

# Decrease in the Etch Rate of Polymers in the Oxygen Afterglow with Increasing Gas Flow Rate

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## Synopsis

In this paper we report the variation of the etch rate of polymers in the afterglow of a radio frequency discharge in oxygen as a function of total flow rate in the range 2–10 cm<sup>3</sup> (STP)/min. The measurements were made at ambient temperature with the O(<sup>3</sup>P) concentration held essentially constant. We report results on three polymers: *cis*-polybutadiene, a polybutadiene with 33% 1,2 double bonds, and a polybutadiene with 40% 1,2 double bonds. We have observed that the etch rate of these polymers decreases significantly with increasing flow rate, strongly suggesting that the vapor-phase products of polymer degradation contribute to the degradation process.

## INTRODUCTION

With the exception of Spencer and Borel,<sup>1</sup> previous workers<sup>2-5</sup> who have studied the etching of polymers in the afterglow of a radiofrequency (RF) discharge in oxygen have assumed that the most important parameters in determining the etch rate are the reactor pressure and the power supplied to the discharge. It has been further assumed that the main effect of increasing the flow of molecular oxygen (O<sub>2</sub>) into the reactor is to decrease the residence time of the oxygen in the discharge, thus possibly decreasing the percentage of O<sub>2</sub> dissociated. With respect to the etch rate of polymers, the influence of this and other possible effects of varying the flow rate has apparently been considered sufficiently unimportant that many workers<sup>2-4</sup> have failed even to report their O<sub>2</sub> flow rate. Spencer and Borel<sup>1</sup> have pointed out that the flow rate of oxygen will become important if a combination of low flow rate and high reaction rate results in depletion of the supply of oxygen atoms [O(<sup>3</sup>P)] reaching the polymer surface. These authors studied the effect of variations in gas flow rate at very high flow rates (10<sup>3</sup>–10<sup>4</sup> cm<sup>3</sup> (STP)/min) on the etch rate of photoresists maintained at elevated temperature. They obtained results which were consistent with the depletion hypothesis.

Yasuda et al.<sup>6</sup> also studied the variation of the etch rate of polymer fibers with gas flow rate. The polymers were exposed *in the plasmas* produced by an RF discharge in various gases. With the power held constant, it was observed by these workers that above a critical flow rate the etch rate of polymers *decreased* with *increasing* gas flow rate. This finding was attributed to a decrease in the concentration of active species in the plasma with increase in flow rate. In addition to dissociated molecules, other active species such as ions, electrons, and high energy photons are present in the plasma produced from an RF discharge, making identification and measurement of the concentration of species reacting with the polymers difficult.

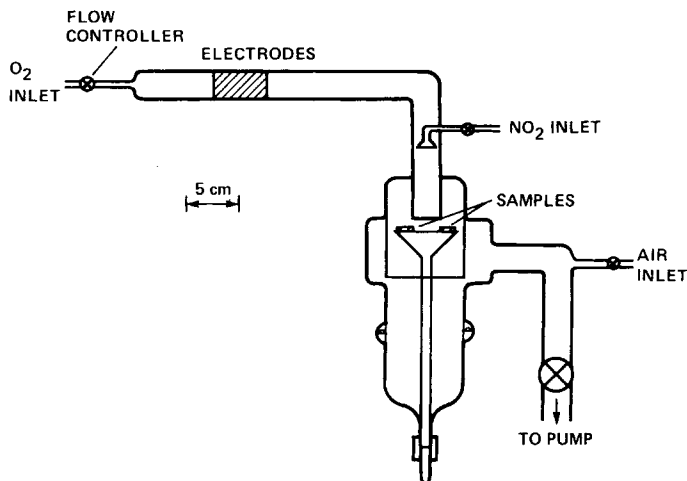


Fig. 1. The multisample reactor.

In this paper we report the variation of the etch rate of selected polymers as a function of the oxygen flow rate in the range 2–10 cm<sup>3</sup> (STP)/min. The polymers studied were: *cis*-polybutadiene, a polybutadiene with 33% 1,2 double bonds, and a polybutadiene with 40% 1,2 double bonds. These polymers were selected from those whose etching under similar conditions was studied previously in this laboratory.<sup>7</sup> The polymers were exposed sufficiently far downstream from the glow discharge so that ions, electrons, and high energy photons would not interact with the sample. It was believed that the principal active species present under these conditions was O(<sup>3</sup>P). The measurements were made at ambient temperature. It was observed that under our experimental conditions the etch rate of the polymers studied decreased significantly (more than a factor of 5) with increasing flow rate, despite the fact that the concentration of O(<sup>3</sup>P) was held essentially constant (total variation less than 30%). We propose that active species other than O(<sup>3</sup>P) are required to account for the decrease in etch rate with flow rate.

### EXPERIMENTAL

Polymer sample preparation and measurement of the etch rate were carried out as described in Ref. 7. The polymers used for this study were chosen so that a range of etch rates would be represented.

Figure 1 is a schematic diagram of the reactor used for etching. This reactor was designed so that the sample was well removed from the RF discharge. In addition, a right angle bend separated the sample from the discharge, thus shielding the sample from ultraviolet radiation produced in the discharge. RF power (13.56 MHz) was capacitively coupled to the oxygen discharge by means of an impedance matching network. The discharge was operated at a net power of 15 W. The mass flow of O<sub>2</sub> into the reactor was measured and controlled by a MKS Instruments, Inc. mass flow controller. At a given flow rate, the pressure in the reactor was controlled by adjusting a valve located between the reactor and the vacuum pump. The pressure was measured by a baratron pressure transducer.

The concentration of  $O(^3P)$  was determined by  $NO_2$  titration.<sup>8</sup> The mole fraction of  $O(^3P)$  at the titration point ( $x$ ) was computed from the titration data as follows: At the end of a titration, the molar flow of  $NO_2$  is equal to the atomic flow of  $O(^3P)$  at the  $NO_2$  inlet. Thus we can determine the atomic flow of  $O(^3P)$  through the plane of the  $NO_2$  inlet,  $F_O(x)$ . Since our system is in a steady state when the discharge is on, the total mass flowing past a given plane in the reactor must equal the mass flow of  $O_2$  into the system which is measured by the flow meter. Hence we have

$$32F_{O_2}(0) = 32F_{O_2}(x) + 16F_O(x) \quad (1)$$

where  $F_{O_2}(0)$  is the molar flow of  $O_2$  into the system,  $F_{O_2}(x)$  the molar flow of  $O_2$  past the plane of the  $NO_2$  inlet at  $x$ , and  $F_O(x)$  the molar flow of  $O(^3P)$  past  $x$ . Using eq. (1), we can express the total molar flow at  $x$ ,  $F_T(x)$ , as

$$F_T(x) = F_{O_2}(x) + F_O(x) = F_{O_2}(0) + 1/2F_O(x) \quad (2)$$

The mole fraction of  $O(^3P)$  in the gas stream flowing past the plane at  $x$ ,  $\chi_O(x)$ , will be given by

$$\chi_O(x) = [F_O(x)]/[F_{O_2}(0) + 1/2F_O(x)] \quad (3)$$

## RESULTS

### $O(^3P)$ Concentrations

At constant total reactor pressure  $P_r$ , the mole fraction  $\chi_O(x)$  produced was found to be independent of  $F_{O_2}(0)$ . This follows the fact that  $\chi_O(x)$ , measured by  $NO_2$  titration, did not change as the flow rate was varied by a factor of 5, from 2 to 10  $cm^3(STP)/min$ , at constant  $P_r$ . This also indicates that there was not a measurable decay of  $O(^3P)$  during the time required for the gas to flow from the point of production in the discharge to the location where  $\chi_O$  was measured by  $NO_2$  titration. The polymer sample was placed downstream from the titration point at a distance about one-half the distance from the origin of the discharge to the titration point. On the basis of the absence of change in the  $\chi_O$  observed when the flow rate was varied by a factor of 5, we conclude that the decay of  $O(^3P)$  is sufficiently slow in our system that  $\chi_O$  is the same at the titration point and the polymer sample position. On the other hand, if this conjecture were not correct and there was appreciable decay of  $O(^3P)$  between the titration point and the sample position it would be expected that the concentration of  $O(^3P)$  at the sample position would decrease with decreasing flow rate because at the lower flow rates the times taken for the gas to travel between the titration point and the sample position would be greater.

The value of  $\chi_O$  was, however, strongly dependent on the total reactor pressure, as can be seen in Figure 2. Also plotted in Figure 2 is the partial pressure of  $O(^3P)$  calculated as the product,  $\chi_O P_r$ . It can be seen that the partial pressure of  $O(^3P)$  decreased by less than 0.04 Torr (30%) over the range of reactor conditions studied ( $P_r = 0.27-1.0$  Torr). In this pressure range, the

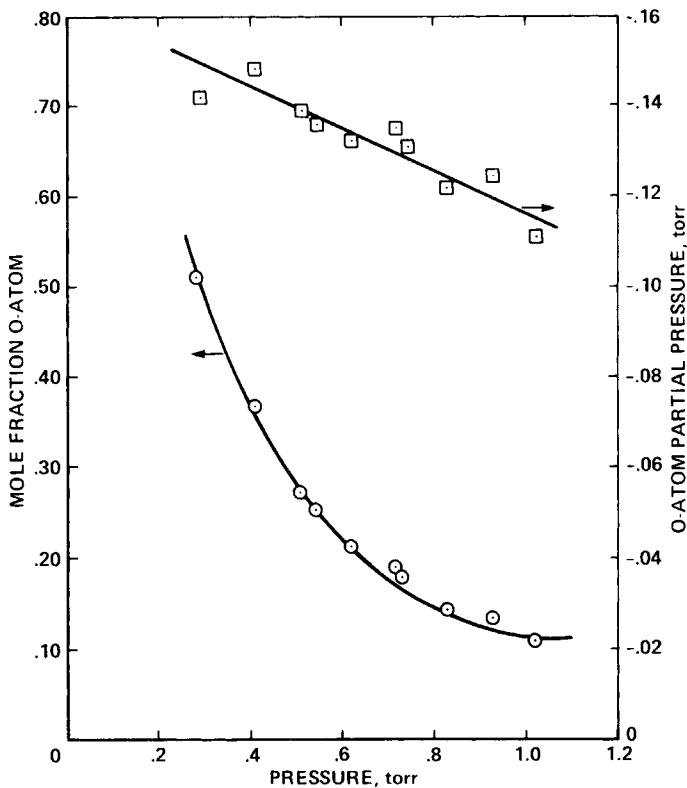


Fig. 2. Mole fraction  $\chi_0(x)$ (○), and partial pressure (◻) of  $O(^3P)$  versus total reactor pressure.

concentration of  $O(^3P)$  obtained was roughly independent of total reactor pressure.

### Etch Rate as a Function of Flow Rate

Plotted in Figure 3 is the etch rate vs. the calculated volumetric flow rate,  $F_V$ , for the three polymers studied ( $F_V = F_T/\rho$ , where  $\rho$  is the molar density of the gas at  $P_R$ ). In all cases the flow rate of  $O(^3P)$  was more than 10 times the amount needed to account for the complete conversion of the products of polymer degradation to  $CO_2$  and  $H_2O$ . It is apparent from Figure 3 that increasing the flow rate *decreased* the etch rate considerably in the case of all the polymers studied. The decrease in the etch rate cannot be attributed to a decrease in  $O(^3P)$  concentration in the vicinity of the polymer since, as already noted, the  $NO_2$  titrations clearly showed no variation in the partial pressure of  $O(^3P)$  with  $F_T$  when  $P_R$  was held constant and less than a 30% variation over the entire range of  $P_R$  studied.

Increasing the volumetric flow rate of the reactant gas mixture through the reactor had the effect of sweeping products of polymer degradation away from the polymer surface. Taking this effect into consideration, the decrease in etch rate with flow can be explained as follows: Reactive intermediates—for example, OH radicals—were produced during polymer degradation. These intermediates reacted with the polymer more rapidly than  $O(^3P)$ . As the flow rate was increased, the intermediates were removed more efficiently from the

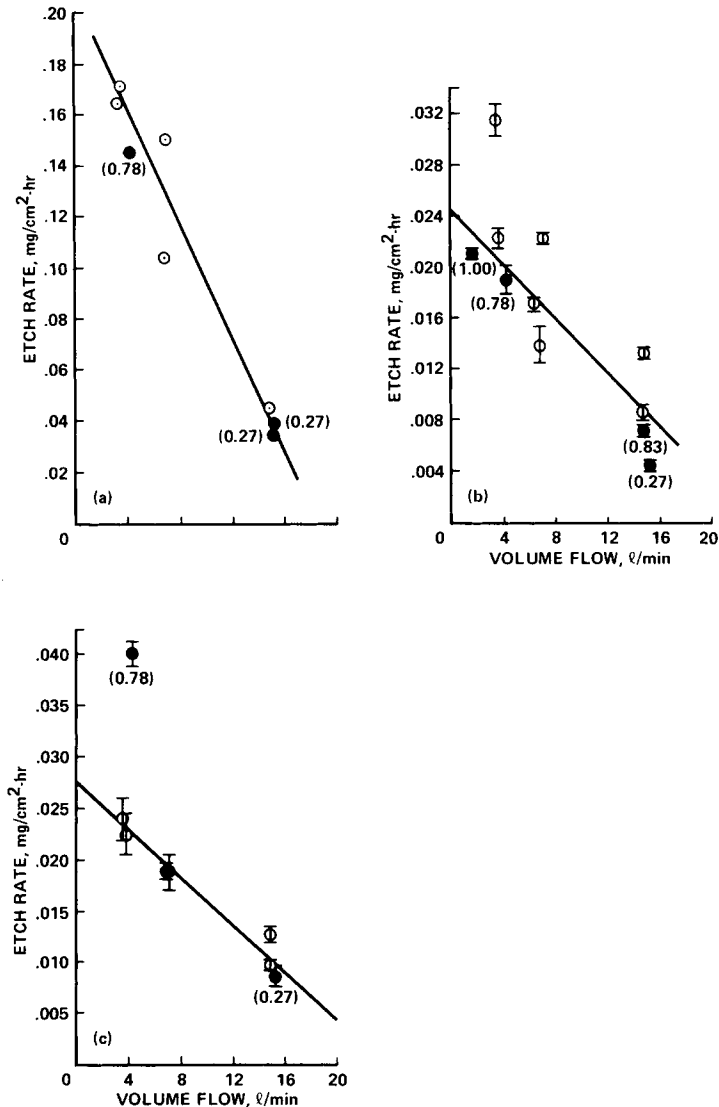


Fig. 3. Etch rate of three polybutadienes vs. volume flow rate  $F_V$ : (○) measurements made at a total reactor pressure of 0.5 Torr; (●) measurements made at reactor pressures other than 0.5 Torr; these pressures are given in parentheses by each data point. The error bars represent the spread obtained from measurements on two different samples exposed in the same run. Where an experimental point appears without error bars a duplicate sample was not run. (a) *cis*-polybutadiene; (b) a polybutadiene with 33% 1,2 double bonds; (c) a polybutadiene with 40% 1,2 double bonds. The lines were drawn using a least-squares best fit of a straight line to the data.

reaction site, resulting in a *decreased* etch rate with an increase in flow. OH is a known product of the reaction of  $O(^3P)$  with hydrocarbons,<sup>9</sup> and has been observed as a product of polymer etching in a RF discharge in oxygen.<sup>5</sup> At room temperature most of the reactions of OH with hydrocarbons are 2 orders of magnitude greater than those of  $O(^3P)$ .<sup>10</sup>

Products of polymer degradation have been observed to increase the etch rate of polymers exposed to a plasma. For example, in the case of

poly(oxyethylene) being etched in a *plasma*, Yasuda et al. reported that this polymer exhibited the highest etch rate when etched in a plasma of its own degradation products and residual air.<sup>11</sup> Their results also support the hypothesis that the products of polymer degradation contribute significantly to the etch rate.

### CONCLUSIONS

We have demonstrated that the etch rate of selected polymers in the oxygen afterglow can be strongly dependent on the flow rate of oxygen through the reactor. In the range of flows studied, the etch rate *decreased* by more than a factor of 5 for all polymers studied with increasing gas flow. Since the measured concentration of O(<sup>3</sup>P) decreased less than 30% and the etch rate changed by a factor of 5 under the conditions studied it is unlikely that O(<sup>3</sup>P) is the principal active species responsible for polymer etching. It is proposed that a product derived from the reaction of O(<sup>3</sup>P) with the degradation products of the polymer itself was responsible for the enhanced rate of degradation at the lower flow rates.

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