

# Combustion and Fire Retardance of Poly(2,6-dimethyl-1,4-phenylene ether)–High-Impact Polystyrene Blends. I. Morphological Aspects

A. B. BOSCOLETTO,<sup>1</sup> M. CHECCHIN,<sup>1</sup> M. TAVAN,<sup>1</sup> G. CAMINO,<sup>2,\*</sup> L. COSTA,<sup>2</sup> and M. P. LUDA<sup>2</sup>

<sup>1</sup>Centro Ricerche EniChem, Via della Chimica 5, 30175 Porto Marghera, Venezia, Italy; <sup>2</sup>Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università, Via P. Giuria 7, 10125 Torino, Italy

## SYNOPSIS

The study, by scanning and transmission electron microscopy (SEM and TEM), of the morphological aspects of thermal degradation of poly(phenylene ether)–high-impact polystyrene blends (PPE/HIPS) occurring on burning gives a detailed mechanistic insight into the process. It is seen that thermal degradation leads to a cellular structure in the material that evolves to a foamed char on burning. The fire-retardant triphenyl phosphate can modify the shape and size of the cellular structure. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Mechanistic studies of the last two decades have shown that combustion and fire retardance in polymeric materials are closely related to their thermal degradation behavior.<sup>1</sup> However, the progress of our understanding of the mechanistic aspects is still unsatisfactory, owing to the complexity of the degradation processes occurring in combustion.

The complexity increases when heterogeneous materials such as most polymer blends are considered. Indeed, it was shown that interactions between reactive species involved in the degradation of one of the phases of the blend with reactive species and/or polymer molecules of another phase may lead to unexpected results.<sup>2</sup> Furthermore, in the case of the most common approach to fire retardance by means of additives, different solubilities of the additive in the phases of the blend might play an overwhelming role in the retardant action. Therefore, in the case of blends, the mechanistic study should also involve the use of techniques that allow the morphological characterization of the material to examine the effect

of the degradation process on the phases of the blend.

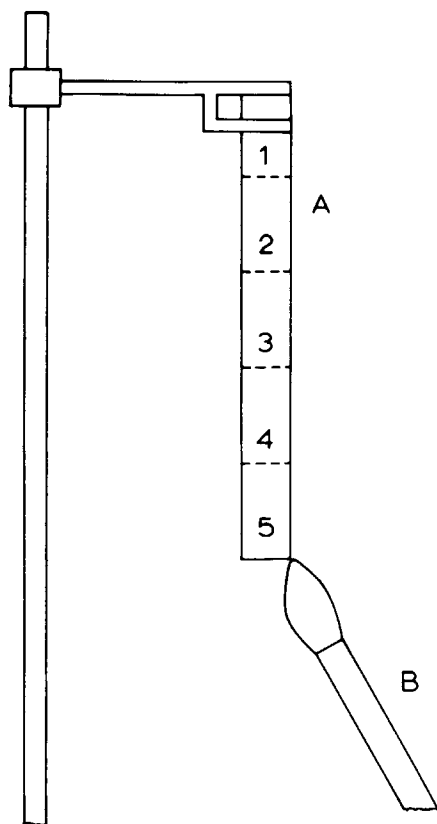
In this article, we report on the morphological aspects of the thermal degradation of a 65/35 w/w blend of poly(2,6 dimethyl-1,4-phenylene ether) (PPE) with high-impact polystyrene (HIPS) burning in the Underwriters Laboratories UL 94 test.<sup>3</sup> This test was chosen because it is most often used to characterize the combustion behavior in specifications concerning polymeric materials. The effect of the fire-retardant triphenyl phosphate (TPP), widely used in the PPE/HIPS blend, was also studied.

## EXPERIMENTAL

### Materials

An experimental sample of PPE ( $M_w = 50,000$ ;  $M_w/M_n = 2.8$ ) and an industrial sample of HIPS (EniChem, Edistir; PS phase [80%]:  $M_w = 240,000$ ,  $M_w/M_n = 2$ ; rubber phase [20%]). The blend PPE–HIPS 65/35 w/w and mixtures of the blend with TPP (Reomol, Ciba-Geigy) between 4.8 and 16.6% weight concentration were prepared in a twin-screw extruder Werner SZW 40. Specimens for the UL 94

\* To whom correspondence should be addressed.



**Figure 1** Ignition in the UL 94 test: (A) bar specimen divided in five equal sections (zones); (B) gas burner.

test were prepared by injection molding using a press Battenfeld 230/E.

### Combustion Test

The UL 94 test was used, in which a specimen held vertically is ignited by the flame of a gas burner applied twice for 10 s to the bottom (Fig. 1), following a detailed procedure reported in the literature.<sup>3</sup> Materials are classified depending on time for extinguishment of the flame after each ignition and on whether combustion occurs with dripping of flaming particles, capable of igniting surgical cotton placed underneath the specimen.

Time for flame extinguishment decreases from class V-1 to V-0. Ignition of the cotton leads to class V-2 independently of the extinguishment time if it is shorter than or equal to that of class V-1; otherwise, the material is nonclassified. Thus, fire retardance is often arbitrarily considered to improve in the sequence V-2, V-1, V-0. However, the real fire hazard of V-2 classified materials might depend on type of application, i.e., on whether combustible

material is available for fire propagation by flaming dripping. The temperature inside the bar specimen during the test was monitored by a thermocouple (Cr-Al, 0.6 mm) introduced in a hole made in the center of the bar at mid-height.

### Thermography

The temperature of the surface of the specimen not involved in the flame or of the charred burned section immediately after extinguishment of the flame in the UL 94 test was measured by infrared thermography. An Agema 880 apparatus was used, equipped with an MCT detector, cooled at liquid nitrogen temperature, operating in the 8–12  $\mu\text{m}$  range. The emissivity value,  $\epsilon = 0.95$ , was used for the computation of the temperature values.

### Microscopy

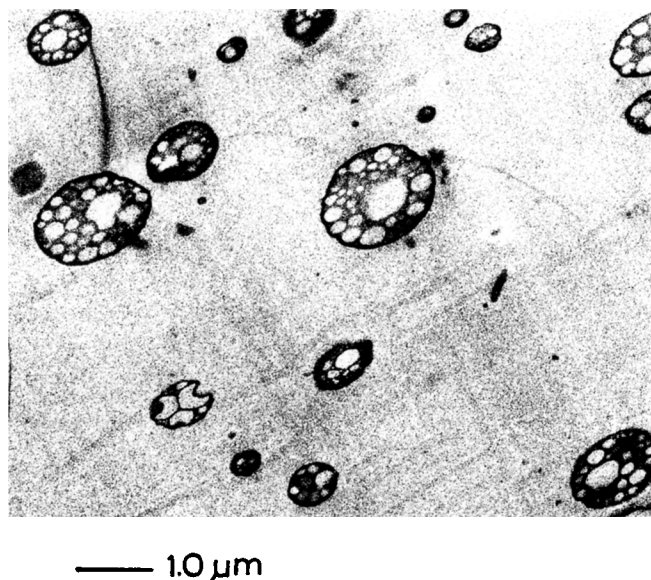
Transmission electron microscopy (TEM) was carried out with a Philips EM 400 instrument operated at 80 keV on thin sections (ca. 70 nm) cut by means of an ultramicrotome EF/C4 Reichert-Jung and exposed to vapors of a 2% water solution of  $\text{OsO}_4$  to stain PBU regions.<sup>4</sup> Scanning electron microscopy (SEM) of the fracture surface of samples cooled at liquid nitrogen temperature was carried out using a Zeiss DSM 950 instrument provided with Northern Tracor Z II energy dispersive system (EDS) for electron probe microanalysis.

## RESULTS AND DISCUSSION

The TEM micrograph of Figure 2 shows the morphology of the blend. The continuous phase is constituted by PPE in which the PS matrix of HIPS is completely soluble.<sup>5–7</sup> Rubber domains present in the HIPS sample of diameters up to 1–2  $\mu\text{m}$  having a typical “salami”-structure<sup>8,9</sup> are observed in which the dark PBU phase surrounds the occluded PS subdomains. Most of the PBU-*g*-PS copolymer in the rubber domains is located within the PBU phase and at the interface between PBU and PS or PPE-PS matrix.<sup>10,11</sup>

### Effect of Combustion on Morphology

SEM micrographs of Figure 3 show that combustion induces formation of regular, spherically shaped cavities of 150–250  $\mu\text{m}$  within the specimen. The number of voids increases ongoing from the top of



**Figure 2** TEM micrograph of the original PPE-HIPS blend (65/35 w/w). Magnification:  $\times 10,000$ .

the specimen [Fig. 3(a-1)], which is just reached by the flame of the self-sustained combustion, to the central and bottom zones [Fig. 3(b-1) and (c-1), respectively]. In the latter, which is the most involved in the combustion, cavities are distributed almost in the entire specimen.

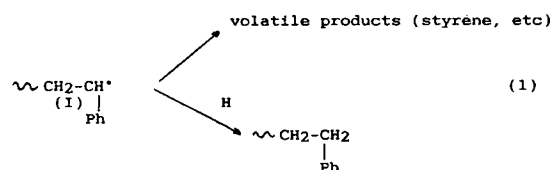
The internal surface of the cavities is not smooth; it is, instead, characterized by the presence of small bulges whose height tends to decrease from top to bottom of the specimen, as shown at higher magnification of the SEM observations [Fig. 3(a-2), (b-2), and (c-2)]. From the TEM micrographs of Figure 4, it can be deduced that these bulges are due to the rubber domains, which protrude from the internal surface of the voids. This is shown, e.g., by the pointer of Figure 4(a-2), indicating a bulge on the internal surface of a void in the top section of the specimen.

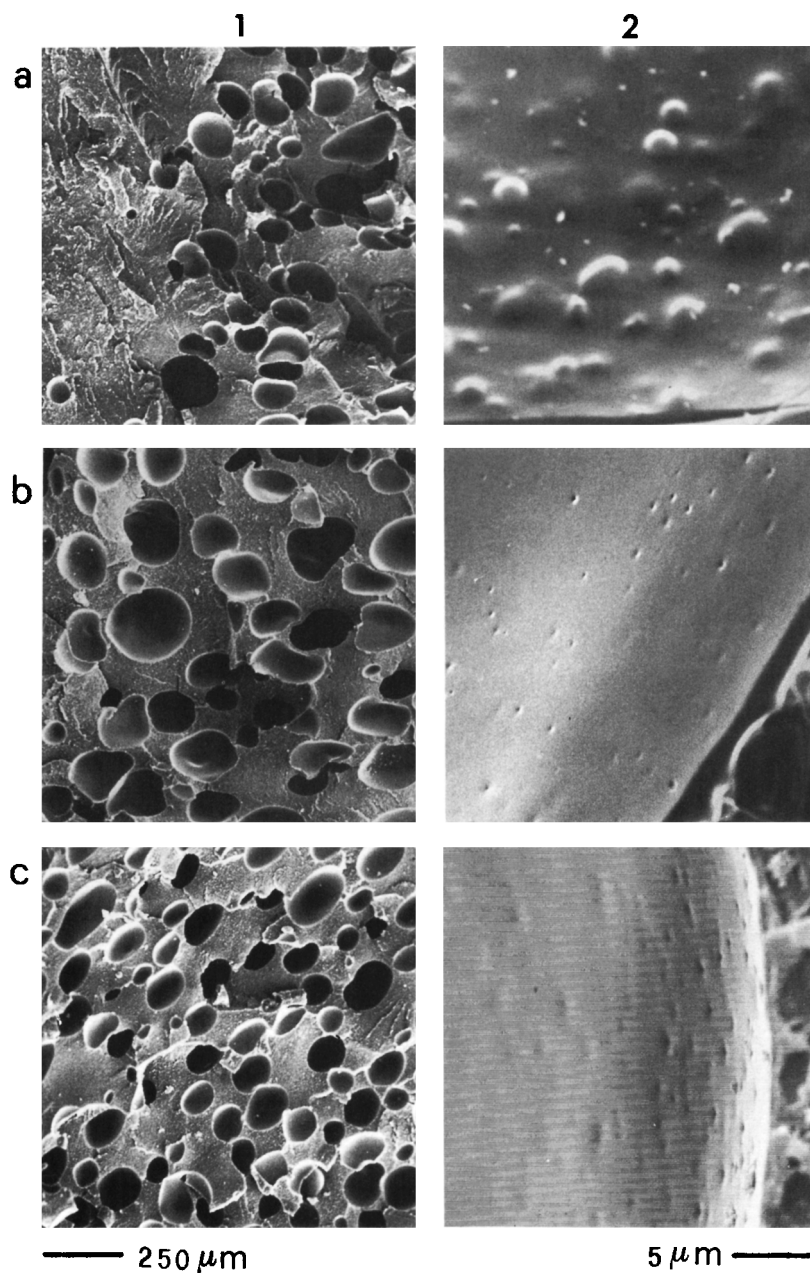
These morphological features can be explained assuming that in the UL 94 test heat induces thermal degradation to gaseous products of the polymer material of the whole specimen. Gases from the outer part of the specimen diffuse freely to feed the flame, whereas gases created inside the specimen seem to experience restricted diffusion. Thus, the voids could be created by the buildup of pressure due to these gases, against the thermoplastic matrix PPE-PS. This can be deformed because it reaches and exceeds the temperature of the glass transition (PS: ca.  $100^{\circ}\text{C}$ , PPE: ca.  $210^{\circ}\text{C}$ ), in agreement with temperature measurements either on zone 3 (Fig. 1) of specimens during self-sustained combustion after

the second ignition, when the zone is not reached by the flame (Table I), or at the end of the test (Ref. 12 and legend to Fig. 3). The concentration of the voids increases from the top section of the specimen to the bottom, in agreement with parallel increasing of the temperature, which increases the rate of thermal degradation of the polymeric material and, hence, the rate of formation of gases.

A larger thermal stability of the rubber domains as compared to the miscible blend PPE-PS is evident from SEM and TEM examinations of the top section of the specimen [Figs. 3(a) and 4(a)]. Here, the temperature does not exceed  $150^{\circ}\text{C}$ , allowing accumulation of the more stable rubber phase. This might be explained on the basis of stabilization of the PS phase by PBu.

In fact, the PS chains should be the most unstable chemical structure in both the PPE-PS matrix and the rubber phase. However, literature data indicate that in both cases a stabilization effect is shown on the thermal degradation of PS by PPE<sup>13</sup> or PBu,<sup>14,15</sup> respectively. The stabilization was shown to be due to termination by hydrogen transfer to the polystyryl radicals (I) that propagate the thermal degradation of PS<sup>16</sup>:

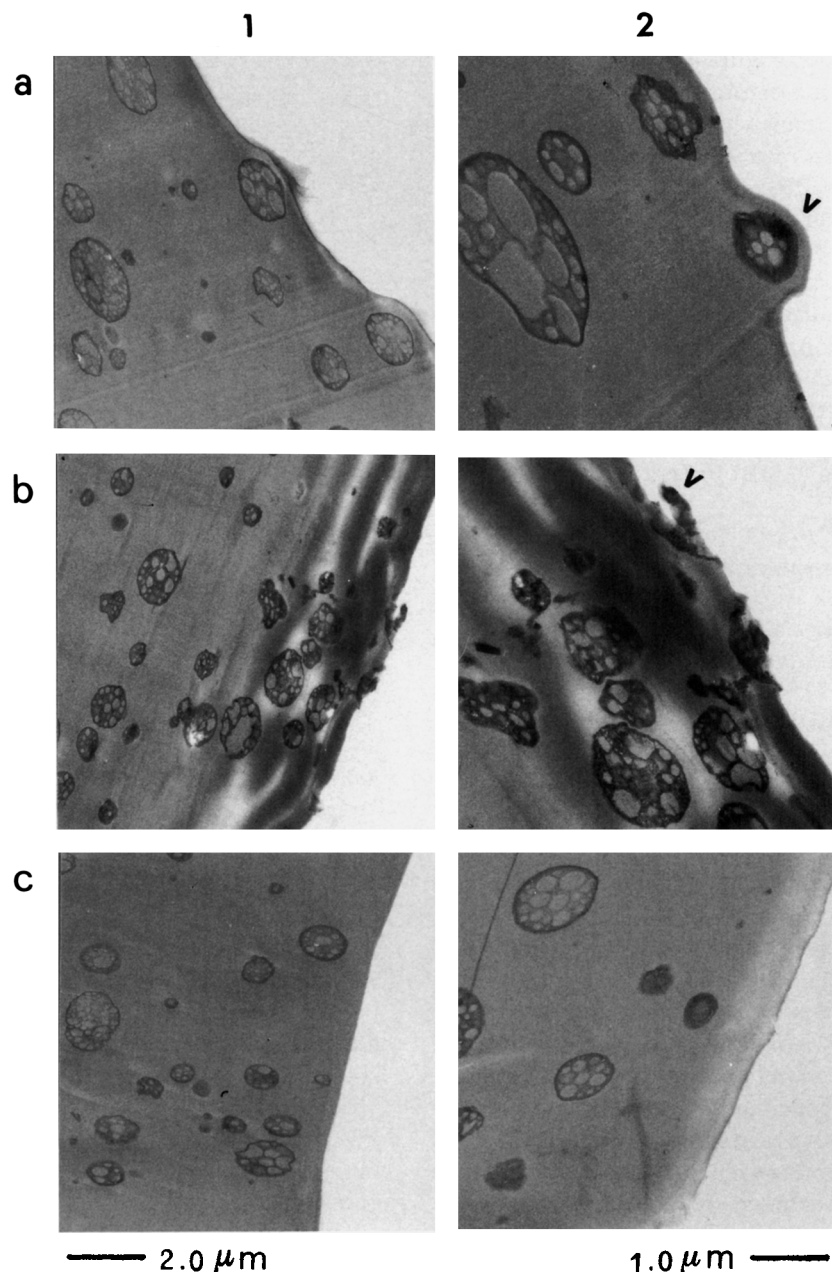




**Figure 3** SEM micrographs of surface fracture along the specimen of PPE/HIPS blend after the UL 94 test: (1) transverse section of specimen,  $\times 38$ ; (2) internal surface of void,  $\times 2000$ . (a) Zone 1 of the specimen of Fig. 1 ( $\leq 150^\circ\text{C}$ ); (b) zone 2 ( $\leq 250^\circ\text{C}$ ); (c) zone 5 ( $\leq 410^\circ\text{C}$ ). Temperatures measured on the surface of the specimen at the end of the test by thermography.<sup>12</sup>

In the case of PPE, it was suggested that the mobile benzylic hydrogen atoms of the methyl groups are transferred to macroradicals (**I**)<sup>13</sup> (Scheme 1). Whereas it was shown that the allylic hydrogen atoms of 4-vinylcyclohexene, which is formed by degradation of PBU, can terminate macroradicals (**I**) in degrading PS-PBU blends.<sup>14,15</sup> In our case, the

temperature reached by the specimen, at least in the top section [Fig. 3(a)], might not be high enough for formation of 4-vinylcyclohexene. However, PBU chains and PBU-*g*-PS also have mobile allylic and tertiary hydrogen atoms, respectively, which can be transferred to (**I**) as the benzylic hydrogens of PPE (Scheme 1).



**Figure 4** TEM micrographs of the wall of voids in the sections of Figure 3: (1)  $\times 5,000$ ; (2)  $\times 10,000$ .

The above morphological observations suggest that, at relatively low temperatures, stabilization of PS by PBU in rubber domains is larger than by PPE, in agreement with thermogravimetric data.<sup>17</sup> This can be explained if we assume that mobility of allylic and benzylic hydrogen atoms are similar at these temperatures. A larger concentration of allylic hydrogen atoms is indeed available in PBU for termination of macroradicals (I) (1 allylic H atom per C

atom, for ungrafting units) as compared to benzylic hydrogen atoms in PPE (0.75 benzylic H atom per C atom). This explanation also assumes that extensive interactions between macroradicals (I) and polymer molecules (e.g., PBU), across phase boundaries are unlikely, in agreement with the literature data.<sup>2</sup> Otherwise, the rate of PS degradation in the PPE-PS matrix and in the rubber phase would tend to become equal, owing to hydrogen transfer across

the phase boundary, and the accumulation of the rubber phase shown in Figure 3(a) would not occur.

The increase of temperature ongoing from top to bottom of the specimen tends to suppress the discrimination between rate of degradation of the two main phases of the PPE-HIPS blend. This is well shown by the pointer in the TEM of Figure 4(b-2), indicating a rubber domain that decomposes at a rate close to that of the continuous matrix, avoiding the formation of a bulge. At the highest temperatures of the bottom section, both phases seem to degrade at the same rate, as shown by the TEM of Figure 4(c). Accordingly, the evidence of bulges on the internal surface of the voids inside the specimen decreases from Figure 3(a-2) to (c-2).

### Effect of TPP on Morphology

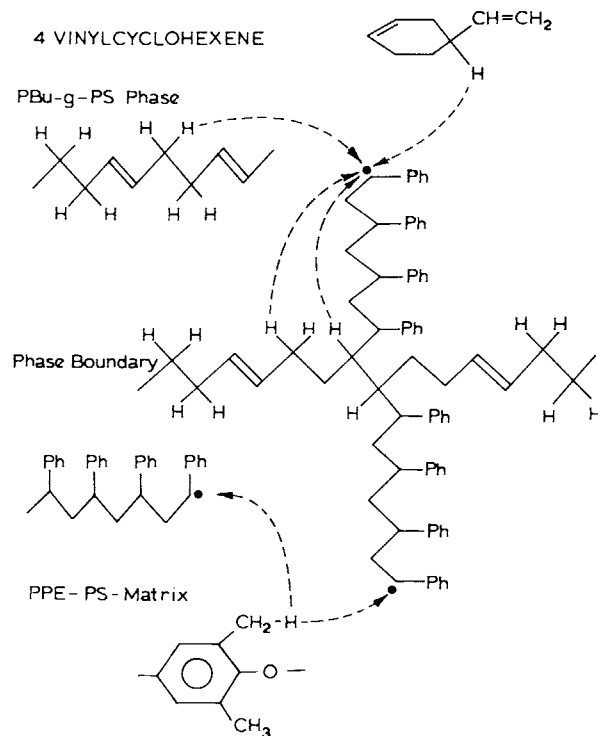
Formation of cavities within the UL 94 specimen during the test is limited to the bottom of the specimen (zone 5, Fig. 1), whereas the upper zones (1-4) are unaltered in the presence of TPP. This is a consequence of the fact that only the bottom zone of the specimen is involved in the combustion in the presence of the fire retardant and it reaches lower temperatures (Table I).<sup>12</sup> For example, the maximum temperature measured on the surface of zone 5 by thermography, just after flame extinguishment, is 320°C in the blend containing 16.6% of TPP as compared to 410°C in the absence of TPP.<sup>12</sup>

The size and shape of the voids inside the specimen are modified with increasing concentration of TPP. Figure 5(a) shows that at 4.8% of TPP the morphology of the specimen is similar to that without TPP of Figure 3(c), which corresponds to similar range of temperature reached by the respective zones of the two specimens, whereas irregular cav-

**Table I** UL 94 Classification and Temperature Measured by a Thermocouple (Internal) or Thermography (Surface) on Zone 3 During Self-sustained Combustion, Flame-free Zone (Fig. 1) of PPE/HIPS Specimens

TPP (%)	UL 94 (3.2 mm)	Temperature (°C)	
		Internal	Surface
—	n.c. <sup>a</sup>	240	220
4.8	V-1	150	160
16.6	V-0	90	125

<sup>a</sup> n.c. = nonclassifiable.

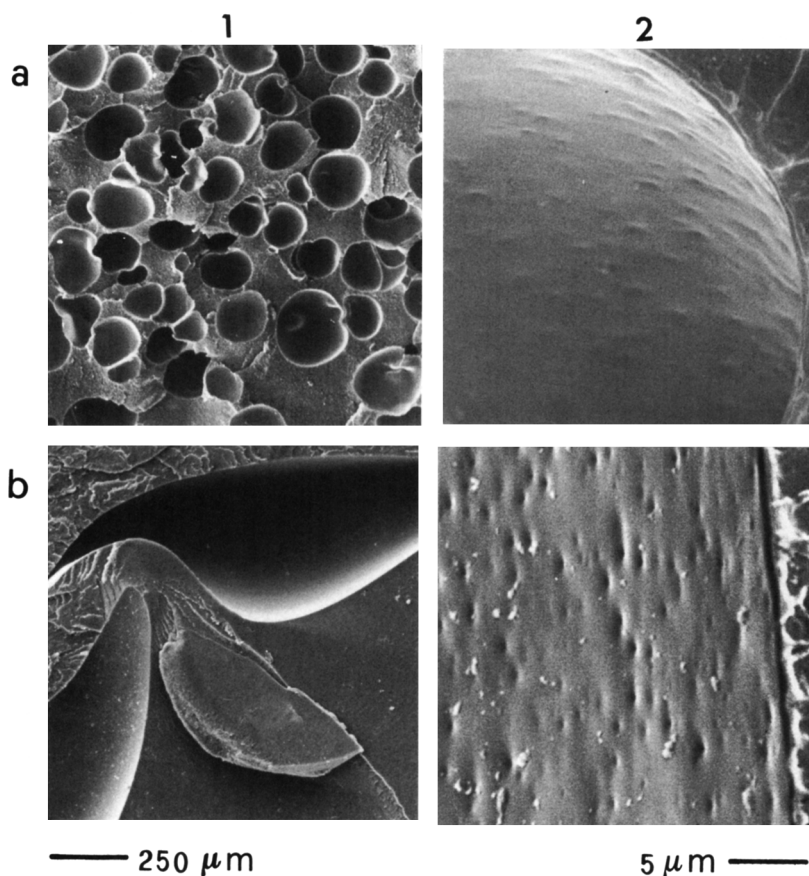


**Scheme 1** Thermal degradation of PPE-HIPS blends. Termination by mobile hydrogen atoms from the different species.

ities one order of magnitude larger are formed in the presence of 16.6% of TPP [Fig. 5(b-1)].

The effect of TPP on the morphology of the specimens cannot solely be due to decrease of temperature. Indeed, the shape and size of the cavities was shown to be independent of the temperature in the absence of TPP, down to temperatures [ $\leq 150^\circ\text{C}$ , Fig. 3(a-1)] lower than those of fire-retarded specimens [ $\leq 320$ , Fig. 5(b-1)]. The role of TPP could be either physical or chemical. For example, TPP could plasticize the matrix, modifying its rheological properties, which determines the formation of the cavities. Furthermore, volatilization of TPP may contribute to increase the size of the voids. Otherwise, TPP could modify the formation of the volatile products from the material, inducing a fire-retardant action already in the condensed phase.<sup>18</sup>

TPP does not seem to modify the trend observed above of the rubber domain phase to volatilize at a lower rate than the PPE-PS matrix, as shown by the bulges of Figure 5(a-2) and (b-2). In particular, TEM images of Figure 6 indicate that there is similarity between the zones of the specimens corresponding to Figures 4(c) and 6(a) or 4(b) and 6(b), respectively, which is reflected by similarity of temperature values.



**Figure 5** SEM micrographs of zone 5 (Fig. 1, bottom) of specimens of PPE-HIPS blends containing TPP: (1) Transverse section of specimen, magnification (a)  $\times 38$  and (b)  $\times 50$ ; (2) internal surface of voids in (1),  $\times 2,000$ . (a) 4.8% TPP; (b) 16.6% TPP.

Phosphorous microanalysis showed that TPP is distributed uniformly between the phases of the blend. Therefore, the most evident effect of TPP on shape and size of cavities in the burned UL 94 specimens is not due to preferential solubility of TPP.

### Surface Morphology

PPE/HIPS blends produce a relatively large amount of charred residue on burning that accumulates on the surface of the UL 94 specimen. The char has a foamed structure likely to be originated by the same mechanism seen above for void formation within the specimen. Indeed, Figure 7(a) shows a bubble growing against the external surface of the specimen. The carbonization of the walls of the bubble should provide the foamed char.

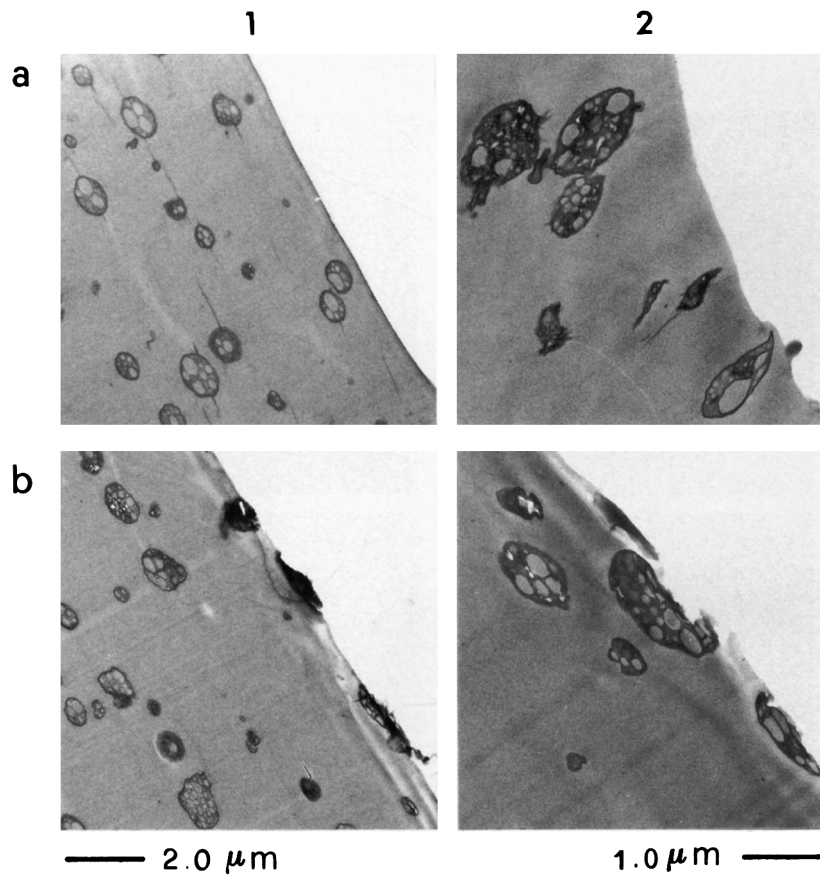
Figure 7(b) shows that the cells of the foamed char have a size of the order of 1 mm with walls about  $5 \mu\text{m}$  thick, which also show the presence of numerous small closed cells. The size of these "sec-

ondary" cells ( $\leq 5 \mu\text{m}$ ) might suggest that they are originated by the decomposition of the rubber domain phase within the PPE-PS matrix in which voids are created.

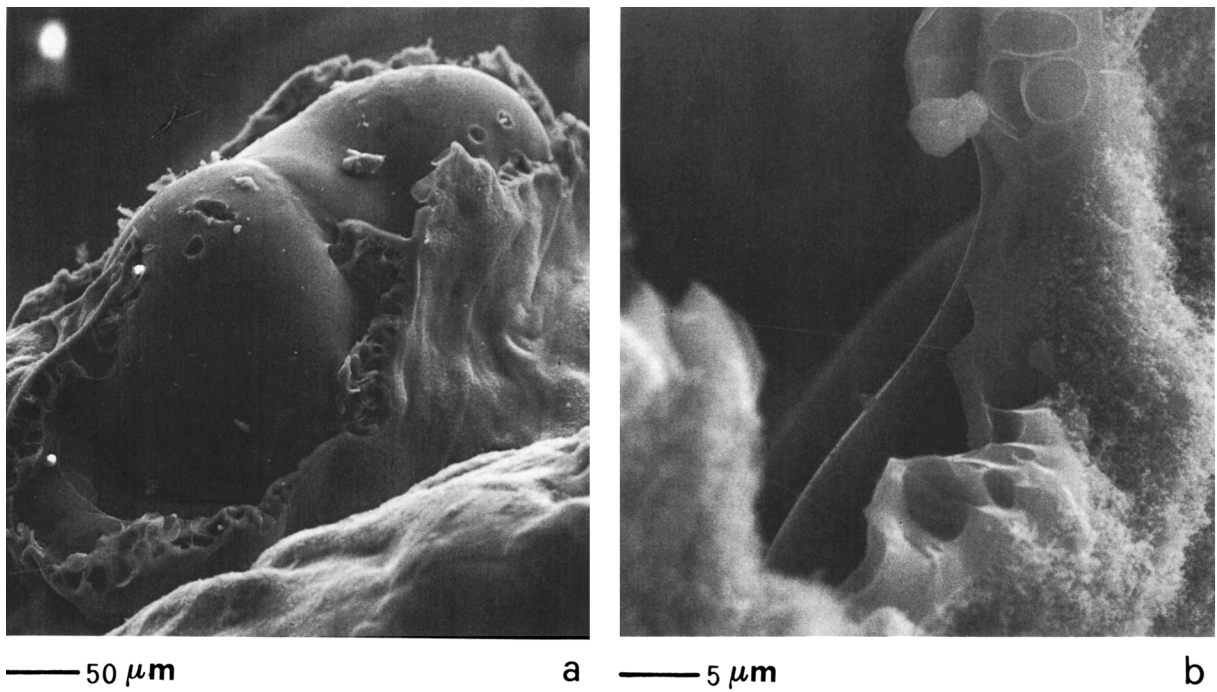
The external surface of the specimen is uniformly covered by a carbonized dust ( $< 0.2 \mu\text{m}$ ) that is likely to be the product of the combustion of the foamed char produced by thermal degradation of the blend. The presence of TPP does not introduce observable variations of the structure of the foamed char.

### CONCLUSIONS

Comparison of the morphology of the PPE-HIPS blend before and after burning gives a detailed insight on the mechanism of degradation during combustion that could not be obtained otherwise. Thermal degradation inside the material forms gases that create a cellular structure in the whole specimen. A relatively lower rate of degradation is found for the



**Figure 6** TEM of the wall of voids in the sections of Figure 5. Magnification: (1)  $\times 5,000$ ; (2)  $\times 10,000$ .



**Figure 7** SEM of surface of UL 94 specimens close to the flame zone, after testing. Magnification: (a)  $\times 200$ ; (b)  $\times 2000$ .



rubber domains as compared to the PPE-PS matrix, which is more evident at the lower temperatures.

The cellular structure is the precursor of the foamed char that is formed on the outer surface of the burning material. The char contains large voids whose walls (ca. 5  $\mu\text{m}$  thick) show the presence of numerous "secondary" closed cells. The secondary cells might derive from degradation of rubber domains, whereas the degradation of the PPE-PS matrix might supply the charred walls. Complete combustion of the char leads to a carbonized dust.

TPP reduces the temperature of combustion and tends to modify both the shape and the size of the cells in the material exposed to heat, possibly because of its volatilization and chemical interaction with the degrading material. However, TPP seems not to modify sensibly the structure of the foamed char.

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