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Effect of Triethanolamine and Benzaldehyde on the Storage Stability of Polystyrene- Ammonium Perchlorate Propellant

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Abstract. The effect of triethanolamine and benzaldehyde on the stability of polystyrene has been studied by dynamic thermogravimetry (TG). Slower decomposition of polymer in the presence of these compounds indicates their inhibiting ability on the oxidation of the polymer. The burning rate measurements of polystyrene (PS)/ammonium perchlorate (AP) propellants at ambient temperature and pressure shows an increase with the storage time. The percentage change in the burning rate of the propellants containing aldehyde and amine is less during the ageing which indicates the increased stability of the propellants. The safe-life time of the propellants for the ballistic stability has been calculated from the activation energy for the ageing process using an Arrhenius type equation. The safe-life of the propellants containing triethanolamine and benzaldehyde is more than the neat propellant.

1. Introduction

In a review, the present status about ageing of composite solid propellants has been discussed’, Most of the ageing studies are on the changes occuring on the binder’s properties:“‘. Yokoyama et al[8] prepared CTPB propellants to study the effects of hardeners and antioxidants on the mechanical properties during the ageing. A systematic study by Kishore et al[9-11] on the ageing of polystyrene based composite propellants revealed that the ageing process is controlled by the oxidizer decomposition. This conclusion has been derived from the studies on the propellants containing additives which bring about desensitization in the decomposition rate of the oxidizer. Addition of any additive which protects the binder either from oxidation or from other chemical reactions may ‘also decrease the rate of ageing. In order to see the effect of additives which can protect the binder from oxidation reaction during the ageing. we have carried out accelerated ageing studies in presence of triethanolamine (TEA) and benzaldehyde. These compounds are found to be most effective antioxidants among other classical antioxidants such as 2,6-ditertiarybutyl-*p*-cresol and *N*-phenyl naphthylamine for polystyrene[12,13]. For the purpose of understanding of ageing process, a simple model propellant (PS/AP) consisting of only oxidizer and binder with the antioxidants was chosen.

2. Experimental

2.1. Materials

Polystyrene (PS) was prepared from inhibitor free freshly distilled styrene[9]. Benzaldehyde was purified by the usual[14] method. Triethanolamine (TEA) and divinylbenzene (DVB) were purified through distillation.

Polymer samples with additives were prepared by weighing the viscous prepolymer and the additive (I wt%) into a beaker. The mixture was mechanically stirred until a homogeneous distribution of the additive occured. This was cast in soft glass tubes and was cured by keeping at room temperature for a day and later at 50°C for one week after which the glass tubes were broken and the polymer strands were obtained. Since the polymer did not cure in the presence of TEA, DVB was added to facilitate the curing process. The control polymer strands without additives (PS and PS + DVB) were also made.

Processing of the AP/PS propellants[15], ageing studies[9] and measurement of the burning rates of the propellants at ambient pressure[16] are described elsewhere.

Dynamic TG studies in oxygen atmosphere were carried out on a home-made TG assembly similar to that described by McBain and Bakr" with a sample weight of 20 mg and a heating rate of 5°C/min.

3. Results and Discussion

Dynamic TG thermograms of polymer samples with and without antioxidants are shown in Fig. 1 which indicate some salient features. As expected, crosslinked polymer with DVB undergoes oxidative degradation in a slower rate than polystyrene[18]. The antioxidants drastically desensitize the polymer degradation. The inception of the weight loss at a higher temperature in the presence of antioxidants indicates the inhibition of the oxidation reactions. The mechanism of inhibition of oxidation is different for triethanolamine and benzaldehyde.

Amines and alcohols are the most commonly used antioxidants which act as a hydrogen or electron donors[19] to compete with polymer substrate for consuming

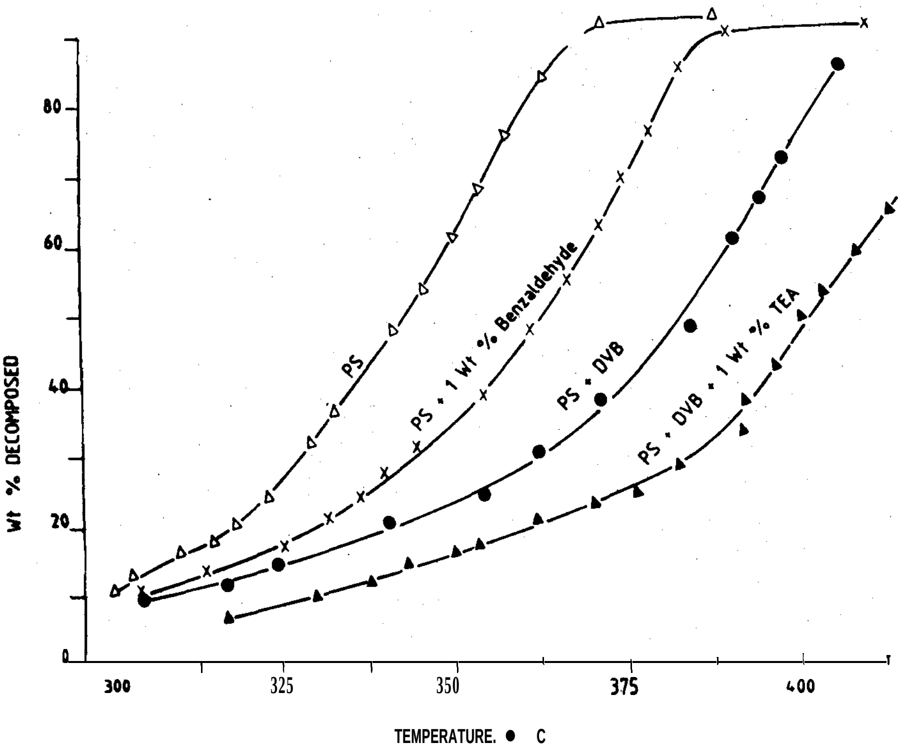
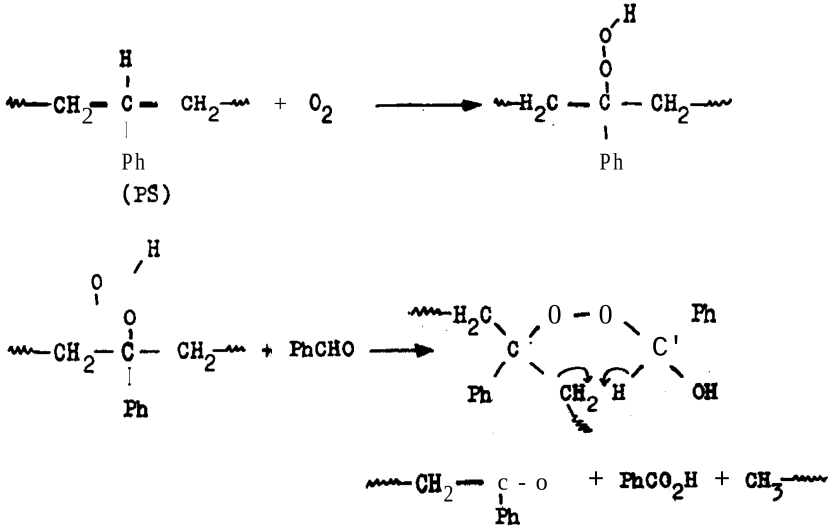


Figure 1. Dynamic TG plots of PS and PS + DVB in presence of tea and benzaldehyde.

peroxy radicals $(R\dot{O}_2)$ to terminate the propagation reaction and thus bring about stabilization in oxidative degradation. De La Mare[20] in his studies on the reactions of tertiary butyl hydrogeroxides in the presence of tertiary amines observed the formation of secondary amine, tertiary butyl alcohol and aldehyde. The reaction occured through. the attack of the unshared pair of electrons present in the amino nitrogen atom on the peroxy linkage resulting in the cleavage of the linkage to give alkoxide and alkyl hydroxide ammonium, the latter further undergoes rearrangements to give secondary amine, aldehyde etc. This indicates that tertiary amino compounds inhibit oxidation reaction also by decomposing the hydroperoxide formed in the polymer. It is noted that the products formed as a result of the reactions mentioned above further interact with the hydroperoxide and suppress the oxidation.

The inhibiting ability of benzaldehyde is viewed in a different manner. Polystyrene in oxygen atmosphere undergoes decomposition to give styrene and benzaldehyde as the major products. Jellinek[13] in his studies on PS observed that in oxygen atmosphere, decomposition rate slowed down after sometime indicating inhibition of oxidation by the products. It has been established that alkyl hydroperoxides or peroxyhemiacetyl adduct with aldehyde undergoes decomposition to give stable products*‘. The most plausible mechanism of inhibition action of aldehyde on PS oxidation is given below ;



The inhibiting ability of TEA and benzaldehyde on the oxidative degradation reaction of PS revealed that these are effective antioxidants which can be used to protect PS during ageing.

In propellants these may suppress the deterioration rate of binder resulting in little change in the ballistic properties of propellants during ageing. One of the ballistic properties which can be easily determined to note any effect during ageing in the burning rate($\dot{r}$) of the propellants. Accelerated ageing studies were carried out on propellant systems containing I percent of antioxidants at 150°C. This higher temperature was chosen to get measurable change in $\dot{r}$. It has been shown that *E* value for ageing does not change between 64” and 150°C, implying that the mechanism or the rate controlling step of ageing process remains unaltered throughout the temperature range[22].

The $\dot{r}$ measurements of the aged propellants were done at ambient pressure and temperature. It may be pointed out that at higher pressures, the burning rate of AP/PS propellants was very fast to record any difference between differently aged samples. Hence, measurements were done only at ambient pressure. Moreover, studies on the effect of transition metal oxides on CTPB based propellants have shown the propellant burning rates to have the same trend at ambient as well as at high pressure in presence of additives?“. Thus, it is expected that $\dot{r}$ behaviour of the aged and unaged propellants would be that same at ambient as well as at higher pressures, although the actual magnitude of change may be different.

The $\dot{r}$ data of various propellant systems aged at 150°C as a function of storage time were recorded. The change in $\dot{r}$ as a function of storage time was calculated

Table 1. Data on the burning rates of various propellant systems aged at 150°C for different storage times.

System	Storage time (days)	Percentage change in $\dot{r}$
AP/PS	Unaged	0.0
	7	11.8
	14	23.6
	20	33.6
AP/PS + DVB	Unaged	0.0
	7	9.6
	14	19.2
	20	27.5
AP/PS + Benzaldehyde	Unaged	0.0
	7	8.4
	14	16.8
	20	24.0
AP/PS + DVB + TEA	Unaged	0.0
	7	5.6
	14	11.2
	20	15.8

(Table 1). It shows that $\dot{r}$ increases with storage time and the dependence is linear within the time scale to which ageing was carried out. Earlier in our laboratory ageing studies have been carried out on PS/AP propellants at different temperatures as a function of storage time and the increase in $\dot{r}$ has been explained on the basis of formation of a peroxy compound during the ageing[22]. The plot of the percentage change in $\dot{r}$, as a function of storage time was found to follow zero order kinetics. From this plot, for a particular percentage change in $\dot{r}$, storage time t could be obtained at different temperatures T. The inverse storage time t^{-1} gives the rate of ageing. The E value for the ageing process (temperature range 60-160°C) was found to be 13 ± 2 kcal.mole^{-1}. This E value for the change in $\dot{r}$ during ageing was used to estimate the safe life time of the propellant for the ballistic stability. Arrhenius equation in the following form was used for calculating the safe life time for a chosen percentage change in $\dot{r}$ at ambient storage temperature.

$$\log t_2 = \log t_1 + \frac{E}{2.303R}\left(\frac{T_1 - T_2}{T_1 T_2}\right) \qquad (1)$$

where t_1 is the storage time at T_1°K for a particular percentage change in $\dot{r}$ and t_2 is the safe life time at ambient temperature (298°K). The. safe life data for various systems are presented in Table 2 for various percentage changes in $\dot{r}$. From Table 2. it is evident that incorporation of antioxidants increase the safe life. Table 2 also

Table 2. Safe life data of different propellant systems for the changes in burning rate.

System	Safe life for various percentage changes in r (years) 2.5%	5%	10%	15%
AP/PS	2.52	5.04	**10.08**	**15.12**
AP/PS + DVB	**3.13**	6.26	12.52	18.78
AP/PS + DVB + TEA	**5.21**	**10.42**	20.84	31.26
AP/PS + Benzaldehyde	3.47	6.93	13.89	20.84

shows that the relative effect of TEA is more than benzaldehyde. Better inhibiting ability of TEA may be attributed to the fact that TEA contains both amine and alcoholic groups known for their antioxidant capabilities whereas benzaldehyde is not a stabilizer in the conventional sense and its mechanism is unique as it is self generating type of compound product from the polymer substrate itself.

4. Conclusions

Triethanolamine and benzaldehyde inhibit oxidative degradation of PS by decomposing any peroxide group introduced into the polymer chain to stable products. This inhibition of oxidation increases the stability of propellants, as a result lesser change in the burning rate is observed with respect to the storage time. The storage stability of PS/AP propellants increases tremendously in presence of triethanolamine and benzaldehyde.

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