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Copolymer of Styrene and Oxygen as Potential Rocket Fuel

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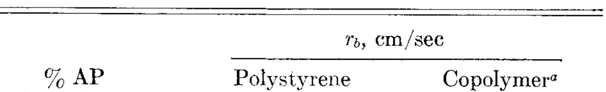
Very little attention has been paid to the use of oxygen copolymers (peroxidic polymers) as hybrid fuels or in solid composite propellants as fuel binders. This Note describes preparation of oxygen copolymers with styrene and presents strand burning rate data for composite propellants using them with ammonium perchlorate.

Experimental

The copolymers were prepared from styrene (Bareilly Synthetic Rubber Ltd.), commercial grade oxygen and benzoyl peroxide as follows.[1] Oxygen was then passed slowly into 200 g of styrene at 50°C for 10 to 60 min, then 2 g of benzoyl peroxide was added, and the mixture was kept on a water bath for 3–5 hr. When it became sufficiently viscous, it was poured into molds and cured at 70–80°C for 2–3 days. The following reaction is supposed to take place,



$$H_2C = CH\cdot C_6H_5 + O_2 \rightarrow \left(CH_2 - \overset{\overset{C_6H_5}{|}}{CH} - O - O \right)_n$$

Molecular weight could be varied by passing oxygen for different time intervals.

Table 1 Burning rates of polymer/ammonium perchlorate solid propellants at 30°C, 1 atm

% AP by weight	r_b, cm/sec Polystyrene propellant	 Copolymer[a] propellant
65	0.046	0.047
70	0.086	0.113
75	0.093	0.160
80	0.118	0.280

[a] Oxygen was passed for 60 min at 50°C for preparing the polymer.

Table 2 Comparison of propellant properties

Polymer[a]	Hardness R_b scale	Load to deform, tons	Mass burning rate, $\dot{m}$, g/sec
Polystyrene	55	3.5	0.111
Oxygen copolymer-I	43	2.5	0.106
Oxygen copolymer-II	40	2.0	0.094

[a] In the preparation of copolymers I and II oxygen was passed for 15 and 20 min at 50°C, respectively.

The densities of the polymer samples were determined by Nichalson's hydrometer. The weight average molecular weight M_w was determined by viscosity method by using the following empirical relationship,

$$[\eta] = 1.03 \times 10^{-4} M_w^{0.74} \tag{1}$$

where the constants, 1.03×10^{-4} and 0.74 refer to the polystyrene-benzene system, and $[\eta]$ is the intrinsic viscosity. The molecular weights so determined are only rough estimates because the constants would also depend on the nature of the polymer. The molecular weights are found to be of the order of 10^5.

Solid-propellant strands were prepared by mixing powdered ammonium perchlorate (AP) which was obtained from Central Electro-Chemical Laboratories, Karaikudi, with the viscous resin in a mortar and curing in molds for 10–15 days. Then a coating of inhibiter was applied to prevent burning down the side, and the strands, kept in vertical position, were ignited from the top. The linear burning rate (r_b) results are given in Table 1.

To simulate hybrid rocket operation with a copolymer fuel, center-perforated, cylindrical grains, 3.8 cm long with a port diameter of 0.5 cm, were made. Oxygen was passed through the grain at 12 liter/min. The grain was then ignited and the change in diameter with oxygen flow time t was noted. This was used to calculate the mass burning rate,

$$\dot{m} = \pi \rho l (r_2^2 - r_1^2)/t \tag{2}$$

where ρ and l are the density and length of the polymer sample, and r_1 and r_2 are the initial and final port radii. Propellant hardnesses were determined with a Rockwell hardness testing machine using a $\frac{1}{16}$-in. ball diameter and a 100-kg load on the Rb scale. Elastic deformability was measured on a high-pressure testing machine; the minimum weight in tons at which the sample (diameter, 2.02 cm; length, 6.61 cm) began to deform was noted. The results are given in Table 2.

For thermal degradation studies copolymer samples of ≈0.3 g were weighed and introduced in a preweighed test tube. The test tube was kept in a muffle furnace a fixed temperature for a definite time. The results computed from the weight losses (as described later) are given in the Table 3. The gaseous degradation products were analyzed by passing them through water and absolute alcohol. From the conventional organic analysis formaldehyde was identified in the aqueous solution, whereas benzaldehyde and styrene monomer were detected in the alcoholic solution.

Table 3 Thermal degradation results

Polymer[a]	Density, g/cm³	$k \times 10^5$ 230°C	 350°C	Energy of activation of thermal degradation, kcal/mole
Polystyrene	1.05	0.44	5.0	16
Copolymer-A	1.06	0.74	5.4	13
Copolymer-B	1.09	1.01	5.9	12
Copolymer-C	1.10	1.39	6.8	11

[a] In the preparation of copolymer-A, copolymer-B, and copolymer-C oxygen was passed for 10, 25, and 60 min, respectively, at 50°C.

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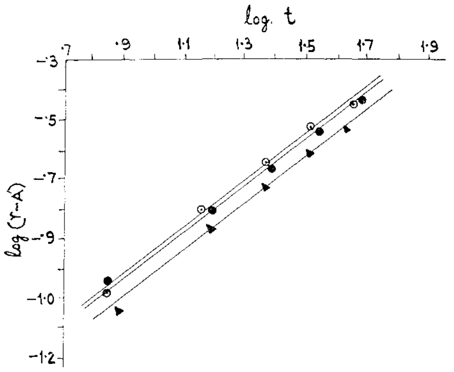

Fig. 1 Variation of port diameter with time. ⊙ **polystyrene,** ● **copolymer I,** ▲ **copolymer II.**

Discussion

Table 1 shows that r_b for the copolymer propellant is much higher than that for the polystyrene propellant when the AP content exceeds 70%; when the AP content is increased to 80%, r_b is more than double that of the polystyrene propellant. The enhancement of r_b is expected in view of presence of oxygen atoms in the polymer chain.

Figure 1 shows that the experimental data for the change of port radius r with the time t for the hybrid operation satisfies the following equation[2]:

$$\log(r - A') = \log B + x \log t \tag{3}$$

where A' is a constant taken as the initial port radius, and B and x are constants depending on the nature of the polymer. From the intercept and slope, B and x could be estimated, and the linear regression rate $\dot{r}$ was obtained by differentiating Eq. (3): so that

$$\dot{r} = dr/dt = xBt^{x-1} \tag{4}$$

From Fig. 1 it is evident that $\dot{r}$ decreases as the amount of oxygen in the copolymer increases. This can be explained as follows. According to Marxman et al.[3]

$$\dot{r} = \dot{Q}_w/\rho\Delta H \tag{5}$$

where $\dot{Q}_w$ is the heat transfer per unit area from the flame to the wall, and ΔH is the effective heat of gasification. Thus, $\dot{r}$ would be inversely proportional to ΔH, since for copolymers $\dot{Q}_w$ and ρ would not vary much. ΔH for the copolymer would be greater than polystyrene since in the former —C—O— and —O—O—bonds are present. Furthermore, the greater the amount of oxygen in the copolymer, the greater would be the number of such bonds and (hence the value of ΔH), and $\dot{r}$ would be smaller. It may be noted that for an estimate of ΔH for copolymers, a knowledge of flame temperature at the boundary layer is needed.

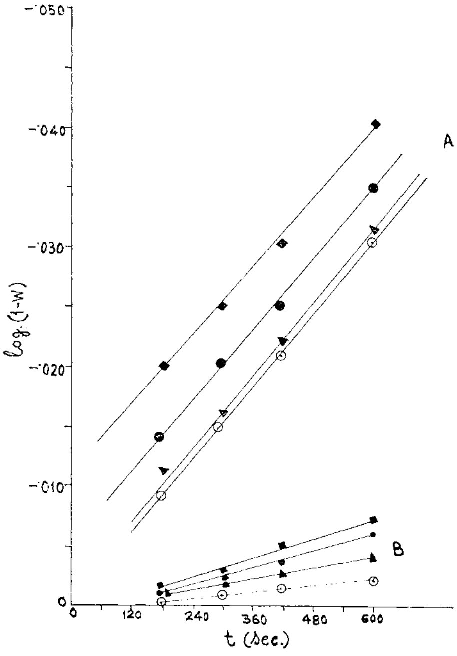

Fig. 2 Variation of weight loss fraction with time. ⊙ **polystyrene,** ▲ **copolymer A,** ● **copolymer B,** ■ **copolymer C. The group of curves A and B correspond to 350°C and 230°C, respectively.**

The weight loss fraction W is defined as

$$W = (m_1 - m_2)/m_1 \tag{6}$$

where m_1 and m_2 are the weights of polymer samples before and after heating for a definite period. Figure 2 shows that W is related to time in the following manner[4]

$$\log(1 - W) = -kt \tag{7}$$

where k is the characteristic rate constant. Equation (7) is consistent with a first-order rate law governing the rate of chain degradation independent of the depolymerization process involved. The lines in Fig. 2 do not exactly pass through the origin at higher temperatures because the induction period becomes more prominent.[4]

The energy of activation E for degradation can easily be estimated with the help of the following equation:

$$k = A \exp(-E/RT) \tag{8}$$

where A is the frequency factor, R is the gas constant and T is the absolute temperature. The low E makes the copolymer feasible for efficient thrust modulation as it favors pressure sensitivity.[5] Table 3 shows the values of E for different polymers. The value of E is found to decrease when the oxygen content in the copolymer is increased.

It has been shown by Rabinovitch,[4] that if degradation involves reverse depolymerization or unzipping process, the following equation should hold:

$$1 - W = \exp\left[-(P_0 - 1)k^*t\right] \tag{9}$$

where P_0 is the initial degree of polymerization and k^* is a constant. If this mechanism operates, k would be equal to $(P_0 - 1)k^*$ and hence k should increase as P_0 increases. It is clear from Table 2 that k for copolymer C is greater than that for copolymer A. This is in accord with the above hypothesis since P_0 would be greater in C than in A. Qualitative analysis of the degradation products shows that formaldehyde and benzaldehyde are produced. Since the benzaldehyde and formaldehyde are obtained in the degradation products, it appears that fission occurs at the —O—O— bond and the —C—C— bond adjacent to phenyl ring.[1]

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