

## NOTES

### *Effect of Location of Flame Retardants in Polymers on the Oxygen Index*

In our continuing work of evaluating flame retardants and flame retardance techniques, one of the aspects we have looked into has been the effect of the location of the flame retardant within a substrate upon its flame retardance efficiency. The location of poly(vinyl bromide) (PVBr) in a polyester filament had an important effect upon the oxygen index (*O.I.*) of the fiber.<sup>1</sup> The same was true also for poly(diethylvinyl phosphonate) (PDEV) and poly(dimethylvinyl phosphonate) in a polyester filament.<sup>2</sup> As the thermal stability of PVBr and PDEV homopolymers appeared to be essentially the same, the general effect of the location of the grafted PVBr and PDEV upon the oxygen index was also the same: the more the homopolymers were incorporated inside the filament, the higher the *O.I.*

In a continuation of these studies, we have now looked at two other types of substrate materials (a polysulfone and a "polyvinyl"), widely different substrate dimensions (2400  $\mu\text{m}$  tubing vs. 13.5  $\mu\text{m}$  filament), and a different flame retardant incorporation technique (solution deposition vs. radiation grafting).

## EXPERIMENTAL

### Materials

**PVBr.** The homopolymer used was prepared in bulk polymerization using  $\gamma$ -irradiation and a total dose of 4.8 Mrads. The material had an inherent viscosity of 0.11 (0.635 g/100 ml tetrahydrofuran) at 30.0°C.

**Tubing.** A medical-grade Tygon (vinyl chloride-vinylacetate copolymer) tubing was used as received.

**Hollow Fibers.** Two sizes (254  $\mu\text{m}$  and 614  $\mu\text{m}$  O.D.) of polysulfone hollow fibers were used. The larger-size fiber was used uncoated, and the smaller-size fiber was used uncoated and coated with a carbonized poly(furfuryl alcohol) coating.

### Coating Procedures

For the surface coating of the tubing and hollow fiber as well as the shell and uniform deposition cases, a 33% tetrahydrofuran (THF) solution of PVBr was used. The amount of the surface coating was determined by the number of passes of the tubing or fiber through the solution. The shell-like deposition in the uncoated hollow fiber was achieved by a slow moving of the fiber through the solution and taking care that the ends of the fiber would not come in contact with the solution. The uniform deposition was achieved by submerging the fiber into the solution for a brief period. For the core deposition of PVBr in the tubing, a 50% solution was used which was drawn up into the tubing. The treated substrates were then dried in a vacuum oven at 50°C/16 hr.

### Determination of *O.I.*

*O.I.* measurements on the 254- $\mu\text{m}$  hollow fiber were performed in the helix sample holder described before.<sup>3</sup> A bundle of six fibers was used in these determinations. For the 614- $\mu\text{m}$  fibers and the tubing, the measurements could be performed in the holder or without it, as the samples were self-supporting and individual specimens were used. When attempting to determine the *O.I.* on very small samples (less than 100 mg) using the helix sample holder, care should be taken in performing the determination on a sample portion that is not touching the helix material itself, or erratic results

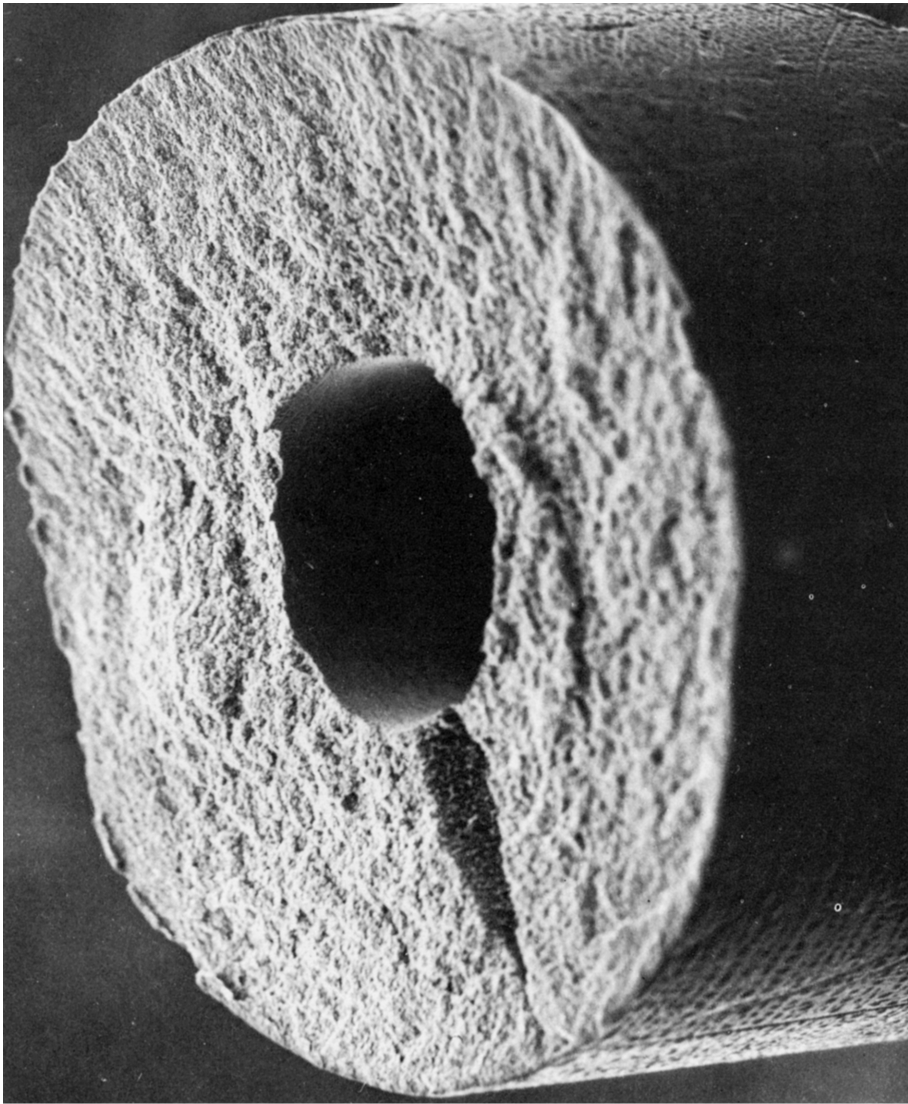


Fig. 1. Cross section of a polysulfone hollow fiber.

will be obtained because of the helix material acting as a serious heat sink for the small sample size burned. The precision of all of the *O.I.* values reported is within  $\pm 0.3$  *O.I.* unit.

### RESULTS AND DISCUSSION

The hollow fibers that we used were fibers that had been prepared for water desalination applications. As a result, they consisted of a rather thick, highly porous or cellular wall and a comparatively small central hole. For the actual desalination application, the outside of the fiber is coated with a thin, pinhole-free, coating. In Figure 1 is depicted an SEM picture of the cross section of the uncoated 254- $\mu\text{m}$  hollow fiber that we used in our work. As the PVB<sub>r</sub>—the one we used in the deposition studies—assumed a dark-purple color upon drying in a vacuum oven at 50°C, its distribution in the cross section of the substrate could be easily visualized in an optical microscope. This change in the color of PVB<sub>r</sub> upon heating is characteristic of the homopolymer itself, whether it has come

in contact with solvents of different polarities or no solvents at all (bulk homopolymer). Thus, we feel the proposed correlation between the color and the location of the homopolymer is valid.

The PVBr location-versus-*O.I.* data are summarized in Tables I and II. As can be seen, in the case of the tubing, incorporation of about 6% of PVBr in the center of the tubing resulted in an *O.I.* about 2 units higher than when deposited on the outside of the tubing. These results are in agreement with the PVBr grafting results in polyester filaments observed before.<sup>1</sup> Furthermore, with the surface-deposited PVBr, approximately twice the amount of PVBr was needed to achieve the same *O.I.* as when it was deposited in the core of the tubing.

TABLE I  
Oxygen Index Versus Flame Retardant Location. Solution-Deposited PVBr and Medical Grade "Tygon Tubing"<sup>a,b</sup>

% Deposited	Oxygen index	
	Outside	Center
0	20.8	20.8
6.5	—	24.3
5.8	22.2	—
9.4	23.4	—
16.0	25.2	—

<sup>a</sup> Poly(vinyl chloride)-poly(vinyl acetate) copolymer O.D. 2400  $\mu\text{m}$ .

<sup>b</sup> I.D. 650  $\mu\text{m}$ .

TABLE II  
Oxygen Index Versus Flame Retardant Location. Solution-Deposited PVBr and Polysulfone Hollow Fibers

% Deposited	Shell-like	O.D. 614 $\mu\text{m}$ I.D. 157 $\mu\text{m}$	Uniform	
0	23.5		23.5	
32	29.7		—	
29	—		32.5 ( $\Delta 2.8$ )	
	Carbonized Surface	O.D. 325 $\mu\text{m}$ I.D. 92 $\mu\text{m}$	Uniform	O.D. 254 $\mu\text{m}$ I.D. 79 $\mu\text{m}$
0	22.2		20.0	
32	33.5		—	
34	—		36.6 ( $\Delta 5.3$ )	

In the case of the 614- $\mu\text{m}$  hollow fibers, uniform deposition of the PVBr in the fiber led to an *O.I.* of at least 2.8 units higher than when it was deposited nonuniformly in a shell-like distribution from the outside in.

In the case of the 254- $\mu\text{m}$  uncoated and carbonized poly(furfuryl alcohol)-coated fibers, we already see a difference of 2.2 units in the *O.I.* as a result of the carbonized coating on the fiber. When the PVBr is deposited strictly on the surface of the coated fiber and is then compared with the fiber in which the PVBr is distributed uniformly in the fiber, we obtain a 5.3-unit difference in the *O.I.* These results are similar to those of the polyester grafting work.<sup>1</sup> Some of the earlier grafting results are reproduced here in Table III.

The grafting work was performed on 13.5  $\mu\text{m}$  100% poly(ethylene terephthalate) filaments. Thus, the core location of PVBr led to its most efficient utilization, followed by a uniform distribution, then a surface coating, and the least efficient solution-coated surface. This generalization appears to be true now not only for a 100% polyester, but also for a polysulfone and a polyvinyl. It appears

TABLE III  
Flame Retardant Location Versus Efficiency<sup>a</sup>

	Solution coating	Uniform	Grafts Surface	Core
VBr				
<i>O.I.</i>	25.2	26.3	23.5	21.9
% FR	55	18.8	18.8	1.2
DEVp				
<i>O.I.</i>	29.4	27.6	24.3	—
% FR	70	16	21	—
<i>O.I.</i> Control	= 20.4			

<sup>a</sup> VBr = Grafted PVBr; DEVp = grafted PDEVp.

to be true on a 13.5- $\mu\text{m}$  scale as well as on a 254-, 614-, and 2400- $\mu\text{m}$  scale. It also appears to be true whether the flame retardant is grafted or solution deposited.

In summary, it is concluded that the more thermally labile a flame retardant is (e.g., PVBr, PDEVp), the more efficient it becomes and the more it is concentrated at the center of a substrate of dimension at least from 13.5 to 2400  $\mu\text{m}$ . Thus, factors that will slow the rate of the flame retardant loss from the flame front will contribute to improved flame retardance efficiency. We have demonstrated here the effect of one such factor—the location of the flame retardant in the substrate. From our other work, at least two other factors appear to have a similar effect upon the flame retardance efficiency: (1) the structure of the flame retardant itself, and (2) a low volatility coreactant in a formulation.

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#### References

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