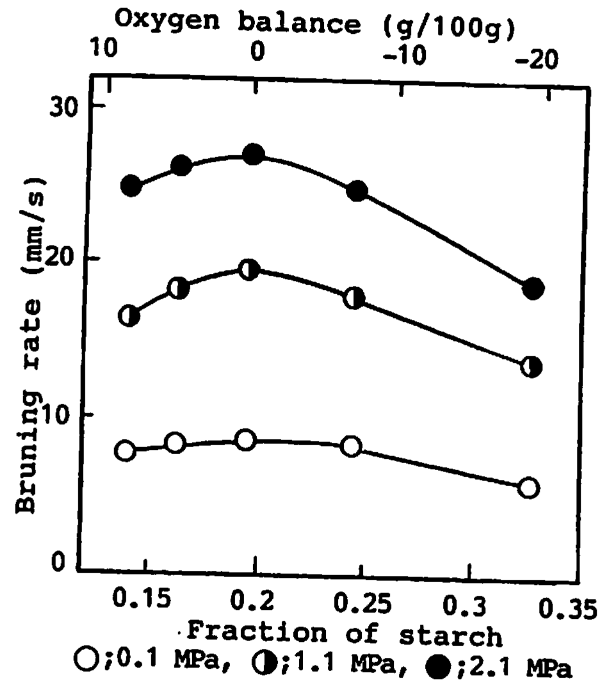

Fig. 5 Burning rate of $KBrO_3$/cornstarch mixtures

3.2 The heat of reaction

Fig. 4 shows the results of the heat of reaction measured under three pressurized conditions. The heat of reaction had a maximum when the oxgen balance was equal to zero. This result was similar to the area of the exothermic peak in the DTA curves. Hence, it was suggested that these reactions proceeded according to eq.(1) . The heat of reaction showed a slight increase with increasing ambient pressure.

3.3 The burning rate

A linear burning rate is affected by the bulk density and the diameter of the burning tube. A preliminary investigation showed that the linear burning rate was constant from 60% to 70% of theoretical maximum density, when the diameter of burning tube is greater than 6 mm.

Fig. 5 shows the results of the burning rate measurement for various compositions under pressurized conditions using argon. The burning rate had a maximum value at the stoichiometric mixture at all conditions. The burning rate was affected by the ambient pressure and increased with increasing pressure. This indicates that the gas phase reaction has a considerable influence on the combustion analogous to the solid propellant combustion. Fig. 6 shows the results of the burning temperature measurement under atmospheric conditions. The burning

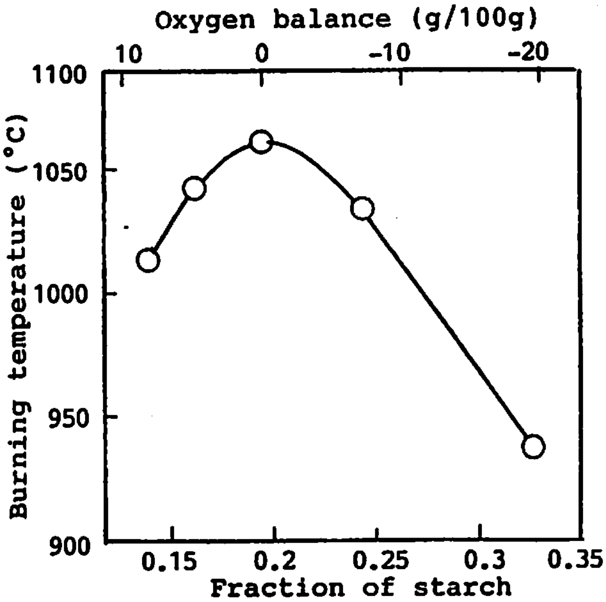

Fig. 6 Burning temperature $KBrO_3$/cornstarch mixtures

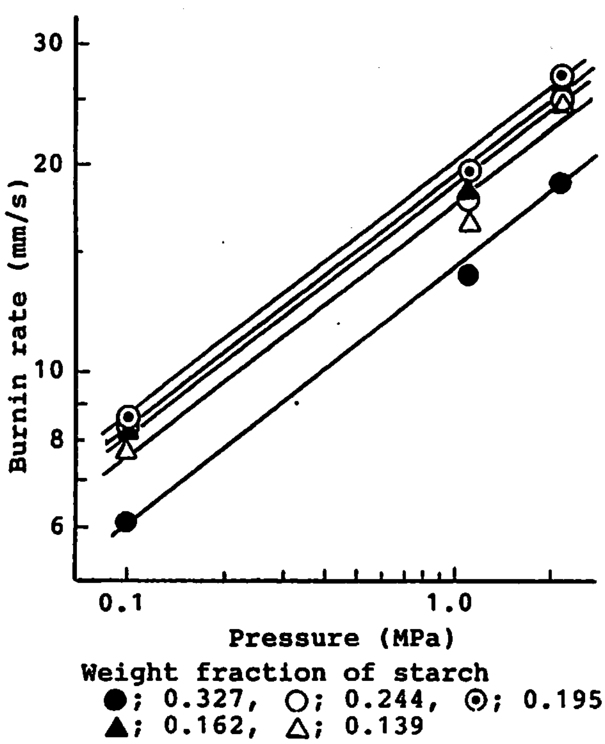

Fig. 7 Burning rate characteristics of $KBrO_3$/cornstarch mixtures

temperature was also affected by the composition

Table 2 Pressure exponent of burning rate

Weight fraction of onstarch	Pressure exponent
0.327	0.364
0.244	0.347
0.195	0.365
0.162	0.363
0.139	0.365

similar to the burning rate and heat of combustion[3].

Fig. 7 shows the vieille plots for the burning rate data. In order to express the influence of the pressure on the burning rate, the pressure exponent was calculated using vieille's equation (Table 2) of $V=aP^n$. It became clear that the pressure exponent was about 0.36 and was independent of the composition.

4. Conclusion

The thermal reactivity and the combustion reactivity of potassium bromate/starch binary mixtures were studied by thermal analysis, the heat of reaction, the burning temperature and the burning rate to obtain the basic data as the one of the concrete breakagents.

These binary mixtures vigorously react just after melting of the potassium bromate. As the heat of reaction, the burning temperature and the burning rate had a maximum value at the stoichometric composition in eq.(1), it became clear that the reaction proceeded mainly according to eq.(1).

Furthermore, the burning rate was dependent on the ambient pressure, and the pressure exponent was about 0.36 for each composition.

References

1) "The General Explosive", p37 (1995), ed. by Japan Explosives Industry Association

2) F. Solymosi, "Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase", John Wiley & Sons (1977) p.373

3) Hidetsugu Nakamura, J. Ind. Expl. Soc. Japan, 52, 173 (1991)

臭素酸カリウムとコーンスターチとの反応

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コンクリート破砕薬の主剤として，臭素酸カリウム－コーンスターチ混合系の熱反応性および燃焼反応性を，熱分析，燃焼熱，燃焼温度や燃焼速度を測定して考察した。

両者は臭素酸カリウムの融解時に激しく反応し，燃焼熱，燃焼温度，燃焼速度ともに(1)式にともなう量論組成で最大値を示し，熱反応，燃焼反応が主に(1)式にともなって進行することが判明した。

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