# Burning and Degradation Mechanism of Polyester Propellants

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In the combustion of propellants, whether hybrid or solid, polymer degradation is an important step in those cases where polymers are used as fuels.[1] Useful information about polymer degradation has accumulated only recently.[2,3] However, very few comprehensive studies have been performed.[4] Rabinovitch has developed a theory of polymer degradation based on the concept of critical fragment size.[5] Houser has given a procedure of calculating the mass regression rate of the propellant from kinetic data on degradation.[6,7]

The results of the present investigation show that the degradation follows first order kinetics and involves reverse depolymerization. The kinetic data can be correlated with mass regression rate provided the surface temperature is known.

## Experiment and Results

Polyester resin was prepared by refluxing a definite ratio of phthalic anhydride and maleic anhydride with propylene glycol and removing water and excess glycol by distillation under reduced pressure. The unsaturated polyester was cross-linked with styrene. The polyester thus obtained was cured in the temperature range 60–70°C in an air oven.

Thermal conductivity and specific heat of polyester samples were determined by Lees method[8] and Regnault's method,[9] respectively. The density of polyester was determined by measurement of the volume and weight of the cylindrical cast. The results are recorded in Table 1.

The degradation kinetics was studied in the following manner. The polymer was cut into pieces of approximately equal size and weight. The pieces were kept in a muffle furnace maintained at a constant temperature. After heating for a definite time, the pieces were taken out, cooled in a desiccator and weighed accurately. The observations were repeated at different temperatures and for different intervals of time. The fraction degraded was estimated at definite time intervals and at various temperatures. The fraction degraded $w$ is given by

$$w = (m_1 - m_2)/m_1$$

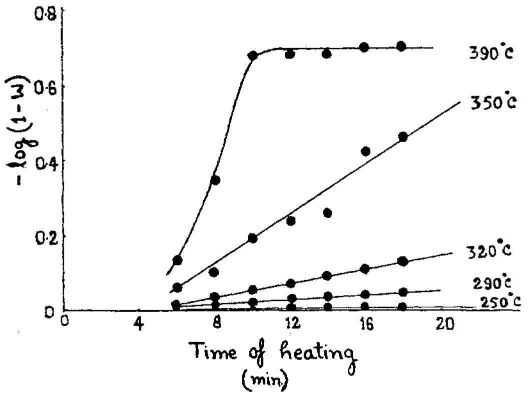

**Fig. 1 Test of equation log (1-ω) = -*kt* for polymer A.**

where $m_1$ is the initial weight of the polymer block and $m_2$ is the weight of the polymer block after time $t$. Experiments also were performed with polymer pieces of different sizes. In order to ascertain whether the degradation is purely thermal or oxidative or both, degradation studies also were performed in a vacuum. Typical degradation data for polymer A are plotted in Fig. 1. The experiments were performed at different temperatures. The results are given in Table 2.

For burning rate measurements in oxygen, a tubular cast of the polyester was taken. The flow rate of oxygen was 22 g./min. The internal radius of the tube was determined at various time intervals. Mass burning rate $\dot{M}$ was calculated by using the following equation:

$$\dot{M} = [\rho\pi l(r_2^2 - r_1^2)]/\Delta t$$

where $r_1$ is the initial radius at time $t$, $r_2$ is the radius at time $t + \Delta t$, $l$ is the length of the polymer block and $\rho$ is the density. Knowing the surface area, the mass burning rate per unit area could be estimated.

The surface temperature was measured in the following manner. A tubular cast of the polymer was prepared and the temperature at various points was measured by copper-constantan thermocouple taking the regression surface as the reference. The results are given in Fig. 2. The surface temperature was obtained by extrapolation.

## Discussion

We shall first consider the mechanism of polymer degradation. Experimental values of $w$ are found to depend on $t$ in the following manner: $\log(1 - w) = -kt$ where $k$ is constant. A typical plot is shown in Fig. 1. $k$ is found to depend on the nature of the sample. Some typical values are given in Table 2. $k$ is found to increase with an increase in the temperature. The energy of activation $E$ for the degradation reaction was obtained by using the Arrhenius equation, $k = A \exp(-E/RT)$ where $A$ is the frequency factor, $R$ is the gas constant, and $T$ is the absolute temperature. $E$ and $A$ were estimated to be 24 ± 1 $k$cal/mole and $4.3 \times 10^6$ sec$^{-1}$, respectively. In order to ascertain whether the degradation process is diffusion-controlled, $k$ was estimated for polymer pieces of different thickness. $k$ is found to be the same in all cases showing that the degradation process is not diffusion-controlled. Further, the degradation studies in a vacuum gave the same values for $k$ as in air. This shows that the degradation is purely thermal.

The mechanism of thermal degradation can be partly understood if results are analyzed in terms of the theory of Rabinovitch which invokes the concept of critical fragment size (c.f.s.). The c.f.s. is the chain length of the volatile product of chain degradation, above which it is more economical to continue breaking backbone C—C bonds than to remove the fragment from its environment. Assuming random scission, the following equation[5] is obtained:

$$w = 1 - \exp(-ik't)[i + 1 - i\exp(-k't)] \qquad (1)$$

where $i$ is the maximum chain length of the c.f.s. expressed in units of monomer length, which is equal to the ratio of C—C bond energy and heat of vaporisation of monomer. $k'$ is a certain constant. Three cases arise;

1) when $k't \ll 1$ and $i \gg 1$, Eq. (1) reduces to

$$1 - w = ik't\exp(-ik't)$$

**Table 1 Physical properties of polyester**

| Property | Value |
|---|---|
| Specific heat | 0.25 cal/g deg |
| Thermal conductivity | $0.96 \times 10^{-3}$ cal/sec cm °C |
| Density | 1.265 g/cm$^3$ |
| Thermal diffusivity | $3.0 \times 10^{-3}$ cm$^2$/sec |

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**Table 2 Values of $k$ for polymer samples**

| | Polymer A | Polymer B | Polymer C |
|---|---|---|---|
| Temp., °K | $k \times 10^3$, min$^{-1}$ | $k \times 10^3$, min$^{-1}$ | $k \times 10^3$, min$^{-1}$ |
| 523 | 0.95 | 1.06 | 2.50 |
| 563 | 3.00 | 5.00 | 5.75 |
| 593 | 9.40 | 11.30 | 13.40 |
| 623 | 32.00 | 37.00 | 46.00 |
| 663 | 137.00 | 148.00 | 152.00 |

2) when $k't \gg 1$ and $i \gg 1$

$$1 - w = i \exp(-ik't)$$

3) when $k't \gg 1$ and $i \ll 1$

$$1 - w = \exp(-ik't)$$

Since $i$ would not depend on the nature of the polymer sample, the kinetics should be independent of degree of polymerization for all the three cases considered previously, provided random scission occurs.

The experimental results show that although the plot of $\log(1 - w)$ against $t$ is a straight line, the slope depends on the nature of the polymer sample showing that the mechanism of degradation does not involve random scission.

If one assumes unzipping process, i.e., reverse depolymerization one can show that[5]

$$w = 1 - \exp[-(P_0 - 1)k^*t] \qquad (2)$$

where $P_0$ is degree of polymerization. Equation (2) shows that the $\log(1 - w)$ vs $t$ plot would be a straight line passing through the origin. It is also clear that $(P_0 - 1)k^*$ would vary from polymer to polymer. Experimental data recorded in Table 2 clearly show that Eq. (2) is satisfied. Hence it follows that mechanism of degradation involves reverse depolymerization. The reverse depolymerization can occur in two ways: 1) random initiation and unzipping, 2) end initiation and unzipping. Since the bonds connecting the linear chains (cross links) will be broken in a random fashion because of the steric factors, it appears that random initiation and unzipping process should occur in the degradation process.

We shall now examine whether the degradation data can be connected with the regression rate measurements.

Since the degradation follows first order kinetics we can write

$$\dot{M} = kM = MA \exp(-E/RT) \qquad (3)$$

where $M$ is the mass of the reacting polymer. If a rectangular polymer block is taken, Eq. (3) can be written as

$$\dot{M} = ax\rho A \exp(-E/RT) \qquad (4)$$

where $a$ is the area and $x$ is the thickness. Thus, $\dot{m}$ is given

$$\dot{m} = M/a = x\rho A \exp(-E/RT) \qquad (5)$$

Equation (5) gives the regression rate at the plane $x = x$ where the temperature is $T$. The net regression rate $\bar{m}$ would be given by

$$\bar{m} = \int d\dot{m} = \rho A \int_0^l \exp(-E/RT)dx \qquad (6)$$

$\bar{m}$ can be estimated provided the definite integral can be evaluated. Houser has calculated $\bar{m}$ as the sum of the rates of a series of thin isothermal slabs, each at the appropriate temperature along the profile. Evidently this procedure is cumbersome. A better procedure would be to plot $\exp(-E/RT)$ against $x$ and evaluate the definite integral. For this method experimental values of $T$ for various values of $x$ ought to be known beforehand. This information is sometimes not available. Fortunately, in the present case, the experimental measurements of $T$ at various values of $x$ showed that

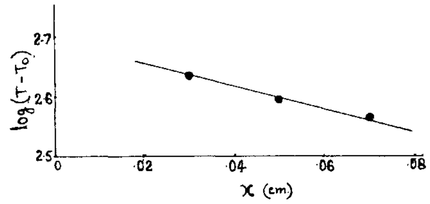

**Fig. 2 Estimation of surface temperature using Eq. (7).**

$$\log(T - T_0) = \log(T_s - T_0) - \kappa' x \qquad (7)$$

where $T_6$ is surface temperature, $T_0$ is initial temperature, and $T$ is the temperature at any plane $x$, $\kappa'$ is constant. The validity of Eq. (7) is confirmed by Fig. 2. The integral in Eq. (6) cannot be evaluated using Eq. (7). However, values of $T$ can be calculated at any value of $x$. With this information the integral can be evaluated by a graphical method. The integral in Eq. (6) was evaluated in this manner.

On substituting the relevant quantities in Eq. (6) using Table 1, $\bar{m}$ is found to be $1.91 \times 10^{-2}$ g/sec cm$^2$. The experimental value of hybrid regression rate is $1.6 \times 10^{-2}$ g/sec cm$^2$. The agreement is satisfactory.

We may now discuss Fig. 2 more thoroughly. Since a straight line is obtained, extrapolation of the curve gives $T_s$ when $x \rightarrow 0$. $T_s$ is found to be 800°K. The nature of the plot in Fig. 2 supports the following temperature profile equation suggested by Houser[7]:

$$(T - T_0) = (T_s - T_0) \exp(-\dot{r}x/\alpha) \qquad (8)$$

where $\alpha$ is thermal diffusivity which is equal to $\kappa/c\rho$ ($\kappa$ is thermal conductivity and $c$ is specific heat), $\dot{r}$ is linear burning rate. In order to check the internal consistency, using the experimentally determined values of $\dot{r}$, the surface temperature was calculated. Equation (8) gives a value of 800°K which is in excellent agreement with the extrapolated value quoted previously. It may be noted that Eq. (8) is derived by considering only heat transfer by conduction. Since in the process of pyrolysis polymer heat is absorbed also, a term must be introduced into the equation to take this into account. Equation (8) has been modified by Houser in this manner.[7] Unfortunately surface temperature measurements are not sufficiently extensive and precise to warrant any detailed analysis of the results on the basis of Houser's modified expression.

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