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S. Fakirov^a; R. J. Shields^a; C. Fuchs^b; K. Friedrich^b; D. Bhattacharyya^a

^a Centre for Advanced Composite Materials and Department of Mechanical Engineering, The University of Auckland, Auckland, New Zealand ^b Institute for Composite Materials (IVW GmbH), University of Kaiserslautern, Kaiserslautern, Germany

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S. Fakirov

R. J. Shields

Centre for Advanced Composite Materials and Department of Mechanical Engineering, The University of Auckland, Auckland, New Zealand

C. Fuchs

K. Friedrich

Institute for Composite Materials (IVW GmbH), University of Kaiserslautern, Kaiserslautern, Germany

D. Bhattacharyya

Centre for Advanced Composite Materials and Department of Mechanical Engineering, The University of Auckland, Auckland, New Zealand

In this article an attempt was undertaken to improve the barrier properties of polyolefin films against oxygen by creating internal micro-platelets of a second polymer component using the previously developed concept of micro-fibrils reinforced polymer-polymer composites (MFC). By means of melt blending of partners with mutually complementing barrier properties, and by extrusion and pressing

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Present address for C.F. and K.F.: AMME, The University of Sydney, Sydney, NSW 2006, Australia.

Address correspondence to D. Bhattacharyya, Centre for Advanced Composite Materials and Department of Mechanical Engineering, The University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: d.bhattacharyya@auckland.ac.nz

the extrudate in order to convert the dispersed spherical particles of the minor component into platelet-like ones with thickness of about 1 μm , it is possible to improve the barrier properties of the neat major component. The described morphologic transition of the dispersed phase is proven by Scanning Electron Microscopy. Attempts to manufacture thin films from such pressed blends with improved barrier properties in industrial-scale experiments via extrusion blow molding or slit-die extrusion failed so far. This was due to the fact that void formations occurred during the processing, as already reported for blends of thermoplastics with liquid crystalline polymers. For this reason, using compression molding, films were prepared from the pressed strips, in which the platelets can be converted into thin sheets depending on the processing conditions. Compression molded plates or films of polypropylene/poly(ethylene terephthalate) (70/30 by wt) composites with an MPC structure (MPC = micro-platelets reinforced composites) showed up to four times better barrier properties against oxygen than films of the neat PP.

Keywords: barrier properties, microplate reinforced composites, polymer blends

INTRODUCTION

Barrier polymers are organic polymers displaying the ability to restrict the passage of gases, vapors, and organic liquids. Their importance as an article of commerce is recognized by the food-packaging and related industries. These polymers, when used alone or in combination with other polymers or materials, provide an efficient and economical method for the packaging and shelf-life extension of food and beverages [1].

Permeation is the rate at which a gas or vapor passes through a polymeric material. The permeation of a gas or vapor through a polymer depends on the polymer, the penetrating gas, and the environment. A polymer configuration leading to good polymer backbone packing decreases permeability. The simpler the molecular structure, the better the packing. Crystallinity is an important factor because crystallites are impermeable and reduce the permeation rate. Permeation also depends on the nature of the penetrating gas. The rate of passage of a permeating species through a polymer matrix is governed by (i) its solubility in the polymer, and (ii) the relationship between the size of the penetrating gas molecule and the interstices in the polymer. Permeation rates are affected also by humidity and temperature.

Permeability is the proportion constant in the general equation for mass transport of a penetrating gas across a barrier:

$$\frac{\Delta M}{\Delta T} = P \left(\frac{A \Delta p}{L} \right) \quad (1)$$

where P = permeability of the barrier, $\Delta M/\Delta t$ = the mass of the penetrating gas crossing a barrier per unit time, A = area of the barrier, L = thickness of the barrier, and Δp = partial pressure difference across the barrier. Permeability, as a property of a material, is a product of permeance and thickness [2].

Organic polymers are classified by the degree to which they restrict the passage of gases. The categories range from high barrier (low permeability) to low barrier (high permeability). The category in which a polymer is classified may vary according to the penetrating gas. Typical low barrier polymers are plasticized PVC, polypropylene, polyethylene (low and high densities, linear low density), and polystyrene. To the category of good and high barrier polymers belong polyesters, for example, poly(ethylene terephthalate) (PET), polyamides, for example, Nylon 6 (PA6), PVC (rigid), poly(vinyl fluoride), poly(vinylidene chloride) [3].

No single resin is capable of producing the right balance of physical and mechanical properties, appearance, and economics for all types of packaging. The logical and practical approach is the combination or modification of existing polymers by polymer blending or alloying, chemical modification, or structuring using melt-processing techniques [4]. An example for a reasonable complementation of the barrier properties of two polymers is given in Table 1.

The principal use of barrier polymers is in packaging, especially of medicines, food, and beverages, but they are becoming increasingly important in the packaging of chemicals, insecticides, and automotive supplies. These thermoplastic materials are versatile and can be fabricated into many shapes and forms. The package may be rigid, such as a bottle, semi-rigid and thermoformed from a sheet, or flexible as a pouch.

Fabrication processes for rigid plastics include compression molding, thermoforming, sheet extrusion, steam-chest expansion,

TABLE 1 Permeability of PET and PP with Barrier Properties [5]

Medium	Units	PET		PP	
		Nonoriented	Oriented	Nonoriented	Oriented
Oxygen	$\text{cm}^3 \text{ mm}/\text{m}^2 \text{ d bar}$	4–4.5	1.8–3.5	80–90	35–45
Carbon dioxide	$\text{cm}^3 \text{ mm}/\text{m}^2 \text{ d bar}$	10–11	5–8	300–320	170–180
Water vapor 20°C, 85% rel. humidity	$\text{g mm}/\text{m}^2 \text{ d}$	3	0.9–2	0.10–0.15	0.04–0.07

three-dimensional packaging (cartons, spin welding, blow molding, extrusion blow molding, stretch blow molding, and injection-stretch blow molding), heat-set molding, the blow mold-fill-seal-system, barrier enhancement, and monolayer modifications [6–7].

This is the reason for the steady increasing efforts for creating polymer materials with improved barrier properties. To them belong the experiments with liquid crystalline polymers (LCP) because of their excellent gas-barrier properties [8]. But the relatively high current price of commercially available LCP makes it interesting to combine them with other polymers of lower price in blends or in laminates. Other drawbacks of LCP are their non-transparency and anisotropic mechanical properties [9]. Blends or laminates based on LCP and non-polar polymers such as polyethylene (PE) are expected to be a particularly difficult case because of the poor phase adhesion, which may cause cracking or even delamination [10].

To the first reports on the transport properties of blends of LCP and PE belongs that of Flodberg et al. [10]. They studied the oxygen and water vapor permeabilities of a series of blends with a wide range of compositions produced by compression molding and film blowing. The two polymers are completely immiscible and, even though a compatibilizer was used, some blends showed poor barrier properties essentially due to the weak adhesion between the polymers. This was confirmed by scanning electron microscopy (SEM) and by density measurements, showing the presence of voids, which in some cases formed continuous pathways in the structure [10].

In a subsequent study the same authors [11] followed the morphology and the oxygen permeability of blends of extrusion-grade high density polyethylene (HDPE) and two LCPs (the copolyesters Vectra A950 and Vectra RD501). The blends were prepared by melt mixing and injection molding. SEM observations revealed that LCP was present in the blends as mixed oriented bands and small spheres at low LCP contents (4–9 vol%), whereas blends with more than 18 vol% LCP showed LCP lamellae of macroscopic lateral sizes (mm). The decrease of oxygen permeability was around 50% at 9 vol% LCP, and at 27 vol% LCP the decrease with respect to the neat HDPE was between 90 and 100%. It was also found that microvoids were present in all the blends despite the use of a very high injection pressure (180 MPa). However, their impact on the oxygen permeability was negligible [11], in contrast to the case of blown films from similar blends [10].

With the development of nanomaterials' technologies, and more specific, of polymeric nanocomposites, it looked attractive to apply the same approach for preparation of polymeric materials with

improved barrier properties. A special attention was paid to the natural layered silicates (clays) being crystalline materials consisting of 1 nm thick layers (or sheets) with a length in the range from 30 to ~2,000 nm, depending on the particular silicate.

It was the Toyota Group, which in 1997 demonstrated that incorporation of small amounts of clay particles (2–6 wt%) into a thermoplastic polymeric matrix can generate enhanced properties such as thermal and UV resistance, low permeability toward gases, and to some extent improved mechanical properties. Similarly to the case of mechanical properties, where the improvement is typically 20% and in rare cases above 30% (at about 5 wt% loading) [12], the reduction of permeability toward gases is in the same range. For example, De Kee [13] studied the oxygen permeability of layered silicate/PE nanocomposite films and found that 5 wt% clay does not improve the properties of HDPE. The oxygen permeability of an LDPE/clay/compatibilizer 90/5/5 system is only ~15% lower than that of the neat LDPE [13].

Quite similar is the report of Kalendova et al. [14] who followed the effect of morphology on the barrier properties of PVC/montmorillonite/montmorillonites; it was concluded that improvements of about 30% are common.

It is already well known and widely documented that the crucial step in the preparation of polymer nanocomposites is the dispersion of the natural-layered clay in the polymer matrix. Chemical or mechanical approaches are used for this purpose. Usually one starts with an *intercalation*, where the polymer chains swell the intersheet or gallery spacing and lead to a well-ordered alternating polymer/silicate-layered nanostructure. This is followed by an *exfoliation* step, where the silicate sheets are completely delaminated and individually dispersed in the polymeric matrix.

Tomova and Reinemann [15] studied the effect of the clay content, particles aspect ratio, and their orientation on the barrier properties of HDPE/clay nanocomposites used for injection blow-molded containers. Similar model study of the barrier properties of polymer/layered silicate nanocomposites has been carried out by Bharadwaj [16]. In both cases it was found that with an increase of the aspect ratio from 1 to 400 the relative permeability drops from 0.8 to 0.3; the latter drops 5 times (for an aspect ratio of 1,000) and only twice (for an aspect ratio of 200) when the volume fraction of clay amounts to 0.010. Quite similar are the results for the same particles when they are displayed perpendicularly to the gas diffusion direction, and slightly worse in the case of a chaotic arrangement of the platelets. But in the case when they are

oriented parallel to the diffusion direction, no barrier effect can be observed [15].

As a matter of fact, the two approaches for preparation of polymeric materials with improved barrier properties, that is, the blending of LCP with thermoplastics and the nano-composites comprising layered silicates, use the same concept, that means, the reduction of permeability arises from the longer diffusive path that the penetrating gas must travel in the presence of the filler. This situation is schematically illustrated in Figure 1 for a barrier from a homopolymer and barrier from polymer blend where the minor component is dispersed in the matrix as parallel displayed plates with possibly high aspect ratio positioned perpendicular to the gas diffusion direction.

It is quite obvious that a sheetlike morphology is particularly efficient at maximizing the path length due to the large length-to-width ratio compared to other shapes of fillers, such as spheres or rods.

Starting from the reported data, and mostly taking into account the previously outlined disadvantages of the blends with LCP (namely (i) relatively high prices of LCPs, (ii) their unavoidable anisotropy of mechanical properties, and (iii) the rough [microns to mm range] and morphologic inhomogeneous dispersed particles), as well as the serious drawbacks of the polymer nanocomposites (whose preparation requires not routine approaches), it looked very challenging to exploit the same concept (Figure 1) but using common thermoplastics. The only requirements to such blends are: (i) the two partners should be distinguished by mutually complementing barrier properties as, for example, the case is with PP and PET (Table 1), (ii) they should be thermodynamically immiscible, and (iii) they should have different

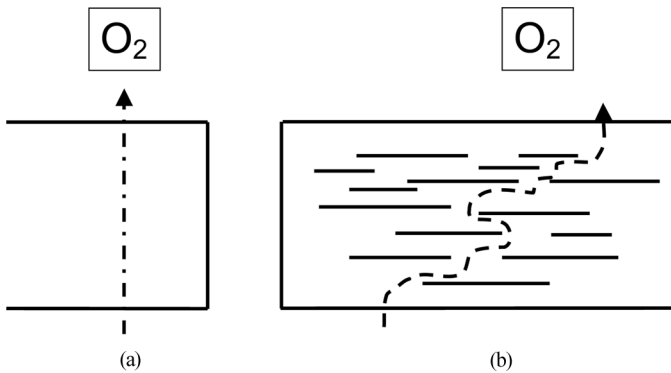


FIGURE 1 Schematic of the diffusion path of oxygen molecules through a homopolymer (a) and through a blend with the depicted morphology (b).

(at least 40°C) melting temperatures. Such blends of *flexible-chain* thermoplastics do not suffer from the aforementioned drawbacks, as mentioned for the LCP blends and the polymer nanocomposites.

For the realization of this target this study used experience gained during the development of the concept of microfibrils reinforced composites (MFC) [17–27]. Briefly, the latter consists of the following.

In contrast to the common polymer composites where the reinforcement is represented by glass- or other fibers, in the case of MFC the role of the reinforcement is played by microfibrils. Because the microfibrils are not available as a separate material, they have to be created, similarly to the isotropic matrix thereafter. The preparation of MFC includes three basic steps: (i) melt blending with extrusion of two immiscible polymers having different melting temperatures T_m (*mixing step*); (ii) cold drawing of the extrudate with good molecular orientation of the two components (*fibrillation step*); (iii) thermal treatment at a temperature between the T_m s of the two blend partners (*isotropization step*).

Whereas during the second step (fibrillation step) the two polymers are converted into a highly oriented state, that is, one deals with a highly oriented blend, the third step results in melting of the lower-melting component and its transformation into an isotropic matrix, reinforced with the microfibrils of the higher-melting component. Technologically, this transition to an MFC structure can take place during processing of the drawn blend via injection- or compression molding. The essential requirement is that the processing window is not too close to the T_m of the microfibrils, otherwise they will melt and return to their starting spherical shape.

The MFC concept is a relatively new one, and it seems to be a useful approach for processing of polymer blends and manufacturing of polymeric materials and articles with environmental friendly properties because no mineral reinforcements or additives are needed. Another characteristic feature of these materials is the extremely homogeneous distribution of the reinforcement in the matrix polymer, which fact is of a particular importance for the intensive studied nanocomposites nowadays. The problem, dealing with the common nanocomposites, regarding the fine and homogeneous dispersion of the reinforcing elements does not exist in the case of the MFC approach because the fine and homogeneous dispersion of the reinforcing component in the matrix starts from the very beginning as spheres, and later as micro- or nanofibrils. In addition, dealing with MFC or nanofibrillar composites one profits from the extremely high *aspect ratio* values (between 100 and 1000). And last but not least, contrasting to other polymer-polymer composites, MFC comprise only flexible-chain thermoplastics [17–27].

EXPERIMENTAL DETAILS

Materials

Recycled material from PET bottles (type FR 65, with a melting range of 236–252°C, supplied by Rethmann Plano GmbH, Germany), a commercial grade PP (type Novolen with melt flow index 5, provided by Basell, Germany) and commercial grades of polyethylene (HDPE and LDPE) were used as reinforcing component and matrix materials, respectively.

Sample Preparation

Although the MFC concept is basically preserved, in the case of MPC the manufacturing process is modified to reach the demanded blends structure. Again, as in the case of MFC, the difference in the melting temperatures of the two partners should preferably be at least 40°C, and it is also necessary that both polymers are not thermodynamically miscible. In addition, the processing of the blend partners has to be possible in the same temperature range without the occurrence of thermal or oxidative degradation in any of them. The manufacturing of MPC comprises three basic steps: (i) melt blending with extrusion (*mixing step*), (ii) pressing of the extruded bristle in order to transform the existing spheres into plates (*microplating step*), and (iii) thermal treatment at a temperature between the T_m s of the two blend partners in order to convert the lower-melting component into an isotropic state (*isotropization step*). These three basic manufacturing steps are schematically illustrated in Figure 2.

In the first step, the two polymers are blended, and the bristle with a diameter of ca. 2 mm leaves the extruder reaching two water-cooled rollers where the bristle is pressed with a defined load. As a result, the bristle gets flattened into a 20 mm wide and 0.5 mm thick strip. Because of the cooled surface of the rollers the flattened extrudate solidify immediately.

During the third step, melting of the lower melting component takes place, and thus it transforms into an isotropic matrix reinforced with the microplates of the higher-melting component. As a matter of fact, only after this treatment stage a polymer-polymer composite material is produced. This means, the isotropization takes place during processing of the cut strips via compression molding into macroscopic plates.

In order to enhance the matrix contribution to the overall mechanical behavior of the plates with MPC structure and to improve the adhesion between the starting strips, sheets of neat biaxially oriented

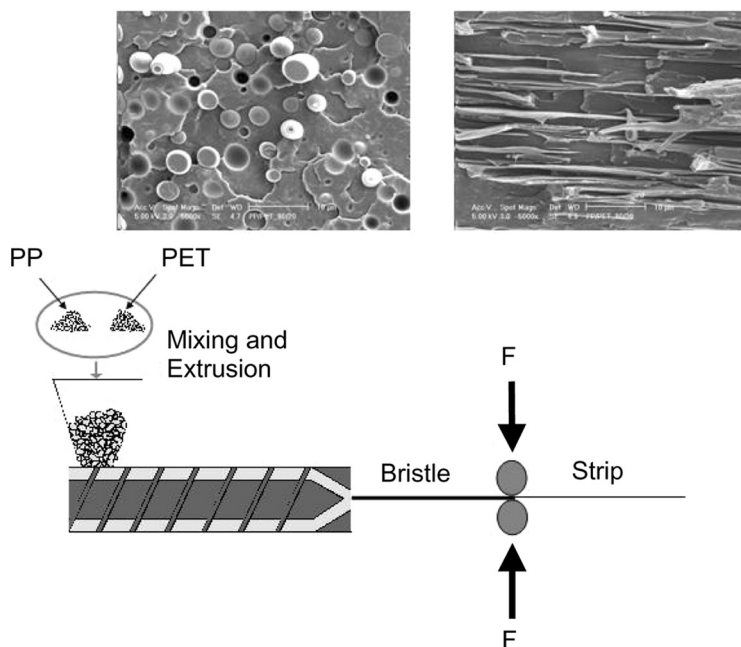


FIGURE 2 Schematic of the experimental setup for manufacturing of strips with MPC structure, and SEM micrographs of the cryo-fracture of PP/PET (70/30 by wt) samples: (a) (left), (b) (right).

PP (BO-PP) film were placed on the two outer sides of the strips layer as well as on the inner side. The compression molding was carried out with a pressure of 600 kPa. The pressure was held during heating up to 190°C and kept at that level for 10 min, before cooling down to room temperature after which the pressure was released.

In addition to the lab-scale compression-molded experiments, attempts also were undertaken to manufacture extrusion blow molded films from LDPE/PET blends as well as slit-die extrusion of PP/PET blends using industrial scale equipment. For doing so the strips prepared according to the aforementioned description, were palletized and dried before feeding the respective extruder. For sake of comparison, films of the neat LDPE and PP were also manufactured.

Methods

Scanning Electron Microscopy

Scanning electron microscopic observations were performed on a Philips XL3OS FEG scanning electron microscope (SEM) with an

acceleration voltage of 5 kV. Samples from the various manufacturing and processing stages of MPC were immersed and fractured in liquid nitrogen in order to study their surface morphology. All the specimens were coated with a thin platinum layer prior to SEM analysis.

Differential Scanning Calorimetry

Calorimetric analysis was performed from -50°C up to 280°C at a scan rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere using a DSC Q1000 (TA Instruments) on samples of around 5 mg, dried under vacuum at 100°C for 24 h.

The degree of crystallinity, $w_c(DSC)$, was evaluated by means of the following equation:

$$W_c = \frac{\Delta H_{\text{exp}}}{\Delta H_{\text{id}}} \quad (2)$$

where ΔH_{exp} and ΔH_{id} were the measured and ideal (for 100% crystalline samples) values of the heat of fusion, respectively. For PP and PET the values of ΔH_{id} were adopted as 209 J/g and of 140 J/g [28], respectively.

Barrier Properties Characterization

The barrier properties toward oxygen were tested by mostly using a homemade apparatus. A plate of 1.5 mm thickness and 80 mm diameter was placed between two chambers. In the lower chamber an oxygen sensor is measuring the incoming oxygen through the tested sample from the upper chamber. The oxygen sensor during the experiment is surrounded by nitrogen.

In a first step, both the upper and lower chambers are flushed with nitrogen. The valves of the lower chamber get closed when the oxygen sensor shows no more oxygen concentration in the chamber. Afterward, the upper chamber is flushed with oxygen and after a defined time of flushing, the chamber gets loaded with oxygen under $10 \text{ kPa}/\text{inch}^2$ pressures. All the valves are closed during the experiment. The oxygen concentration gets measured until a constant oxygen concentration is reached.

RESULTS AND DISCUSSION

Verification of the MPC Concept: A Sphere-Plate Morphological Transition

The main purpose of these preliminary experiments was to check the possibility for a drastic change of the morphology of the dispersed

phase—from globular to platelet- or sheetlike. Only in such a case one can expect a serious positive change of the barrier properties of polymer blends against gases.

As mentioned in the Introduction, polyolefins as PE and PP belong to the category of the low barrier polymers, whereas PET possesses good barrier properties (Table 1). Further, Table 1 shows that with regard of the barrier properties for rigid and semi-rigid packaging applications, PET exhibits good properties for both, gas and water vapor permeation resistance. At the same time, PP, and particularly PE, show poor barrier properties toward gases and excellent properties regarding water vapor. Taking the fact into account that these polymers constitute the major part of polymers used for packaging purposes, it seemed challenging to combine their properties, that is, PE or PP films or semi-rigid containers reinforced with microplates of PET. Such materials will be characterized by improved gas- and water vapor-barrier properties.

The very first lab-scale experiments for preparation of compression-molded films from such blends (distinguished by the desired morphologies along the processing line) were quite promising, as can be concluded from Figure 3.

In Figure 3, the cryogenic fracture surfaces, as observed in SEM at various stages of MPC manufacturing, are shown. The commonly observed [17–26] spherical shape of the dispersed polymer (Figure 3a) is converted into microplates (Figures. 3b and c) when the pressing is performed at 80°C, or into thin multilayers (Figure 3d) if the pressing takes place at 200°C.

Industrial-Scale Experiments for Manufacturing of Polymer Films with Improved Barrier Properties

The aforementioned rather positive results of the morphological transformation of the dispersed polymer (Figure 3) encouraged the authors to perform experiments on industrial-scale equipment. The target was to manufacture extrusion blow-molded or slit-die-extruded films of PE/PET and PP/PET blends, respectively, starting from blends having an MPC structure.

For this purpose, the matrix materials (PP or LDPE) were mixed with PET in various wt. ratios in a twin-screw extruder, and continuously pressed strips of the blends were manufactured as described in the experimental part. The strips were palletized and dried before feeding into the blow molding line (for the LDPE-based films) or the slit-die extruder (for the PP-based films). Because, as it will be demonstrated later, these experiments did not offer the expected

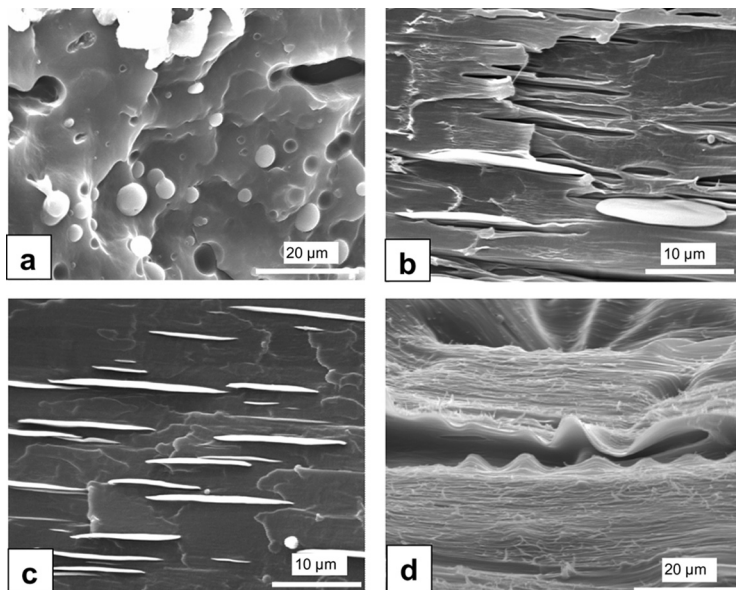


FIGURE 3 SEM micrographs of cryo-fracture surfaces of bristles of PP/PET (40/60 by wt) blends, hot pressed at various temperatures: (a) no pressure (as extruded bristle), (b) and (c) pressed at 80°C, (d) pressed at 200°C.

improvement of the barrier properties, they will not be described here in more detail. Nevertheless, these experiments allowed the derivation of a couple of important conclusions:

1. The different blend compositions have to be prepared by means of melt blending in a twin-screw extruder, but not via diluting of a given composition with a neat matrix material just before feeding the film forming equipment.
2. Blends containing more than 30 wt% PET cannot be processed for film manufacturing via extrusion blow molding or slit-die extrusion.
3. The attempts to use processing temperature not higher than 220°C (in order to prevent melting of PET microplates and their converting back to spheres) failed because the manufactured films contained a large amount of solid PET particles. For this reason, processing temperatures of 240°C and die temperature of 180°C (for the neat matrix films) or of 220°C (for the blends) were used.
4. These increased temperatures led to significant change of the starting layered structure of the blends due to melting of PET, which, in turn, deteriorated the barrier properties.

In Table 2, some of the results of testing the barrier properties (permeability of oxygen) of slit-die extruded and extrusion blow moulded films are summarized.

From the data presented, one can conclude that the blow-molding approach cannot be used for manufacturing of films of the LDPE/PET blends because during the blowing pores (voids) are created. The same holds for the slit-die extrusion of the PP/PET blends.

Somewhat better were the results of the slit-die extrusion of the LDPE/PET blends, particularly with lower PET content (15 wt%), where improvements of the permeability against oxygen of about 20–25% were observed (Table 2, sample 9).

What could be the reason for the failure of these experiments? In the first place, one has to consider the relatively high processing temperature (240°C). This temperature coincides with the melting range of the used PET grade. At such temperature the starting morphology (plates of PET) change back to more or less spherical particles. The same situation has been manifold observed in the SEM for MFC when the processing temperature is above the melting of PET, that is, the microfibrils melt and convert back into spherical particles [26–27].

Obviously, the main reason for the poor barrier properties, even worse than those of the neat film (Table 2, samples 2, 3, 7, and 8) is related to the formation of pores and/or micro-voids during the film

TABLE 2 Permeability toward Oxygen of Slit-Die Extruded or Extrusion Blow Molded 100 μm Thick Films of Neat PP or LDPE and of their Blends with PET Processed at 240°C (Testing Apparatus: GDP-C of Brugger Feinmechanik, Munich, Germany)

Sample #	Blend comp.	Composition (wt%)	Slit-die	Blow mold	Permeability ($\text{cm}^3/\text{m}^2 \text{ d bar}$)	Note
1	PP	100/0	+	–	669	—
2	PP/PET	90/10	+	–	—	No vac. possible
3	PP/PET	75/25	+	–	—	Not homog. film No vac. possible
4	LDPE	100/0	–	+	2068	—
5	LDPE/PET	90/10	–	+	—	Not homog. film No vac. possible
6	LDPE/PET	70/30	+	–	1710	—
7	LDPE/PET	75/25	+	–	—	Not homog. film No vac. possible
8	LDPE/PET	90/10	+	–	—	Not homog. film No vac. possible
9	LDPE/PET	85/15	+	–	1610	—

manufacturing. This observation has been already reported by Flodberg et al. [10–11] for blends of thermoplastics with LCP. They explain the poor barrier properties of the two completely immiscible polymers (even when containing compatibilizer) by the weak adhesion between the blend partners, resulting in the formation of voids, which play the role of “channels” for the diffusion of gas molecules.

One can assume that during the film formation (via blowing or extrusion), when the blend melt leaves the die with a temperature of about 220°C, the matrix polymer (PP or LDPE) is much more flexible than the dispersed PET particles (which are supposed to be at these temperatures in a solid state). Due to the extensional forces the matrix separates from the PET particles, creating in this way voids. In order to avoid such a separation of the matrix from the dispersed particles one has to perform the film formation at much lower temperatures, applying, as compensation, much higher pressures. For this reason the authors came back to the lab-scale hot pressing.

However, it is still believed by the authors that a processing window can be found in the future, by which these industrial scale methods will too lead to improved barrier properties. This is a matter of improving the starting material and a better control of the subsequent processing variables. Unfortunately, this was not possible within the scope of this project.

Lab-Scale Hot Pressing of PP/PET Films with Improved Barrier Properties

The reason for using again the hot pressed film production was not only the failure of the industrial-scale experiments, but also the more promising preliminary testing of hot pressed films, as can be concluded from Table 3.

These results demonstrate the need for a more systematic control of the temperature characteristics of the blend components. More specifically, it is important to know more about the blend morphology after roll pressing (strips manufacturing) as well as the final hot pressing of the films or plates, starting from strips.

A good idea about the thermal behavior, the phase state, and the degree of crystallinity of a semi-crystalline polymer can be obtained from the DSC analysis. For this reason such measurements were performed on the main starting components, as well as on their intermediate and final products, also on some of them after annealing (Figure 4).

The very general conclusion drawn from all the DSC curves is that the two polymers are in a semi-crystalline state, regardless of whether

TABLE 3 Permeability toward Oxygen of 300 μm Thick Films, Hot Pressed at Various Temperatures under a Load of 30 kN and a Retention Time of 5 min. Materials: neat PP, LDPE, and PET as well as of the Blends LDPE/PET (Testing Apparatus: GDP-C of Brugger Feinmechanik, Munich, Germany)

Sample #	Blend comp.	Composition (wt%)	Pressing temp.($^{\circ}\text{C}$)	Permeability ($\text{cm}^3/\text{m}^2\text{d bar}$)	Note
1	LDPE	100/0	140	560	From 2 specimens
2	PP	100/0	180	142	—
3	PET	100/0	Commerc. Film	25.6	From 2 specimens
4	LDPE/PET	70/30	160	369	From 3 specimens
5	LDPE/PET (layers of strips)	70/30	160	28	From 2 specimens

they are in a neat or blended state. Although the neat PET demonstrates some additional crystallization during the heating in the DSC instrument (Figure 4a), in the blends with PP it shows a very poor crystallinity as can be concluded from its melting peaks (Figure 4c–e). This observation suggests that PET does not reach a substantial crystallinity level (Table 4) during the cooling down of its melt after

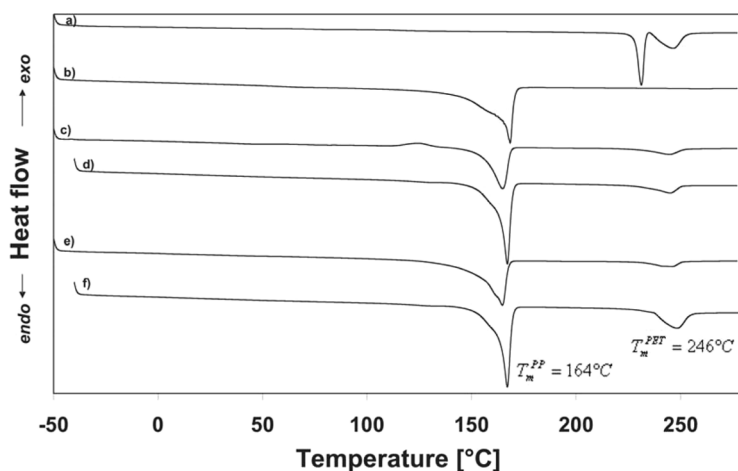


FIGURE 4 DSC curves in a heating mode of: (a) starting neat PET pellets, (b) starting neat BO-PP film, (c) starting nonpressed (as extruded) bristle of the blend PP/PET (70/30 by wt), (d) the same after pressing, (e) compression molded plate comprising the strips with microplates of the blend PP/PET (70/30 by wt) and the film of BO-PP, (f) as (e), but annealed at 200 $^{\circ}\text{C}$ for 6 h.

TABLE 4 Melting Temperature, T_m , and the Degree of Crystallinity, \mathcal{W}_c (DSC), of the Starting, Intermediate, and Final MPC Products, as Evaluated from the DSC Curves of Figure 4

Sample	Melting temperature (°C)		Crystallinity (%)	
	T_m^{PP}	T_m^{PET}	\mathcal{W}_c^{PP}	\mathcal{W}_c^{PET}
BO-PP	168.5	—	70.4	—
PET-pellet	—	231/246.42	—	24.5
Nondrawn bristle	164.9	245.0	50.0	38.1
Drawn bristle	167.1	245.1	71.5	39.9
Pressed plate	164.7	246.1	72.7	27.5

extrusion or even after compression molding (Figure 4e). In order to make its melting peak better visible, samples from the compression-molded plate were subjected to annealing before taking the DSC curves. The result is shown in Figure 4f, where the expected effect can be observed, that is, both blend components are characterized by increased crystallinity.

It should be noted that the presence of an amorphous phase could not be resolved *via* its glass transition temperature, T_g , even for the PET component (Figure 4). The reason for this can be related mostly to (i) the relatively small amount of PET in the blends under investigation (30% by wt), and (ii) the partial crystallinity, which, effectively, reduces the amount of the amorphous fraction of PET (Table 4), Figure 4a.

In Figure 5 the SEM micrographs reflecting the four different cases of the manufacturing process are displayed. Figure 5a shows the situation just after extrusion (where PET is homogeneously distributed in the PP matrix as particles, mostly of spherical shape and with a diameter of about 5 μm , similarly to the manifold documented [17–27] microfibrils reinforced polymer-polymer composites). PET particles with elliptical or slightly elongated shape of almost the same diameter are also observed (Figure 5a). After pressing of the extruded bristles, the PET particles were flattened into plates with a thickness of 1–3 μm (Figure 5b).

It is interesting to note here that this sphere-plate transformation takes place to a different extent at the edges and in the middle part of the formed strip, as can be concluded from Figure 5c. First of all, on the strip edges the matrix dominates, that is, the population of PET particles is smaller than in the middle parts of the strip. Further, the flattening process is not that complete, which, obviously, is due to

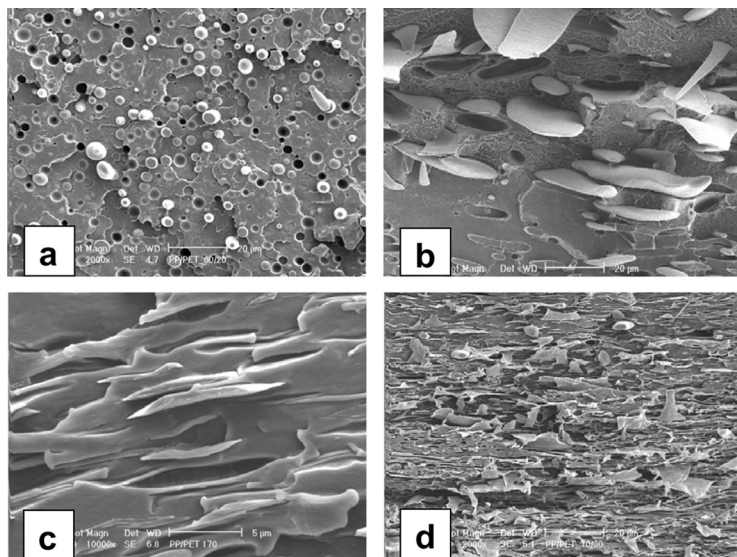


FIGURE 5 SEM micrographs of cryo-fracture surfaces of roll-pressed bristles of PP/PET (70/30 by wt) blend at various stages of MPC manufacturing: (a) as extruded bristle, (b) border section of the manufactured strip, (c) and (d) middle section of the strip.

the lower temperature of the material at the edges as compared to the middle parts.

The produced PP/PET strips were hot pressed in order to obtain thinner and large enough testing plates for measuring the barrier properties. The SEM micrographs of the cryofracture surfaces are shown in Figure 5d. In contrast to the case of converting the bristles into strips just by pressing them in a continuous cold rolling process, during the additional static hot pressing one can apply much higher pressure and temperatures. That is why the flattening process of the platelets goes much further, that is, the PET particles become thinner and larger in area, which is very favorable for the barrier properties improvement (compare Figures 5b with 5d).

Hot pressed PP/PET (70/30 by wt) plates, with the morphologic structures demonstrated in Figure 5d, were used for testing of the oxygen permeability.

Figure 6 illustrates the oxygen concentration in the lower chamber versus the experimental time for the neat PP and for the microplate-reinforced polymer-polymer composite of PP/PET (70/30 by wt). A quite well-expressed difference in the permeability behavior of the

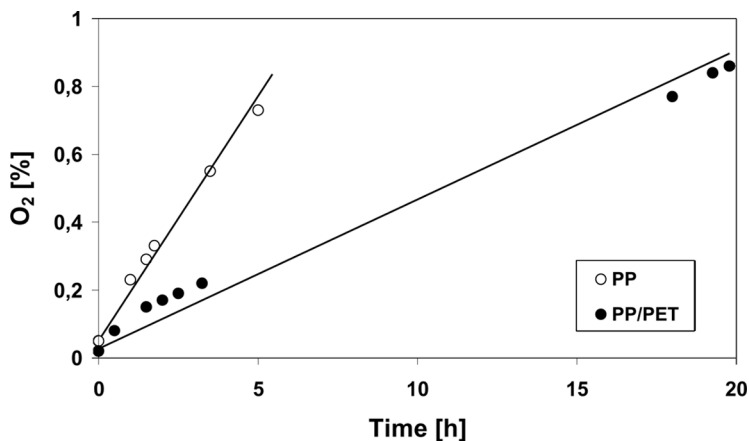


FIGURE 6 Oxygen concentration in the lower chamber vs. time; ○) neat PP; ●) microplate reinforced composite of PP/PET (70/30 by wt%).

two samples can be observed. As one can see, the plot for the PP/PET sample increases half as that for the neat PP does. What is more important, the diffusion of oxygen through the hot pressed PP/PET sample needs more than four times longer time than through the neat PP sample having the same thickness. Furthermore, the increase of the oxygen concentration in the lower chamber behaves in a linear dependence versus the diffusion time (in the time frame in which of the experiments were performed).

CONCLUSIONS

The results of testing the barrier properties of hot pressed PP/PET (70/30 by wt) films (Figure 6) demonstrate that the MPC concept (Figure 1) works. The creation of optimal conditions (blend partners and composition, pressure, temperature, etc.) for the transformation of the starting spherical particles into plate- or sheetlike formations, possibly placed parallel to each other, allows one to create packaging materials such as films or thin-walled containers, with improved barrier properties.

As the industrial-scale experiments demonstrated, the applied processing temperature should not be very high (i.e., considerably above the melting of the matrix component) because voids are created at the interface boundary between the matrix and the reinforcement. At the same time, it should be noted that these industrial-scale experiments indicated the possibility for manufacturing breathable polymer

films being of interest as materials for disposable medical clothing. The extrusion blow molded and slit-die extruded LDPE/PET films preserved their mechanical integrity and appearance although they contain a large number of pores and microvoids, making them breathable, but not useful, as barrier materials. However, there is still enough room for improving this purpose in the future.

With respect to the continuation of these studies, it seems to be of interest to check to what extent the superior barrier properties of the hot-pressed plates can be preserved after injection molding of the pelletized roll-pressed strips. Contrary to the hot pressing, where the plates are getting even thinner and larger in area as well as preserving their perfect alignment parallel to each other, during the injection molding it is hoped that the plates will preserve their starting dimensions, but, it is assumed they will lose their very favorable orientation for the barrier properties.

Another challenge in this direction is to check the barrier properties of polymer (PP or PE) films reinforced with PET microfibrils, that is, the case when one deals with the transformation of the starting spheres into microfibrils instead into microplates. Due to the large surface area of the microfibrils (with a diameter of 1–3 μm and a length of a couple of hundred of μm), it could happen that the barrier properties are also improved. Such materials will have also the advantage (in comparison to those with MPC structure) that the effect of the reinforcement orientation on the barrier properties (with respect to the gas diffusion direction), will not exist anymore. Furthermore, the mechanical reinforcement in the case of MFC is much higher than that of MPC, that is, it will be possible to manufacture, for example, containers with thinner walls, preserving the level of their barrier and mechanical properties.

More attractive in this respect seem to be the nanofibrils-reinforced composites (NFC) where the reinforcement represents nanofibrils with diameters of 50–150 nm and a length of a couple of hundred μm [29].

An additional advantage of the barrier materials with MFC or NFC structure is related to the fact that the dispersed component (PET) is in a highly oriented state, as was repeatedly documented [17–27]. In such a state, PET possesses, in average, a two times lower permeability toward oxygen, carbon dioxide, and water vapor, as compared with the non-oriented state (Table 1); that is, the barrier effect of polyolefin films reinforced with PET micro- and/or nanofibrils has to be significantly increased in comparison to the polyolefin films containing PET particles in a non-oriented state.

The realization of the outlined tasks is in progress.

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