Effect of phosphorous-containing modified poly(vinyl alcohol) on the mechanical and flame retardant properties of polypropylene

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Abstract. Blends of polypropylene (PP) and different phosphorous-modified poly(vinyl alcohol) (PVA) derivatives synthesized on purpose, were prepared by both solvent and melt mixing, and fully characterized. Thermogravimetric analysis showed that the addition of the phosphorous-modified PVAs significantly increased thermal stability and charring of PP, probably due to their dehydration and the subsequent formation of a protective layer onto PP. SEM analysis demonstrated poor phase compatibility between PP and the polymeric additives, however acceptable dispersion of the polymeric additives was obtained. It was also observed that grafting of the modified PVA on PP occurred due to radical reactions arising during melt processing. Mechanical characterization showed that the elastic behavior of the blends was not altered with respect to neat PP, while ductility was reduced; on the other hand, impact resistance was considerably improved by blending. Slightly higher LOI values were obtained for the blends even with phosphorous content as small as 1 wt%; reduced dripping was also observed during the burning tests for the blend samples. Moreover, cone calorimeter test results showed that heat release rate, total heat release, and fire growth rate decreased compared with PP, in particular for the blends containing residual –OH groups on the PVA backbone. Therefore, these blends can find application where the combination of toughness and fire retardancy is required, such as in the automotive industry.

Keywords: polymer blends and alloys, poly(vinyl alcohol), polypropylene, flame retardant polymers, material testing

1. Introduction

Polypropylene (PP) is one of the most widely used polymer because of its low cost, ease of processing as well as high water and chemical resistance. PP is used in several applications, for example housing, electronic pieces, wire and cables, automotive industry. However, it is inherently combustible [1–4], giving rise to problems such as evolution of smoke and toxic gases formed during combustion that are of particular concern among government regulatory bodies, consumers and manufacturers. A solution to

reduce PP flammability is to incorporate flame retardants (FR) in the polymer structure [5–7]. As well known in the literature, FR can be introduced in the polymer matrix through a chemical modification of polymer (reactive FR) or by blending (additive FR) [8–11]. Phosphorous-containing flame retardants are widely used since they are more environmentally friendly compared to halogen-based flame retardants. The phosphorous based FR may operate in the vapor phase, suppressing the combustion of the flammable mixture through a radical mechanism which

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interferes with the exothermic reactions. In the condensed phase, these FR can promote the formation of a charred layer on the polymer surface, which acts as a barrier against diffusion of volatile products as well as shielding the polymer surface from heat and air [3, 5, 6, 9].

Polymeric flame retardant additives are particularly interesting: the advantage of using them rather than conventional non-polymeric species is that they show better resistance to extraction, migration and volatilization due to their high molecular weight [12, 13]. In a previous paper, a set of polymers which showed promising action as flame retardant additives, obtained by chemically modifying poly(vinyl alcohol) (PVA) with 4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (BIC), was synthesized and characterized [14]. The choice of PVA as a starting preformed polymer was due to its high availability, low cost, and relatively high reactivity. Moreover, PVA is potentially able to form char due to the presence of free hydroxyl groups. On heating, they can undergo dehydration reactions giving rise to unsaturated materials, especially in presence of phosphorous-containing moieties which can act as a dehydration catalyst source [15]. The chemical structures of the prepared polymers are depicted in Figure 1. The choice of these structures was motivated by their expected different polarities, which could in turn confer different compatibility

properties on blending with commodity polymers. PVA main chain and BIC moieties are quite polar. On the other hand, grafting of less polar aliphatic and aromatic ester groups onto PVA backbone lead to polymers showing a wider range of polarity.

In this work we chose PP as a thermoplastic material to be flame-retarded on blending with the above mentioned PVA derivatives. To this aim, we prepared blends by mixing the polymeric additives with PP in a suitable solvent and studied their flame retardancy behavior by thermogravimetry (TG) and limiting oxygen index (LOI) techniques. After assessing the efficiency of the PVA derivatives as flame retardant melt mixed blends were also prepared. Molecular weight, compatibility and mechanical properties of the melt mixed blends were determined through gel permeation chromatography (GPC), differential scanning calorimetry (DSC), X-Ray diffraction (XRD), dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), impact and tensile tests. Finally, their flame retardancy properties were also assessed.

2. Experimental section

2.1. Materials

Moplen type polypropylene EP1X30F (MPP, containing 2 wt% ethylene, $M_w = 250\,000$ Da, melt flow at $230^\circ\text{C} = 7.00\text{--}10.0$ g/10 min) was provided by Montell (Italy). High molecular weight isotactic

Figure 1. Chemical structure of the synthesized polymers

Table 1. Degrees of modification and phosphorous content of the additives

Additive	P obtained from ICP-AES [wt%]	Degree of modification		
		x ^a	x ^b	y ^b
A1	11.5	0.52		
A2	8.0	0.23		
A1'	11.0	0.47		
A2'	9.3	0.32		
B	8.6		0.44	0.27
C	8.7		0.51	0.10

^aObtained from % P determined through ICP-AES^bObtained from ¹³C NMR

polypropylene (HIPP, $M_w = 580\,000$ Da; $T_{m\,onset} = 160\text{--}165^\circ\text{C}$) and all solvents were purchased from Sigma-Aldrich (Italy), and used as received. Polymeric flame retardant additives A1 and A2, used for the preparation of the solvent-assisted blends, were synthesized as previously described [14]. The additives A1', A2', B and C, used for the melt mixed blends, were prepared through the same procedure, but using a higher amount of reagents (5 g of PVA). The degrees of modification and phosphorous content of the additives, determined through inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ¹³C NMR, are listed in Table 1.

2.2. Blends preparation

2.2.1. Blends prepared by dissolution

4.5 g of HIPP and 1,1,2,2-tetrachloroethane (100 mL) were introduced in a round bottomed flask provided with magnetic stirrer. The mixture was heated under stirring up to 100°C to completely solubilise PP, then it was cooled down at 80°C , and the appropriate amount of selected additive was added. The mixture was further driven to reflux and stirred for two hours. Subsequently, the solvent was removed by rotary evaporation and the resulting material was dried under vacuum at 70°C for 1 h, then at room temperature for 24 h. In all cases, proper amounts of HIPP and polymeric additive were selected to prepare 5 g of blend. About 1 g of blend was pressed in a preheated press at 165°C and 2.5 atm for 1 hour in order to get bars ($70 \times 6 \times 3$ mm³). These processing conditions were chosen in order to avoid thermal

degradation of the additives. Table 2 lists the blends prepared in this way. These samples were characterized by means of TG and LOI measurements.

2.2.2. Blends prepared by melt mixing

Melt mixing was carried out in a Brabender Plasto-graph EC (Germany) twin screw mixer at 175°C with a screw rate of 40 rpm. Proper amounts of polypropylene (MPP) and polymeric additive were selected to prepare 50 g of blend. The flame retardant additives were added after the MPP melted, and the resulting blend was further mixed for 5 minutes. Then the material was removed, left to cool and cut in pellets. The pellets were hot-pressed using a Collin P200E bench top press, under a pressure of 100 bar at 165°C for 3 minutes, to obtain thin films (average thickness 150 μm), or at 175°C for 5 minutes, to obtain plates of 3 mm thickness. Thin films samples were used to perform Fourier transform infrared (FTIR) spectroscopy, TG, DSC, XRD and tensile tests, while the plates were cut in bars and used for DMTA, Charpy impact tests, cone calorimeter tests and LOI measurements. The blends prepared in this way are listed in Table 3.

2.3. Characterization techniques

Transmission FTIR analysis was performed using a Nicolet Nexus FTIR spectrophotometer (USA). Spectra were collected using 32 scans at 4 cm^{-1} resolution, in the $400\text{--}4000\text{ cm}^{-1}$ range.

The number-average (M_n), weight-average (M_w) molecular weights and intrinsic viscosities were estimated by GPC using a Waters Alliance GPC V2000 system (USA), equipped with refractive index and viscosimetric detectors, using two consecutive Polymer Laboratories (UK) mixed columns with 1,2-dichlorobenzene (DCB) at 145°C as eluent ($0.8\text{ mL}\cdot\text{min}^{-1}$). The equipment was calibrated with polystyrene standards.

LOI measurements were performed in triplicate in vertical tests on a Stanton Redcroft FTA (UK) flammability unit provided with an oxygen analyzer, previously calibrated with polystyrene standard

Table 2. Blends prepared by solvent dissolution

Blend	Additive	Additive content [wt%]	Phosphorous content [wt%]
Bl1	A1	8.6	1.0
Bl2	A1	4.3	0.5
Bl3	A2	6.2	0.5

Table 3. Blends prepared by melt mixing

Blend	Additive	Additive content [wt%]	Phosphorous content [wt%]
Bl4	A1'	9.0	1
Bl5	A2'	10.8	1
Bl6	B	11.6	1
Bl7	C	11.6	1

bars. The dimensions of the polymer bars prepared by hot pressing were $70 \times 6 \times 3 \text{ mm}^3$.

Cone calorimeter (CC) tests were performed in duplicate by a Fire Testing Technology (UK) cone calorimeter. The samples with the dimension of $60 \times 60 \times 3 \text{ mm}^3$ were exposed to a radiant cone at a heat flux of $35 \text{ kW} \cdot \text{m}^{-2}$.

TG analysis of blends prepared by dissolution was carried out on a Mettler TGA/SDTA851e/LF/1100 (Switzerland) device at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ up to 800°C under nitrogen atmosphere (flow rate = $100 \text{ mL} \cdot \text{min}^{-1}$). For the blends prepared by melt mixing, TG analysis was performed on a Perkin Elmer Pyris Diamond TG-DTA thermogravimetric analyzer (USA) under the same conditions, but in this case prior to the heating ramp the samples were subjected to a 30 minutes isotherm at 80°C to remove the moisture that could be absorbed after the melt processing. DSC analyses were performed on a Mettler Toledo DSC Star 822e (Switzerland) calorimeter at a heating/cooling rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in a nitrogen atmosphere. Melting temperatures and enthalpies were calculated from second heating scans. The crystallinity degree of MPP and its blends was calculated by using $\Delta H^\circ_{\text{melting}} = 209 \text{ J g}^{-1}$, reported as the melting enthalpy of 100% crystalline PP [16].

XRD experiments were performed using a Philips PW 1710 (Netherlands) diffractometer with a rotating anode generator and a wide-angle power goniometer. The used radiation was unfiltered $\text{Cu K}\alpha$, with 40 kV voltage and 20 mA intensity. The scan rate was $1^\circ \cdot \text{min}^{-1}$ over a diffraction angle 2θ ranging between 2 and 40° . The evaluation of the degree of crystallinity for each sample was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve. The separation of the crystalline peaks from the amorphous part was achieved by curve fitting using Gaussian functions by means of Origin 8.0 software.

A Perkin Elmer Pyris Diamond DMTA (USA) in the dual cantilever flexural mode was used to study the dynamic mechanical thermal behavior of the blends. Rectangular specimens 50 mm long, 10 mm wide, 3 mm thick were analyzed. The samples were conditioned in an environmental chamber at 25°C and 50% relative humidity (RH) for 7 days prior to testing. The tests were run at a heating rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ from -80 to 140°C under nitrogen. Oscillation frequency and amplitude were 1 Hz and $5 \mu\text{m}$, respectively. T_g was taken as the peak value of $\tan \delta$ curves.

Charpy impact tests were performed on a CEAST 6545 (Italy) apparatus according to ASTM standard test method D256-06. A standard notch (3.5 mm long) was applied to the rectangular shaped rod sample with dimensions of $60 \times 60 \times 3 \text{ mm}^3$. The notch was in the opposite direction to the striking hammer. A Philips XL20 (Netherlands) Scanning electron microscope (SEM) was used to examine the morphology of the cross-section of specimens subjected to impact tests. Samples were metallised before the observation with a gold–platinum mixture by means of a BalTec MED020 (UK) coater.

Tensile tests were performed on an Instron 5564 (USA) dynamometer equipped with a 100 N load cell on test specimens prepared according to ASTM D882-02 standard test method. The test samples were ‘dog-bone’ shaped 22 mm long, 4 mm wide. The thickness (0.1–0.2 mm) was measured at different points for each specimen and its average value was introduced in the Instron Merlin calculation software. The tests were performed using 5–8 specimens for each sample. The measurements were carried out at an elongation rate of $20 \text{ mm} \cdot \text{min}^{-1}$ at room temperature after the samples were conditioned for 24 hours at 50% RH.

3. Results and discussion

3.1. Characterization of the blends obtained by dissolution

As a preliminary study, we prepared blends of PP with flame retardant additives by solvent dissolution, using a polypropylene grade with high molecular weight and melting point (HIPP). The HIPP blends were prepared by dissolution in hot 1,1,2,2-tetrachloroethane (Table 2). Additive contents lower than 10 wt% were used, since higher amounts would have affected negatively the mechanical properties of PP. Therefore blends containing 1 or 0.5 wt% of phosphorous were prepared, to evaluate the effect of the additive amount on the flame retardancy of polypropylene.

The obtained blends were studied by TG and LOI techniques. The thermogravimetric curves under nitrogen are shown in Figure 2, and the relative data are listed in Table 4. From the figure, a slight weight loss was observed for the blends at about 250°C , associated to polymeric additives decomposition (mainly dehydration of the vinyl alcohol moieties). Moreover, in the blends the main weight loss process was significantly delayed ($>100^\circ\text{C}$), and a residual

Table 4. Thermogravimetric and LOI results of neat HIPP and its blends

Sample	Additive	Phosphorous content [wt%]	T _{onset} ^a [°C]	T _{max} ^b [°C]	Char yield at 600°C [%]	LOI [%]
HIPP			297	415		17.3±0.3
B11	A1	1.0	408	463	6.0	18.7±0.4
B12	A1	0.5	416	463	2.5	17.7±0.2
B13	A2	0.5	421	463	2.9	18.2±0.4

^aOnset temperature of the main weight loss process^bTemperature of the maximum rate of weight loss **Figure 2.** TG curves of neat HIPP and its blends in nitrogen atmosphere

char was formed at high temperature, while pure HIPP completely volatilized below 500°C. These results suggest that the additives can confer flame retardancy to PP. In this respect, A2 was likely more effective than A1, since B13 showed higher T_{onset} and char yield with respect to B12. This slightly higher effectiveness shown by A2 can be related with its larger hydroxyl content (see Table 1), if we reasonably assume that dehydration is the first step of the additives decomposition.

The results of LOI measurements are reported in Table 4. The LOI values of the blends were slightly higher than that of neat HIPP. Therefore, LOI data also confirmed that flame retardancy was conferred by A1 and A2 to HIPP. In particular, the highest LOI value was obtained for the blend containing the highest phosphorous amount (B11), while at low phosphorous content the LOI value was higher when the blend contained more hydroxyl groups (B13). This result was in agreement with TG data.

3.2. Chemical characterization of melt mixed blends

Once the effectiveness of the additives as flame retardants was assessed, the modified PVAs were blended to PP through melt mixing, which is a more

technologically feasible processing technique compared to solvent blending. For melt mixing, we selected a Moplen type polypropylene containing 2 wt% ethylene (MPP) as matrix. MPP had higher flexibility than HIPP, and Moplen type PPs have been used for different applications in automotive industry [17–20] MPP was blended with A1', A2', B and C at 175°C and 40 rpm for 5 min. For each blend, the amount of the polymeric additive was selected in order to get a phosphorous content of 1 wt%. In Table 3 the blends formulations are listed.

In order to probe the possibility that MPP or the polymeric additives partially degraded during the blending process, the obtained blends were characterized by FTIR and GPC. In general, FTIR spectra of the blends showed peaks due to MPP and the corresponding additive. The main MPP bands appeared at 3000–2850 cm^{-1} (C–H stretching) and 1500–1350 cm^{-1} (C–C stretching). All the blends showed signals due to the additives at 3600–3400 cm^{-1} (O–H), 1730 cm^{-1} (C=O) and 856 cm^{-1} (skeleton vibration of caged bicyclic phosphate). It should be noted that no additional bands appeared in the blends with respect to virgin MPP and additives. This suggests that degradation upon blending, if any, occurred to a low extent. As an example, Figure 3 shows the spectrum of virgin MPP, the polymeric additive B and the corresponding blend (B16).

GPC analysis was performed in DCB at 145°C. The obtained data are collected in Table 5. For the sake of comparison, GPC analysis was also performed on unprocessed MPP and on a MPP sample processed analogously to the blends.

The polydispersity (M_w/M_n) of the unprocessed MPP is rather high, typical of a PP synthesized in the presence of Ziegler-Natta catalysts [21]. As can be seen, molecular weights and polydispersity of processed MPP were lower than those of unprocessed polymer pellets. Thus, melt-mixing processing of neat MPP brought about slight degradation of the polymer. The decrease of polydispersity is consistent with ‘con-

Figure 3. FTIR spectrum of virgin MPP, the additive B, and the corresponding blend B16

trolled PP degradation' principles, where the highest molecular weight chains are statistically more likely to undergo radical-mediated scission [22]. Although the polymeric additives were rather insoluble in DCB, when they were incorporated into the blends a significant fraction turned to be dissolved

Table 5. GPC data of neat MPP and its blends

Sample	Additive	M_w^a [Da]	M_w/M_n^b	M_{peak}^c [Da]
Unprocessed MPP	—	254 000	6.8	159 000
Processed MPP	—	218 000	4.5	136 000
B14	A1'	218 000	4.8	139 000
B15	A2'	229 000	5.2	144 000
B16	B	235 000	4.8	145 000
B17	C	278 000	4.6	159 000

^aweight-average molecular weight

^bpolymer polydispersity

^cpeak of the GPC curve

in the solution subjected to GPC characterization. Nevertheless, as can be observed from Figure 4a and Table 5, the GPC curves of the blends were similar to that of neat processed MPP, leading to comparable M_w and polydispersity, and neither peaks related to the presence of the additive, nor bimodal patterns of the molecular-mass curves were observed. The blend B17 is an exception to this general behaviour, since its GPC chromatogram showed a minor portion of higher molecular weight chains. These findings suggest that the polymeric additives could interact with the polypropylene phase, forming physical or chemical associates having a slightly larger hydrodynamic volume than that of plain MPP, which were not separated during the elution run. This could also explain the increase in M_w observed for B17, in which the bulky pendant substituent can modify the size of the dissolved polymer adduct, thus yielding increased values of molecular weight [23].

A further confirmation of this hypothesis can be obtained by the Mark-Houwink-Sakurada (MHS) plots, Figure 4b, in which the intrinsic viscosity is plotted as a function of M_w . MHS plots are widely used for the analysis of polymer structure, as they reflect structural changes in the polymer, such as branching and chain rigidity [24]. The slope described by the Mark-Houwink exponent can vary between 0 for solid spheres and 2 for rod-shaped structures.

From the figure, it is observed that while all samples showed comparable curve slope values of about 0.71 (typical of linear flexible chains in good solvents), the processed MPP sample displayed higher values of viscosity throughout the range of

Figure 4. GPC chromatograms (a) and Mark-Houwink-Sakurada plots (b) of neat MPP and its blends

Figure 5. Scheme of the possible reactions involved in PVA grafting onto PP

M_w values analyzed. This suggests that polypropylene molecules in the blends present chain branching [25], due to the interaction of MPP with the modified PVAs. This can be due to some radical reactions that may occur between additives and matrix, as depicted in Figure 5. Usually, radical formation occurs in the presence of an initiator, identified as [In] in the figure [26, 27], which in this case may be represented by the metal particles of the equipments used for processing. Also, we should take into account that a small part of the PVAs additives may undergo dehydration reactions, leading to double bond formation, which can react with the polypropylene free radicals that could be formed during processing at high temperature.

3.3. Crystallinity of the melt mixed blends

In order to study the effect of the additives on the polypropylene crystallinity, DSC and XRD experiments were performed. The DSC thermograms of the processed MPP showed a melting endotherm spanning between 143 and 161°C. The DSC data of the blends revealed that the melting temperature of polypropylene was not apparently affected by the addition of the flame retardant additives (see Table 6), indicating the absence of interactions such as co-crystallization within the polypropylene phase [28], as well as poor compatibility of the flame retardants with polypropylene. Since the glass transition signal from DSC traces was rather weak and broad, the T_g s of the blends were determined through DMTA (see Section 3.4).

Melting enthalpy values were used to calculate the crystallinity of MPP and blends. As can be seen from Table 6, the degree of crystallinity of MPP remained unaltered after blending with the flame retardant additives, with the exception of the blend B16, for which a slight increase in crystallinity was observed.

From the X-ray diffractograms (Figure 6) can be observed that the monoclinic α form of PP was present in all samples, and no peaks associated with the hexagonal β form (usually detected at $2\theta = 16.1^\circ$) were visible [29]. This is in agreement with the observation that isotactic polypropylene prepared with the traditional heterogeneous Ziegler-Natta catalysts generally exist in the stable α form [30]. The degree of crystallinity for each sample was obtained also by XRD as detailed in the experimental part. In this approach, the amorphous contribution to the scattering was taken into account through a broad diffraction band. From Table 6, which shows the degrees of crystallinity obtained by XRD and DSC, it can be observed that the results obtained by the two techniques are comparable. Moreover, the blends did not present significant changes in comparison with virgin MPP, with the exception of B16, which contain the polymer B as an additive. The latter has a different chemical structure compared to

Figure 6. X-ray diffractograms of virgin MPP and its blends

Table 6. Melting temperatures and enthalpies, T_g and crystallinity degrees of MPP and its blends

Sample	T_{peak} [°C]	ΔH_1^a [J·g ⁻¹]	ΔH_2^b [J·g ⁻¹]	T_g^c [°C]	Crystallinity from DSC ^d [%]	Crystallinity from XRD [%]
MPP	154	83	83	-2.3	40	37
B14	153	73	80	-2.8	38	43
B15	154	70	78	-2.7	37	37
B16	154	81	89	0.1	43	46
B17	155	73	80	-5.6	39	41

^aMelting enthalpy per gram of blend

^bMelting enthalpy per gram of MPP

^cGlass transition temperature obtained from DMTA

^dCrystallinity degree obtained from ΔH_2

the other phosphorous containing additives. In fact, the presence of aliphatic butyl chains is able to increase the compatibility of the additive with the matrix, as also showed by SEM analysis (see Section 3.4). This entails that the additive particles can increase PP crystallinity acting as heterogeneous nucleating agents.

3.4. Dynamic mechanical thermal, morphological and mechanical properties

In order to get reliable T_g values for the MPP blends, DMTA measurements were carried out. The dynamic viscoelastic curves for the neat MPP and the blends with the modified PVAs are shown in Figure 7. All the storage modulus versus temperature curves experienced a gradual decline with temperature increasing from -80 to 130°C [31]. MPP exhibited two distinct relaxations peaks. The α -relaxation, at about 81°C , relates to slip mechanism of polymer chains in the crystallites [32]. The β -relaxation (-2.3°C) is assigned to the motion of the main chain in the amorphous regions, thus can be regarded as the glass transition temperature [33].

The $\tan\delta$ curves of the blends showed slight T_g value changes with respect to the parent polypropylene (Table 6). In particular, a small increase was ascribed to B16, while B17 displayed a slightly anticipated glass transition (peak at -5.6°C). The latter result suggests that in the B17 blend the segmental mobility in the amorphous phase was increased, due to the presence of polymer chains bearing bulky aromatic pendants, as already evidenced by the GPC analysis. On the other hand, the increase in T_g observed for B16 can be related to the increase in crystallinity of this sample, as detected through DSC and XRD analysis (see Section 3.3). It is expected that crystallization can impose constraints on chain

mobility, thus yielding increased values of glass transition temperature [34].

It is also worth noticing that in the case of B15, i.e. the blend containing the additive with the lowest degree of modification (see Table 1), a sharp peak in the mechanical loss spectrum was observed at about 80°C , accounting for the T_g of the unmodified PVA chain segments.

The morphology of neat MPP and its blends was evaluated by SEM observation of the fracture surfaces of samples subject to impact tests. The results are presented in Figure 8.

As can be observed, pure MPP presents a smooth and homogenous surface, evidencing a brittle fracture of the sample. Figure 8 b and 8d are similar to virgin MPP, however small, well dispersed additives particles covered by a layer of polypropylene matrix could be observed. In Figure 8c and 8e large additive particles are poorly dispersed within the MPP matrix, thus indicating a strong incompatibility between the polymers. In particular, several voids ascribed to removal of the additive due to the mechanical stress are present on the surface of B15. Therefore, it should be concluded that although all the blends are incompatible, the dispersion of polymeric additives is acceptable in B14 and B16, while severe incompatibility is observed for B15 and B17. It should be noted that, regarding the flame retardancy of a material in general, the low phase compatibility is not a drawback, yet it can negatively affect the mechanical properties of the final blend. However, from SEM analysis it is also evident that samples B15 and B17 show a more ductile fracture, as confirmed by the appearance of multiple fracture planes.

The mechanical properties of the blends prepared by melt mixing were characterized in order to evaluate the effect of the flame retardant additives, with a special view on the poor compatibility observed by SEM analysis. To this aim, tensile and impact tests were carried out on films and rod-shaped samples, respectively. Table 7 displays tensile modulus, yield stress, ultimate stress and elongation at break for all samples. It was observed that pure MPP was able to bear deformations up to 625%, showing typical behaviour of ductile polymers: stress whitening followed by necking and drawing. On the other hand, a brittle behaviour was observed for the blends, and the tensile specimens failed just after the linear elastic region of the stress–strain curves. Since GPC

Figure 7. Elastic modulus (E') and loss factor ($\tan\delta$) versus temperature for neat MPP and its blends obtained by melt mixing

Figure 8. SEM micrographs of the fracture surface of plain MPP (a) and its blends: B14 (b), B15 (c), B16 (d), and B17 (e)

Table 7. Mechanical tests results for MPP and its blends

Sample	Elastic modulus [MPa]	Yield stress [MPa]	Ultimate stress [MPa]	Elongation at break [%]	Resilience [$\text{kJ}\cdot\text{m}^{-2}$]
MPP	970±0.2	25±1.9	32±5.8	625±166.7	1.8±0.2
B14	1063±0.3	26±1.0	21±1.1	12±2.5	2.1±0.1
B15	1135±0.2	21±1.3	19±1.2	5±0.8	2.7±0.2
B16	1027±0.2	22±0.9	19±0.5	16±3.9	2.3±0.2
B17	1032±0.2	17±2.9	16±2.4	4±1.2	2.4±0.3

results showed that polypropylene molecular weight was not affected by the presence of the additives, this behaviour can be due to the poor interfacial interaction between matrix and flame retardant additives.

As shown by SEM observations, the flame retardant additives were not well blended, but only dispersed in the matrix. In such a case, strength and elongation at break for filled systems depend on the

state of the polymer-particle interface, since when the adhesion between filler and matrix is poor, a reduced stress transfer occurs at the interface, facilitating void opening and crack propagation [35, 36]. Regarding elastic modulus and yield stress, the values obtained for the blends did not vary significantly with respect to that of the starting MPP. In particular, all the blends showed a slight increase in modulus, suggesting that the additive particles can act as weakly reinforcing fillers, whereas yield stress decreased to some extent. On the other hand, the ultimate stress and the elongation at break noticeably decreased compared to the starting MPP. It can be mentioned that the blends B14 and B16 showed slightly better elongation at break with respect to the other blends, which is probably due to better compatibility between the corresponding additive and the matrix, as observed by SEM micrograph analysis. Therefore, tensile tests showed that the elastic behaviour was not altered by the addition of the flame retardants, whereas the plastic behaviour was changed significantly. It must be noted that in several applications where PP must be flame retarded, elastic and impact properties of the material are crucial, while the plastic behaviour is not [37, 38]. Actually PP-based blends are widely used in many cases where good resistance to physical impulsive shocks is needed. For example, in automotive industry PP-based blends are constituents of many items, such as bumpers, in which the impact resistance is very important. Thus, it is convenient to evaluate impact properties of the materials where high toughness is required. The toughness of the starting MPP and its blends is displayed in Table 7 in terms of impact resilience. All blends showed higher toughness compared to MPP and B15 and B17 showed the highest resilience values. This can be related to SEM observations, which showed a more ductile fracture even though poor compatibility was observed for these blends. As already mentioned for the tensile tests, these results can be explained by considering that the size of the stiff particles dispersed into the matrix is in the range of tenths of microns, which make the additive particles acting as fillers. This can confer greater toughness to the matrix even with poor filler-to-matrix interaction. In fact, the impact energy can be partially dissipated in a mechanism, where the crack advancement is hindered by the presence of the stiffer additive particles. Crack

deflection and twisting occur as a growing crack encounters the matrix-particle interfaces, which act primarily ahead of the crack tip to impede crack advance [39].

In summary, impact tests showed that the prepared blends can find application where toughness properties are required, while they increase slightly MPP flame retardancy, as it will be seen later.

3.5. Thermal and flammability properties of the melt mixed blends

Thermal stability and flame retardancy behaviour of the prepared melt mixed blends was characterized by TG analysis, LOI and cone calorimeter measurements.

Figure 9 shows the thermogravimetric curves of melt processed MPP and its blends in nitrogen atmosphere. From the curves it can be observed that neat MPP showed one weight loss step between 400 and 500°C, while all blends displayed an additional degradation step in the 200–300°C temperature range. This additional weight loss process has been attributed to the decomposition of the additives initiated by thermal dehydration reactions, as confirmed by massive water evolution detected through mass spectrometry [11].

This step appeared at a slightly lower temperature in B15 with respect to the other blends, probably due to its higher content of –OH groups. Table 8 shows the onset temperature of weight loss, the temperature of the maximum rate of weight loss for both steps, and the char yield at 600°C.

As can be seen in Figure 9 and Table 8, the second weight loss step of the blends, which is related to MPP degradation, was slightly delayed with respect to virgin MPP. Therefore, as it was observed for the blends obtained by dissolution, it is likely that the dehydration of additives led to a charred layer which

Figure 9. TG curves of MPP and its blends

Table 8. Thermogravimetric and LOI results of neat MPP and its blends

Sample	Additive	Step 1		Step 2		Char yield at 600°C [%]	LOI [%]
		T _{onset} [°C]	T _{max} [°C]	T _{onset} [°C]	T _{max} [°C]		
MPP				403	460	–	17.2±0.3
B14	A1'	237	246	432	480	4.2	19.4±0.2
B15	A2'	225	240	429	481	9.3	19.2±0.4
B16	B	236	249	431	481	0.9	19.0±0.4
B17	C	233	249	432	483	3.5	18.8±0.5

can protect polypropylene from degradation. From this point of view, no differences can be observed between the different additives used.

At the end of the second degradation step, neat MPP completely volatilized at 500°C, whereas the blends yielded a residue at 600°C. The highest amount of residue was associated to B15, as higher content of –OH groups favoured charring. B16 showed a lower char yield, probably due to the aliphatic nature of the side groups introduced. Therefore, as already discussed for the blends prepared by dissolution, the polymeric additives can confer flame retardancy also to the melt mixed blends.

As can be seen in Table 8, even with a small content of phosphorous (1 wt%), LOI values increased to some extent in comparison with the plain polypropylene. Reduced dripping was also observed during the burning tests for the additivated samples. Thus, LOI values confirmed that the additives A1', A2', B and C are able to increase MPP flame retardancy in the melt mixed blends.

Cone calorimeter (CC) test is an effective method to study the flammability of materials. To further investigate the effect of the phosphorous modified PVAs on the flame behavior of PP, CC tests were performed using a heat flux of 35 kW·m⁻². The heat release rate (HRR) and the mass loss curves of MPP

and the blends are shown in Figure 10, while the relevant data obtained from CC measurements are listed in Table 9.

It was observed that the peak of heat release rate (PHRR) for neat PP was 1109.1 kW·m⁻², and its total heat release (THR) was 100.7 MJ·m⁻². All the blends showed reduced values of both HRR and THR compared to MPP. In particular, B15 displayed a PHRR value about 25% lower than MPP, while a 24% decrease of the THR was measured for B14. These results suggest that the presence of phosphorous atoms associated with higher amounts of –OH groups increased the flame retardant properties of the blends. Based on the HRR curves, the fire growth rate (FGR) was calculated as the PHRR to PHRR_i ratio [40, 41], to assess the fire hazard of the samples. In general, lower FGR values indicate that the time to flashover is delayed, then more time is allowed for people to escape fire. Slightly lower values of FGR were associated to the presence of the modified PVAs, and B15 showed a value of 5.29 kW·m⁻² s⁻¹, which represented a decrease of about 25% with respect to MPP. These results further demonstrated that blending polypropylene of PP with the phosphorous-modified PVA derivatives reduced the FGR of the blends provided that a significant number of free –OH groups is present. On the other hand,

Figure 10. Heat release rate (a) and mass loss (b) curves of neat MPP and its blends obtained from cone calorimeter tests

Table 9. Cone calorimeter data of neat PP and its blends

Sample	TTI ^a [s]	PHRR ^b [kW·m ⁻²]	PHRR _t ^c [s]	THR ^d [MJ·m ⁻²]	FGR ^e [kW·m ⁻² ·s ⁻¹]	Average SPR ^f [m ² ·s ⁻¹]	Char residue [wt%]
MPP	48±3	1109.1±74.2	160±2	100.7±1.8	6.93±0.4	0.019±0.001	not data
B14	24±1	862.8±31.2	130±28	78.4±7.1	6.64±1.1	0.021±0.003	2.3±0.3
B15	29±3	841.0±105.4	159±25	94.9±3.4	5.29±1.6	0.022±0.001	3.7±0.2
B16	24±1	927.9±19.5	163±3	97.6±1.3	5.69±0.1	0.022±0.002	3.2±0.2
B17	25±1	904.3±50.1	139±23	92.4±6.5	6.51±1.2	0.021±0.002	3.1±0.4

^atime to ignition^bpeak of the heat release rate curve^ctime to peak of the heat release rate curve^dtotal heat release^efire growth rate^faverage smoke production rate

slightly increased values of the averaged smoke production rate (SPR) indicated that the additives can promote smoke release to some extent. As a final remark, it was observed that the residue after combustion increased for all the blends in comparison with MPP, demonstrating that the additives can enhance the stability of the residue also in presence of oxygen.

4. Conclusions

The results obtained on the flammability behavior of polypropylene through the use of purposely synthesized phosphorous-containing polyvinyl alcohol polymers are reported. The characterization of blends of polypropylene and different phosphorous-modified PVA derivatives bearing aliphatic (valeroyl group) or aromatic (benzoyl group) substituents showed that phase compatibility depended on the kind of substituting groups on the PVA backbone. It was also observed that grafting of the modified PVA on MPP may occur due to radical reactions arising during melt processing. TG, cone calorimeter and LOI measurements demonstrated that thermal stability and flame retardancy of the blends was improved, confirming that the phosphate moieties can act as carbonization promoters, in particular when a suitable amount of free hydroxyl groups is present. Tensile tests demonstrated that the elastic properties of the starting MPP were slightly influenced, while plastic behaviour was negatively affected. Impact test showed that the toughness of the blends was higher than that of pure MPP, likely due to a crack deflection and twisting mechanism.

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