CALORIMETRIC INVESTIGATION OF SULFUR VULCANIZATION OF NATURAL RUBBER

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要　　約

　最近에 와서는 黃에 依한 고무의 加黃反應이 發熱反應이라는데 主眼點을 두어　近來　高分子化學 分野에서 그 活用度가 높은 熱分析機 (特히 DSC, DTA)가 加黃發熱現象研究에 많이 利用되고 있다. 그러나 고무의 加黃反應을 速度論的으로 연구하여 理論的 基礎를 確立하여 두는 것이 必要하다는 것은 여러 學者들이 前부터 느껴왔으나 고무彈性體는 한번 加黃되면 一般的인 溶媒에 依한 溶解가 어렵기 때문에 反應物(黃, 加黃促進劑)이나　生成物의 濃度測定에 依한 加黃反應의 速度論的 研究가 어려웠다. 그래서 本　研究에서는　DSC (Differential Scanning Calorimetry)를 利用하여 얻은 天然고무의 加黃發熱 thermogram을 Borchardt-Daniel이 제안한 방법으로 分析하여 kinetic data(즉, rate constant k, frequency factor ko, Activation Energy Ea)를 얻었다. 또한 이 kinetic data가 가황촉진제의 種類에 따라 어떻게 달라지는지, 實際工程에서 適正加黃時間, 溫度, 加黃促進劑의　種類, 配合量 決定에 活用할 수 있는 方案에 對해서도 관심을 두고 檢討하였다.
　한편 DSC에 依한 方法의 信賴度를 검토하기 위하여 DSC用으로 쓰여진 것과 同一한 시료를 使用하여 Oscillating Disk Rheometer에 의한 Cure Curve를 얻고 이 Cure　Curve를 分析하여 얻은 kinetic data를 앞서 구한 data와 比較檢討하였다.

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SUMMARY

The effects of several vulcanizing accelerators on the determination of kinetic parameters of natural rubber vulcanizate was studied by DSC. Kinetic parameters were determined by means of the calculation procedures of Borchardt-Daniels and Oscillating Disk Rheometer (ODR) cure curve analysis, using both DSC exothermal thermogram and ODR cure curve. In order to examine the credibility in the DSC method the same compound which was used for DSC method was used for the comparison with the results of ODR data.

Upon this method, kinetic rate constant (k), and Arrehenius parameter (Ea, ko, n) have been determined for rubber compounds via a new method using DSC thermogram and ODR cure curve. In the comparison of DSC and ODR results, kinetic parameters has shown good agreements between two results.

Consequently, from the present studies, it is shown that the DSC thermoanalytical method can provide an alternate new method of kinetic study of rubber vulcanization.

INTRODUCTION

In recent years many thermoanalytical studies have been achieved through Differential Scanning Calorimetry in observing vulcanization process, particulary for accelerated sulfur cure of NR compounds.[1-4] And research workers became to recognize the needs for the establishment of the basic theory on the vulcanization reaction rate in terms of thermoanalytical methods. But for the reaction rate study approprieate analytical methods were not properly set up because of insolubility of rubber vulcanizate which for the determination of the concentration of reactants, etc. This study is then considered to obtain a calculation method of kinetic data according to Borchardt-Daniels method[5] with DSC thermogram.

For identification of the study, comparison of the experimental data between DSC and ODR has been made.

EXPERIMENTALS

Materials

The recipe used in this study is given in Table 1. Natural rubber used was of RSS #1 grade. Commercial accelerators were used without any further purifying treatment and are abbreviated as follows:

tetramethylthiuram disulfide as TT (NOCCELER TT, OUCHI SHINKO)

N-oxydiethylene-2-benzothiazoyl sulfenamide as MSA (NOCCELER MSA, OUCHI SHINKO)

dibenzothiazyl disulfide as DM (NOCCELER DM, OUCHI SHINKO)

Table 1. Recipe for NR compound [PHR]

Compound	1	2	3	4	5
NR (RSS #1)	100	100	100	100	100
Stearic acid	1	1	1	1	1
Zinc oxide	5	5	5	5	5
Sulfur	2.5	2.5	2.5	2.5	2.5
Accelerator	1	1	1	1	1
	(TT)	(MSA)	(DM)	(M)	(D)

2-mercaptobenzothiazole as M (NOCCELER M, OUCHI SHINKO)

1,3-diphenyl guanidine as D (NOCCELER D, OUCHI SHINKO)

Equipment

A mettler TA-3000 system and Monsanto 100 were used for DSC and ODR respectively (Fig. 1) The temperatures used for ODR were 150, 160 and 170°C, and the operating conditions of mettler TA-3000 system are as follows:

| Operating	Condition
Starting temperature	150°C
End temperature	250°C
Purge Gas	Nitrogen (50mℓ/min)
Heating rate	10K/min

RESULTS AND DISCUSSION

Reaction rate from ODR cure curve

Fig. 3 illustrates the rate constants of NR vulcanization system with five different accelerators. The data were obtained by isothermal ODR cure curve analysis (Fig. 2). Curing temperature was 160°C. Through Fig. 3, k values are given and has shown in Table 2. Arrhenius plots of Table 2 has shown in Fig. 4. The ODR cure curve analysis has also given a estimated kinetic parameter applying Arrhenius equation as shown in Table 3. The equation applied is;

$$k = \frac{2.303}{t} \log \frac{M_{HF} - M_L}{M_{HF} - M_H} \quad \dots\dots\dots\dots (1)$$

that is, $\log \dfrac{M_{HF} - M_L}{M_{HF} - M_H} = \dfrac{k}{2.303} \cdot T \dots (2)$
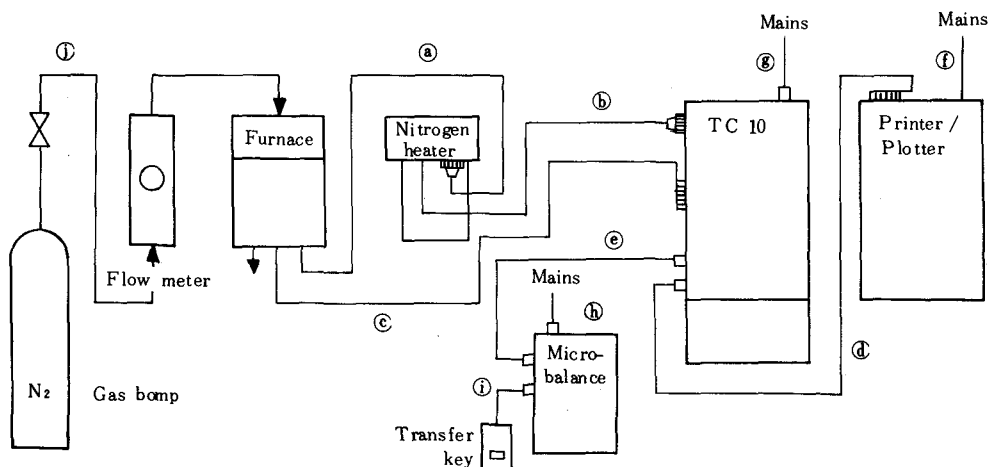
ⓐ Power cable for furnace   ⓑ Power cable for DSC 30 cell
ⓒ Signal cable for DSC 30   ⓓ Connecting cable to printer / plotter
ⓔ Connecting cable to microbalance   ⓕ Mains cable for printer / plotter
ⓖ Mains cable for TC 10   ⓗ Mains cable for microbalance
ⓘ Hand or foot transfer key   ⓙ Gas tube for DSC 30 cell

Fig. 1. Schematic diagram of thermal analyser unit

It has shown that a specimen compounded fast onset accelerator like thiuram indicated relatively lower values of Ea and conversely moderate or slow acting accelerators like sulfenamides or diphenyl guanidine higher values of Ea.
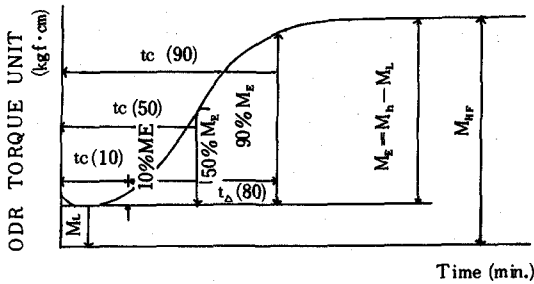

Fig. 2　Rheometer cure curve showing the quantities which are measured in order to evaluate the rate constants for the reaction giving rise to the curve.
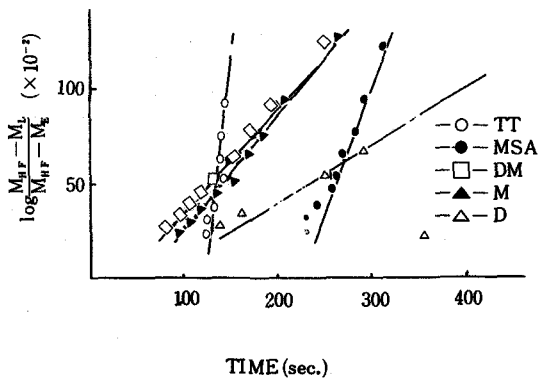

Fig. 3　Plots for rate constants of NR vulcanization with different accelerators the data obtained by isothermal ODR cure curve analysis. Curing temperature 160℃.
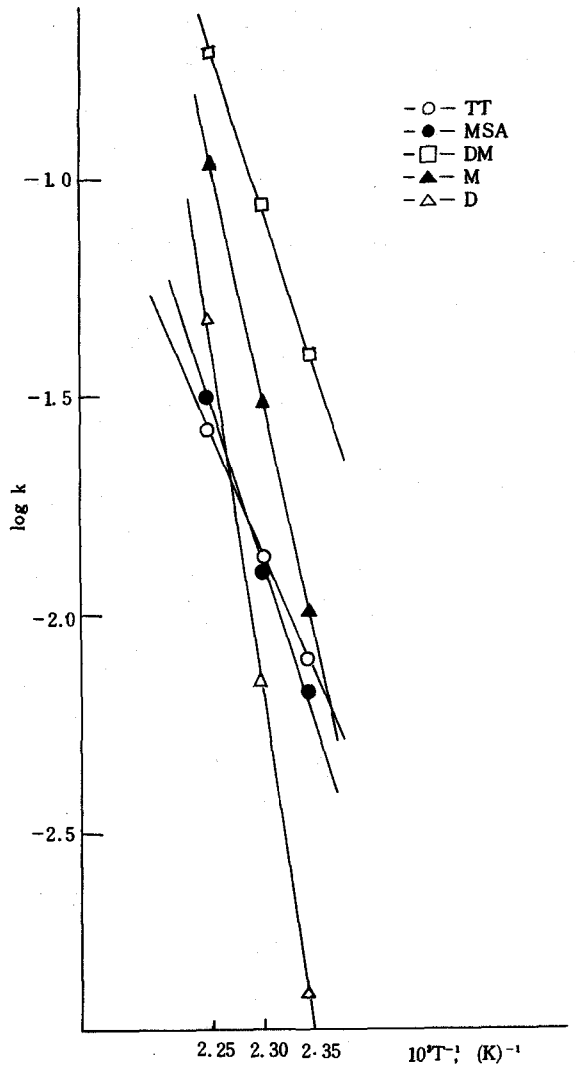

Fig. 4　Arrhenius plot showing effect of accelerator's type in NR compounds.

Table 2. Experimental values for rate constant k by Rheometer cure curve analysis in NR compounds.

Polymer	Rheometer cure temperature (K)	Accelerator	k (sec^{-1})	log k (sec^{-1})
		TT	4.0×10^{-2}	−1.40
		MSA	1.0×10^{-2}	−2.00
	423	DM	7.8×10^{-3}	−2.10
		M	6.4×10^{-3}	−2.19
		D	1.4×10^{-3}	−2.86
		TT	8.5×10^{-2}	−1.07
		MSA	3.0×10^{-2}	−1.52
NR	433	DM	1.4×10^{-2}	−1.86
		M	1.3×10^{-2}	−1.89
		D	6.9×10^{-3}	−2.16
		TT	1.99×10^{-1}	−0.70
		MSA	1.12×10^{-1}	−0.95
	443	DM	4.67×10^{-2}	−1.33
		M	3.16×10^{-2}	−1.50
		D	2.63×10^{-2}	−1.58

Table 3. Estimated kinetic parameter by ODR cure curve analysis using Arrhenius equation.

Accelerator	Overall activation energy, E_a (KJ/mol)	Frequency factor, log k_o
TT	59.0	8.6
MSA	65.8	11.4
DM	71.6	12.0
M	84.5	17.0
D	126.0	27.0

Reaction rate from DSC thermograms

The measuring method of activating energy for polymer thermal dicomposition by means of DSC dynamic scanning which is disclosed by Borchardt and Daniels[5] was applied to obtain kinetic parameter of rubber vulcanization.

Reaction rate, k is determined by the relation between curing temperature and the amount of evolution heat as shown in Fig. 5, and then the values of Ea and ko were obtained through Arrhenius plots.

Equation applied was;

$$k = \frac{A^{x-1}}{m_o} \cdot \frac{dH/d\theta}{(A-a)^x} \quad \text{...............} \quad (3)$$

Since reaction order is one,
therefore equation (3) is

$$k_1 = \frac{dH/d\theta}{A-a} \text{.................................} \quad (4)$$

Fig. 6 illustrates Arrhenius plots showing effect of five (5) different accelerators in NR compound. The obtained was by differential enthalpic analysis. Table 4 is the kinetic data derived from Fig. 6. Fig. 6 has also shown that the hypothesis which vulcanization reaction of sulfur/accelerator system will be first order reaction might be correct. Coran[6] and Paik, Choi[7] support well this fact through their experiments.

As a results of the kinetic study on NR vulcanization of sulfur/accelerator system in terms of reaction rate by means of ODR and DSC, since the value of two kinetic data are identical, DSC method will be able to use in industries as a quality control method.

Table 4. Estimated kinetic parameter by differential enthalpic analysis using Borchardt-Daniels equation.

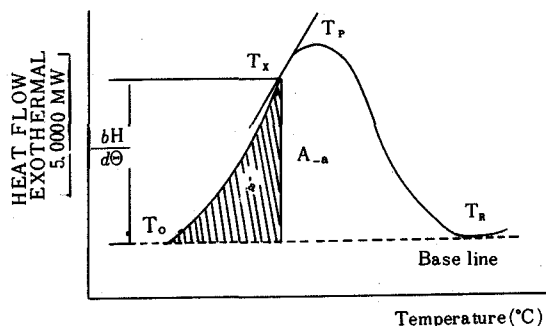| Kinetic parameter / Accelerator	Overall Activation Energy Ea (KJ/mol)	Frequency Factor log k_0
TT	51.7	2.0
MSA	59.3	2.6
DM	68.9	3.5
M	82.3	5.0
D	134.0	9.5

Fig. 5. DSC thermogram showing the quantities which are measured in order to evaluate the rate constants for the reaction giving rise to the curve.

Fig. 6. Arrhenius plots showing effect of accelerator's type in NR compounds, the data obtained by differential enthalpic analysis.

CONCLUSIONS

The results of this work can be summerized as follows:

1. Vulcanization reactions of NR compounds with sulfur/accelerators system have been processed in first order reaction.

2. It has shown that a specimen compounded fast onset accelerator like thiuram indicated relatively lower values of Ea and conversely moderate or slow acting accelerators like sulfenamides or diphenyl guanidine higher values of Ea.
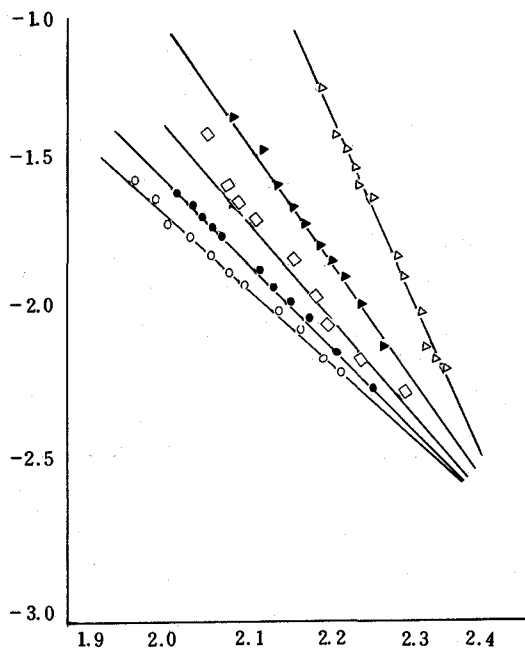
3. It was found that the values of kinetic data obtained both from DSC and ODR methods were identical. Therefore, as Brazier[2] mentioned, the DSC thermogram provides an alternate method for quick analysis for quality control of rubber compounds for the industry.

NOTATIONS

A : Total enthalpy change

a : Partial enthalpy change

Ea : Overall activation energy of vulcanization

k_o :   Frequency factor

$X.n$:   Order of the reaction

t :   Time

T :   Kelvin temperature

m_o :   Initial mass of sample in the pan

M_L :   Minimum torque

M_{HF} :   Maximum torque

M_H :   Torque attained at a stated time

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