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High Barrier Polyamide/Polyolefin/Organoclay Nanocomposites

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Summary: New composites coupling the alloy and nanocomposite technologies have been successfully produced with regular co rotating twin screw extruder. These new composites, Polyamide(PA6)/Polyolefin(PO)/compatibilizer/nanoclay, have been blown to end up with monolayer films. The thermo mechanical performances of these new composites do not reveal any improvement at high temperature resulting from the presence of nanoclays, as required by emergent needs in automotive field. More interesting are the high barrier properties obtained with these new composites. For specific permeating species, the association of alloy and nanocomposite technologies lead to new materials with superior barrier performances comparing to the materials making up the alloys. Physical explanation of such behavior is detailled in this paper.

Keywords: barrier; nanocomposite; organoclay; permeation; polyamide; polyolefin

1. Introduction

For now more than thirty years, in polymer science, polymer blending has been considered - both from an academic and industrial point of view - as the most efficient, low cost and "time to market" attractive route to develop new materials with superior overall performances [1]. Among all the studied polymer couples, polyamides (PA) and polyolefins (PO) has received the largest attention because of the expected addition of performances of the parent polymers (high mechanical, thermo-mechanical performances and chemical resistance for PA and low moisture uptake and ease to process for PO). This attractive wedding has led ARKEMA to develop 15 years ago a complete product range of these materials under the trade name ORGALLOY®. Beside these expected initial performances, ARKEMA Research has demonstrated the benefits of these polymer blends to control and improve different material performances like surface properties [2], permeability [3,4] or impact resistance [5].

Beside polymeric components, inorganic fillers are frequently used in polymer and polymer blends with advantages that include cost savings and improved (thermo) mechanical performances. Nevertheless, using regular micrometer type fillers often leads to performances compromise like the well know modulus/impact dilemma. Developed in the early 80's in Toyota laboratories, the concept of material reinforcement with "exfoliable" nanoclays has gained much attention because of its expected win/win approach. Open and patents literature [6] has revealed all the potential performances of these new "magic" nanocomposites : superior balance of modulus/impact, improved thermo-mechanical performances (HDT, Vicat), fire resistance properties, different thermal and processing behavior (CLTE) and – last but not least – permeability reduction attributed to the "tortuous pathway" concept [7].

As a consequence, it is noteworthy to notice resemblances between the two concepts of polymer blending and nanocomposites. It was very attractive to try to

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marry them through the development of compatibilized PA/PO/organoclay blends and evaluate their thermo-mechanical and barrier performances. That is clearly the topic of this paper.

2. Experimental

2.1. Materials

PA/PO/organoclay alloys have been prepared with Durethan® KU 2-2601 (Bayer) – a medium viscosity PA6 enriched with nano size clay particles - PE or PP as the dispersed phase polymer and a compatibilizer according to the internal ARKEMA know-how. Regular PA6 has been used as a reference to prepare compatibilized PA6/PO alloys without any nano clays. The ratio PA/PO is always defined to ensure that PA6 is the matrix of the blend in which PO is finely dispersed thanks to the compatibilizer.

2.2. Compounding and Processing

All blends were prepared with a Coperion Werner & Pflederer ZSK 30 laboratory modular co rotating twin screw extruder (L/D = 44) using 250–270 °C barrel set temperature, 300 rpm rotation speed and a throughput of 15 kg/h. Alloys have been blown on a laboratory Collin extruder to end up with 50 μm thickness monolayer films.

For sake of clarity, the Table 1 reports the reference of the films considered in this study and the raw materials associated.

2.3. Material characterization

Dynamic Thermo Mechnanical Analysis (DTMA) have been performed on extruded films during a temperature sweep from −100 °C to 220 °C at a fixed frequency of 1.6 Hz.

Permeability datas of the blown films have been recorded according to the standard methods ASTM D3985 for oxygen permeability and ASTM E96 for solvent permeability.

Morphologies of the blown films have been analyzed by Transmission Electron Microscopy with WEISS LEO 902 80 kV apparatus.

3. Results and Discussion

As mentionned in the introduction, this paper is focused on 2 main properties: the thermo mechanical and the permeation performances of these new composites.

Thermo Mechanical Properties

The first section of this paragraph is dedicated to the thermo-mechanical properties of the compatibilized PA6/PO alloys with or without nanoclays. The Figure 1 shows the evolution of storage and loss moduli (E′ and E″ respectively) as a function of temperature for PA6/PE and PA6/PE/nanoclay.

The addition of nanoclays in PA6/PE blends does not lead to a change in the secondary and main mechanical relaxations.

Figure 1 also clearly indicates a slight increase in storage modulus induced by the nanoclays over the temperature range considered (from −100 °C to 220 °C). Nevertheless near the melting zone, the benefit of nanoclays is completely erased by the sharp decrease of the modulus and the

Table 1.
The references in the first column will be used in the following article.

Reference used in the paper	Raw materials
PA6	Medium viscosity PA6
PA6/nanoclay	Durethan® KU 2-2601
PA6/PE	Medium viscosity PA6 + PE + compatibilizer
PA6/PE/nanoclay	Durethan KU 2-2601 + PE + compatibilizer
PA6/PP	Medium viscosity PA6 + PP + compatibilizer
PA6/PP/nanoclay	Durethan KU 2-2601 + PP + compatibilizer

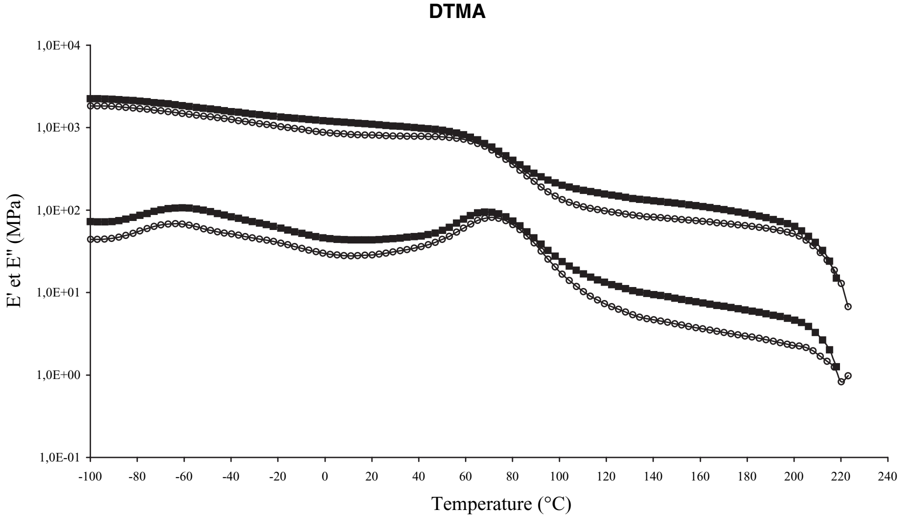

Figure 1.
E′ and E″ as a function of temperature. ■ = PA6/PE/nanoclay ○ = PA6/PE.

mechanical behaviour of the two blends is essentially governed by the modulus of the PA6 matrix. In this high temperature domain, the expected increase in storage modulus by the addition of nanoclays is not observed. As a conclusion, the association of alloy and nanocomposite technologies do not allow to generate new composites with significantly improved thermo mechanical properties at temperature close to the melting area. These two concepts do not provide innovating formulations route to design new materials for high temperature application.

Permeation Properties

The second section of this paragraph is related to the permeation properties of these new composites. Due to the fact that Orgalloy® materials are currently used in wide-ranging fields, different permeating species could have a practical and industrial interest. Two permeation cases will be presented and discussed in this paper : oxygen and styrene permeation. These two cases are linked to industrial applications for Orgalloy®, packaging and Sheet Molding Compounds (SMC) release films respectively (see Figure 2 for SMC release films).

Oxygen Permeation

The Figure 3 shows the oxygen permeation values measured at room temperature and 0% relative humidity for PA6/PP, PA6/PP/nanoclay, PA6 and PA6/nanoclay. PA6 and PA6/nanoclay have been evaluated in term of oxygen permeation in order to have references to compare with the new alloys.

The positive effect of nanoclays on the barrier properties is observed for both PA6 and the compatibilized PA6/PP blends. In fact, a 30% decrease in oxygen permeation

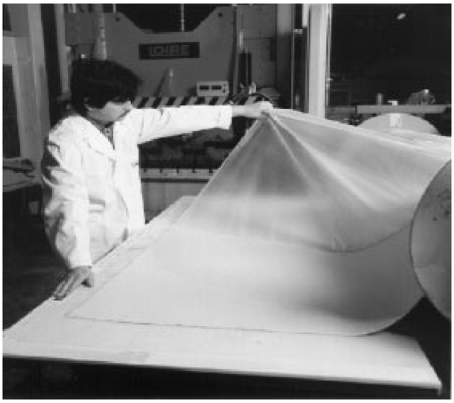

Figure 2.
SMC release film application : Film barrier to styrene required.

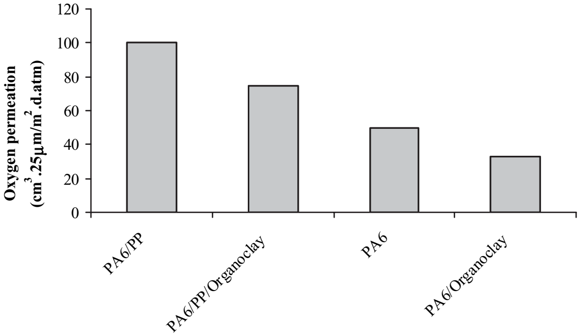

Figure 3.
Oxygen permeation at room temperature and 0% relative humidity for PA6/PP, PA6/PP/nanoclay, PA6 and PA6/nanoclay.

by the addition of nanoclay has been obtained for the considered blend and also for pure PA6. This result has been already reported in literature. As example, the Durethan® permeation performances extracted from the Bayer's data sheet [8] are perfectly in line with our measurements and confirm the 30% reduction in oxygen permeation obtained by the addition of nanoclays in PA6. This improved gas barrier performance resulting from the presence of nanoclays is commonly called "tortuous pathway" [7] concept.

PP based Orgalloy® (compatibilized PA/PP) is less oxygen barrier than PA6 due to the presence of PP dispersed phase which is highly permeable to oxygen (Figure 3). Based on the permeation value and the volumic fraction of the two phases, theorical permeation model [9,10] can be used to estimate the permeation value of the blends. The Table 2 gathers the theorical and experimental oxygen permeation values for PA6/PP and PA6/PP/nanoclay. The agreement between theorical and experimental values is good.

Styrene Permeation

The Figure 4 shows the styrene performances in term of permeation for 6 materials: PA6/PE, PA6/PP, PA6/PE/nanoclay, PA6/PP/nanoclay, PA6 and PA6/nanoclay.

A styrene permeation decrease is observed by the addition of nanoclays (Figure 4). Whereas the oxygen permeation decrease was similar for PA6 and for the compatibilized blends, the improvement of styrene barrier performances depends strongly on the materials considered. In particular, the permeation decrease is much higher for the blends compared to pure PA6 (see Table 3).

As a direct consequence of the permeation decrease difference, Orgalloy® nanocomposites become more styrene barrier than PA6 nanocomposites and especially in the case of PA6/PE/nanoclay Orgalloy®. In fact, whereas the styrene permeation of PA6/nanoclay is equal to 0.13 g · mm/m^2 · day, the styrene permeation of Orgalloy® PA6/PE/nanoclay is equal to 0.03 g · mm/m^2 · day. The association of

Table 2.
Comparison between theorical and experimental oxygen permeation values for the blends.

	Oxygen permeation (experience) cm^3 · 25 µm/m^2 · day · atm	Oxygen permeation (theory) cm^3 · 25 µm/m^2 · day · atm
PA6/PP	100	120
PA6/PP/nanoclay	75	80

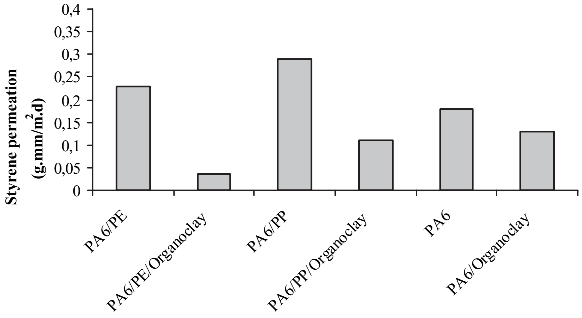

Figure 4.
Styrene permeation at 40 °C for PA6/PE, PA6/PP, PA6/PE/nanoclay, PA6/PP/nanoclay, PA6 and PA6/nanoclay.

alloy and nanocomposite technologies allows to produce a new composite PA6/PE/nanoclay Orgalloy® 4 times more barrier than the PA6/nanoclay composite and 8 times more barrier than the PA6/PE blend. This example clearly underlines the great benefit obtained through the synergy of the two nanocomposite and alloy technologies.

It is worth noting that Orgalloy® materials have at the first order the same permeation level than PA 6 before the addition of nanoclay (around 0.2 $g \cdot mm/m^2 \cdot day$ for PA6 and the two Orgalloy® grades). This remark confirms that the difference observed for the nanocomposite materials comes from the coupling effect between nanocomposite and alloy technologies and not from the alloy technology only.

Nevertheless a pendant question is : why is the nanoclay effect different between PA6 and Orgalloy®? The next section is dedicated to provide a physical explanation on this latter point.

Table 3.
Permeation decrease resulting from an addition of nanoclays. PA6 and two Orgalloy® grades are considered.

	Permeation decrease
From PA6 to PA6/nanoclay	35%
From PA6/PE to PA6/PE/nanoclay	85%
From PA6/PP to PA6/PP/nanoclay	60%

The permeation of a composite is given by the equation [11,12] :

$$P = \frac{P_{\text{matrix}}}{\left(1 + \frac{\Phi_d}{2} \times \frac{\mathrm{L}}{\mathrm{W}}\right)} \qquad \text{(eq.1)}$$

where : P_{matrix} is the permeation of the matrix polymer Φ_d is the volumic fraction of the clays L/W is the aspect ratio of the nanoclays (length divided by width).

Knowing the permeation of the composite and the permeation of the matrix (data are extracted from Figure 4) and according to equation 1, it is possible to calculate a "theorical" aspect ratio of the nanoclays in the different materials: PA6/nanoclay, PA6/PE/nanoclay and PA6/PP/nanoclay. The Table 4 gathers these calculated "theorical" aspect ratios for the 3 materials under consideration.

Obviously the higher the aspect ratio, the higher the permeation decrease (comparison of Tables 3 and 4). This comment only reflects the fact that the permeation reduction induced by the addition of the nanoclays essentially arises from the aspect ratio parameter of the fillers (see eq.1). The physical meaning of this calculation is confirmed by the good agreement between the calculed aspect ratio values (Table 4) and the well known aspect ratio of the used nanoclays (typically between 100 to 1000).

Besides, the large L/W differences between the 3 matrices can not be explained by the intrinsic shape of the nanoclays, in fact the two PA6/PO Orgal-

Table 4.
Calculated aspect ratio of the nanoclays in the 3 polymer matrix : PA6, PA6/PE Orgalloy® and PA6/PP Orgalloy®.

	L/W
PA6/nanoclay	50
PA6/PE/nanoclay Orgalloy®	600
PA6/PP/nanoclay Orgalloy®	200

loy® filled with nanoclays have been produced by using the same Durethan®, PA6/nanoclays, as a raw material (see Table 1). In other words, the nature, the shape and the exfoliation degree of the nanoclays introduced in the 3 matrices are the same. To go further on the analysis, TEM observations giving a picture of the morphology of these new alloys have been carried out on the extruded films (Figures 5 and 6). Figure 5 indicates that the nanoclays are only localized in PA6, the matrix of the alloys. We can conclude that the nanoclays exfoliated in PA6 by the raw material supplier remains in PA6 matrix during the compounding stage necessary to prepare the Orgalloy® materials.

Figure 6 demonstrates a high orientation of nanoclays along the extrusion axis. In addition, this picture illustrates the high degree of deformation/alignement of the PO nodules in this PA6/PO extruded film. This leads to a original structure which can be assimilated to a multilayer structure containing two types of layers : PA6 + nanoclay layers on the one hand and PO layers on the other hand. Owing to the similar characteristic dimension between the layers thicknesses and the nanoclays sizes, a perfect orientation of the nanoclays along the extrusion axis is observed : the nanoclays are confined in stretched PA6 domains. The major consequence is the increase of the aspect ratio of the nanoclay in the Orgalloy® in comparison to the intrinsic aspect ratio of the nanoclays. The classical tortuous pathway revealed in PA6 is replaced by a ‘‘multilayer’’ structure with a ‘‘continuous’’ nanoclays pathway in these polymer blends (L/W increases in the cases of Orgalloy® materials as shown by the calculation, see Table 4). This original structure is at the origin of the high styrene barrier performance of these new composites.

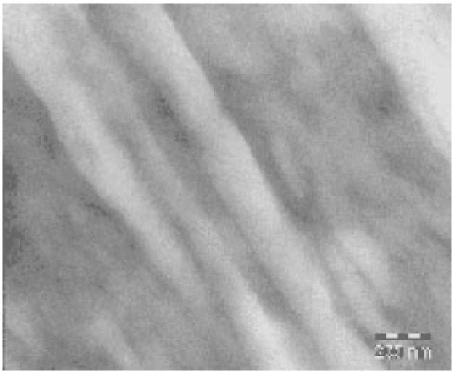

Figure 5.
Localisation of the nanoclays in PA6 (PA6 is darker than PO). TEM observation. Sample : extruded films.

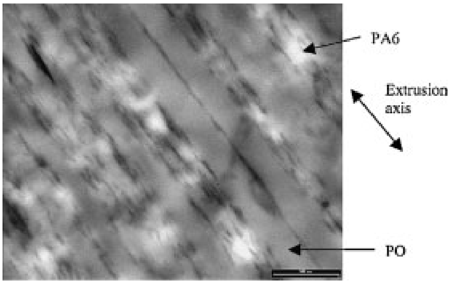

Figure 6.
Alignement of nanoclays in the blends. TEM observation. Sample : extruded films.

The great synergistic effect by coupling the alloy and the nanocomposite technologies has been clearly revealed with styrene as a permeating component. In this case, Orgalloy® filled with nanoclays is the most barrier materials and is also more barrier than the materials making up the alloys. It is worth noticing that this unusual behaviour is not universal ; that means that it depends on the permeating component. As an example, the oxygen permeation results do not show such a behavior.

The physical explanation of this specific and unusual behaviour in term of styrene permeability has already been detailled [3,4]. Briefly, the styrene molecules can not be absorbed by polyolefin nodules in spite of the high affinity between polyolefin and styrene because the swelling of polyolefin associated with the styrene absorption is prevented by the rigid non swollen PA6 matrix, which maintains its rigid behavior in contact with styrene, a non-plasticizer for PA6. As a consequence, the polyolefin nodules act as unpermeable components, as fillers and then create a ‘‘new’’ tortuous pathway. This behavior is observed with styrene which generates a high swelling and a large dimensional change of polyolefin if styrene is absorbed by the polyolefin and is not observed with small oxygen molecules because the absorption of oxygen in polyolefin is not associated to any significant polyolefin dimensional change.

4. Conclusion

The permeation through nanocomposite alloy materials strongly depends on permeating component. The association of alloy and nanocomposite technologies can lead to new materials with superior barrier properties comparing to the materials making up the alloys.

ARKEMA Research has studied and patented these new nanocomposite alloys and actively promotes this new concept in barrier packaging applications.

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