Some Observations on the Ignition of Composite Solid Propellants

K. Kishore, S. Sankaralingam, R. Nagarajan and K. Mohandas

Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore-560 012

ABSTRACT

Heat-up times derived from studies on the ignition characteristics of a few model composite solid propellants, containing polystyrene, carboxy-terminated polybutadiene, plasticised polyvinyl chloride and polyphenol formaldehyde as binders, show that they are directly proportional to the mass of the sample and inversely proportional to the heat flux. Propellant weight-loss prior to ignition and high pressure ignition temperature data on the propellants, ammonium per chlorate, and binders show that the ignition is governed by the gasification of the binder pyrolysis products. The activation energy for the gasification of the pyrolysed polymer products corresponds to their ignition behaviour suggesting that propellant ignition is controlled by the binder.

1 INTRODUCTION

Ignition of composite solid propellants has been the subject of research by a number of workers and three principal models have been postulated: (i) solid-phase reaction model, (ii) heterogeneous surface reaction model, and (iii) gas-phase reaction model. In all the models, it is assumed that the heat-up time of the solid phase is the dominant factor of propellant ignition and this has been supported by various experimental techniques. Diffusion and chemical reaction times are neglected except in extreme cases like large heat flux or low oxidiser concentration. In this paper an attempt has been made to measure the heat-up time for composite solid propellant ignition.

Pressure has been found to promote the ignition of composite solid propellants significantly, suggesting that gas-phase reactions are important during ignition. In this paper, the effect of pressure on the ignition of composite solid propellants and their constituents, viz., ammonium per chlorate (AP) and the binder, have been examined. The effect of transition metal salicylates on ignition of propellants has also been examined.

The importance of polymer gasification process arises due to its role in understanding the polymer combustion processes. The kinetic studies on polymer degradation have been generally done at low temperatures at which the degradation rates are low. Obviously, these results cannot be satisfactorily extrapolated to combustion conditions. The surface temperature during burning of polystyrene (PS) samples in air is around 480 °C and for most polymers it is in the range of 400-500 °C. Hence during combustion the bulk polymer can be imagined to be isothermally heated at these temperatures. So, an attempt was made to study the kinetics of gasification, from isothermal TG experiments, in the temperature range 440-570 °C. These experiments were aimed at understanding the role of binder in propellant ignition processes.

2. EXPERIMENTAL DETAILS

Carboxy-terminated polybutadiene (CTPB)/ammonium perchlorate (AP), polystyrene (PS)/AP, p-phenol formaldehyde (PPF)/AP and polyvinyl chloride (PVC)/AP propellants were prepared as described elsewhere. Analar grade AP (Veb Labor
Chemie Apolda, Germany) of particle size 53-105 μm was used. Polymer samples were prepared by curing the prepolymers in a similar fashion as that of the propellants. Preparation and characterization for Co, Ni, Mn and Fe salicylates (Cosal, Nisal, Mnsal and Fesal) are described elsewhere\(^\text{14}\).

The ignition delay measurement apparatus consists of a small furnace having a stainless steel platform at the centre, the temperature of which could be maintained to a desired level within ±2 °C variation. Inert atmosphere was provided in the furnace by flushing it with nitrogen gas (10 ml/min). A guide tube was used to drop the sample at the centre of the hot platform. Cubical shaped propellant samples of 25 mg weight were used and their dimensions were kept constant in all the runs.

Ignition temperatures of AP, PS and propellants at various pressures were measured in a high pressure differential thermal analysis (DTA) assembly. Oxygen or nitrogen was filled in the pressure vessel to about 7 atm and released, and this procedure was repeated several times to expel the air in the pressure vessel after which the pressure of the gas was maintained at a preset level (Table I). DTA runs were taken at a heating rate of 10 °C/min. At the time of ignition, \(\Delta T\) trace gave a sudden exotherm and even the pen, recording the temperature axis, showed a sharp change in the slope. Explosion sound was clearly heard at the time of ignition. The experiments were reproducible to ±1 °C. A typical trace is shown in Fig. 1.

Ignition delay measurements of the polymer samples, at various isothermal temperatures, were carried out as described elsewhere\(^\text{15}\). Weight-loss prior to ignition was measured as described elsewhere\(^\text{15-17}\). A 50 mg sample (disc of 3 mm diameter) was used in each run. Sample weight was continuously recorded with respect to time after the introduction of the sample into the furnace. The ignition event was located by an abrupt change in the weight-loss trace as shown in Fig. 2.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>N(_2)</th>
<th>O(_2)</th>
<th>N(_2)</th>
<th>O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/AP</td>
<td>614</td>
<td>599</td>
<td>606</td>
<td>601</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>593</td>
<td>610</td>
<td>573</td>
</tr>
<tr>
<td></td>
<td>629</td>
<td>588</td>
<td>616</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>631</td>
<td>575</td>
<td>621</td>
<td>565</td>
</tr>
<tr>
<td></td>
<td>635</td>
<td>569</td>
<td>626</td>
<td>559</td>
</tr>
<tr>
<td></td>
<td>636</td>
<td>567</td>
<td>632</td>
<td>553</td>
</tr>
</tbody>
</table>

Table 1 Ignition temperature (IT) of composite solid propellants as a function of pressure (sample weight : 10 mg)

For heat of decomposition (\(\Delta H_d\)) measurements of the propellants, Stanton Redcroft DTA model 671 was used. The phase transition peak of AP was used as an internal standard for the area measurements. Ignition of the sample was completely avoided by taking lesser amount of samples (0.5 to 1 mg). Under such conditions decomposition of the propellant only occurs. The experiments were done in nitrogen atmosphere at a heating rate of 20 °C/min. A typical run is shown in Fig. 3. For ignition temperature (IT) measurements, at atmospheric pressure, the same assembly was used and a heating rate of 20 °C/min was employed. For higher mass propellant sample (5 mg or above), the ignition always occurred and hence higher mass was used for ignition temperature measurements. A typical ignition trace is shown in Fig. 4.
3. RESULTS AND DISCUSSION

The results of ignition delay measurements are plotted in Fig. 5. Extrapolation to zero mass gives a hypothetical ignition delay ($\tau$) for which the heat-up time is zero. The ignition delay at zero mass could be taken as the chemical delay devoid of any physical delay. Figure 5 shows that heat-up time or physical delay varies directly with the sample mass and inversely with temperature. It is apparent from Fig. 5 that the physical delay will outproportion the chemical delay for a large mass and low heat flux; the heat flux increases with the increase in the furnace temperature. The physical delay can also be estimated from the ‘weight-loss prior to ignition’ experiments (Fig. 2); the time for the inception of the propellant weight loss after it has been introduced into the furnace, is identified as the physical delay. The physical delay obtained by this method is found to support the results from the hot plate measurements.

In polymer ignition, the weight loss before ignition has been found to be in the range of 5-20 per cent. Korobeinichev and Aniseforov have studied the effect of oxidiser on the degradation of binders and they found that notable decomposition of AP does not begin until most of the binder (PS) is degraded. But $\text{HClO}_4$ very strongly accelerates the degradation of PS. These observations show that the binder gasification plays a significant role during ignition. This gets further support from the weight-loss data, prior to ignition, which show variance with different binders (Table 2), the weight-loss expectedly is minimum in the cross-linked binders (CTPB, PPF). The PVC/AP propellant shows the highest weight-loss prior to ignition (Table 2). It may be noted that in PVC, a large amount of $\text{HCl}$ is liberated at much lower temperatures than the ignition temperature and this may be the reason for the abnormally high value for the weight-loss.
Typical high pressure DTA traces are given in Figs 6 and 7 and Table 1. The $T_{ig}$ of PS, AP and PS/AP as a function of pressure are shown in Fig. 8. It can be seen from Table 1 that $T_{ig}$ of the propellants increases with pressure in nitrogen but decreases in oxygen. The binder $T_{ig}$ is lowered with the increase of oxygen pressure (Fig. 8). Since binder will not ignite in nitrogen atmosphere the effect of nitrogen pressure on binder ignition cannot be examined. Since the polymers will only gasify in nitrogen the increase of pressure would obviously suppress the gasification. It has been shown that polymer ignition controlled by the gasification process. Hypothetically, it leads to the conclusion that the $T_{ig}$ increases directly with the inert gas pressure. A comparison of the $T_{ig}$ in oxygen and nitrogen (Fig. 8) and the above observations reveal that the ignition behaviour of the propellant is very similar to the ignition of the binder. Further support of this conclusion come from the following evidence.

Ignition delay ($\tau$), devoid of physical delay, was measured at various temperatures for various propellants. The $\tau$ could be related with the activation energy ($E_{ig}$) for ignition by an Arrhenius equation in the following manner:

$$1/\tau = B \exp \left(-E_{ig}/RT\right)$$

where $(1/\tau)$ represents the rate of the pre-ignition reactions and $B$ the pre-exponential factor. From the slope of the plot of $\ln (1/\tau)$ vs $1/T$, the $E_{ig}$ (Table 2) has been obtained for various propellants. In all the three propellants the same oxidiser, AP, has been used and if the rate-controlling step lies in AP decomposition, one would get the same value of $E$ for all the propellants...
KISHORE, et al: IGNITION OF COMPOSITE SOLID PROPELLANTS

Figure 4. Typical DTA trace for the ignition of PS/AP propellant, at 1 atm.

<table>
<thead>
<tr>
<th>Propellant system</th>
<th>Weight-loss before ignition (%)</th>
<th>( E_g ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/AP</td>
<td>5.8</td>
<td>20.0</td>
</tr>
<tr>
<td>PVC/AP</td>
<td>8.4</td>
<td>14.0</td>
</tr>
<tr>
<td>PPF/AP</td>
<td>2.0</td>
<td>11.0</td>
</tr>
<tr>
<td>CTPB/AP</td>
<td>3.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Table 2. Weight-loss before ignition in propellants with different binders (temperature: 623 + 2 K; sample weight: 50 ± 1 mg; and atmosphere: nitrogen)

with different binders. But in the present case this is not so; the \( E_g \) varies with the binder (Table 2) and the magnitude (10-20 kcal/mol) is lower compared to the

The \( E \) values for the gasification of polymers are available elsewhere\(^9\),\(^16\); surprisingly, the activation energies are consistently low. This suggests that the rate of gasification must be controlled by a low activation physical process, like volatilisation. The thermal degradation of polymers generally has activation energies of the order of 50 kcal/mol which involve the scission of chemical bonds as the rate-controlling step. This cannot be so with the gasification of the polymers. The vaporisation energies of the monomers of the common polymers, like PS, PMMA, etc. are about 10 kcal/mol\(^3\).

At the surface temperature encountered in the ignition process, the degradation of the polymer and the subsequent volatilisation of the degraded fragments takes place simultaneously. Generally low \( E \) values are encountered in the ignition process which is an indicator that the rate-controlling step in the vaporisation of the degraded fragments rather than the bond breakage. Ignition delay \( (r) \) is a sum of physical delay \( (r_p) \) and chemical delay \( (r_c) \), i.e.
Figure 6. Typical DTA traces for the ignition of AP and PS at higher pressures.

\[ \tau = \tau_1 + \tau_2 \]  

As arbitrary limit, the physical delay can be visualised as the point at which the sample has generated just enough fuel species for ignition. The rate of the ignition process can be given by the following rate expression:

\[ \frac{1}{\tau} = B \exp \left( -\frac{E_{ig}}{RT} \right) \left[ P \right]^x \left[ O_2 \right]^y \]  

where \((P)\) and \((O_2)\) respectively are the concentration of the polymer and oxygen and \(x\) and \(y\) are their respective exponents. The weight-loss data prior to ignition indicated that a very small amount (10 per cent of the original weight) decomposes prior to ignition showing that \(P\) remains practically constant. Excess \(O_2\) flux was maintained in the experiment and hence \(O_2\) also remains constant in the experiment. Then Eqn (3) reduces to Eqn (1).

The Arrhenius plots were generated from the ignition delay (\(\tau\)) data of PS and PS plus additives to determine the \(E_{ig}\) values by plotting \(\ln \tau\) vs \(1/T\). The \(E_{ig}\) values range between 4 and 8 kcal/mol (Table 3) and are comparable to the reported \(E\) values for the ignition of various polymers\(^{16,22}\). These low activation energies suggest that the ignition phenomenon is controlled by some physical process\(^{16}\). From the similarity between the \(E\) values for ignition and gasification of polymers\(^{16}\), it may be considered that the rate controlling step in polymer ignition is polymer gasification\(^{1,16}\). Fire
KISHORE, et al: IGNITION OF COMPOSITE SOLID PROPELLANTS

NITROGEN ATMOSPHERE  HEATING RATE : 10 °C/min  AA' : CTPB/AP
OXYGEN ATMOSPHERE  WEIGHT OF SAMPLE: 10 mg  BB': PVC/AP
A, B, C, D : 1 atm  CC': PS/AP
A', B', C', D': 14 atm  DD': PPF/AP

Figure 7. Typical DTA traces at 1 atm and 14 atm pressures for the ignition of propellants.

 retardant additives, like ammonium phosphate (MAP & DAP) and NH4Br lower the ignition delay of PS, and consequently the $E_g$ for ignition (Table 3) is also lowered.

Data on the ignition temperature (IT) of PS/AP and CTPB/AP propellants are shown in Table 4. In all the existing models of the ignition of composite solid propellant theories, the heat-up time of the solid phase is considered important compared to the time of the diffusion and chemical reactions. By suitable additives in the propellant if it is possible to alter the exothermic heat of reaction in the solid phase, one may consider the solid phase ignition model in preference to others. Since the condensed phase heat release is very high in the presence of Fusel (Table 4) the decrease in IT is found to be drastic.

Isothermal decomposition of these propellant samples was carried out at different temperatures (Fig. 9) and the time taken for 10-50 per cent decomposition was obtained; inverse of this gave the rate $^1$ of decomposition $(1/\Delta t)$. The activation energies $(E)$ were determined by Jacobs-Kureisky method$^{24}$. The plot of $\ln (1/\Delta t)$ vs $1/T$ are shown in Figs 10 and 11. The $E's$ for the samples are also indicated in these figures. It may be mentioned that the temperatures chosen for the TG studies are in the range of the ignition temperatures of the propellants. An average $E$ of $(33 \pm 3)$ kcal/mol can be assigned to the propellants; the $E$ values are not significantly altered in the presence of the additives.

Miller, et al$^5$ have shown that the ignition delay of polymers depends upon the rate of production of combustible gases. We have determined$^3$ the
Figure 8. Effect of pressure on the ignition temperature of PS/AP propellant and its ingredients.

Table 3. Activation energy ($E_a$, kcal/mol) for the ignition of polymers

<table>
<thead>
<tr>
<th>Polystyrene (PS)</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS + 0.6 mol % MAP</td>
<td>5.2</td>
</tr>
<tr>
<td>PS + 0.06 mol % DAP</td>
<td>5.4</td>
</tr>
<tr>
<td>PS + 0.06 mol % NH$_2$Br</td>
<td>4.5</td>
</tr>
</tbody>
</table>

weight-loss and the rate of weight-loss prior to ignition of PS in the presence of several additives, which significantly change the ignition delay. Ignition was observed to occur at a particular critical rate for a given polymer sample for a selected temperature and sample geometry. It may therefore be considered that the rate of decomposition at the point of ignition will be the same in the presence of the additives. The temperatures were found out from Figs 10 and 11 corresponding to the rate of the uncatalysed propellant at its ignition temperature. The derived IT's as against the experimental values are shown in Table 4. Although the actual magnitude does not tally in all the cases, the trend of the IT, in the presence of the additives, remains the same. This shows that the solid phase ignition model could be preferred for the propellants, particularly in those cases where large amount of solid phase heat release occurs. It may be pointed out that one could get a better correlation between the experimental and calculated IT's in the presence of additives, if the initial decomposition rate is measured accurately which, however, was not possible in the set-up used in the present studies.
KISHORE et al: IGNITION OF COMPOSITE SOLID PROPELLANTS

The metal salicylates not only affect the ignition but also the mass burning rate (m). Table 4 clearly shows that only Fesal increases the mass burning rate (m) significantly. Hewkin et al have made photographic and visual observations of the burning surface of double base (DB) propellant in the presence of lead acetyl salicylate as burning rate catalyst; they observed that the catalyst increases the temperature of the hot spots present at the surface. Furthermore, they observed that lead acetyl salicylate, which almost doubles the linear burning rate (m), increases the surface temperature (T) from 750°C to 790°C.

The salicylates enhance the burning rate primarily by modifying the chemical reactions occurring at the surface. Pifer and Lennon have observed that catalysts, like PbO and lead salicylate, in DB propellant are responsible for the higher T and calorific value of the product. Kubota et al have also observed that Pb salicylates alter the surface reaction zone in DB propellants. The above discussion clearly shows that salicylates in the presence of metal ions at or near the burning surface increase the rate of the chemical reactions occurring at the surface. The calorific value of the product is proportional to T as shown in Table 4.
in the presence of Fesal. $T_s$ is dependent on the regression rate of the propellant according to the following equation:

$$\dot{m} = \dot{r} = Z_s \exp\left(-\frac{E_s}{RT_s}\right)$$

(4).

where $\dot{m}$, $A$ and $\rho$ are the mass burning rate, burning surface area, and density of the propellant and $E_s$ and $Z_s$ are the activation energy and pre-exponential factor. $T_s$ is determined by the decomposition behaviour of the propellants. Since Fesal shows the highest increase in solid phase heat of decomposition (Table 4), it is responsible for generating higher $T_s$ in the propellant and consequently higher $\dot{r}$ compared to other salicylates.

4. DEFENCE APPLICATIONS

Initiation of ignition in solid propellants and sensitivity towards ignition of the aged propellants are the two areas where above studies may provide useful information. Since ignition characteristics of propellants strongly depend upon the binder, and catalysts. These factors may have significant bearing on the igniter design and ageing modulation of the propellants.

5. CONCLUSION

It may be concluded that the propellant ignition is strongly dependent on the chemical nature of the binder. The sensitisation of the ignition and also the burning rate of the propellant in the presence of salicylate additives are successfully explained from the solid-phase ignition model since the condensed phase heat release was found to be substantial in the presence of additives.
REFERENCES


