

# The Role of Intumescence on the Flammability of Vinyl and Vinylidene Polymers

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## Synopsis

Thermal stability and flammability properties of six structurally related vinyl and vinylidene polymers fail to show correlation. Instead, it is found that the combustion of these polymers is dominated by their char-forming ability. A remarkable intumescent effect is observed in PVC<sub>2</sub>, PVF<sub>2</sub>, and PVC which accounts for the high flame extinguence of these polymers.

## INTRODUCTION

Poly(vinyl chloride) (PVC), poly(vinylidene chloride) (PVC<sub>2</sub>) and poly(vinylidene fluoride) (PVF<sub>2</sub>) are inherently flame-resistant materials, and this is generally attributed to their high halogen content.<sup>1-3</sup>

In fact, the halogenidric acid generated by thermal degradation of the polymer chains under actual combustion conditions acts as a diluent of fuel and causes also a reduction of the oxygen diffusion to the burning surface.<sup>4</sup>

A flame-poisoning effect of these acids might be also considered, but combustion experiments performed in atmosphere of air and HCl, HF, or HBr have shown that this effect is appreciable only in the case of HBr.<sup>3,5</sup>

However, polymers structurally similar to PVC, PVC<sub>2</sub>, and PVF<sub>2</sub>, such as poly(vinyl fluoride) (PVF), poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA), which are also able to generate large amounts of acids or water during the combustion, are flammable materials.<sup>1</sup>

It appears therefore that, besides the nature of volatile compounds generated, other factors may be determining the flammability properties of the polymers under scrutiny.

In an attempt to provide a basis to understand the combustion behavior of these polymers, some parameters characteristic of the combustion phenomenon such as oxygen index (OI), amount of combustion residue, and polymer surface temperature under forced flame conditions, have been measured.

The results reported in this work lead to conclude that, besides the gen-

eration of noncombustible materials, a remarkable intumescent effect occurring in  $\text{PVC}_2$ , PVC, and  $\text{PVF}_2$  is responsible for the high flame extinguence of these polymers.

### EXPERIMENTAL

**Materials.** Poly(vinyl chloride) and poly(vinyl acetate) were obtained from Aldrich Chemical Co.. Poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene fluoride), and poly(vinyl alcohol) 100% hydrolyzed were obtained from EGA Chemie.

**Thermogravimetry.** A Perkin-Elmer Thermal Analyzer TGS-2 was used to determine the thermal behavior of the samples. Experiments were carried out on about 2 mg of sample under nitrogen flow (60 mL/min) and furnace heating rate of  $10^\circ\text{C}/\text{min}$  up to  $750^\circ\text{C}$ .

**Limiting Oxygen Index (OI) Measurements.** Measurements were carried out on a Stanton-Redcroft apparatus (mod. FTA) in oxygen/nitrogen atmosphere, according to the ASTM D 2863 method.

**Polymer Surface Temperature Measurements.** Measurements were performed on moulded pellets (about 500 mg) placed on a porcelain disc and burned in air atmosphere with a butane flame maintained in a fixed vertical position on it for all the experimental time. The temperature, measured by a chromel-alumel thermocouple ( $\phi = 0.5$  mm) placed in a fixed position inside the sample, was recorded as a function of the time.

**Combustion Residue Measurements.** Combustion residue measurements were carried out by introducing the sample (a pressed pellet of about 300 mg) in a crucible placed in a furnace heated to a fixed temperature and under an air flow rate of 3 L/min. After a fixed time the crucible was withdrawn, rapidly cooled, and weighed.

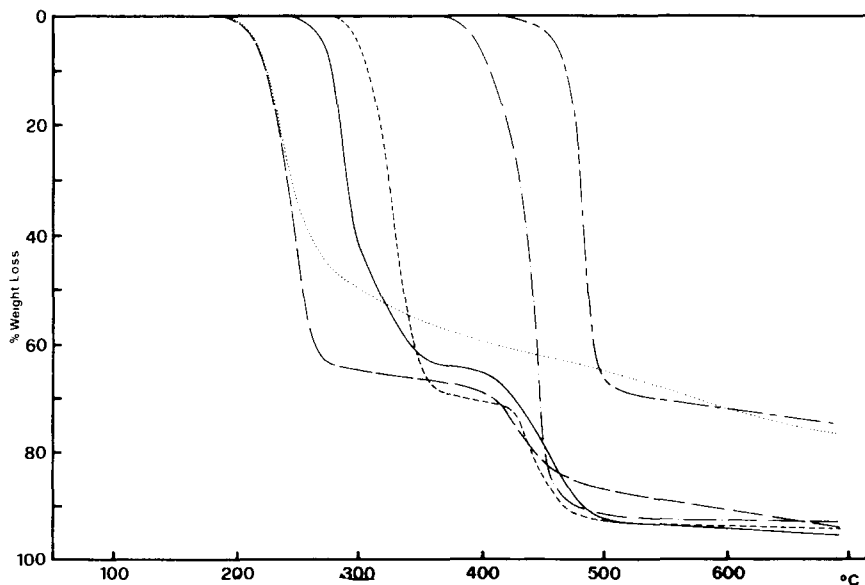


Fig. 1. Weight loss curves for ( $\cdot\cdot\cdot$ )  $\text{PVC}_2$ , ( $- - -$ ) PVA, ( $—$ ) PVC, ( $- - -$ ) PVAc, ( $- \cdot$ ) PVF, and ( $- -$ )  $\text{PVF}_2$ . TG experiments under  $\text{N}_2$  flow (60 mL/min) and heating rate  $10^\circ\text{C}/\text{min}$ .

TABLE I  
Thermal Stability and Combustion Data of Vinyl and Vinylidene Polymers

Sample	PDT <sup>a</sup> (°C)		OI <sup>b</sup>	R% <sup>c</sup>
	1st step	2nd step		
PVA	260	430	21	5
PVAc	340	440	21	7
PVF	455	—	23	3
PVC	295	465	42	15
PVF <sub>2</sub>	500	—	45	20
PVC <sub>2</sub>	245	—	60	30

<sup>a</sup> TG experiments under N<sub>2</sub> flow (60 mL/min), heating rate 10°C/min.

<sup>b</sup> Limiting oxygen index.

<sup>c</sup> % residue with respect to initial weight of sample at a combustion temperature of 500°C.

## RESULTS AND DISCUSSION

Thermal stability and flammability properties of polymeric materials are often related, and, for instance, it is often found that a higher thermal stability corresponds to a lower flammability for a series of polymers having a comparable structure.<sup>1</sup>

The thermal stability of vinyl and vinylidene polymers can be estimated from their thermogravimetric curves (Fig. 1) on the basis of the temperature of maximum rate of polymer decomposition (PDT). PDT values of polymers investigated are collected in Table I. It can be noted that the thermal stability increases in the order PVC<sub>2</sub>, PVA, PVC, PVAc, PVF, and PVF<sub>2</sub>. Flammability indexes (OI values in Table I) for vinyl and vinylidene polymers, however, are not correlated with the corresponding PDT values, indicating that factors are actually influencing the flammability properties of these polymers.

In order to characterize the flammability and the combustion behavior of the polymers investigated, oxygen index (OI), combustion residues and polymer surface temperatures under forced burning conditions were measured. OI values may be considered as an index of the flame resistance of a material<sup>5-7</sup>; it represents the minimum fraction of oxygen in an oxygen/nitrogen atmosphere that is just sufficient to maintain (after ignition) the combustion of the specimen.

The OI values measured, for vinyl and vinylidene polymers, are in agreement with literature data and are collected in Table I. These data point out the flame-resistant property of PVC, PVC<sub>2</sub>, and PVF<sub>2</sub> with respect to the other vinyl polymers investigated. Visual observation during the burning experiments showed that in PVC<sub>2</sub>, PVC, and PVF<sub>2</sub> an abundant char residue was formed at the burning polymer surface. Instead, only a thin crust of char appeared in PVA. In PVAc and PVF the polymer surface appeared to be in a melt form with very little amount of carbon dispersed on it. These observations were confirmed by measurements of char residue amounts in experiments under forced combustion. Figure 2 shows the char residue as a function of the combustion temperature (see Experimental). It can be noted that, for PVC, PVF<sub>2</sub>, and especially for PVC<sub>2</sub>, the char amount is higher with respect to the remaining polymers.

The char forming property of a polymer may significantly influence its

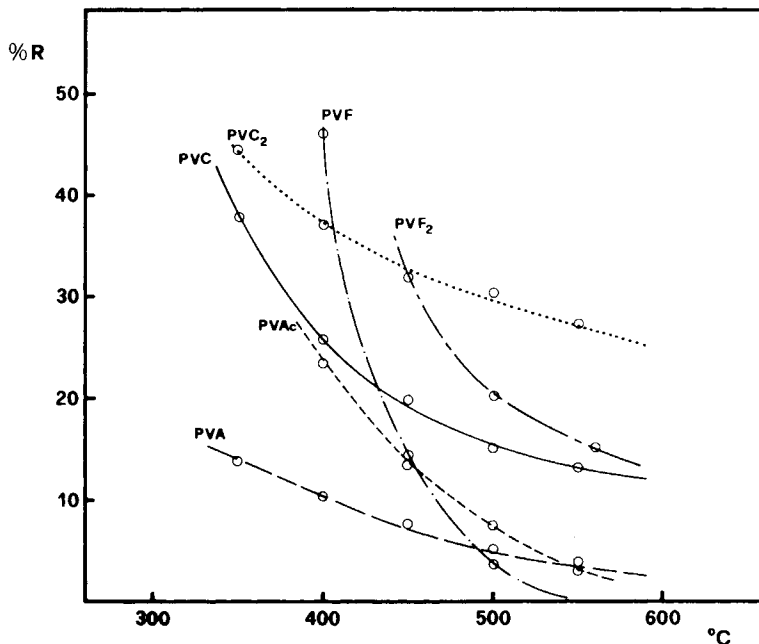


Fig. 2. Char residue vs. combustion temperature for vinyl and vinylidene polymers.

flame resistance. In fact, besides reducing the amount of fuel formed, the accumulation of char at the burning surface may form a thermal insulating char layer that inhibits the combustion process (intumescence).<sup>1,3,8-11</sup> Under these circumstances, heat and oxygen transfer towards the undecomposed polymer bulk becomes hindered and the diffusion of the fuel into the flame is slowed down. The insulating properties of the char layer may be evidenced by measurements of polymer surface temperature during the combustion.<sup>10-12</sup> Such measurements were performed on molded pellets burned in air atmosphere with a butane flame maintained lightly touching the burning surface during all the combustion time. The temperature was measured by a thermocouple placed just below the burning surface.<sup>10,11</sup>

Figure 3 shows the temperature profiles obtained for the polymers investigated; polypropylene (PP) is also reported for comparison.

The PP sample (Fig. 3) reaches high temperature values within a short time because it burns without leaving char residue. PVF and PVAc show a temperature profile similar to PP, while PVC<sub>2</sub>, PVC, and PVF<sub>2</sub> exhibit low temperatures also after long flame-exposition times. In the PVA case, the temperature profile results intermediate.

Data in Figures 2 and 3 point out evidence that the phenomenon occurring at the burning surface of the polymers investigated play a key role in the combustion process, and this explains also the lack of correlation between thermal stability and flammability.

It can be concluded that the high flame extinguence observed for PVC<sub>2</sub>, PVF<sub>2</sub>, and PVC is mainly due to their ability to form an abundant char during the combustion. In these circumstances, the large amount of non-flammable gases generated from the thermal decomposition of the polymer causes the swelling of the char to form an expanded layer (intumescence).

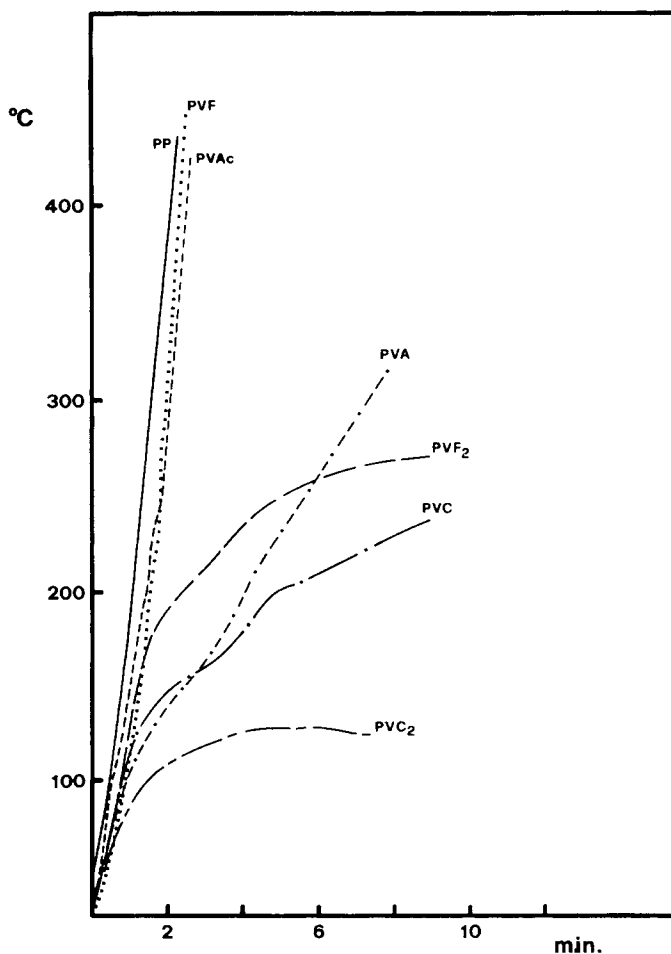


Fig. 3. Polymer surface temperature vs. combustion time for vinyl and vinylidene polymers.

On the contrary, only little amounts of char are formed in the combustion of PVA, PVF and PVAc (Fig. 2). Visual observations show, furthermore, that the char formed results dispersed into the melt polymer surface, so that no insulating effect (Fig. 3) is obtained for these polymers, and their weak flame resistance is therefore understandable.

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