

CHAPTER 4

Use of Organosilicone Composites as Flame Retardant Additives and Coatings for Polypropylene

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4.1 Introduction

Organosilicone polymers and their organic–inorganic hybrid structures are promising components of flame retardant (FR) formulations. This is attributable to their superior properties, compared to polymers with an organic main chain, in terms of their thermal stability and electrical properties. Industrially the most important silicone is the polydimethylsiloxane (PDMS). Its conversion to polyborosiloxane (pBSil) *via* a polycondensation reaction has given rise to interest not only in the academic but also in the industrial field. The mechanical and rheological properties of pBSil have been widely studied, although their behaviour in thermo-oxidative atmospheres is less investigated.^{1,2} Depending on the composition of the siloxane compounds, they may act during combustion as a shielding powder (PDMS) or protective ceramic layer (pBSil). The boron atom in the pBSil is an essential component of ceramic layer formation: without it the PDMS transforms into fine silica powder.³ Advantageous synergetic action of pBSil with ‘carbon-based’ intumescent flame retardants have also been reported, the pBSil acts as an additive enhancing the consistency of char.⁴

Recent advances in flame retardant polymeric materials have focused on the flame retardancy of polymer–clay nanocomposites (PCN). The heat release rate reducing effects of clays in PCN are well known, moreover the clays in combination with intumescent flame retardants have a significant influence on the char structure due to their bubble-nucleating effect.⁵ The needle-like sepiolite clay may promote the formation of increased amounts of char of better uniformity and strength.

The use of different boron-containing compounds such as metal-borates (zinc-, alumino-, magnesium-borate and organo-borates like melamine-borates) are increasingly applied in

polymers, particularly for fire retardant purposes. They may act as smoke suppressants, afterglow suppressants, corrosion inhibitors, or as synergistic agents.⁶⁻⁸ Inorganic boron salts act in the condense phase by changing the degradation pathway of polymers and thus promoting the formation of char and reduction of CO₂ and CO.^{9,10}

Although all of the three mentioned species (the polyorganosiloxanes, the clay and the melamine-borate) have been used as synergists in fire retardant compositions, their combination without FR-active atoms (*e.g.* P, Br) has not been investigated yet. In this study of pBSil, various composites containing needle-like clay and melamine-borate were prepared and characterised as flame retardant components in polypropylene. The combustion characteristics of the relevant polymer blends and composites were compared to those of pristine polypropylene. Contact angle measurements have been performed, beyond the FR characterization, in order to determine the multifunctional character of the developed pBSil composites.

4.2 Experimental

4.2.1 Materials

Polypropylene (PP) of Moplen HP400R type was received from Basell Polyolefins, MFI: 25 (230 °C, 2.16 kg). Hydroxyl-terminated polydimethylsiloxane (PDMS, HO–(Si(CH₃)₂O)_{*n*}–H)) with a viscosity range of 400–650 mPa s was received from Wacker Silicone GmbH (trade-mark: Wacker Silicone OEL CT 601 M). Boric acid (BA), melamine and absolute ethanol were received from Sigma Aldrich and used without further purification. The melamine-borate (MB) was prepared in our laboratory and was used as an incorporated additive. The MB was obtained using the following procedure:

first, the melamine (12.6 g, 0.1 mol) was dissolved in 600 ml boiling distilled water and the boric acid (12.2 g, 0.2 mol) in 100 ml distilled water. After mixing them the solution was left to cool down to room temperature under constant stirring. The white flocculated MB was completely precipitated then decanted and filtered. The obtained MB was then washed with cool water and left at room temperature to dry. The needle-like clay sepiolite (OSEP) in organomodified form was supplied by Tolsa (trade-mark: Pangel B40). As the peroxide radical initiator, 1,3,5-tris(tert-butylperoxy)benzene, trade name: Luperox F90P (Elf Atochem) was used. When applied, its amount in the composites was 0.5% of the pBSil content.

4.2.2 Sample Preparation

The formation of boron linkages between the PDMS chain required a treatment in boiling ethanol. The boric acid was dissolved in boiling ethanol, and then the PDMS was added dropwise. The mixture, under continuous stirring, was heated until a transparent solution was obtained. The reaction was carried out in excess boric acid. In the case of applying the additives, the MB and/or OSEP were added before the removal of ethanol in order to get a homogenous mixture. The majority of ethanol was removed by heating the samples up to 140 °C and any remaining ethanol was subsequently removed by evaporation in a vacuum chamber at 60 °C. The polyborosiloxane (pBSil)-based samples were solidified after the evaporation. The compositions of prepared samples are summarised in Table 4.1.

[Table 4.1 near here]

4.2.3 Preparation of PP Compounds

Melamine-borate and organomodified sepiolite containing-polyborosiloxane (pBSil–MB–OSEP) systems were introduced into polypropylene (PP). The amount of pBSil–MB–OSEP system in PP was increased by a multi-step process in the mixing chamber of Brabender Plastograph. A mixing temperature of 190 °C and a mixing speed of 60 m⁻¹ were used, the samples were homogenized for 10 m and then melt-compressed at 200 °C.

4.2.4 Preparation of Multilayer Structured Composites

The efficiency of the pBSil–OSEP–MB system was investigated also in the form of a multilayer structure. The upper layer was pBSil-based composite while the internal layer was pristine polypropylene. The multilayer structured samples were prepared in a Colin P200E type press at 195 °C and 50 bars for 10 m by compression of 10 × 10 × 0.4 cm PP sheet and pBSil–OSEP–MB sheet 10 × 10 cm. The thickness of the pBSil-based outer layer was 0.5 mm.

4.2.5 Characterisation

The thermal stability of materials was examined by thermogravimetric analysis (TGA) (Setaram Labsys TG DTA/DSC) under air atmosphere and with a heating rate of 10 °C m⁻¹. The combustion parameters (HRR: heat release rate, TTI: time-to-ignition and THI: total heat release) of samples were determined by a mass loss calorimeter (according to ISO 13927, FTT Inc.) under a heat flux of 50 kW m⁻². Contact angle values were determined by the sessile drop method goniometrically using 5 µL volume of water in a Kruss Contact Angle Meter.

4.3 Results and Discussion

4.3.1 Thermo-oxidative Stability

The analyses for determining the influence of boron inclusion on the thermo-oxidative stability of PDMS were designed, considering former experiments, determining the role of different end-groups on its thermal degradation.^{11,12}

The TGA results in Figure 4.1 show, in agreement with the literature, that the oxidative thermal degradation of PDMS takes place in two stages. In the first step volatile products, mostly cyclic compounds, are evolved and fragments of lower molecular weight are formed. In the second step further depolymerisation and breakdown of the PDMS chain takes place.

[Figure 4.1 near here]

Comparing the oxidative degradation of pBSil to that of PDMS, the first degradation step had completely disappeared. The residue at 550 °C was decreased in the case of pBSil, probably because boron can form volatile compounds which are easily lost.¹³ The characteristic mass loss data obtained in an air atmosphere are presented in Table 4.2.

[Table 4.2 near here]

The boron coupled to the polysiloxane chain of pBSil forms a network through borosiloxane linkages. The temporary B···O inter-chain dative bonds in polyborosiloxane also establish the linkages of a network structure. The incorporated boron favours reactions such as Si–CH₃ dehydrogenation to Si–CH₂ and the splitting off of the methyl groups from PDMS through conversion to radicals and giving additional binding sites as shown in Equations 4.1–4.3.¹⁴



A significant enhancement in the thermal stability and the disappearance of the first degradation step are observed in TG curves at low temperature (see Figure 4.1), which can be ascribed to the cross-linking structure of pBSil, which hinders the splitting of the cyclic oligomers and the formation of disadvantageous volatile products. This effect is more pronounced in the presence of MB and OSEP.

4.3.2 Combustion Characteristics of Polypropylene-based Composites

The pBSil–OSEP(5%)–MB(5%) sample was selected to prepare PP-based composites. The samples made of PP and polyborosiloxane composites are summarised in Table 4.3, where the values are given in weight percent.

[Table 4.3 near here]

The HRR (heat release rate) curves of the composites are shown in Figure 4.2. The amount of pBSil–OSEP–MB has a significant influence on the combustion properties: the peak of HRR decreased with the increasing percentage of pBSil–OSEP–MB in the composite, furthermore reduction in THR (total heat release) and EHC (effective heat of combustion) can also be observed, however the TTI (time-to-ignition) is shifted slightly to a lower time range. All of the quantitative results are tabulated in Table 4.4. The lower HRR [kW m^{-2}], and THR [MJ m^{-2}], indicate less fire hazard but with a slightly shortened TTI [s].

[Figure 4.2 near here]

[Table 4.4 near here]

The curves of PP/pBSil–OSEP–MB composites lie between two references, pure PP and pBSil–OSEP–MB. The shape of the curves is changing gradually with the increasing amount of pBSil–OSEP–MB. In the case of pristine PP a shoulder can be observed before the maximal HRR value; as the pBSil content of the composites is increased this shoulder is gradually broadened. The presence of pBSil–OSEP–MB causes a steady-state heat release until the peak at the end of the combustion, which is also decreased.

Applying peroxide as radical initiator (sample: NKMB073) the thermal stability and the combustion properties improved further. As shown in Table 4.4 the peak of HRR was

reduced from 898 to 230 kW m⁻², the time at which this occurred increased from 146 to 256 s and a remarkable decrease occurred in the THR value. Indeed it is noteworthy that at the beginning of combustion the composite NKMB073 exhibits a HRR as low as that of the pure pBSil–OSEP–MB reference. The peroxide probably acts by building linkages between polymer chains both within the silicone phase and at the interfaces of the two polymers, but the validation of this assumption requires further experiments.

The advantageous effect of the pBSil systems in PP can be accounted for by the formation of a non-carbonaceous white ceramifying intumescent structure on the surface during the combustion which acts as a protective ceramic layer. At the end of combustion the polypropylene leaves no residue whereas the PP/pBSil–OSEP–MB samples leave a white solid consistent char-like residue with an enlargement of 3–5 cm as shown in Figure 4.3.

[Figure 4.3 near here]

4.3.3 Multilayer Structure: PP/pBSil–OSEP–MB

The efficiency of the pBSil–OSEP–MB composite was also investigated in a multilayer structure form, using it as coating layer on the PP surface. In previous studies on boron-containing PDMS the authors found that the boron content helps to form a protective, coherent, heat resistant ceramic layer on the polymer during the combustion.^{4,15} These results initiated the use of polyborosiloxane composites as a coating layer on the PP surface.

During processing we found that the pBSil–OSEP–MB composite readily forms a continuous layer on the surface of PP. The 500 μm layer formed on the PP core of 4 mm corresponds to less than the half of the lowest pBSil–OSEP–MB concentration (NKMB061) in Table 4.3. Formation of such multilayer structures resulted in improved combustion characteristics (see Figure 4.4): more than 30% reduction of the peak of HRR and considerable delay of the peak (from 217 to 454 s) compared to PP can also be observed. Furthermore, in this case the TTI did not decrease but increased to 60% of the original value.

[Figure 4.4 near here]

The wettability study of this surface revealed that the coated layer is less adhesive than that of pristine PP, as shown in Figure 4.5, taken by the equipped digital camera. The contact angle of water drop on the PP surface is 90° while the coated surface has a contact angle value of 115° .

[Figure 4.5 near here]

The results suggest that multilayer structures may provide protection more efficiently, especially against the early degradation of the polymer, than the mixtures of the same composition. Such surface layers may perform multifunctional roles acting both as a flame retardant and as an adhesion-modifying (dust/graffiti releasing, self-cleaning) layer.

4.4 Conclusion

The thermo-oxidative degradation of PDMS is affected by the inclusion of boron atoms. The pBSil, formed by a polycondensation reaction, exhibits higher stability in the initial stages of decomposition as the boron-containing units hinder the splitting of the cyclic oligomers. At higher temperatures, however, the mass loss of pBSil is larger than that of PDMS.

For improving the fire retardancy of PP the pBSil was combined with melamine borate and fibrous clay (sepiolite). Increasing concentration of PP/pBSil–OSEP–MB in PP decreases the peak of HRR gradually and also the THR value. These results suggest that the formation of a non-carbonaceous, white, ceramifying intumescent layer on the surface of PP may act similarly to the conventional carbonaceous foam, but its heat stability is higher. Further improvement was achieved by the introduction of a radical initiator into the system. This probably acts through building linkages between polymer chains.

The PP/pBSil–OSEP–MB system forms readily a continuous layer on the surface of PP. Applied as a surface layer it acts as a flame-retardant protective coating and also enables the control of adhesion at the surface. This double effect of the developed coating is advantageous in construction, automotive and other relevant industries.

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Table Captions

Table 4.1 The composition of pBSil and its composites with melamine-borate (MB) and/or organomodified sepiolite (OSEP).

Table 4.2 Characteristic TG data of polyorganosiloxane polymers and composites.

Table 4.3 The compositions of PP/pBSil–OSEP–MB in wt%.

Table 4.4 Combustion properties of PP/pBSil–OSEP–MB composites.

Figure Captions

Figure 4.1 TGA and DTA curves of polydimethylsiloxane (PDMS) and polyborosiloxane (pBSil) polymers and systems containing 5 wt% organomodified sepiolite (OSEP) and/or melamine-borate (MB) component under air atmosphere, with a heating rate of $10\text{ }^{\circ}\text{C m}^{-1}$.

Figure 4.2 Rate of heat release vs. time curves of PP/pBSil–OSEP–MB composites as the percentage of pBSil–OSEP–MB was varied from 0–55 wt% (see Table 4.3); irradiation heat flux: 50 kW m^{-2} .

Figure 4.3 Images of the combustion residue of (a) PP and of (b,c) PP/pBSil–OSEP–MB after treatment under cone heater (heat flux: 50 kW m^{-2}). Image (c) shows the non-carbonaceous, ceramified intumescent structure. (Reproduced with permission from ref. 3).

Figure 4.4 Heat release rate results of the reference polymer and the multilayer structure; irradiation heat flux: 50 kW m^{-2} .

Figure 4.5 Photo of water drop on (a) PP coated by pBSil–OSEP–MB material and (b) uncoated PP as reference. (Reproduced with permission from ref. 3).

Table 4.1

<i>Sample code</i>	<i>PDMS</i> <i>wt%</i>	<i>BA</i> <i>wt%</i>	<i>MB</i> <i>wt%</i>	<i>OSEP</i> <i>wt%</i>
PDMS	100	-	-	-
pBSil	90.9	9.1	-	-
pBSil-MB(5%)	86.4	8.6	5	-
pBSil-OSEP(5%)	86.4	8.6	-	5
pBSil-MB(5%)-OSEP(5%)	81.8	8.2	5	5

Table 4.2

<i>Sample</i>	<i>Temp for Mass Loss</i>		<i>Temp for maximal rate of mass loss</i>	<i>Residue at 550 °C</i>
	<i>[°C]</i>			
	<i>15%</i>	<i>50%</i>	<i>[°C]</i>	<i>[%]</i>
PDMS	398	542	509	48
pBSil	415	488	481	38
pBSil–OSEP	424	498	489	36
pBSil–MB	431	476	472	33
pBSil–MB(5%)–OSEP(5%)	421	477	475	30

Table 4.3

<i>Sample code</i>	<i>PP</i>	<i>pBSil-OSEP-MB</i>	<i>pBSil-OSEP-MB</i>		
			<i>pBSil</i>	<i>OSEP</i>	<i>MB</i>
NKMB060	0	100*	90	5	5
NKMB061	75	25	22.5	1.25	1.25
NKMB062	60	40	36	2	2
NKMB063	45	55	49.5	2.75	2.75
NKMB073	45	55*	49.5	2.75	2.75

* 0.5% peroxide content

Table 4.4

<i>Sample</i>	<i>TTI</i> [s]	<i>Pk. HRR</i> [kW m ⁻²]	<i>Pk. Time</i>	<i>THR</i> [MJ m ⁻²]	<i>Residue</i> [%]
PP	34	898	149	115.3	0
NKMB060	22	132	62	23.3	19.8
NKMB061	24	586	208	84.1	2.3
NKMB062	25	441	227	76.3	3.7
NKMB063	20	332	263	67.1	6.1
NKMB073	20	230	256	43.8	7.9

Figure 4.1

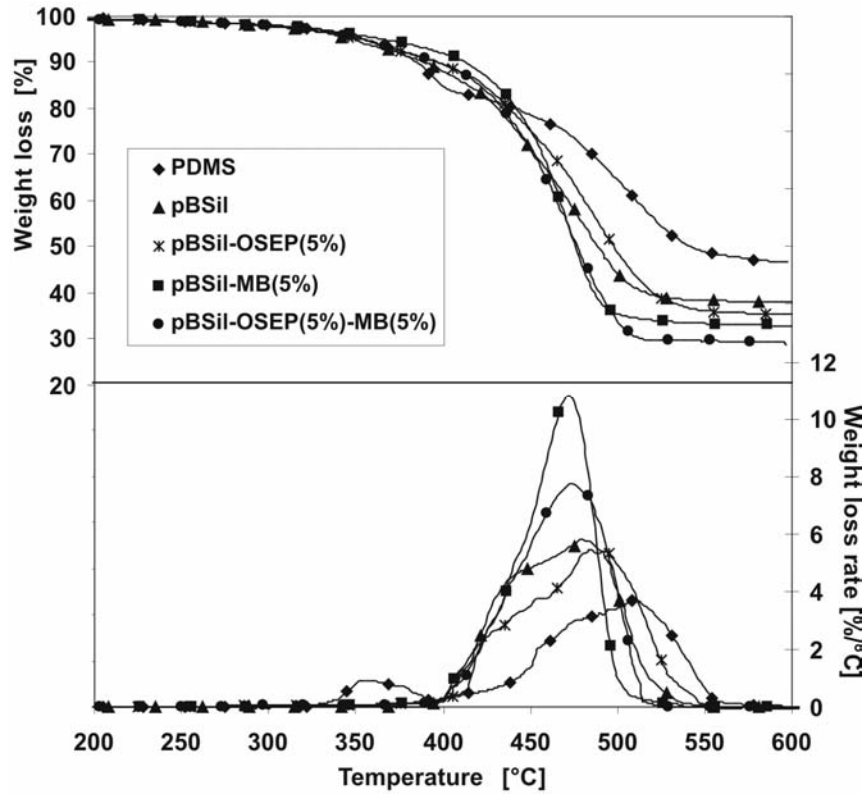


Figure 4.2

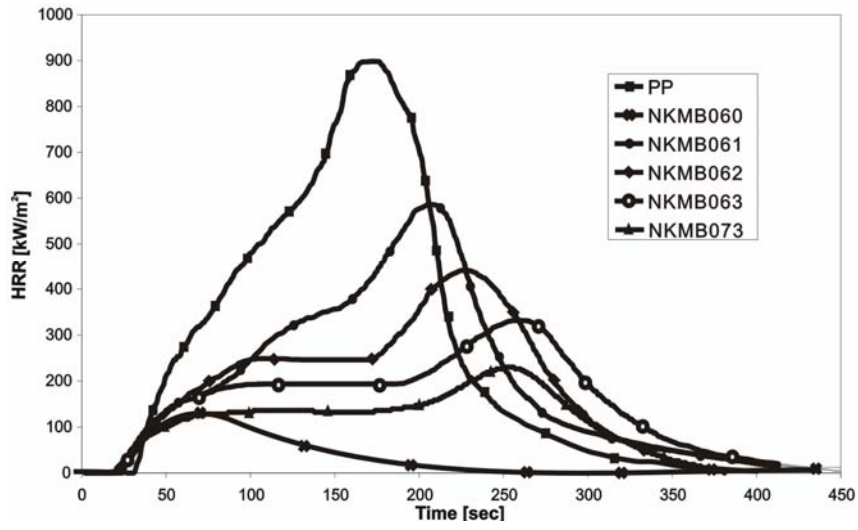
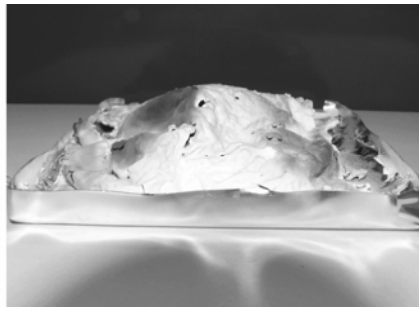


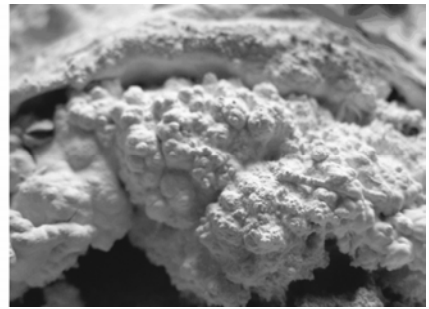
Figure 4.3



(a)



(b)



(c)

Figure 4.4

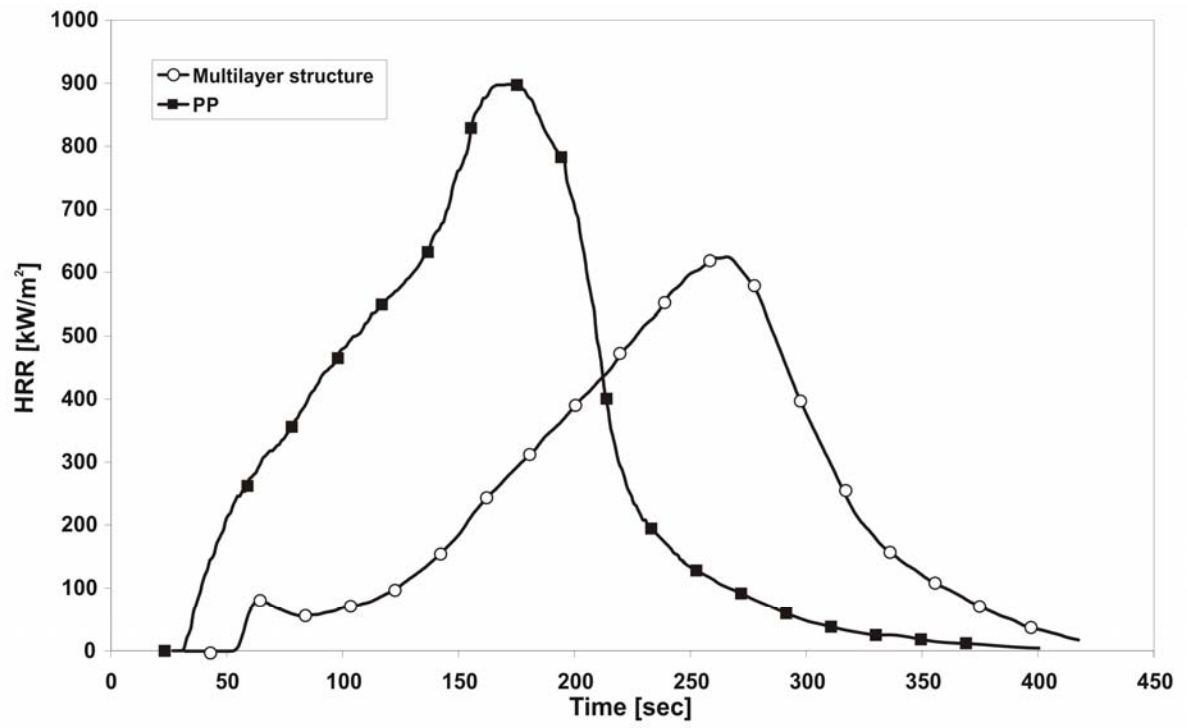
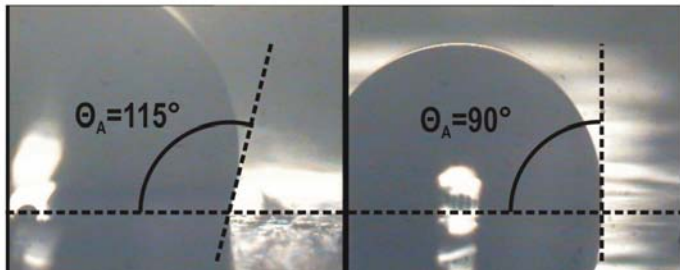


Figure 4.5



Abstract

In this work, polyborosiloxane composites were investigated as polymeric flame retardants for polyolefins. The polyborosiloxane (pBSil) produced by the reaction of boric acid with silanol-terminated polydimethylsiloxane shows increased thermal stability in the initial stage of the degradation. Needle-like clay sepiolite (OSEP) inorganic filler and melamine-borate (MB), when applied with pBSil, further improves its performance. The composites of pBSil, OSEP and MB exhibited flame retardant activity, without the presence of phosphorus or halogen atoms, either as additives in a polypropylene (PP) matrix or as a coating layer on PP.

The relationship between the amount of pBSil composite in the PP matrix and combustion characteristics was determined. Formation of a non-carbonaceous intumescent protective surface layer of white, ceramic structure was obtained after combustion of the PP/(pBSil–OSEP–MB) composite. This protective structure provides a positive impact on the shape and peak of heat release rate curves. The combustion and surface characteristics (wettability) of multilayer systems indicated that the pBSil surface layer may perform multifunctional roles acting not only as a flame retardant component but also as an adhesion modifying (dust/graffiti releasing, self-cleaning) layer.