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THERMAL DEGRADATION OF POLYTETRAFLUOROETHYLENE IN FLOWING HELIUM ATMOSPHERE
I. DEGRADATION RATE

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Abstract—The thermal degradation of polytetrafluoroethylene in flowing helium atmosphere was studied in the temperature range 510-600℃. The products of thermal degradation were analyzed by an on-line gas chromatography and the rates of degradation were obtained. At relatively lower temperatures (less than 530℃) the rate curves as a function of time showed two peaks. This phenomenon was explained in terms of diffusion limitation of the gaseous products. Further research was carried out by scanning electron microscopy (SEM) in order to observe the diffusion limitation and these facts were confirmed by observing the matrix of partially degraded polymer. The rate curves which have two peaks indicated that the diffusion limitation was disappeared above ca. 50% conversion. The activation energy in diffusion limitation free region was 78.1 kcal/mole and it was very similar to the result obtained by Madorsky (80.5 kcal/mole). The activation energy was also consistent with that obtained by thermogravimetry.

Key words: *Polytetrafluoroethylene, Thermal Degradation, Diffusion Effect, Rate, Activation Energy*

INTRODUCTION

When polymer is thermally degraded, the rate of thermal degradation is very important quantity to describe the progress of reaction. The rate of thermal degradation of polytetrafluoroethylene (PTFE) has been studied by several investigators [Madorsky et al., 1953; Florin et al., 1954; Wall and Michaelson, 1956; Michaelson and Wall, 1957; Madorsky and Straus, 1960; Siegle et al., 1964; Goldfarb et al., 1962; Madorsky, 1964], because of its relatively high thermal stability.

In 1953, Madorsky studied on the rates and activation energy of thermal degradation of PTFE in vacuum and the temperature range 400-500℃ using pressure method and loss-of-weight method [Madorsky et al., 1953]. He reported that the rate of thermal degradation of PTFE was the first order with respect to the sample weight and that the activation energy was 80.5 kcal/mole. Thereafter, the similar researches have been performed on the relatively small size of PTFE sample under vacuum condition and at relatively low temperature in order to reduce extra factors, such as the diffusion limitation and side reaction [Siegle et al., 1964; Goldfarb et al., 1962]. Many efforts were also made to identify the degradation mechanism of PTFE [Siegle et al., 1964; Goldfarb et al., 1962; Madorsky, 1964; Wall, 1972; Kim and Rhee, 1980].

However, it has been known that the rate of thermal degradation of polymer is a complex function including the chemical reaction rate, the diffusion rate through the polymer matrix, and the vaporization rate of volatile fragments from the surface [Goldfarb et al., 1962]. In some papers, it was shown that the slow diffusion of products in the sample may lead to some changes in the rate behavior with respect to the conversion for thick samples [Wall and Michaelson, 1956; Siegle et al., 1964]. The degradation rate had a zero-order depending on the sample weight at the relatively low temperatures and had a pseudo retarded character for thick samples.

In this paper, the relatively larger size of PTFE was thermally degraded in a flowing helium atmosphere. This report describes new information on the diffusion limitation of gaseous products, the state of polymer depending on degradation time, the effect of helium flow rate as carrier gas and the influence of initial sample weight.

EXPERIMENTAL

1. Reagent

PTFE used was obtained from Mitsui Fluorochemicals Co., Ltd. (Teflon 7A-J) and in the form of powder for molding. The sample was placed and tested in a furnace at 300℃. None of the volatile gases were detected by GC. Thus, the sample was used without further purification.

2. Thermal Degradation of PTFE in Helium-Flowing Reactor

The reactor system used for the experimental studies is shown schematically in Fig. 1. The sample boat was a stainless steel rectangular groove (2.7 cm length×1.4 cm width×0.7 cm depth) and was placed inside the nickel tube decomposition chamber (2.54 cm dia×128 cm long). The needle valve and capillary manometer were placed in front of the decomposition chamber to control the flow rate of carrier gas (0-150 ml/min). The reactor was heated using Lindberg electric furnace and temperature controller. The temperature was controlled from 200 to 1200℃ by three

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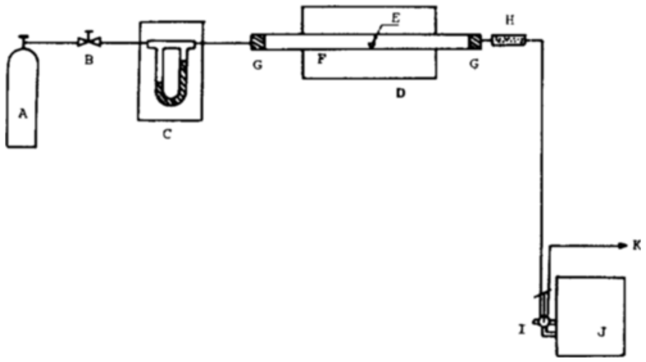

Fig. 1. Apparatus for the pyrolysis in He carrier gas flow.

(A) Helium cylinder
(B) Needle valve
(C) Capillary manometer
(D) Furnace
(E) Sample boat
(F) Ni reactor
(G) Rubber stopper
(H) KOH column
(I) Six-port valve
(J) Gas chromatograph
(K) Vent

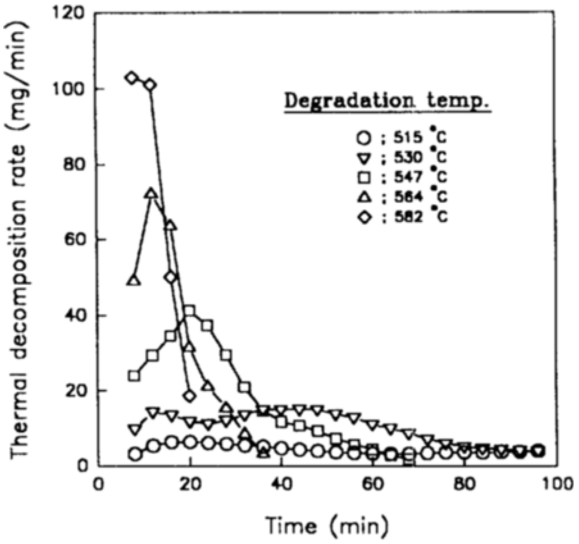

Fig. 2. Effect of degradation temperature on the rate of thermal degradation of PTFE.

Degradation conditions; He flow rate = 100 ml/min.; initial weight = 1 g.

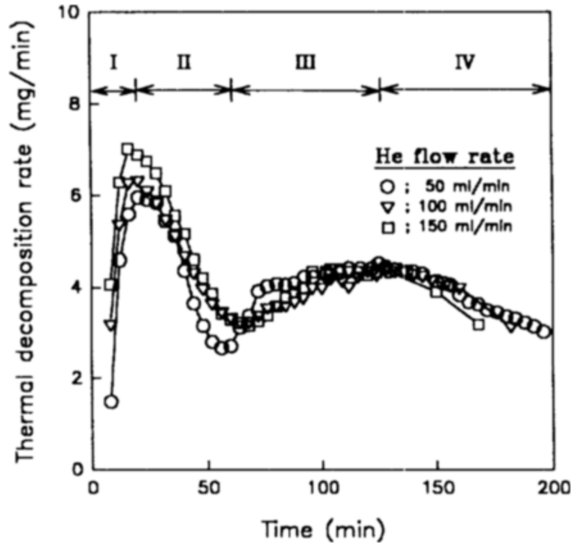

Fig. 3. Effect of helium flow rate on the rate of thermal degradation of PTFE.

Degradation conditions; T = 515℃; initial weight = 1 g.

electrical heaters.

The decomposition products from the reactor were passed into GC through KOH column in order to remove solid particles and HF that might be carried along in the gas stream. The products were sampled with a 720 μl gas sampling valve connected to Varian 920 gas chromatograph equipped with TCD.

For each experiment, the reactor was purged with helium for a while to flush out the hold-up in the gas phase. The degradation temperature and the flow rate of carrier gas were set for the experiment. When the conditions were reached at steady state, the rubber stopper of exit side was opened and the sample boat filled with PTFE was pulled into the middle zone of reactor. After the rubber stopper was closed again, the decomposition gases were sampled and analyzed by GC in every 4 min. For GC analysis, helium was the carrier with a flow rate of 30 ml/min. Porapak Q column (0.25 cm×2 m) was used.

Under most conditions, the main products were tetrafluoroethylene, perfluoropropene and cyclic-perfluorobutane. The rate of thermal degradation was calculated as following equation.

$$F = \frac{Q\Sigma C_i M_i}{1 - \Sigma C_i RT/P} \text{ (mg/min)} \qquad (1)$$

where Q is the flow rate of carrier gas in the reactor, R is the gas constant, T is temperature and P is pressure. C's and M's are the molar concentrations and the molecular weights of the products, respectively. The molar concentrations at any time were calculated by the peak heights of products in chromatogram and the sample loop volume of six port valves (720 μl).

3. Thermogravimetry

Thermal analyzer 990 with TGA 951 of Du Pont was used to determine the weight loss during the thermal degradation of the PTFE. Initial sample weight was about 12 mg and nitrogen as carrier gas was flowed at rate of 100 ml/min.

RESULT AND DISCUSSION

1. Thermal Degradation of PTFE in the Helium-Flowing Reactor

The rates of the thermal degradation of PTFE under the various conditions were plotted as a function of time. Fig. 2 demonstrates the behavior of rate curves with respect to the temperature under carrier gas of 100 ml/min. Figs. 3 and 4 show the effects of carrier gas flow rate on the thermal degradation of PTFE at 515 and 564℃, respectively. It can be seen that the flow rate of carrier gas does not severely influence on the rate of thermal degradation.

In Fig. 2, it shows that the rate curves at relatively lower temperatures (515 and 530℃) have two peaks, while the rate curve at higher temperatures has one peak. Because the degradation rate at the high temperatures was fast and the retention time of GC was relatively long (4 minutes), the continuous analysis was not possible. But it is expected that the rate curves are the same in pattern with the only differences in the progressive time

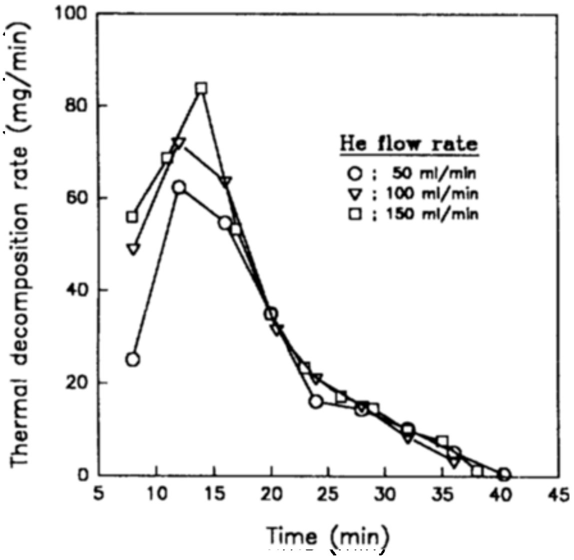

Fig. 4. Effect of helium flow rate on the rate of thermal degradation of PTFE.
Degradation conditions; T=564°C; initial weight=1 g.

of degradation. These curves can be divided into four regions. Region I is considered as the pre-conditioning region (from the starting point to the apex of first peak) because the sample temperature increases sharply from the room temperature to the degradation temperature. Region II is the decomposition region (the down slope side of the first peak) because the decomposition rates decrease with the increase of time. If the rate of the thermal degradation is the first order for the remaining sample weight, it is expected that the rate decreases exponentially with the increase of time. In general, the rates of the thermal degradation of PTFE at the relatively higher temperatures (547, 564 and 582°C) fit the exponential curve well. At relatively lower temperature, however, the decomposition rates decrease temporary for a short period of time. Region III is the growing-rate region (from the valley to the apex of second peak) due to the decomposition rates increase again to establish the second peak. Region IV is another downslope side of the peak and it is considered as the second decomposition region. In this region the decomposition rate decreases exponentially with the increase of time.

From these results, the thermal degradation can be explained in terms of the diffusion limitation of gaseous products in the polymer matrix. In order to confirm these phenomena, the polymer matrixes partially degraded were observed by SEM. The samples (1 g) were degraded for 15, 24, 44 and 58 min at 530°C and were cooled to room temperature. The samples cooled were crosscut and observed by SEM. The results are shown in the Fig. 5. In case of the sample after 15 min degradation, which corresponds to the first apex in the rate curve, the apparent volume was the same as the initial volume. The small pores of about 10 μ were non-uniformly distributed in the polymer matrix. In case of the sample after 24 min degradation, which corresponds to the valley in the rate curve, the pores increased in size and the apparent volume appeared to be slightly larger than initial volume. However, the pores were not interconnected yet. In case of the sample after 44 min degradation, which corresponds to the second apex, the pore size became much larger than the previous one and the apparent volume was not changed. Even though

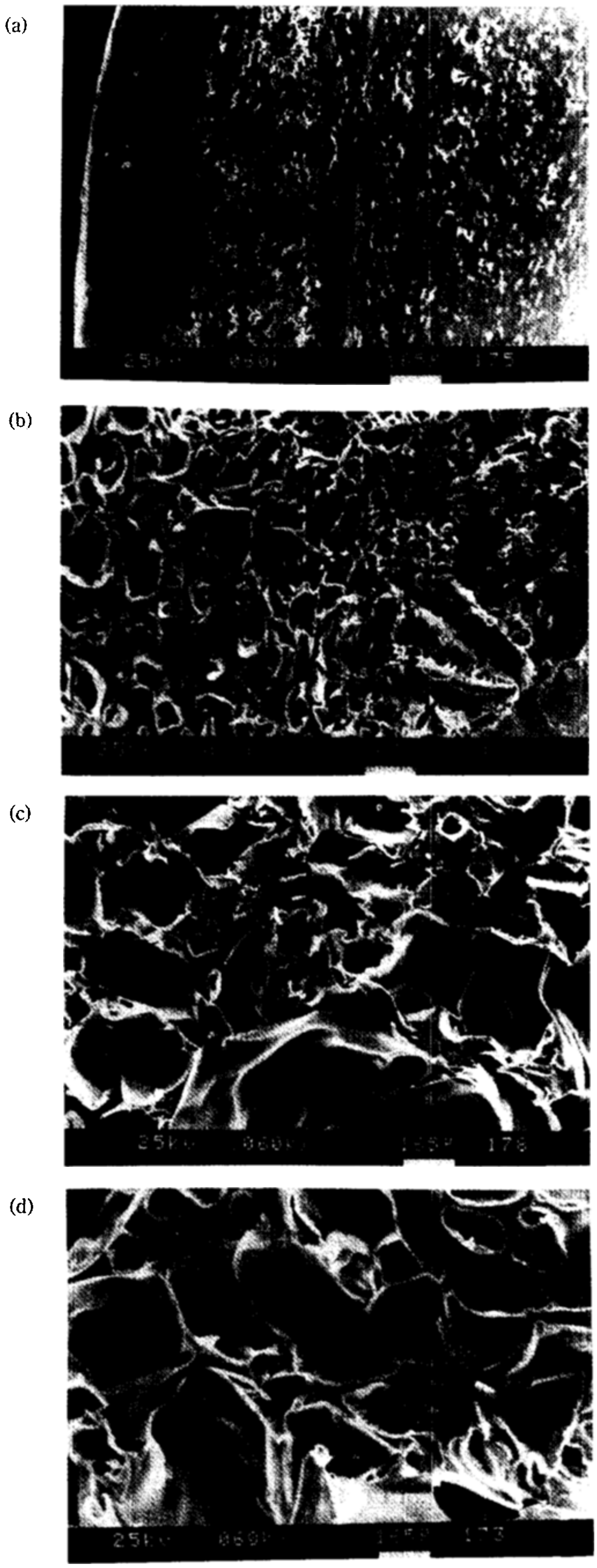

Fig. 5. SEM pictures of PTFE partially degraded at 530°C and under He flow rate of 100 ml/min.
Degradation time: (a) 15 min, (b) 24, (c) 44, (d) 58.

Table 1. Comparison of the maximum rates of thermal degradation of PTFE

Temperature (C)	Maximum rate (g/min) Experimental	Maximum rate (g/min) Calculated[a]
515	0.00633	0.01324
530	0.01423[b]	0.03459
547	0.03459	0.09846
564	0.07213	0.26890
582	0.10303	0.74410
600	0.20483	1.97666

a) Using the rate constant by Madorsky [Madorsky and Straus, 1957].
b) Value at the second peak.

the degradation was further progressed, the apparent volume was almost same as that of the sample after 24 min degradation. However, the pores were enlarged and then interconnected each other. In case of the sample after 58 min degradation, which corresponds to the plateau, the pore size was little larger than that of the sample after 44 min degradation and the apparent volume was smaller than initial volume. Thereafter, the sample was eventually converted to the transparent liquid phase and the liquid phase of sample was remained even at the room temperature. It is assumed that the polymer does not have its properties because the size of polymer chain decreases too much throughout the long period of degradation.

Each region of the rate curves with two peaks can be explained on the basis of diffusion limitation of gaseous products. In the region I, the active sites for the thermal degradation of PTFE is initiated and formed in the polymer matrix of sample. So it is assumed that a small portion of the thermal degradation takes place under this region. In region II, the thermal degradation of PTFE occurs actively. Most of products are isolated in the pores around the active sites and partially diffused out to the surface of polymer matrix because the products are captured inside the dense matrix of the undegraded polymer. It is considered as a strong-diffusion-limitation region. As the degradation progressed, the pores increase in size and then, begin to be interconnected. In the region III, the rate of thermal degradation increases with time because the diffusion of gaseous products in the sample becomes much easier than that in Region II. It seems that the gaseous products inside the large pores are readily out from the sample matrix that those captured inside the isolated pores. The region III is a partial-diffusion-limitation because the diffusion limitation still remained. In Table 1, the maximum rates of PTFE degradation in this experiment are compared with those calculated using the rate constants of Madorsky. The conditions for PTFE degradation are virtually the same in all cases with the differences in the pressure and sample size. It indicates that the diffusion of gaseous products is readily occurred under vacuum condition and in the small size of sample. Lastly, the region IV is expected to be the no-diffusion-limitation region because the pores are big enough and the products are released easily.

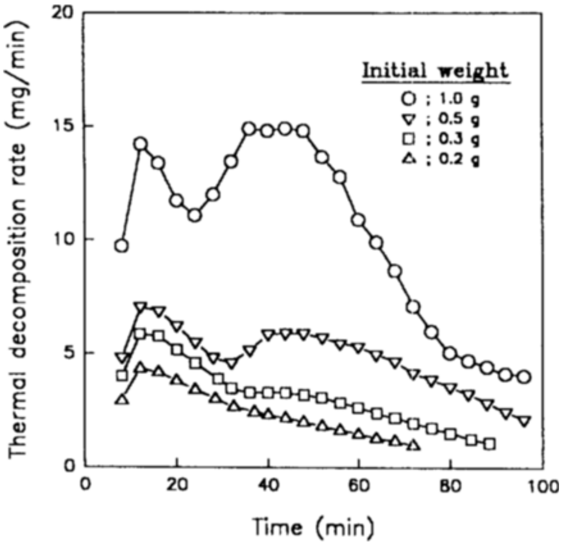

Fig. 6. Effect of the initial weight on the rate of thermal degradation of PTFE.
Degradation conditions; T=530C; He flow rate=100 ml/min.

Table 2. Conversion up to the second peak in the rate curves

Temp. (C)	He flow rate (ml/min)	Initial weight (g)	Degraded weight (g)	Conversion (%)
515	50	1.0	0.517	51.7
	100	1.0	0.529	52.9
	150	1.0	0.495	52.9
530	50	1.0	0.495	49.5
	100	0.3	0.157	52.3
	100	0.5	0.250	50.0
	100	1.0	0.521	52.1
	150	1.0	0.509	50.9

In order to examine the effect of sample thickness on the rates of thermal degradation, the various initial weights were used. The results are shown in Fig. 6. As the initial weight decreases, the second peak diminishes gradually. However, the position of the second peak does not move with the initial sample weight. In Fig. 2, we already showed that the position of the second peak moved toward the left with the increase of temperature. Comparing these two results, it can be known that the position of the second peak is related with the conversion. The conversions up to the second peak under various conditions, which can be calculated from the areas under the rate curves, are shown in Table 2. It shows that the values are not depending on the flow rate of carrier gas, temperature and the initial weight of sample. However, it shows that these values are related to those at about 50% conversion. If it is assumed that the active sites are uniformly distributed in the sample and that the pores at the second apex in the rate curve are completely interconnected, the conversion up to the second apex can be easily calculated.

$$\text{Conversion} = \frac{\text{Number of pores} \times \text{Size of pore}}{\text{Initial size of sample}}$$

$$= \frac{\left[\frac{L}{d}\cdot\frac{W}{d}\cdot\frac{H}{d}\right]\left[\frac{4}{3}\pi\left(\frac{d}{2}\right)^3\right]}{L \times W \times H}$$

$$= \pi/6 \cong 0.52 \qquad (2)$$

Here, L, W and H are the length, the width and the height of the initial sample, respectively. The d is the diameter of pore just interconnected. Therefore, it is expected that up to 52% conversion, the rate curves are influenced by the diffusion limitation due to the dense matrix of polymer.

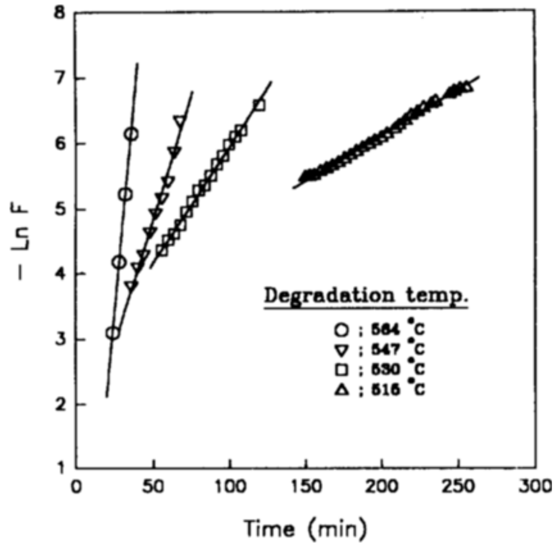

Fig. 7. Plot of –Ln F vs. time for Eq. (5).

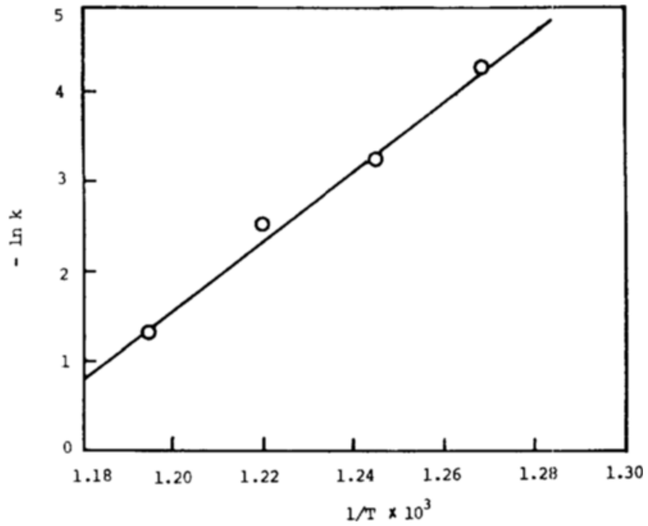

Fig. 8. Arrhenius plot for the thermal decomposition of PTFE.

In order to verify whether the region IV is free from the diffusion limitation, the activation energies were calculated in the region after 52% conversion. If the rate of thermal degradation of PTFE is the first order for the remaining weight w, the rate equation is given by

$$F = -\frac{dw}{dt} = kw \tag{3}$$

where k is the rate constant of degradation and t is time. Eq. (3) can be integrated:

$$w = w_0 \exp(-kt) \tag{4}$$

where w_0 is the initial weight of the sample. Eq. (4) is substituted for w into Eq. (3) and the logarithm is taken.

$$\ln F = \ln(kw_0) - kt \tag{5}$$

If ln F is plotted against t, the rate constant k can be obtained from the slope. The ln F vs. t for each temperature after the conversion of 52% is represented in Fig. 7. The Arrhenius plot for the temperature dependence is given in Fig. 8. From the slope of Arrhenius plot the activation energy is obtained as 78.2 kcal/mole (Table 3). This value is very close to Madorsky's result (80.5 kcal/mole) measured under vacuum at 400-500℃. Therefore, it implies that region IV is free from the diffusion limitation.

Table 3. The activation energies from various sources

Source	Methods	Sample size (mg)	Temperature range (℃)	Atmosphere	Activation energy (kcal/mole)
Madorsky[a]	Pressure & Loss-of-weight	7	400-500	in vacuum	80.5
Siegle[b]	Manometric & Weighting	30-100	360-510	in vacuum	83.0
Ballistreri[c]	LPTD-MS	1.5	Overall	N_2 flowing	74.8
This work	GC	1,000	510-560	He flowing	78.2[d]
	TGA	12	Overall	N_2 flowing	75.5

a) Madorsky et al., 1953; Madorsky and Straus, 1960.
b) Siegle et al., 1964.
c) Ballistreri et al., 1984.
d) Value obtained from the diffusion limitation free region.

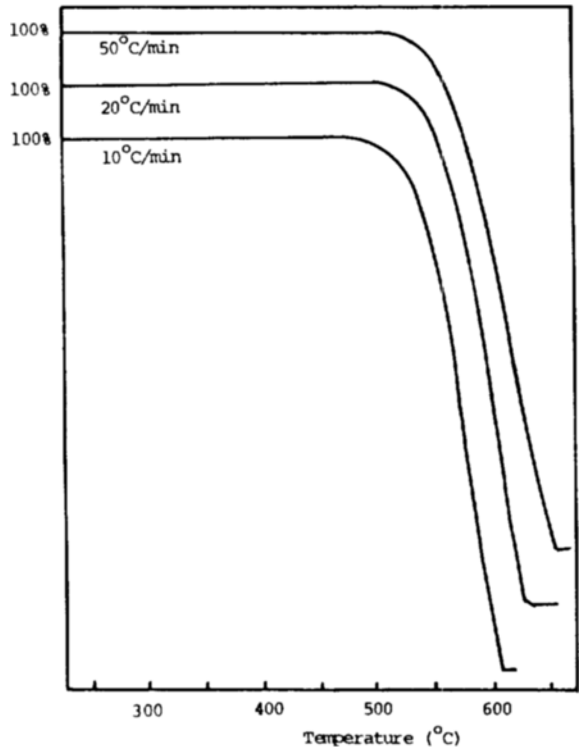

Fig. 9. Thermogravimetric analysis for PTFE.
(a) Heating rate=10℃/min, (b) 20, (c) 50.

2. Thermogravimetric Analysis

The results of the thermogravimetric analysis of PTFE are shown in Fig. 9. In case of the heating rate of 10℃/min, the thermal degradation of PTFE was started from about 490℃. Kissinger used the following equation in order to calculate the activation energy from TGA curves [Kissinger, 1957].

$$\frac{d\ln(\beta/T_m^2)}{d(1/T_m)} = -\frac{E}{R} \tag{6}$$

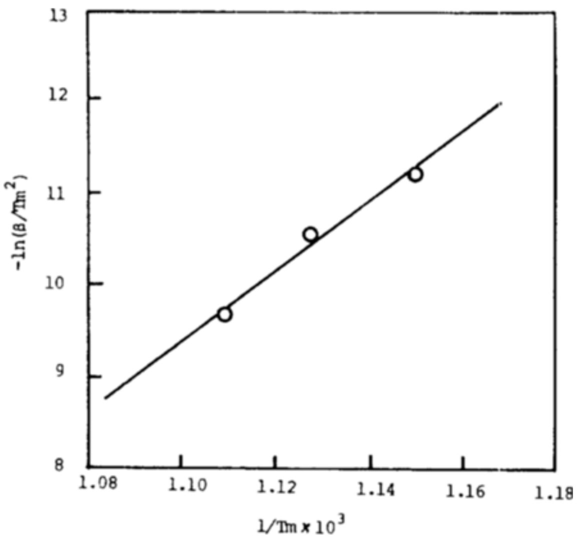

Fig. 10. Linear plot of Eq. (6) as derived from TGA.

where β is the heating rate (°C/min), E is the activation energy, R is the gas constant, and T_m is the temperature at the deflection point of the TGA curve. The value of T_m was obtained from Fig. 9. The calculated activation energy is 75.5 kcal/mole. The activation energies from various sources are shown in Table 3. The activation energies obtained in the inert gas flowing and the relatively higher temperature range are slightly lower than those obtained in vacuum and in the temperature range less than 500°C. It is expected that the difference of the activation energies may be due to the different temperature range and the flow rates, in which PTFE is thermally degraded. In fact, it indicates that the difference of the activation energies can be expressed in terms of the degradation mechanism of PTFE or the product distribution of the degradation. However, the further research is discussed in the companion paper [Jun et al., 1995].

CONCLUSION

The thermal degradation of PTFE has been carried out in the flowing helium and the temperature ranges 510-600°C. The rate of thermal degradation could be explained in terms of the diffusion limitation of gaseous product. The half of conversion for the initial sample weight occurred in the diffusion limitation region and the values for the conversion up to the diffusion limitation region was almost same not depending on the degradation temperature, the flow rate of carrier gas, and the initial weight of sample.

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