

## Innovative Films with Tunable Permeability for Fresh Vegetable Packaging Applications

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**ABSTRACT:** Blends of a commercial polypropylene (PP), typically used as food contact material, with increasing amounts of poly(4-methyl-1-pentene) (PMP) are prepared in a twin-screw extruder to obtain thin films with improved gas permeation for fresh vegetable packaging. Permeability, haze, and transparency of monolayer films produced by casting are investigated under conditions mimicking the industrial ones. O<sub>2</sub> and CO<sub>2</sub> permeability can be tuned by increasing PMP content in the blends from 5 to 20 wt %. Transparency and haze are practically unchanged in the presence of low content of PMP. Moreover, tensile and rheological tests show that PMP does not significantly affect the related properties of blends compared to the neat PP matrix, thus allowing for the industrial applicability of these new formulations. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39503.

**KEYWORDS:** blends; extrusion; films; gas permeation; poly(propylene) (PP)

Received 28 August 2012; accepted 4 May 2013

DOI: 10.1002/app.39503

### INTRODUCTION

Minimally processed raw fruits and vegetables (MPRFVs) represent a rapidly growing segment of the fresh product industry with multi-billion dollar annual sales and an even faster increase in the market share expected within the next few years.<sup>1–3</sup> The peculiar characteristic of minimally processed vegetables is that, even after harvesting and processing, their tissues still stay alive, therefore continuing their metabolic functions, such as respiration, transpiration, and enzymatic activity. Nevertheless, their shelf-life is limited to a few days; as a consequence, these products present specific packaging requirements to preserve the combination of fresh-like quality and nutritional properties.<sup>1–10</sup>

Polyolefins, which are the most frequently used plastics as food contact materials,<sup>5,6,9–11</sup> are hardly enough permeable to gases and vapors<sup>12,13</sup> to well match with the respiration rate of fresh fruits and vegetables. Indeed, most polyolefin-based packages do not guarantee an optimal O<sub>2</sub> and CO<sub>2</sub> internal atmosphere, especially when the products have a high respiration rate.<sup>4,7,14</sup>

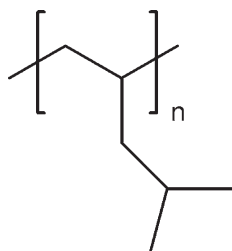
Three routes have been mainly followed to develop polyolefin-based packaging materials for respiring products: (i) films containing proper additives;<sup>1,15–17</sup> (ii) microperforated films;<sup>1,18,19</sup> and (iii) the use of modified atmosphere packaging (MAP).<sup>1,3,7,8,14,18,20</sup>

In the first route, the polymer matrices are mixed with an inert inorganic material, such as CaCO<sub>3</sub> and SiO<sub>2</sub>, to generate micro-porous films. The gas permeabilities can be tuned by adjusting filler content and particle size, as well as degree of film stretching. The average pore size usually obtained ranges from 0.1 to 1.5 μm.

In the second case, films with very high rates of gas transmission are attained through microperforation methods. The diameter of the micropores generally ranges from 40 to 200 μm and, by altering size and thickness of the microperforating needles, gas permeability can be tuned to meet well defined product requirements.

Such packaging solutions can provide the needed permeability properties and are thus widely used. However, they have the disadvantage of a certain degree of production complexity, often augmented by the necessity of multilayer co-extrusion to match the required material properties.

The third solution to extend the shelf-life of breathing fresh-cut produces consists in modifying the atmosphere inside the package; in MAP systems, usually the O<sub>2</sub> level is kept low in order to reduce the undesired oxidative reactions and the growth of aerobic micro-organisms. Passive MAP, being based only on the type of package material, requires a careful selection of films



**Figure 1.** Chemical structure of poly(4-methyl-1-pentene) (PMP).

with suitable gas permeability and selectivity to obtain optimal  $O_2$  and  $CO_2$  concentrations for a particular product. In active MAP systems gas-scavengers or emitters are intentionally added into the polymeric packaging film or within the food container to control the level of  $O_2$ ,  $CO_2$ , ethylene, etc. in the headspace atmosphere.

All the above-mentioned packaging materials may be not easy to recycle and/or to destroy at their life-end or, in the case of microperforation, they do not guarantee the hygienic conditions of the packed food items. Furthermore, in the case of MAP, sometimes, especially for fresh products with high respiration rate, the  $O_2$  level in the package may be too low (or  $CO_2$  level too high) thus inducing fermentative metabolism with possible growth of pathogenic micro-organisms.

In this study, we explore a further route: the possibility of improving the gas permeation performances of monolayer films, particularly intended for packaging of breathing fresh cut vegetables, through melt blending of properly selected commercial polyolefin grades. Indeed, melt blending<sup>21–23</sup> is a quite simple and costly effective technology; moreover, monolayer films based on blends are attractive alternatives to multilayer co-extruded films, also used to match the permeability requirements in food packaging applications.<sup>17,24,25</sup> A similar approach has been already exploited by us in a previous work, in which melt blending of a low density polyethylene matrix with an ethylene/norbornene copolymer endowed with high barrier properties resulted in monolayer films with reduced permeability to gases.<sup>26</sup>

On the other hand, blending a commercial polyolefin, commonly used for packaging applications, and a thermoplastic characterized by a very high permeability is expected to improve the permeability to gases and vapors of the ensuing blends with respect to that of the polyolefin matrix.<sup>27–29</sup>

Here, in order to endow polypropylene (PP) films with higher permeability, a commercial poly(4-methyl-1-pentene)-based material (PMP) was chosen.<sup>30</sup> In fact, isotactic PMP, first described by Natta et al.,<sup>31,32</sup> displays a unique combination of physical properties due to its distinctive molecular structure (Figure 1), characterized by the bulky *iso*-butyl side branches.

PMP provides the lowest density (*ca.*  $830 \text{ kg m}^{-3}$ ) among all thermoplastic resins,<sup>30</sup> i.e., it offers the largest specific volume. As a consequence, PMP has a very high gas permeability (its  $O_2$  permeability is one order of magnitude higher than that of polyethylene or polypropylene common grades);<sup>30,33</sup> this makes PMP an excellent material for gas separating applications, like permeable films, membranes and hollow fibres.<sup>34–38</sup>

The possibility of tuning the gas permeation properties of flexible films based on a cheap PP matrix by varying PMP content in melt-extruded blends was thus investigated. The selection of proper processing conditions for the production of blends and films required a preliminary study of molecular, thermal, and rheological characteristics of the starting materials that were correlated with the corresponding parameters of the resultant blends and combined to phase morphology investigations on both blends and films. Permeation and optical properties as well as mechanical behavior were evaluated on the film samples in order to compare the properties of the different blends with those of the neat PP matrix. In view of application in industrial processes, the performances of films containing commonly used processing aids were compared to those of a commercial film grade destined to packaging of fresh cut vegetables.

## EXPERIMENTAL

### Materials

A random propylene-based copolymer, MOPLEN RP340H (PP,  $d = 0.900 \text{ g cm}^{-3}$ ,  $MFR = 1.8 \text{ g (10 min)}^{-1}$  at  $230^\circ\text{C}/2.16 \text{ kg}$ ), kindly supplied by Lyondellbasell Industries S.r.l. (Italy), was used as matrix.<sup>39</sup> This PP grade exhibits excellent clarity, proper mechanical properties, and is suitable for food-contact applications. A poly(4-methyl-1-pentene)-based thermoplastic with the trade name of TPX MX004® (PMP,  $d = 0.834 \text{ g cm}^{-3}$ ,  $MFR = 25 \text{ g (10 min)}^{-1}$  at  $260^\circ\text{C}/5.0 \text{ kg}$ ), which was supplied by Mitsui & Co. Italia S.p.A. (Italy), was used as second component. In some cases, the prepared blends were added with proper amounts of an antifog additive (AF, a polyethylene-based masterbatch containing 27 wt % of glycerol monooleate) and/or a slip agent (SA, a polyethylene-based masterbatch containing 2 wt % of erucamide), both of them kindly supplied by I.T.P. S.p.A. (Italy).

### Preparation of Blends

PP/PMP blends with different compositions (from 5 up to 20 wt %) were prepared in a lab-scale twin-screw extruder (Brabender DSE 20, diameter = 20 mm, L/D = 40). After some preliminary extrusion tests, the following conditions were used: temperature profile = 130, 190, 220, 230, and  $230^\circ\text{C}$ ; die temperature =  $240^\circ\text{C}$ ; screw speed = 150 rpm. Some PP/PMP blends containing also proper amounts of the above-mentioned antifog and slip aids were prepared in the same conditions for comparison purposes with commercial films. Specifically, 3 wt % of the masterbatch containing the SA and 5 wt % of that containing the AF were added, separately or together (the percentages are referred to the whole blend).

### Molecular Characterization

Molecular masses and molecular mass distribution ( $M_w/M_n$ ) of starting materials and their blends were determined by gel permeation chromatography (GPC) using a high temperature (GPC-HT) Waters 2000 instrument equipped with two on-line detectors: a differential viscometer and a differential refractometer. The samples were dissolved in *o*-dichlorobenzene and the measurements carried out at  $145^\circ\text{C}$  with a flow rate of  $0.8 \text{ mL min}^{-1}$ . The GPC columns (3 PL Gel Olexis) were calibrated with narrow polydispersity polystyrene standards. The calibration curve obtained from polystyrene was converted to

polypropylene by using the Mark–Houwink constants for polypropylene.

### Thermal Characterization

Thermal properties of PP, PMP, and their blends were investigated by differential scanning calorimetry (DSC) carried out with a Mettler–Toledo DSC 821<sup>e</sup> instrument. Measurements were performed under nitrogen atmosphere (flow rate 40 mL min<sup>-1</sup>) at scan rates of 20°C min<sup>-1</sup>. To delete any previous thermal history, all samples were heated well above their melting temperature that is up to 180°C for the neat PP matrix and up to 260°C for the neat PMP and the PP/PMP blends. During the subsequent cooling, crystallization temperature ( $T_c$ ), and corresponding enthalpy ( $\Delta H_c$ ) were determined. Another heating run allowed measuring glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and corresponding enthalpy ( $\Delta H_m$ ).

### Rheological Characterization

The rheological parameters were determined on a Rheometric AR2000 rotational rheometer (TA Instruments) equipped with an aluminium plate-and-plate fixture and a melt transducer. The rheological measurements were conducted on disks of 25 mm diameter and 1 mm thickness obtained by compression molding in a laboratory press. Parallel plate geometry (25 mm diameter and 500  $\mu\text{m}$  gap) was used for rheological experiments carried out at 250°C. Measurements (frequency sweep from high to low frequency) were performed under nitrogen in oscillatory mode at 10% strain level, which was determined to be in the linear viscoelastic region, in the frequency range 630–0.05 rad s<sup>-1</sup>.

### Film Production

Film production was set up on a laboratory scale, using a cast film extrusion system constituted by a single-screw extruder (Brabender 19/25/D, diameter = 19 mm, L/D = 25) equipped with an UNIX take-off unit. Films of typical commercial thickness (70 or 45  $\mu\text{m}$ ) and 10 cm wide were produced. After some preliminary tests, operating conditions were chosen as follows: cylinder temperature = 250°C; die temperature = 260°C; screw speed = 40 rpm; chill roll temperature = 32°C; take-off speed = 2.6–3.0 m min<sup>-1</sup>.

### Morphological Analysis

The morphology of pellets and films was observed by using a Jeol JSM-6380LV scanning electron microscope (SEM) operating at 20 kV accelerating voltage. The observations were carried out on the fracture surfaces of the specimens, in the transverse direction. Both pellet and film samples were fractured in liquid nitrogen. The surfaces were gold-coated by using a sputtering coating unit model AGAR PS3.

### Optical Properties

The haze and transparency of the films were determined by using a Gardner Haze Gard-Plus instrument. The haze and luminous transmittance were measured according to ASTM D1003.

The UV spectra (200–400 nm) of the thinner films (45  $\mu\text{m}$  thick) were recorded with a Varian Cary 400 BIO spectrophotometer.

### Antifog Tests

The antifog efficiency of the films was evaluated through the cold fog test, also commonly called “beaker test” and used for

transparent polymer films. Water (200 mL) at room temperature was poured into a 250 mL beaker, which was then covered with the polyolefin film to be tested, taking care that the film was tightly closed on the glass, and kept at 4°C for 2 h. The antifog property of the film was evaluated by a visual comparison with five different possible situations represented by reference images corresponding to the following test standard levels: A very poor; B poor; C poor; D good; E excellent. Level E corresponds to the absence of visible drops and complete visibility through the analyzed film.

### Coefficient of Friction

The measurements of the film to film kinetic coefficient of friction (COF) were performed according to the ASTM D1894 for plastic films and sheetings. A flat sled of specific weight (200 g) completely covered with the film to be analyzed was moved on a plane covered as well with another portion of the same film sample. The sled was moved with a constant speed of 150 mm min<sup>-1</sup>, and the resistance to the relative motion between the two bodies in contact was determined. Kinetic COF is defined as the ratio of the force required to move one surface over another to the total force applied normal to those surfaces.

### Mechanical Properties

Uniaxial tensile properties of films (70  $\mu\text{m}$  thick) were determined on a Zwick/Roell Z10 dynamometer according to the ASTM D882. The tests were carried out at 23°C with an initial speed of 10 mm min<sup>-1</sup> and a subsequent crosshead speed of 500 mm min<sup>-1</sup>. Tensile modulus, stress and strain at yield, and strain at break, were evaluated for neat PP matrix and blends. Mechanical parameters were measured on several identical specimens of known thickness and the average values are reported.

### Permeability Tests

Permeability of film specimens with respect to O<sub>2</sub> ( $P_{O_2}$ ) and CO<sub>2</sub> ( $P_{CO_2}$ ) was measured at 23°C and 0% delta relative humidity (RH). In particular, a MOCON OXTRAN 2/20 instrument was used for  $P_{O_2}$  measurements according to ASTM D3985 (the analyzed area was reduced by working with a mask frame); whereas, the evaluation of  $P_{CO_2}$  was performed with a MOCON PERMATRAN C4/41 instrument according to ASTM D2476. Water vapor transmission rate (WVTR) was measured at 38°C and 90% delta RH according to ASTM F1249 by using the same MOCON PERMATRAN C4/41 instrument. For each film measurements were carried out on several specimens and the average values are reported.

## RESULTS AND DISCUSSION

### Blends Preparation and Characterization

A commercial polypropylene grade (PP), commonly used for food packaging applications, and a commercial poly(4-methyl-1-pentene)-based material (PMP), characterized by very high gas permeability values and excellent optical properties,<sup>30</sup> were melt blended by using a lab-scale twin-screw extruder. PP/PMP blends at three different compositions (95/5, 90/10, and 80/20 wt/wt) were prepared in order to improve the gas permeation

**Table I.** Molecular Parameters of PP and PMP Starting Materials and PP/PMP Blends

Sample	$M_w^a$ (kDa)	$M_n^a$ (kDa)	$M_w/M_n$
PP	386	110	3.5
PP/PMP 95/5	393	109	3.6
PP/PMP 90/10	383	110	3.5
PP/PMP 80/20	392	110	3.5
PMP	469	119	3.9

<sup>a</sup>Measured by GPC.

properties of films destined to flexible packaging of fresh vegetable products.

Table I reports the molecular characterization of starting materials and blends. Very similar molecular parameters were observed for the various samples. In particular, the presence of PMP as minor component of the blends does not appreciably affect the molecular weight and its distribution with respect to the neat PP matrix. Moreover, the GPC analysis shows no evidence of thermomechanical degradation which might occur during material processing.

The thermal characterization of the PP/PMP blends was performed by differential scanning calorimetry (DSC), as described in the experimental section, and the obtained thermal parameters are collected in Table II; data related to the two single components are reported as well for the sake of comparison. This study showed that the presence of the minor component PMP does not appreciably affect the characteristic transitions of the PP matrix. In fact, the DSC thermograms of the blends (not shown) evidenced the presence of two distinct melting ( $T_{m1}$  and  $T_{m2}$ ) and crystallization ( $T_{c1}$  and  $T_{c2}$ ) temperatures, corresponding to the transition temperatures of the single polymeric components. This behavior suggests an almost complete immiscibility of the two components in the molten state.<sup>40</sup>

By taking into account the heat of fusion of the single PP<sup>41–44</sup> and PMP<sup>45,46</sup> component perfect crystals and a 5–10% error which normally affects DSC measurements, the enthalpy values reported in Table II indicate that the actual degree of crystallinity keeps practically unchanged at about 35% for all the investigated samples. This means that the film permeability mainly depends on the PMP content.

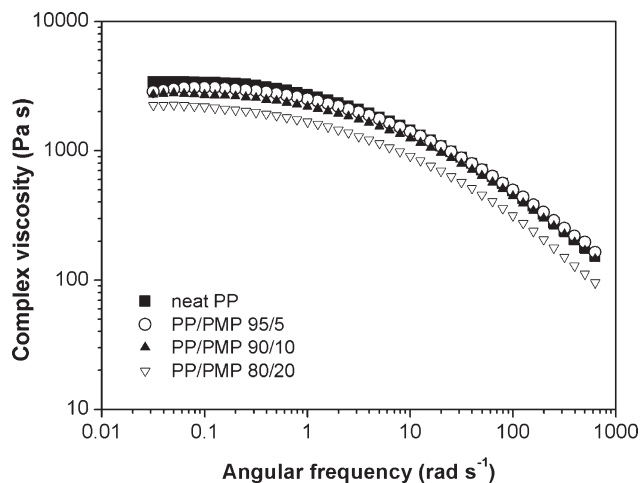
**Table II.** DSC Thermal Characteristics of PP and PMP Starting Materials and PP/PMP Blends

Sample	$T_g^a$ (°C)	$T_m^a$ (°C)		$\Delta H_m^a$ (J g <sup>-1</sup> )		$T_c$ (°C)		$\Delta H_c$ (J g <sup>-1</sup> )	
		$T_{m1}$	$T_{m2}$	$\Delta H_1$	$\Delta H_2$	$T_{c1}$	$T_{c2}$	$\Delta H_1$	$\Delta H_2$
PP	n.d. <sup>b</sup>	148	-	82	-	115	-	83	-
PP/PMP 95/5	n.d. <sup>b</sup>	147	~226	85	n.e. <sup>c</sup>	111	n.d. <sup>b</sup>	80	n.d. <sup>b</sup>
PP/PMP 90/10	n.d. <sup>b</sup>	147	227	76	2	113	~207	76	n.e. <sup>c</sup>
PP/PMP 80/20	n.d. <sup>b</sup>	146	228	67	5	112	210	64	3
PMP	23	-	229	-	30	-	206	-	31

<sup>a</sup>Measured on second heating.

<sup>b</sup>n.d. = not detectable.

<sup>c</sup>n.e. = not evaluated.

**Figure 2.** Complex viscosity versus angular frequency at 250°C of neat PP and PP/PMP blends.

In general, for a biphasic system in the molten state, a homogeneous and uniform distribution of the added phase within the matrix can be achieved when distributive–dispersive mixing is attained. Indeed, the high shear stresses obtained by using a twin-screw extruder can easily guarantee an effective mixing. At this regard, preliminary rheological analyses in dynamic mode were performed on neat PP and PMP components. The complex viscosity curves of the neat PP matrix and of the blends as a function of frequencies are shown in Figure 2. The different blends show a very similar behavior among them and, with respect to the PP matrix, only a slight decrease of complex viscosity values with increasing PMP content is observed. These results confirm the immiscibility of the two components and put into evidence that the presence of PMP does not appreciably influence the rheological properties of the PP matrix, especially for PMP content up to 10 wt %. Therefore, it can be expected that the processing parameters normally adopted for commonly used PP grades could be adequately used also for their blends with PMP.

The gathered evidences of substantial immiscibility of the PP and PMP polymer pair find justification on the base of their solubility parameters. The Hildebrand solubility parameter ( $\delta$ )<sup>47</sup> can be used to estimate binary interaction energies between two substances, thus being a good indicator of solubility, especially

**Table III.** Mechanical Tensile Parameters of Neat PP and PP/PMP Films 70  $\mu\text{m}$  Thick

Sample	$E$ (MPa)	$\sigma_y$ (MPa)	$\epsilon_y$ (%)	$\epsilon_b$ (%)
PP	$1230 \pm 65$	$23 \pm 1$	$8 \pm 0.2$	$300 \pm 30$
PP/PMP 95/5	$1230 \pm 110$	$22 \pm 2$	$8 \pm 0.2$	$325 \pm 29$
PP/PMP 90/10	$1290 \pm 78$	$23 \pm 1$	$7 \pm 0.3$	$305 \pm 19$
PP/PMP 80/20	$1290 \pm 62$	$21 \pm 1$	$7 \pm 0.1$	$271 \pm 20$

for non-polar materials, such as many polymers. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (E_{\text{COH}}/V_m)^{1/2} \quad (1)$$

where  $E_{\text{COH}}$  is the cohesive energy and  $V_m$  the molar volume of a given substance. More the  $\delta$  values of two substances are similar and more these latter are compatible/soluble.

The solubility parameter values available in the literature for polypropylene<sup>48</sup> are in the range from 7.9 to 9.4  $\text{cal}^{1/2} \text{cm}^{3/2}$ , even though an approximate value of 8.2  $\text{cal}^{1/2} \text{cm}^{3/2}$  seems to be the most realistic one. For poly(4-methyl-1-pentene) literature data<sup>49–51</sup> range from 7.4 to 8.0  $\text{cal}^{1/2} \text{cm}^{3/2}$ .

To estimate the miscibility of a polymer pair also the Flory–Huggins<sup>52,53</sup> interaction parameter  $B$ , that is the binary interaction energy density, which appears in the following expression of the Gibbs free energy of mixing, can be used.

$$\Delta G_{\text{mix}} = B\phi_1\phi_2 + RT[(\rho_1\phi_1 \ln \phi_1)/M_1 + (\rho_2\phi_2 \ln \phi_2)/M_2] \quad (2)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\rho_1$ ,  $\phi_1$ ,  $M_1$ , and  $\rho_2$ ,  $\phi_2$ ,  $M_2$  are the density, volume fraction, and molecular weight of polymer 1 and 2, respectively.

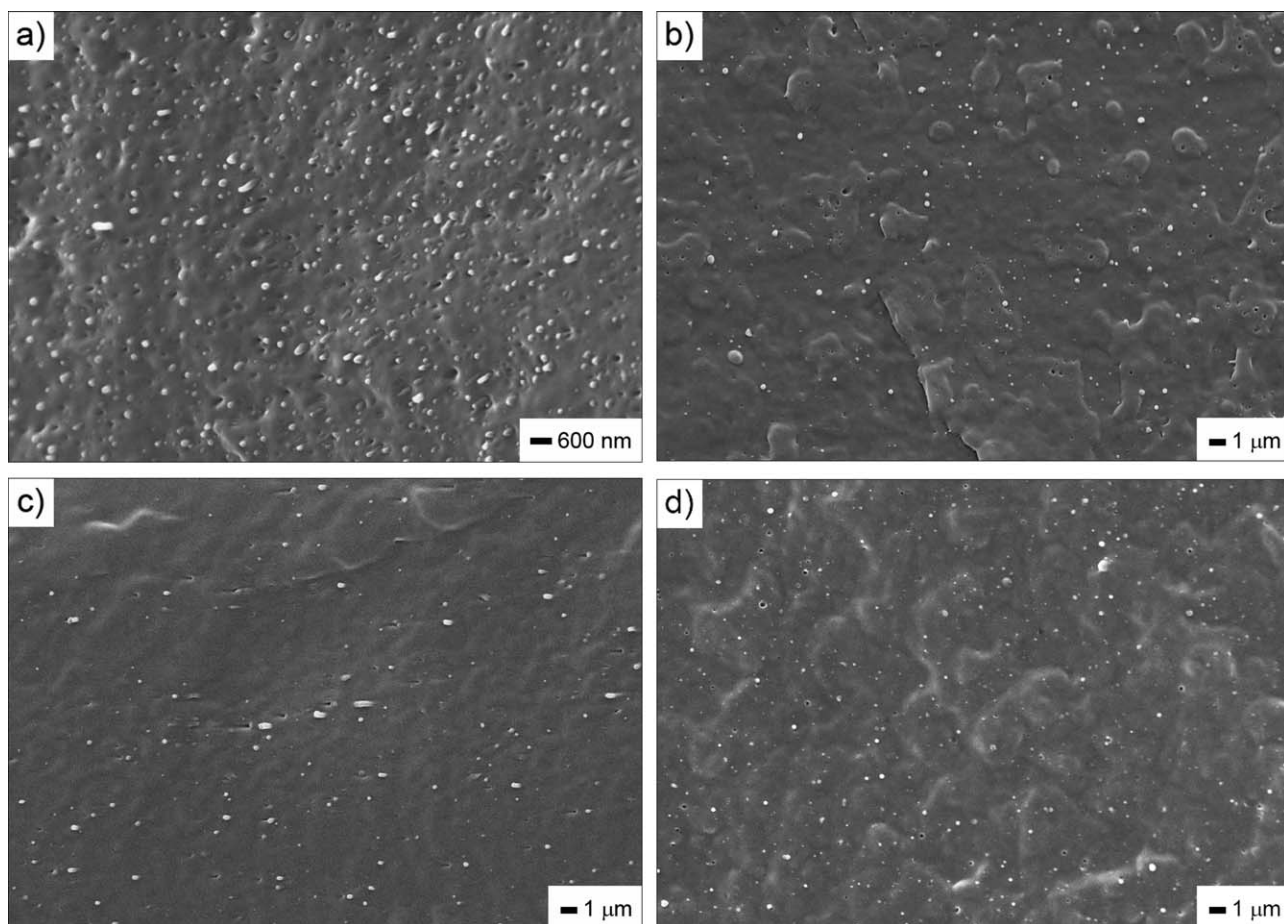
When eq. (2) is evaluated at critical conditions of temperature and blend composition  $\Delta G_{\text{mix}}$  is equal to zero. Under these conditions, the balance between energetic and entropic contributions to mixing is expressed in terms of  $B$  critical ( $B_{\text{cr}}$ ) as:

$$B_{\text{cr}} = RT/2 [(\rho_1/M_{w1})^{1/2} + (\rho_2/M_{w2})^{1/2}]^2 \quad (3)$$

where  $M_{w1}$  and  $M_{w2}$  are the weight-average molecular weights of polymer 1 and 2, respectively. To have miscibility the parameter  $B$  must be less than  $B_{\text{cr}}$ .

Inserting in eq. (3), the experimental density and molecular weight values of the PP and PMP polymers here investigated values of  $B_{\text{cr}}$  of 0.010 and 0.017  $\text{J cm}^{-3}$  can be calculated for room temperature and 250°C, respectively.

When the interaction forces are dispersive in nature, as in the present case, the interaction parameter  $B$  between the two



**Figure 3.** SEM micrographs of (a) PP/PMP 90/10 pellet, (b) PP/PMP 95/5 pellet, (c) PP/PMP 90/10 film, and (d) PP/PMP 95/5 SA AF pellet samples.

polymers can also be expressed in terms of solubility parameters,<sup>47,54</sup> that is:

$$B = (\delta_1 - \delta_2)^2 \quad (4)$$

Inserting the experimental  $\delta$  values of the two polymer components here considered in eq. (4), values of  $B$  ranging from 0.04 to 0.53 cal cm<sup>-3</sup>, corresponding to a range from 0.167 to 2.229 J cm<sup>-3</sup>, are obtained; these values are in any case higher than those above calculated for  $B$  critical by eq. (3), thus indicating the immiscibility of the investigated polymer pair.

### Film Casting and Characterization

Monolayer cast films about 70  $\mu\text{m}$  thick were prepared from neat PP and PP/PMP blends by using a single-screw extruder equipped with a take-off unit, as described in the "Experimental" section.

Uniaxial tensile tests were performed drawing the specimens, cut from the produced films along the extrusion direction. The obtained values of elastic modulus ( $E$ ), yield stress ( $\sigma_y$ ), elongation at yield ( $\epsilon_y$ ), and elongation at break ( $\epsilon_b$ ) are listed in Table III. As one can observe, irrespective of the PMP content, the tensile properties of the PP/PMP blends are practically comparable to those of the neat PP matrix.

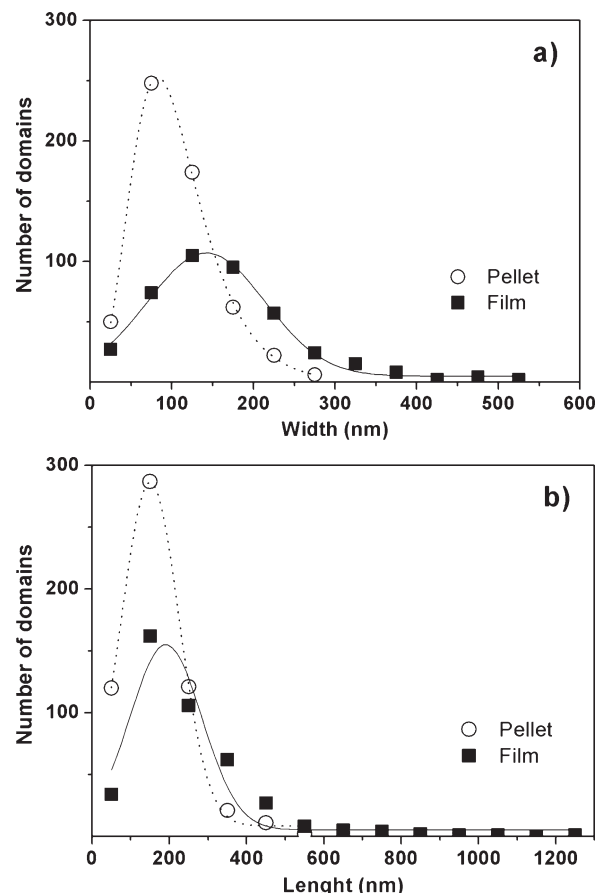
In order to investigate the effect of the processing conditions on the dispersion of PMP in the PP matrix, a morphological study by scanning electron microscopy (SEM) was carried out on fragile fracture surfaces (transverse to the machine direction) of the blend pellets as well as on the corresponding cast films. In all cases, the adopted processing conditions allowed to obtain a quite homogeneous distribution and a good dispersion of PMP domains into the PP matrix (Figure 3) as demonstrated by the fact that, independently of the blend composition, the vast majority of PMP domains have dimensions  $\leq 300$  nm.

From a closer inspection of the SEM micrographs, one can observe that, in some cases, the PMP domains are pulled-out from the PP matrix; this phenomenon, which occurs during fracturing, can be mainly ascribed to the above discussed poor compatibility between the two blend components.

The PMP dispersed domains appear elongated in the machine direction; this is mainly ascribed to the relatively high shear stresses experienced by the polymer melt during extrusion and film casting processes. In addition, the film casting step results in a partial coalescence of these domains with formation of slightly bigger domains, as evidenced by the SEM micrograph reported as an example in Figure 3(c).

The addition to the blends of some processing aids (see below) does not substantially affect the resultant morphology as shown in Figure 3(d).

The coalescence of PMP domains was semi-quantitatively evaluated by automated image analysis (AIA) carried out on SEM micrographs. As described in Figure 4, the size distribution of the PMP domains measured in the film show maxima at values (about 160 and 210 nm for width and length, respectively) higher than those (about 120 nm width and 190 nm length) obtained for the corresponding pellets. Indeed, in any case the vast majority of PMP microdomains in the pellets do not



**Figure 4.** (a) Width and (b) length distribution of PMP domains in sample PP/PMP 90/10: pellet (○) and film (■).

overcome dimensions of 300–400 nm, while a minor part of them reaches 500–600 nm in the film, consequently leading to a slight loss of transparency.

Morphology is likely to have an influence on the optical properties (haze and transparency) of films. Table IV shows that, as expected, the haze of PP-based films increases with PMP content. On the other hand, the transparency decreases with increasing PMP content. However, it is worthwhile to note that both haze and transparency values do not sensibly change and, in particular for the sample containing 5 wt % PMP, they are practically equivalent to the values observed for neat PP.

The permeability of the 70  $\mu\text{m}$  thick films with respect to O<sub>2</sub> and CO<sub>2</sub> was evaluated and the results are presented in Table V. At increasing PMP content a sensible increase of permeability

**Table IV.** Values of Haze and Transparency of Neat PP and PP/PMP Films 70  $\mu\text{m}$  Thick

Sample	Haze (%)	Transparency (%)
PP	11	93
PP/PMP 95/5	10	93
PP/PMP 90/10	21	91
PP/PMP 80/20	22	89

**Table V.** O<sub>2</sub> and CO<sub>2</sub> Permeability, CO<sub>2</sub>/O<sub>2</sub> Selectivity, and Water Vapor Transmission Rate of Neat PP and PP/PMP Films 70 μm Thick

Sample	$P_{O_2}$ (cm <sup>3</sup> m <sup>-2</sup> 24 h <sup>-1</sup> atm <sup>-1</sup> )	$P_{CO_2}$ (cm <sup>3</sup> m <sup>-2</sup> 24 h <sup>-1</sup> atm <sup>-1</sup> )	$P_{CO_2}/P_{O_2}$	WVTR (g m <sup>-2</sup> 24 h <sup>-1</sup> )
PP	1055 ± 65	3750 ± 123	3.6	3.45 ± 0.15
PP/PMP 95/5	1186 ± 74	4446 ± 144	3.8	4.15 ± 0.10
PP/PMP 90/10	1408 ± 90	5771 ± 141	4.1	4.50 ± 0.15
PP/PMP 80/20	1857 ± 115	7072 ± 183	3.8	5.50 ± 0.25

was observed. What is interesting to note is that a PMP content of 10 wt % is sufficient to produce an increase of permeability to O<sub>2</sub> and CO<sub>2</sub> of 40 and 50%, respectively, without appreciably affecting the transparency of the films (Table IV). Moreover, a certain increase in CO<sub>2</sub>/O<sub>2</sub> selectivity was also observed by increasing the PMP content in the blend. A 20 wt % content of PMP nearly doubles the permeability of the matrix, towards both O<sub>2</sub> and CO<sub>2</sub>. Even though, in such a case, the improvement in permeation properties is paralleled by a slight loss of transparency (likely also due to the laboratory scale production of the films).

As for the permeability to water vapor, the observed transmission rate values (Table V) are in line or even higher with those reported (e.g., 5 g m<sup>-2</sup> 24 h<sup>-1</sup> for a film of thickness 30 μm) for materials intended for this kind of packaging applications (fresh cut vegetables). Also the WVTR values increase by increasing the PMP content in the films.

The effect of blend composition on gas permeability can be predicted by some models developed for permeation in heterogeneous media.<sup>27–29</sup> In particular, the Maxwell model<sup>55</sup> [eq. (5)] was originally applied to systems in which the dispersed phase consisted of a low fraction of spherical particles.

$$P_{\text{blend}} = P_c \left\{ 1 + 3\phi_d / \left[ (P_d/P_c + 2) / (P_d/P_c - 1) - \phi_d \right] \right\} \quad (5)$$

where  $P_{\text{blend}}$ ,  $P_c$ , and  $P_d$  are the permeabilities of the blend, continuous, and dispersed phase, respectively;  $\phi_d$  is the volume fraction of the dispersed phase.

When the low permeability component is the continuous phase, as in the present case, the Maxwell model is reported to give underestimated permeability values for the blend permeability.<sup>28</sup>

The experimental value of permeability to O<sub>2</sub> here measured for a film of neat PP matrix (about 2000 cm<sup>3</sup> m<sup>-2</sup> 24 h<sup>-1</sup> atm<sup>-1</sup>, 45 μm, see below Table VI) and an estimated value of roughly 30000 cm<sup>3</sup> m<sup>-2</sup> 24 h<sup>-1</sup> atm<sup>-1</sup> for a corresponding neat PMP film<sup>30</sup> were inserted in eq. (5). In such a way, a permeability of about 2300 and 2600 cm<sup>3</sup> m<sup>-2</sup> 24 h<sup>-1</sup> atm<sup>-1</sup> were obtained for PP/PMP blends of composition 95/5 and 90/10, respectively. These values effectively appear to be much lower than those experimentally measured (Table VI).

The results gathered so far clearly show that the permeability properties of PP-based films can be tuned by increasing the PMP content up to 20 wt %. Then, in order to better compare optical and gas permeation properties of the investigated materials with those of commercial film samples, PP matrix and its blends containing 5 and 10 wt % of PMP were casted into thinner films of about 45 μm, i.e., of thickness comparable to that of a commercial film already on the market for packaging of fresh cut vegetables, here taken as a reference.

Values of haze measured on these films are reported in Table VI. The presence of the minor component PMP enhances, as already observed for the thicker films, the haze values; however, they range within acceptable values (again taking into account that there is room for improving the compounding conditions on a plant scale). UV-visible spectra (data not shown) of the

**Table VI.** O<sub>2</sub> and CO<sub>2</sub> Permeability, Water Vapor Transmission Rate, Haze, Kinetic Coefficient of Friction, and Antifog Level of Neat PP and PP/PMP Films 45 μm Thick

Sample	$P_{O_2}$ (cm <sup>3</sup> m <sup>-2</sup> 24 h <sup>-1</sup> atm <sup>-1</sup> )	$P_{CO_2}$ (cm <sup>3</sup> m <sup>-2</sup> 24 h <sup>-1</sup> atm <sup>-1</sup> )	WVTR (g m <sup>-2</sup> 24 h <sup>-1</sup> )	Haze (%)	COF	AF level
PP	2017 ± 38	-	-	2.6	0.51–0.56	-
PP/PMP 95/5	2876 ± 41	9154 ± 160	9.7 ± 0.20	7.7	0.51–0.57	-
PP/PMP 95/5 SA	3244 ± 92	9115 ± 110	9.5 ± 0.25	8.0	0.23–0.24	-
PP/PMP 95/5 AF	2768 ± 35	9322 ± 180	9.2 ± 0.25	11.3	0.35–0.36	D/E
PP/PMP 95/5 SA AF	2656 ± 80	9201 ± 154	8.3 ± 0.30	13.6	0.33–0.36	D/E
PP/PMP 90/10	3400 ± 97	9489 ± 74	9.9 ± 0.25	10.5	0.45–0.46	-
Reference <sup>a</sup>	3000	12000	5	5.0	0.20–0.40	D

<sup>a</sup> Commercial trilayer film 30 μm thick.

same films were also recorded; they revealed no appreciable differences with respect to the absorbance profile of the film casted from the neat PP matrix.

Permeability values to O<sub>2</sub> and CO<sub>2</sub> of the 45 μm thick films, being comparable or even better with respect to those of the commercial breathable trilayered film taken as reference, appear to be very interesting for the application in fresh vegetable packaging, also by taking into account they are obtained with monolayer films.

Table VI also shows the results relative to PP/PMP 95/5 films prepared from blends containing also processing aids, namely, a slip agent (SA), and/or an antifog (AF) additive, which are normally added in the production of films for this kind of applications. In such a way, films more suitable for a consistent and reliable comparison with commercial samples were obtained, since it was taken into account the possible effect of these commonly used processing additives on the final permeation and optical properties of the ensuing materials. Indeed, the slip agent is fundamental to guarantee the so-called “machinability” during film production at industrial level, whereas the presence of the antifog agent hampers the formation of water drops on the internal surface of the package, thus ensuring a good visibility of the packed food for the consumer and contributing to extend the shelf-life of the packed produces. Data obtained in terms of optical properties, coefficient of friction (COF), and antifog efficiency for the films containing the above-mentioned processing additives are reported in Table VI as well.

The presence of the slip agent reduces the kinetic COF of more than 50%, up to desirable values of about 0.2. Even though the addition of the antifog agent counteracts the effect of slip agent, the COF values of the prepared films are still comparable with that of the commercial film taken as reference. Moreover, it is worth noting, that the films containing the AF gave level D/E (good/excellent) in the cold fog test, also known as “beaker test,” commonly used in industry to evaluate antifog efficiency of this kind of films intended for fresh food packaging.

## CONCLUSIONS

Flexible monolayer films with *increasing and tunable permeability* were achieved by simply melt blending a commercial polypropylene matrix (PP), commonly used as food contact material, with different amounts of a poly(4-methyl-1-pentene)-based material (PMP), also suitable for food contact, and endowed with very high specific volume and excellent optical properties. It has been shown that the use of a polyolefin with highly bulky branches like PMP nearly doubles the permeability to gases and vapors in blends with PMP content below 20 wt %. More interesting, film transparency and haze as well as mechanical properties were not negatively affected by the presence of the PMP in this range of composition. It is worth noting that the overall performances of cast films obtained in conditions mimicking the industrial ones are comparable or even superior with respect to marketed PP-based films having similar thickness. Last but not least, in all these new formulations the presence of the minor component does not significantly affect

the rheological behavior of the PP matrix, thus allowing maintaining its typical processing conditions.

Shelf-life tests will possibly constitute a prosecution of this study, whose first basic focus was the selection of proper components and processing conditions to obtain in a simple and straightforward way monolayer films endowed with tunable permeation properties to match the packaging requirements of “breathing” minimally processed vegetables.

## ACKNOWLEDGMENTS

This study was supported by *Regione Lombardia*: Project 4161-MOD-IM-PACK 2008-2009 and Project 1336-Vegapack 2009-2011.

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