Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: Structure and volume fraction effects


A Université de Rouen, Laboratoire « Polymères, Biopolymères, Surfaces », FRE 3101 CNRS & FR 3038, 76821 Mont-Saint-Aignan Cedex, France
b Équipe de Rhéologie du LIMATB EA4250, Université de Bretagne Occidentale, 6 Av. Le Gorgeu, C.S. 93837, 29238 Brest Cedex 3, France

The water barrier properties of polyamide 12/organo-modified montmorillonite nanocomposites were studied by differential permeation. The water permeability and diffusivity were calculated from permeation kinetics and discussed with respect to the composite compositions. Depending on the clay volume fraction in the 0–5% range and the rotation speed during the composite processing, two different structures were obtained: a partially intercalated structure and a partially exfoliated structure, characterized by a higher level of exfoliation for the higher speed. In agreement with the tortuous path model, the water permeability and the diffusivity decrease with increasing clay volume fraction, \( \phi \), up to 2.5%, for both structures. However, beyond \( \phi = 2.5\% \) for partially intercalated nanocomposites and \( \phi = 4\% \) for partially exfoliated nanocomposites, the permeability no longer decreases, but increases. This effect was larger for the partially intercalated structure than for the partially exfoliated structure. The singular variations in the water permeation properties of nanocomposite membranes were interpreted in considering not only the structural properties, including the polymer crystallinity, but also various nanocomposite/permeant interactions, taking into account the plasticization phenomenon, solubility and free volume variations. It was possible to well simulate the permeation data by considering a water concentration dependent diffusion coefficient. Tensile measurements have shown the influence of the preparation conditions of nanocomposite membranes (clay volume fraction and the rotation speed) on the mechanical properties. As for permeation tests, the best performances were obtained with partially exfoliated nanocomposites compared to partially intercalated ones.

1. Introduction

Polymer/clay nanocomposites have received much attention in both scientific and industrial areas due to their enhanced mechanical [1–4], optical [5–7] and barrier properties [8–10] as well as their flame resistance [11–13]. These improvements are observed at silicate contents as low as 1 vol.%. The structure of nanocomposite membranes was known to play a key role in the improvement of these properties [14,15]. Three kinds of structures are classically encountered:

- **the tactoid structure**, where the clay is agglomerated in the polymeric matrix. This structure corresponds to a conventional microcomposite in which the polymer and the clay tactoids remain immiscible, resulting in poor macroscopic properties of the composite material.
- **the intercalated structure**, where the polymer is located in the clay interlayers, expanding the clay structure, still retaining some order between the platelets.
- **the exfoliated structure**, where the original face-to-face structure of the clay platelets has been completely destroyed and single clay sheets are randomly dispersed in the polymer matrix.

Exfoliated polymer–clay nanocomposite membranes are especially desirable because of their good macroscopic properties, mainly due to the large aspect ratio and interfacial area of the clay particles [16,17]. Nevertheless, complete exfoliation of the clay structure is very difficult to achieve and most polymer–clay nanocomposite membranes exhibit regions where partially intercalated and exfoliated structures coexist. The degree of exfoliation depends on many factors such as the chemical surface treatment of the clay particles and the processing conditions. Indeed, the inorganic clay surface is often modified by organic treatments to improve the affinity of clay towards the polymeric matrix, and the choice of the organic treatment was known to influence the degree of dispersion of the clay [14,18–20]. The techniques and methods used to prepare nanocomposites are also very important in terms
of structural organization. Three strategies are mainly used to prepare nanocomposites: in situ intercalative polymerisation [21–23], melt intercalation [20,24,25], and exfoliation–adsorption method [7,26,27]. The melt intercalation method has many advantages over either in situ polymerisation or exfoliation–adsorption method. First, it is environmentally acceptable due to the absence of organic solvents. Second, it is compatible with current industrial processes, such as extrusion and injection molding. Finally, it was possible to modify the nanocomposite structure by playing with the melt blending conditions.

Articles in the literature showed a complex dependence of the permeability of polymer films on the nanoclay content and the structure of nanofiller–polymer composites. Indeed, usually the barrier effect is improved when the degree of exfoliation is increased [10,15,28] but also when the nanoclay content increases [29–33]. In most works concerning nanocomposites, the barrier properties are examined by using gas [10,15,28,32,33]. In this case, the reduction of permeability is mainly explained by an increase of the diffusion path and modelized by a geometrical approach based on a tortuosity concept [34,16,17,35]. This approach is relatively good since no interaction occurs between the diffusing molecules and the material, which is the case of gas.

In this work, polyamide 12/organo-modified montmorillonite C30B nanocomposite membranes were prepared by a melt intercalation method under different processing conditions leading to partially intercalated or partially exfoliated structures. The effects of the C30B-nanoclay volume fraction, the polymer crystalline properties and the structure of PA12/C30B nanocomposites on the water transport parameters were investigated by differential permeametry, X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). A new feature was underlined in the present study: occurrence of a nanoclay volume fraction threshold beyond which the water permeability of the nanocomposites increased after a steady decrease at low nanofiller content. As far as we know, only improvement in the barrier properties of polymer materials with nanofiller content was reported in the literature.

The classical model that takes into account geometrical parameters of impermeable nanofillers is not able to describe such an increase in permeability [34]. The singular variations of nanocomposite water permeation properties versus clay volume fraction were fitted by a model considering (i) the structural properties, i.e. the polymer crystallinity, the aspect ratio and the rigidity that affect the tortuosity of the diffusion path, and (ii) the nanocomposite/permeant interactions, that alter the permeant solubility, modifying the free volume in the polymer phase by polymer plasticization, and the diffusion properties of the interfacial region around the nanoclay.

As for barrier properties, the effect of composition and preparation conditions on the mechanical properties of nanocomposites will be also examined using tensile measurements. The aim of the present work is to build up a transport model taking into account the changes in the fine structure of the PA12/clay nanocomposites and the plasticization of the matrix by water. This model allows to simulate and to discuss the effects of some structural parameters on transport properties, in particular the increase of the water permeability at high clay volume fractions. A new approach of the relative permeability for nanocomposites has been given on the basis of kinetic and thermodynamic aspects deduced from the analysis of the water permeation fluxes.

2. Experimental

2.1. Materials

The matrix used in this study was a commercial polyamide 12 (Fig. 1), referenced as Rilsan® ACHVO from ARKEMA (Serquigny, France). The melting point of the PA12 grade used in this work is 178 °C and, using thermo-gravimetric analysis (TGA), its weight loss was shown to be less than 0.5% after 45 min at 220 °C [36]. Its weight and number average molecular weights are equal to 37 000 and 20 000 g/mol, respectively [36]. The nanoclay additive used in this study is a commercial modified montmorillonite clay, referenced as C30B, whose specific gravity is ca. 2 g/cm³, supplied by Southern Clay Products (Gonzales, TX, USA). C30B is a methyl bis-2-hydroxyethyl tallow ammonium-exchanged montmorillonite clay with a cationic modifier content of 90 meq/100 g. The tallow chains of surfactant have a composition of ~65%C18; ~30%C16; ~5%C14.

![Chemical structures of the polymer matrix PA12 and the organo-modified montmorillonite C30B.](image)
Nanocomposites have been prepared by mixing the samples in the molten state in a Haake internal mixer (Rheocord EU 5). All nanocomposites were mixed during a residence time of 6 min and at a temperature of 200 °C, chosen to minimize the degradation of both PA12 and organic modifier. Indeed, the quaternary ammonium group is not very stable thermally. Due to the limited thermal stability of the clay-modification surfactant, the processing temperature was fixed at 200 °C, temperature which corresponds to 20 °C above the melting point of PA12. Then, samples were pelletized and processed by compression moulding at 200 °C in order to get 200–250 μm thick plates. The area of nanocomposite membranes was 16 cm × 16 cm. The moulding pressure was gradually applied from 0 to 250 bars during 10 min. The cooling step was kept for 3 min. The blade rotational speed was the processing variable of this study. Two rotational speeds have been used, 32 and 100 rpm, allowing to obtain two slightly different structures at each volume fraction tested. Rheometrical measurements, coupled with microstructural observations, have clearly shown that the PA12/C30B structure was influenced by the clay volume fraction [37] and melt blending conditions [38]. Aubry et al. [37] have shown that these nanocomposite membranes have a complex, intermediate structure composed of a few aggregates and numerous dispersed exfoliated clay layers. Médéric et al. [38] have studied the effect of mixing parameters on structural properties of these nanocomposites. Using the concept of specific particle density defined by Fornes et al. [39], they showed that the degree of exfoliation increases with increasing rotational speed, but also with decreasing volume fraction (Table 1). In conclusion, at any clay volume fraction studied, nanocomposite elaborated with the highest rotational speed exhibited improved rheological properties, signature of a better exfoliation degree. For the sake of clarity, these nanocomposites have been determined under the same experimental conditions and held on a silicon substrate which does not exhibit any diffraction line in the considered diffraction angle range. The diffraction peaks were fitted by Lorentzian equations. We calculated the crystallinity of the samples, \( X_C \), using the classical formula:

\[
X_C = \frac{A_C}{A_C + A_A}
\]

(1)

where \( A_C \) is the crystalline PA12 diffraction peak area, \( A_A \) is the PA12 amorphous halo area.

### 2.2. Preparation of polyamide 12/C30B nanocomposite membranes

Nanocomposites have been prepared by mixing the samples, in the molten state in a Haake internal mixer (Rheocord EU 5). All nanocomposites were mixed during a residence time of 6 min and at a temperature of 200 °C, chosen to minimize the degradation of both PA12 and organic modifier. Indeed, the quaternary ammonium group is not very stable thermally. Due to the limited thermal stability of the clay-modification surfactant, the processing temperature was fixed at 200 °C, temperature which corresponds to 20 °C above the melting point of PA12. Then, samples were pelletized and processed by compression moulding at 200 °C in order to get 200–250 μm thick plates. The area of nanocomposite membranes was 16 cm × 16 cm. The moulding pressure was gradually applied from 0 to 250 bars during 10 min. The cooling step was kept for 3 min. The blade rotational speed was the processing variable of this study. Two rotational speeds have been used, 32 and 100 rpm, allowing to obtain two slightly different structures at each volume fraction tested. Rheometrical measurements, coupled with microstructural observations, have clearly shown that the PA12/C30B structure was influenced by the clay volume fraction [37] and melt blending conditions [38]. Aubry et al. [37] have shown that these nanocomposite membranes have a complex, intermediate structure composed of a few aggregates and numerous dispersed exfoliated clay layers. Médéric et al. [38] have studied the effect of mixing parameters on structural properties of these nanocomposites. Using the concept of specific particle density defined by Fornes et al. [39], they showed that the degree of exfoliation increases with increasing rotational speed, but also with decreasing volume fraction (Table 1). In conclusion, at any clay volume fraction studied, nanocomposite elaborated with the highest rotational speed exhibited improved rheological properties, signature of a better exfoliation degree. For the sake of clarity, these nanocomposites have been determined under the same experimental conditions and held on a silicon substrate which does not exhibit any diffraction line in the considered diffraction angle range. The diffraction peaks were fitted by Lorentzian equations. We calculated the crystallinity of the samples, \( X_C \), using the classical formula:

\[
X_C = \frac{A_C}{A_C + A_A}
\]

(1)

where \( A_C \) is the crystalline PA12 diffraction peak area, \( A_A \) is the PA12 amorphous halo area.

### 2.3. Methods of analysis

#### 2.3.1. Thermo-gravimetric analysis

The amount of organic surfactant in the montmorillonite C30B and the exact mass fraction of C30B in the nanocomposites were determined by thermo-gravimetric analysis, using a TGA-7 Perkin-Elmer from 40 to 700 °C at a rate of 10 °C/min under nitrogen atmosphere.

#### 2.3.2. X-ray diffraction analysis

The crystalline properties of the nanocomposite membranes studied were investigated using a X-ray diffraction D8 Advance diffractometer from Bruker AXS. The source wavelength was \( \lambda = 1.79 \AA \), corresponding to the a line of Co. The sample was placed in a Bragg-Brentano configuration. The 2θ diffraction diagrams were determined between 2° and 60°. The samples were studied under the same experimental conditions and held on a silicon substrate which does not exhibit any diffraction line in the considered diffraction angle range. The diffraction peaks were fitted by Lorentzian equations. We calculated the crystallinity of the samples, \( X_C \), using the classical formula:

\[
X_C = \frac{A_C}{A_C + A_A}
\]

(1)

where \( A_C \) is the crystalline PA12 diffraction peak area, \( A_A \) is the PA12 amorphous halo area.

### 2.3.3. Differential scanning calorimetry

The thermal behavior of samples was analyzed by using the conventional differential scanning calorimeter Perkin-Elmer DSC-7. Samples with a mass of about 12 mg were used. The heating step was done from 50 °C to 200 °C at a rate of 10 °C/min. All DSC runs are carried out under nitrogen atmosphere to minimize the oxidative degradation. Before all DSC experiments, the baseline was calibrated using empty aluminum pans, and the DSC apparatus was calibrated using melting temperature and enthalpy of a high-purity indium standard (156.6 °C and 28.45 J/g).

The degree of crystallinity \( (X_C) \) was determined by using the following equation:

\[
X_C(\%) = \frac{\Delta H_m}{(1 - \phi) \Delta H^{0}_m} \times 100
\]

(2)

where \( \Delta H_m \) was the apparent melting enthalpy, \( \Delta H^{0}_m \) was the extrapolated value of the enthalpy corresponding to the melting of 100% crystalline PA12 (\( \Delta H^{0}_m = 245 J/g \) [40]).

#### 2.3.4. Mechanical tests

Tensile tests of nanocomposites were carried out on a universal testing machine (Instron model 5543). The tests were performed using a load cell of 500 N at a cross-head speed of 5 mm/min and a strain gauge extensometer with a gauge length of 30 mm.

The tensile specimens were machined in composite plates using the template of the French standard NF EN ISO 527-3. Young’s modulus, \( E \), characterizing the rigidity of the material, is the slope of the linear part at the origin of the stress–strain curve. For all nanocomposite samples, the value of the tensile modulus was the arithmetic mean of at least five different specimens.

#### 2.3.5. TEM micrographs

Samples were embedded directly in Spurr resin before sectioning at room temperature on Ultracut UCT microtome (Leica-Vienne). Ultrathin sections were collected on formvar carbon coated 100 mesh nickel grids and directly observed on a Transmission Electron Microscope Tecnai 12 Biotwin (FEI Company–Eindhoven). Image acquisition was performed with a CCD Megaview II camera controlled by analysis software (Eloise, France).

#### 2.3.6. Water permeation

The water permeation measurements were performed with an apparatus developed in our laboratory, called “permeadiffusiometer” [41]. This system, based on a differential permeation method, allows the determination of the diffusion coefficient and the permeability coefficient of a polymer film. The permeameter consists of a measurement cell, a dry nitrogen supply, and a chilled mirror hygrometer (General Eastern Instruments, Massachussetts, USA) (see Fig. 2(a)).

The previously dried film sample of thickness \( L \) was mounted in the cell and dry nitrogen was flushed into both compartments over many hours until a dew point lower than –70 °C was obtained. Next, a stream of liquid water was pumped through the upstream compartment, and then the water concentration in the initially dry
sweeping gas was monitored in the downstream compartment via the hygrometer and a data acquisition system.

The flux $J(L,t)$ at the dry interface was obtained from:

$$J(L,t) = \frac{Q}{S} (p_{\text{out}} - p_{\text{in}})$$

where $S = 30 \text{ cm}^2$ was the film surface area, $R$ is the ideal gas constant, $Q = 9.3 \text{ cm}^3 \text{s}^{-1}$ was the flow rate of the carrier gas sweeping the downstream face and $T_r \sim 298 \text{ K}$ was the temperature of the experiment. The water vapor pressures $p_{\text{in}}$ and $p_{\text{out}}$ are indirectly obtained from the dew point temperature, $T_{dp}$, of the sweeping gas \[41–43\].

2.4. Theoretical background

The mathematical treatment of diffusion transport through the film sample was based on the following assumptions \[44,45\]: (i) the polymer film is dense and homogeneous, (ii) the process is Fickian, (iii) the interfacial sorption equilibrium is instantaneous, and (iv) the mass transfer occurs in a direction perpendicular to the plane sheet.

Concentration and flux profiles, $C(x,t)$ and $J(x,t)$, are described by Fick’s laws and the boundary conditions used are

$$\begin{align*}
  \text{for } t = 0, & & C(x, 0) = 0 \forall x \in [0, L] \\
  \text{at } x = 0, & & C(0, t) = C_{eq} \forall t \\
  \text{at } x = L, & & C(L, t) = 0 \forall t
\end{align*}$$

2.4.1. Permeability

The permeability coefficient was obtained from the steady state flux by

$$P = \frac{J_{st} L}{\Delta \alpha}$$

where $J_{st}$ is the stationary flux and $\Delta \alpha$, practically equal to 1, is the difference in water activity between the two faces of the film.

2.4.2. Diffusivity

In order to examine the possible variation of diffusivity with water concentration, the diffusion coefficient was calculated at two different times of the extent of permeation process (Fig. 2(b)).

The diffusion coefficient was determined from:

- the time $t_i$, corresponding to $J/J_{st} = 0.24$, i.e. to the inflexion point of the transient permeation curve \[41\]:

  $$D_i = \frac{0.091 L^2}{t_i}$$

- the time-lag $t_L$, corresponding to $J/J_{st} = 0.62$ \[43\]:

  $$D_L = \frac{L^2}{6 t_L}$$

When the values of $D_i$ and $D_L$ are practically equal, $D$ can be assumed to be constant. Otherwise, a model that takes into account a possible variation of $D$ with the concentration $C$ of the sorbed molecules can be tested. The diffusion coefficient is usually...
assumed to increase exponentially with the local permeant concentra-
tion in the film during the course of water penetration [46], this was
generally attributed to an increase of the free volume because of
the plasticization of the material by the permeant [47,48]:
\[ D = D_0\gamma^C \]  
(8)
where \( D_0 \) is the diffusion coefficient at nil concentration, \( \gamma \) is the
plasticization coefficient and \( C \) was the local concentration of the
sorbed molecules [43,49].

To determine the two parameters of this diffusion law, we use a
method which was described in more details in a separate paper
[49]. The fitting procedure of the experimental transient flux data
allowed to compute the values of \( D_0, \gamma \) and \( F_p \), called the plasticiza-
tion factor. \( D_0 \), the kinetic parameter of the dry polymer, depends on
the microstructure of the material. The plasticization effect was re-
presented by the value of \( F_p = C_{eq}/C_0 \), which was directly linked to the
slope of the plot of the dimensionless flux \( J_{t}/J_{t,0} \) versus the reduced
time \( \tau = Dt/L^2 \) [43]. The plasticization factor depends both on
the water concentration in the material at equilibrium state, \( C_{eq} \), and
on the plasticization coefficient, \( \gamma \), which was correlated to the free
volume induced by the presence of diffusing molecules inside the
material [41]. Consequently, the equilibrium water concentration
was obtained from the following equation:
\[ C_{eq} = \frac{F_p}{D_0[\gamma^C - 1]}H_0L \]  
(9)

2.4.3. Water sorption

The liquid water sorption measurements were performed by
immersing the various nanocomposite samples in distilled water
at 25 °C. Samples were periodically removed, blotted dry with lint-
free paper, weighed, and immersed again in the beaker. Readings
were initially taken every 30 min for 3 h and afterwards every hour.
The experiment was continued until no mass gain could be recorded
during 5 days. The water concentration \( C_{eq} \) was then calculated from
the mass gain \( M = (M_{eq} - M_0)/M_0 \), \( M_0 \) being the dry mass and \( M_{eq} \)
the mass at equilibrium state of the water sorption kinetic.

The water vapour sorption has been measured by using an elec-
tronic microbalance (Cahn D200 with a mass resolution of 0.1 μg)
in an automated gravimetric dynamic vapor sorption system (DVS;
the sample (5–20 mg) to the measurement reactor, the material
was dehydrated under nitrogen flux until a constant mass was
obtained. The sample environment temperature was controlled at
25 ± 1 °C by a thermo regulated water bath. Then, vapour pressure
was increased in suitable levels up to saturation vapour pressure.
At each step, the mass gain was measured as a function of time until
an equilibrium state was reached. The water content at equilibrium
was used to build the sorption isotherm.

3. Results and discussion

The amount of organic surfactant in the Cloisite C30B and the
exact mass fraction of C30B in the nanocomposite membranes were
determined by thermo-gravimetric analysis. The parameter defin-
ing the C30B content used in the Figs and discussion is the solid
volume fraction \( \phi \) (cf. Table 2).

3.1. PA12/C30B nanocomposite structures

From TEM images of Fig. 3, the intermediate structure com-
posed of some aggregates and dispersed exfoliated layers exists in
our nanocomposite membranes. As revealed by these selected TEM
micrographs and in agreement with previous studies [37,38], it is
interesting to note the presence of more aggregates for partially
intercalated structures than for partially exfoliated ones especially,
at the highest volume fraction of C30B. The scattering of C30B in
the PA12 matrix has been examined from a statistical analysis of
nanoclays observed on TEM images. For that, more than 300 par-
ticles have been counted for each sample studied. Six classes of
particles have been determined as a function of the mean thickness
e; Class (i) for \( e = i \) to \( i + 1 \) nm, the last class (6) being for \( e > 6 \) nm.
For all nanocomposite membranes, the relative proportion of these
classes has been evaluated and is given in Fig. 4. Thus, it can be
deduced, at this observation scale (×60,000), the main presence of
class (1), (2) and (3) (1–4 nm) with the predominance of the class
(2) for which the particle thickness varies between 2 and 3 nm. This
distribution is rather non-dependant of the blend conditions and
of the volume fraction. Nevertheless, for \( \phi \sim 5\% \), it appears that the
partially intercalated nanocomposite (32 rpm) is characterized by
much more particles of thickness higher than 6 nm compared to the
partially exfoliated nanocomposite.

Before discussing the water permeation results, it was necessary
to verify the possible degradation of the C30B during the prepara-
tion of the nanocomposite. TGA measurements have been done in
dynamic (from \( T = 40–700 °C \) at \( 10 °C/min \)) and isothermal (\( T = 200 °C \)
during 10 min) modes. Results presented in Fig. 5(a) and (b) shows
that the blend conditions used in this work seem not to affect the
nanostructure, since the degradation temperature begins at about
250 °C and the isotherm remains practically constant. This results
has been also observed by Edwards et al. [50] who have studied the
degradation products of the C30B.

3.2. XRD and DSC analysis—structure and crystallinity

The crystalline regions of the polymers behave as barriers, and
any change in crystallinity can lead to a modification of the final
properties. It has already been shown that the presence of fillers
could lead to nucleation effects [51], and could partially impede
matrix crystallization; this could affect transport properties, keep-
ing in mind that permeability depends both on diffusivity and solubility, each depending on the concentration of the amorphous
regions [52].

Fig. 6(a) and (b) shows the diffraction patterns of partially interca-
lated and partially exfoliated nanocomposites, respectively, as
a function of C30B content. These diffractograms exhibit a PA12
crystalline peak at \( 2θ \sim 25° \), and an amorphous halo centred at
\( 2θ = 23.5° \) (Fig. 6(c)), leading to a crystallinity of pristine PA12, of
about 31% using Eq. (1). The morphology of crystal structure of PA12
was pseudo-hexagonal \( γ \) forms, characterized by four main reflection
peaks at \( 2θ = 6.5, 12.9, 25, 46.7° \) (Fig. 6(d), corresponding to
miller indices (0 2 0), (0 4 0), (0 0 1) and (2 0 1), respectively [53]).
It can be noticed that the nanocomposite and the pristine PA12
present the same crystal structure. Moreover, the reflection peak at
\( 2θ = 6.5° \) (\( d_{020} = 1.6 \) nm) of the crystalline structure of PA12 is close
to the C30B powder peak, (\( 2θ = 5.7° \), \( d_{001} = 1.8 \) nm). For a micro-
composite structure, the filler diffraction peak (\( 2θ = 5.7° \)) should
stay at the same position; for an intercalated structure, it should be
shifted to lower \( 2θ \) values; and for an exfoliated structure it should
disappear.

At low diffraction angles, the intensity increases due to direct
beam interaction with the sensor. Nevertheless, the relative
intercalation/exfoliation ratio increases with increasing clay con-
centration, as suggested by a smooth shoulder with a gradual
increase in the diffraction intensity at low angles in the XRD pat-
terns. This result shows that the degree of exfoliation is less at the
highest volume fractions, which is in good accordance with the
decrease of specific particle density with increasing volume fraction
(Table 1). At high clay loadings, clay agglomeration to some
extent was usually inevitable.

As shown in the enlarged XRD Fig. 6(a) and (b), the peak around
3.2°, corresponding to an inter-recticular distance of \( d_1 \sim 3.2 \) nm,
Table 2
Measured C30B mass fraction, solid volume fraction of C30B (\( \phi \)) determined by TGA and volume fraction of impermeable nanofillers (\( \phi_i \)) determined from Eq. (10).

<table>
<thead>
<tr>
<th>Measured C30B mass fraction (%)</th>
<th>( \phi ) volume fraction of C30B (%)</th>
<th>( \phi_i ) volume fraction of impermeable nanofillers (%)</th>
</tr>
</thead>
</table>
| **PA12/C30B partially intercalated**
| nanocomposites              |                                   |                                                  |
| 0                             | 0                                  | 0                                                 |
| 1.63                          | 0.81                               | 0.44                                              |
| 2.63                          | 1.31                               | 0.71                                              |
| 4.7                           | 2.35                               | 1.27                                              |
| 8.07                          | 4.03                               | 2.22                                              |
| 9.36                          | 4.08                               | 2.60                                              |
| **PA12/C30B partially exfoliated**
| nanocomposites              |                                   |                                                  |
| 0                             | 0                                  | 0                                                 |
| 1.66                          | 0.83                               | 0.44                                              |
| 2.27                          | 1.13                               | 0.61                                              |
| 5.42                          | 2.71                               | 1.47                                              |
| 8.13                          | 4.06                               | 2.24                                              |
| 9.05                          | 4.52                               | 2.51                                              |

appears for clay concentrations above 2.5%. For lower clay concentrations, this peak is absent or appears rather as a small halo (\( \phi < 2.5\% \)). This halo could be attributed to the polydispersity of inter-reticular distances but also to the lower relative intercalation/exfoliation ratio. Since the XRD diffractograms were normalized from the peak characteristic of the PA12 (\( 2\theta = 6.5\% \)), the intensity of the peak at 3.2\( ^\circ \) increases with the clay content, due to the increase of the number of diffracting particles. This peak originates from the shift of the peak located at 5.7\( ^\circ \) for C30B clay particles (Fig. 6(a) and (b)). This shift reveals the pres-
ence of intercalated structures in all nanocomposites. This result is consistent with TEM images exhibiting numerous aggregates for higher clays contents (φ = 5%) in which intercalated structures appear.

Moreover, at high Cloisite C30B contents, the ratio of the two inter-recticular distances $d_2/d_1$ ($d_2 = d_{020}$ relative to PA12) was equal to 0.5, meaning that the two diffraction peaks originate from multiple diffractions in the samples. From these results, it is rather difficult to differentiate both structures since intercalation was found for all samples exhibiting the same diffraction angles.

The crystalline volume content, $X_C$, determined by XRD, was plotted as a function of C30B volume fraction in Fig. 7. These results show that the crystallinity of the PA12 was slightly increased by the presence of clay particles below $\phi = 2.5\%$. In the case of partially exfoliated structure, the increase was more pronounced and could be attributed to a better nanoclay dispersion (Table 1), leading to a higher content of small crystallites. Above 2.5%, the crystalline volume content tends to decrease with increasing clay content, which should affect the nanocomposite permeability. This effect, which was more pronounced for the more exfoliated structure, was probably due to the presence of numerous dispersed clay entities bringing disorder inside the polymer matrix and so limiting the crystalline phase formation of the PA12 matrix. The crystalline structure of PA12 in nanocomposite membranes seems not to be affected by the presence of C30B. Nevertheless for $\phi > 5\%$, the slight shoulder located at $2\theta = 23^\circ$ (Fig. 6) would reveal the existence of another crystalline structure.

The crystalline structure of PA12 has also been studied by DSC for various content of C30B. Thermograms obtained by DSC during the first heating are presented in Fig. 8. On thermograms, it can be observed the peak of fusion close to 178°C related to $\gamma$ form of PA12 and the relaxation peak close to 166°C. For $\phi > 2.5\%$, if a second melting peak is not observed, the presence of another crystal structure could be masked by the spreading of melting peak. Anyway from diffractograms, because of the low intensity of the amorphous halo centred on $2\theta = 23^\circ$, the $\gamma$ form remains the majority crystalline phase. Finally, no significant change of morphology has been observed either from DSC curves or from DRX.
A second way to estimate the degree of crystallinity, $X_{C_{w}}$, was given by the melting and crystallization enthalpies obtained from DSC thermograms (Fig. 8(a) and (b)). From Eq. (2), the crystallinity of PA12 in partially intercalated and partially exfoliated PA12/C30B nanocomposites has been calculated and plotted as a function of C30B volume fraction in Fig. 9. From these data, it appears that the degree of crystallinity in PA12 was practically unchanged with the presence of nanoclays (close to 18%) but may be reduced very slightly for partially intercalated nanocomposites with volume fraction of charges higher than 4%.

In terms of degree of crystallinity, DSC and XRD results are different. It is well-known that each of the analytical techniques for crystallinity measurement has its own shortcomings. The discrepancy between DSC and XRD for nylon samples having a low crystallinity has been already observed [54] and explained by the fact that nyons obtained by fast cooling processing methods, develop smaller crystallite sizes that tend to broaden the crystalline peaks in X-ray diffractometer scans and thereby introducing some uncertainty in favor of amorphous phase. Differences between the values obtained by these two techniques can be attributed to the difficulty to separate the contribution of each phase (amorphous and crystalline) when the degree of crystallinity is low, especially in XRD measurements. XRD measurements give direct informations concerning the phases and the morphology but in one direction. Moreover, if XRD has the advantage to be a non-destructive method, the presence of crystallites on the sample surface may modify the X-ray penetration and so may give informations limited to a reduced thickness of the sample. Therefore the crystallinity rates determined from XRD may not represent the whole sample.

Concerning DSC, the quantitative analysis may be misinterpreted because of the placement of the baseline and the presence of moisture absorbed during sample preparation. To prevent this, samples were dried in desiccators under vaccum with P2O5. Moreover, by using DSC, the structure of the nanocomposite may change during the heating step, leading to an error in the determination of the crystallinity rate. In other words, the crystallinity measured by DSC corresponds to the overall crystallinity of the material.

In fact, the use of both techniques allowed us to obtain complementary informations for a qualitative analysis. From all these results, we infer that the overall crystallinity rate of our nanocomposite membranes is not, or slightly, affected by the presence of C30B nanofillers which seems induce a gradient of crystallinity in the sample thickness. In the discussion of water barrier properties, the crystallinity from both XRD and DSC results will be taken into account, since not only the overall crystallinity but also the gradient in crystallinity may affect the diffusivity and consequently the permeability.

### 3.3. Tensile tests

In Table 3 are gathered mean values of the Young's modulus, $E$, for partially intercalated and partially exfoliated nanocomposites. The variation of the relative Young's modulus, $E_{n}/E_{m}$, with the volume fraction of C30B is plotted in Fig. 10. The increase in $E$ with the nanoclay content in the composite is a generally observed behavior. Increasing the clay content usually results in an increase in the polymer Young's modulus and in a significant loss of ductility, especially at clay contents above about 3 wt.% [55]. The improvement was found to be even better for the well-dispersed exfoliated nanocomposites, as expected [55–57]. The average orientation of

<table>
<thead>
<tr>
<th>Volume fraction of C30B $\phi_{12}$–$\phi_{300}$ (%</th>
<th>$E$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partially intercalated</td>
<td>Partially exfoliated</td>
</tr>
<tr>
<td>0</td>
<td>1298.6</td>
</tr>
<tr>
<td>0.81–0.83</td>
<td>1465.2</td>
</tr>
<tr>
<td>1.31–1.13</td>
<td>1680.3</td>
</tr>
<tr>
<td>2.35–2.71</td>
<td>1720.3</td>
</tr>
<tr>
<td>4.03–4.06</td>
<td>1835.8</td>
</tr>
<tr>
<td>4.68–4.52</td>
<td>1918.2</td>
</tr>
</tbody>
</table>
Fig. 6. XRD diffractograms of nanocomposites for different C30B contents (a) partially intercalated nanocomposites, (b) partially exfoliated nanocomposites, (c) the partially exfoliated nanocomposite PA12/1.13% C30B, (d) the neat PA12.
Fig. 7. PA12 crystallinity (from X-ray) in PA12/C30B nanocomposites as a function of C30B volume fraction \( \phi \) \( (\circlearrowleft) X_c \) of partially intercalated nanocomposites, \( (-\triangle-) X_c \) of partially exfoliated nanocomposites.

Fig. 8. DSC thermograms of (a) partially intercalated nanocomposites and (b) partially exfoliated nanocomposites.

Fig. 9. PA12 crystallinity (from DSC) in PA12/C30B nanocomposites as a function of C30B volume fraction \( \phi \) \( (\circlearrowleft) X_c \) of partially intercalated nanocomposites, \( (-\triangle-) X_c \) of partially exfoliated nanocomposites.

Fig. 10. Relative Young’s modulus of partially intercalated and exfoliated nanocomposites.

The clay platelets in the polymeric matrix have been shown to have an influence on the nanocomposite mechanical properties [58]. The improvement of the mechanical properties depends also on the quality and quantity of interactions at the polymer/charges interface. Similar results were obtained by Aït-Hocine et al. [59] with PA12/C30B nanocomposites. They observed a clearly increase in the normalized parameter \( E \) with the nanoclay volume fraction \( \phi \), with a threshold of \( \phi \sim 0.01 \), for the transition between two regions defined by two different dependencies on \( \phi \). Moreover, as shown in Fig. 10, the volume fraction effect can be modulated according to the processing conditions used to prepare the samples. Indeed, for a volume fraction of 0.01, Young’s modulus does not depend significantly on the processing conditions, contrary to what is evidenced at higher volume fractions (Fig. 10). This result is in qualitative agreement with that obtained by Aït-Hocine et al. [59] and Dennis et al. [56] on PA6/clay nanocomposites: a higher degree of exfoliation leads to a higher Young’s modulus. It may be attributed to the reduction in the mobility of PA12 polymer chains confined in clay galleries, which is more marked as the structure is more exfoliated.


3.4. Water barrier properties of PA12/C30B nanocomposites

3.4.1. Repeatability

The water permeation measurements have been duplicated for pristine PA12 and for partially intercalated and partially exfoliated nanocomposites at a clay volume fraction $\phi = 2.5\%$; each sample was dried between the measurements. A slight relative increase of permeability, of the order of 10%, was observed systematically for the second run (Table 4). It did not depend on the C30B volume fraction, and would be rather attributed to the PA12 matrix change.

3.4.2. Permeability

Before the discussion of the experimental permeation results and models, it was necessary to well quantify the volume fraction of impermeable fillers. This volume fraction of the impermeable phase due to nanofillers, was calculated according to the following conventional formula:

$$\frac{1}{\phi_i} = 1 + \rho \left( \frac{1 - \mu_i}{\rho_p} \right)$$

with $\rho$ the specific gravity, $\mu$ the weight fraction and the subscripts $i$ and $p$ referring to the impermeable and the permeable phases, respectively. Since the nanocomposites used are mainly composed of partially exfoliated structures, the contribution of the surfactant layer was considered to be that of the permeable phase which represents 25% of the organo-modified montmorillonite C30B. The value of $\rho_i$ of the unmodified montmorillonite was then taken as equal to 2.86 g/cm$^3$ and $\mu_i$ was defined as the nanofiller weight fraction (instead of the inorganic platelet fraction) determined by TGA [28]. The calculated values of $\phi_i$ for partially intercalated ($\phi_{I2}$) and partially exfoliated ($\phi_{100}$) structures ranges from 0.44% to 2.6% (cf. Table 2).

The relative water permeability as a function of C30B volume fraction, $\phi$, is plotted in Fig. 11. At low C30B content, up to $\sim 2.5\%$, the water permeability decreases with increasing clay content for all samples tested, in accordance with the tortuous path model developed by Nielsen and Bharadwaj [34,35]:

$$P_n = \frac{P_m}{1 + (\alpha/2)\rho(2/3)[O + (1/2)]}$$

where $P_n$ is the permeability of the nanocomposite and $P_m$ is the permeability of the PA12 matrix. The key parameters of this model are the dispersed phase volume fraction of impermeable fillers $\phi_i$, the particle aspect ratio $\alpha$, and the orientation parameter of the clay platelets, $O$, which was chosen equal to 0, corresponding to particle random distribution ($O = 1/2[3 \cos^2 \theta - 1]$), $\theta$ angle between the plan of plates and the perpendicular to the diffusive flux).

From our permeation data, in terms of water barrier properties, the best performance was obtained with the partially exfoliated structure for 4% of clay volume fraction: 40% reduction of permeability which was not so high compared to that we expected. However, it is interesting to note that the same barrier effect was found for similar polyamide12/C30B nanocomposites having the same composition but tested with ethanol [60].

Table 4

<table>
<thead>
<tr>
<th>Neat PA12</th>
<th>PA12/2.35% C30B partially intercalated</th>
<th>PA12/2.71% C30B partially exfoliated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$(Barrer)$^a$</td>
<td>First run: 243 ± 5 ; Second run: 270 ± 6</td>
<td>First run: 155 ± 3 ; Second run: 177 ± 4</td>
</tr>
</tbody>
</table>

$^a$ 1 Barrer $= 10^{-10}$ cm$^3$ STP cm/cm Hg cm$^2$ s.

![Fig. 11. Relative water vapour permeability as a function of C30B volume fraction: (○) experimental results and (---) prediction of the tortuous path model for partially intercalated nanocomposites ($\alpha = 237$) or with the mean value $\alpha$ measured from TEM, (□) experimental results and (---) prediction of the tortuous path models for partially exfoliated nanocomposites ($\alpha = 255$) or with the mean value $\alpha$ measured from TEM.](image)

3.4.3. Diffusivity

Figs. 12 and 13 show the $D_l$ and $D_t$ diffusion coefficients of water molecules versus clay content, for partially intercalated and partially exfoliated nanocomposites. For both structures, the values of the diffusion coefficients $D_t$ and $D_l$ tend to decrease when the clay content increases, in apparent contradiction with the permeability behavior observed beyond 2.5%. This observation suggests that, combined with the increase in tortuosity, a possible increase in water sorption with filler content could reduce the diffusivity, attributed to the capacity of nanoclays to retain water molecules, possibly leading to water cluster formation. However, for all nanocomposite membranes tested, it can be observed that,
Fig. 12. $D_I (\text{\L}}$ and $D_L (\text{\S})$ diffusion coefficients as a function of C30B volume fraction for partially intercalated nanocomposites.

Fig. 13. $D_I (\text{\L}}$ and $D_L (\text{\S})$ diffusion coefficients as a function of C30B volume fraction for partially exfoliated nanocomposites.

during the water permeation process, $D_I$ was smaller than $D_L$. The experimental water flux curve has been fitted by using the concentration-dependent diffusion coefficient according to Eq. (9) [41]. As shown in Fig. 14 for the pristine PA12 sample, an excellent agreement between the experimental and the calculated flux was obtained, which was also observed for all nanocomposite membranes tested. The exponential concentration dependence of $D$ was often encountered and usually attributed to the plasticization of the material by the presence of water molecules. This phenomenon has been already observed in the case of another PA12 matrix [62]. The relationship $P=DS$ used in the case of constant $D$, was therefore not valid with our systems.

The limit diffusion coefficient $D_0$, defined at nil concentration, can give informations concerning the microstructure of the polymer. For both nanocomposite structures, $D_0$ diffusion coefficient as a function of clay content was plotted in Fig. 15. The curves exhibit the same behavior as those representing permeability as a function of clay content $\phi$ (Fig. 11). The decrease of $D_0$ with increasing clay volume fractions, up to 2.5%, agrees with the tortuous path model. Above 2.5% for partially intercalated nanocomposites and 4% for partially exfoliated nanocomposites, an opposite tendency was observed, which could be partly attributed to the decrease of crystallinity (Fig. 7) observed from XRD measurements. Another explanation of the increase of $D_0$ for highest clay contents would be due to an increase of the number of hydrophilic sites with the increase of C30B content. For highly filled nanocomposites, the existence of more and more aggregates in partially intercalated structures, compared with the partially exfoliated ones, should probably favor the diffusivity of water molecules along a new pathway consisting in a percolation path through the clay–polymer interfacial zones. The fact that $D_0$ increased from a volume fraction threshold ($\phi = 4\%$ and $5\%$ for partially intercalated structures and $\phi = 5\%$ for partially exfoliated structures), for which the TEM images showed a clear increase of clay aggregates (Fig. 3), suggests a significant contribution of the transport via the clay–polymer interfacial zones. Change in polymer segment flexibility due to the presence of rigid clay lamellae would affect the intrinsic diffusivity of water $D_0$.

The volume fraction dependence of the plasticization factor $\gamma C_{eq}$ was shown in Fig. 16, for both structures. The plasticization effect, due to the presence of sorbed water, increases the free volume during the permeation process and thus favors the chain segment mobility. As shown in Fig. 16, up to 4% of C30B, for both structures, the plasticization factor was very weakly dependent on the C30B content (between 1.5 and 2). Nevertheless, a slight difference appears between both structures: the plasticization effect was found higher for partially intercalated structure. Above 4%, a strong decrease of $\gamma C_{eq}$ with increasing volume fraction was observed for partially intercalated nanocomposite membranes. This surprising result could be explained partly by a reduction of the mobility of the polymer chain segments due to the presence of numerous dispersed clay entities.

In order to give a more precise physical insight into plasticization phenomena, the plasticization coefficient $\gamma$ and the equilibrium water concentration $C_{eq}$ have been plotted separately as a func-
tion of the C30B volume fraction in Fig. 17(a) and (b). The variations of $\gamma$ are similar to those observed for $\gamma C_{eq}$, but they are amplified and clearly show a transition volume fraction at $\sim 2.5\%$ for partially intercalated nanocomposites and at $\sim 4\%$ for partially exfoliated nanocomposites. For moderately loaded partially intercalated nanocomposites, the increase of $\gamma$ reveals an increase of the free volume within the material due to the insertion of water molecules that interact with hydrophilic sites. It is well-known that the presence of pre-existing free volumes is favored in glassy polymer, due to the reduction of the chain segment mobility. In that way, the increase of existing holes resulting from the increase of stiffness of the nanocomposite with the C30B volume fraction would lead to increase $\gamma$. For the partially exfoliated nanocomposite, Fig. 17(a) seems to indicate that volumes occupied by water molecules, located in the region of nanoclays, remain practically unchanged, except for 5% volume fraction. This tendency can be correlated to the better dispersion of partially exfoliated nanostructures, leading to a reduction of the water cluster size [43]. The strong drop of $\gamma$ (expressed in $\text{cm}^3 \text{mmol}^{-1}$), observed for volume fractions larger than 4%, instead of resulting of a decrease of the free volume, would result from both the increase of the sorbed water molecule quantities, due to the increase in the number of hydrophilic sites from C30B, a slight increase in the amorphous phase fraction, and from possible specific interactions between the matrix and water molecules in the modified structure of the nanocomposite system. The change in the equilibrium water concentration $C_{eq}$ as a function of C30B volume fraction is shown in Fig. 17(b). For low C30B contents ($\phi < 4\%$), the equilibrium water concentration is the same for both structures and remains practically constant. The fact that $C_{eq}$ does not much change can be explained by two antagonist effects: the increase of stiffness and crystallinity (from XRD), and at the same time the increase of the number of hydrophilic sites with increasing clay content. On the other hand, for 5% of C30B, a marked increase of $C_{eq}$ is observed only for partially intercalated structure, in accordance with the increase of the water permeability (Fig. 17(b)). The increase of the amorphous phase fraction, thus the sorbed water quantities and the key role of water molecules/clay particles interactions are not sufficient to explain such an increase of $C_{eq}$. For higher volume clay fractions (5%), a higher heterogeneity of the partially intercalated structure would favor the access of water molecules inside the nanocomposite. This assumption was clearly evidenced with the structures shown in Fig. 3, for the partially intercalated nanocomposite with 5% C30B, where several aggregates were observed. According to some authors, the quality of exfoliation depends on the clay content. It seems easier to obtain a better dispersion with a low mass fraction of clay due to the steric effect for high clay content [63, 64].

To verify the water concentration at equilibrium state $C_{eq}$ and confirm the increase in water solubility, liquid water sorption was measured at 25°C. The water concentration $C_{eq}$ was then calculated from the equilibrium state; the data are shown in Fig. 18(a). It appears clearly that the data from the permeation experiments are in good agreement with water sorption measurements, with a slight increase in water solubility at high filler contents, which was more marked for partially intercalated systems. In order to investigate the contribution of the modified nanoclays to water solubility, vapour water sorption measurements have been performed on PA12, non-treated Cloisite Na⁺ and Cloisite C30B, for different water activities and by means of a microbalance (DVS). The sorption isotherms, plotted in Fig. 18(b), show a large increase of the mass gain of Cloisite Na⁺ with relative humidity. For Cloisite C30B, which contains a surfactant, the hydrophobic part of the surfactant induces a significant reduction in the water sorption. Anyway, despite the hydrophobic character of the organic part of C30B, the water solubility of Cloisite remains higher than that of PA12. Thus the increase in water solubility in the nanocomposite membranes with the clay volume fraction, due to the hydrophilic character of C30B, should contribute to the re-increase of permeability.

3.4.4. Key factors for the modelling of relative permeability

Most of the models used are based on a geometrical approach which includes only the aspect ratio, $\alpha$, and the nanofiller vol-

---

**Fig. 16.** Plasticization factor $\gamma C_{eq}$ as a function of C30B volume fraction: (○) partially intercalated nanocomposites, and (●) partially exfoliated nanocomposites.

**Fig. 17.** (a) Plasticization coefficient $\gamma$ as a function of C30B volume fraction: (○) partially intercalated nanocomposites and (●) partially exfoliated nanocomposites. (b) Equilibrium water concentration $C_{eq}$ as a function of C30B volume fraction: (○) partially intercalated nanocomposites and (●) partially exfoliated nanocomposites.
ume fraction, \( \phi \) [65, 66]. Moreover, in these models, such as Cussler [67], Gusev-Lusti [65], Frederickson-Bicerano [65], an orientation of the platelets is fixed whereas in Nielsen and Bharadwaj's model, a dependence of the clay orientation is proposed. In spite of this dependence, the above-mentioned phenomena explain why Nielsen and Bharadwaj's model did not well describe the water transport properties of the PA12-based nanocomposite films. Indeed, this geometrical model based on the tortuosity effect is usually applied to the gas transport.

Permeability of liquids and vapours through filled polymers is much more complex than gas permeability. Liquids and vapours often have appreciable solubility in the polymer, so that the polymer can be plasticized. In addition, a liquid or a vapour may modify the polymer–filler interface, and the solubility or adsorption of liquid or vapour at the interface may be different from the solubility in the bulk polymer. Usually the relative permeability is based on the concept of \( P = DS \), which appeared appropriate for our hybrid systems, since the diffusion coefficient is not constant because of the plasticization effect of water. In this latter case it is more convenient to consider:

\[
P = \langle D \rangle S
\]

with \( \langle D \rangle \) the mean integral diffusion coefficient which is given by:

\[
\langle D \rangle = \frac{1}{C_{eq}} \int_{C_{eq}}^{0} D(c) dC
\]

Using the exponential law of \( D \) (Eq. (9)), the mean integral diffusion coefficient becomes:

\[
\langle D \rangle = \frac{D_0 (e^{F_p} - 1)}{F_p}
\]

Then, the relative permeability can be calculated from Eq. (12):

\[
\frac{P_n}{P_m} = \frac{\langle D \rangle_n}{\langle D \rangle_m} \frac{C_{eqn}}{C_{eqm}}
\]

The simulated values of the relative permeability are plotted in Fig. 19 for both structures. The very good agreement observed between experimental and calculated values validates the pertinence of the exponential law of concentration-dependent diffusion coefficient which initially allows a good fitting of our experimental flux curves. It is thus clear that in the phenomenological models used...
to simulate our permeation data, the diffusivity will depend not only on the tortuosity but also on the water concentration inside the nanocomposite membranes. To have a better approach in the modeling of the water transport of our nanocomposites, several factors affecting the kinetic and the thermodynamic properties should be considered. At this stage of discussion, the modeling step could allow showing the contribution of various parameters that means the phenomenological parameters used are approximate and adjustable parameters; in other words, the phenomenological parameters used are adjustable parameters. The interest of the modeling is to highlight the influence of each parameter and to show the tendency laws.

3.4.4.1. Aspect ratio $\alpha$. Picard et al. [28] analyzed the dispersion of montmorillonite in PA6 from TEM images. They showed that the mean value of $\alpha$ was not constant but varies with the volume fraction $\phi$. The tendency was that $\alpha$ decreases with the increase of $\phi$. As they suggest, from the analysis of the morphology with TEM images, we have calculated the mean value of $\alpha$:

$$\alpha = \frac{\sum n_i \alpha_i^2}{\sum n_i \phi_i} \quad (16)$$

where $n_i$ and $\alpha_i$ are the number and the aspect ratio for nanoclays of $i$ class, respectively. These classes were chosen with $i = 1, 2, 3, 4, 5,$ and 6 platelets. The values of the mean aspect ratio $\alpha$ determined for partially intercalated and partially exfoliated nanocomposites containing different volume fractions of C30B are reported in Table 5. These values are at least ten times lower than those previously computed from Eq. (11), but of the same magnitude than those obtained by Picard et al. [28] for montmorillonite/PA6 systems. It should be noted that the determination of the $\alpha$ value calculated from TEM images was not so obvious because of the clay-platelet curvature, knowing that the thickness of the prepared samples was close to 80 nm. Platelet orientation and flexibility lead to a $\alpha$ value underestimation. According to the blend conditions and above a certain clay content, these platelets may not act as isolated nanofillets that independently affect the diffusion path tortuosity. For these systems, clay platelets overlap each other, leading to a reduced effective surface and consequently to a reduced mean aspect ratio. According to Waché et al. [60], this effect can be integrated in the data fitting by using the corrected mean aspect ratio $\alpha'$ that includes an overlapping parameter $\chi$:

$$\alpha'(\phi) = \frac{\alpha(\phi)}{\chi} \quad (17)$$

In our case, the values of the parameter $\chi$ were estimated from TEM images for both structures at different volume fractions of nanoclays (Table 5).

3.4.4.2. Immobility factor $\zeta$. Kojima et al. [68] showed a correlation between the variation of the water diffusion coefficient and the stress–polymer fraction in nylon6–clay nanocomposites. The correlation is given by the following equation:

$$D = D_0 (1 - C)^{1/u} \quad (18)$$

where $C$ is the stress–polymer fraction, $D_0$ is the diffusion coefficient due to the amorphous phase and $u$ is a morphologic parameter. In that case, a decrease of $D$ is so observed with $C$ and thus with the clay content. Xu et al. [69] took into account the stress–polymer effect by adding a factor of polymer chain–segment immobility, $\zeta$, in the tortuosity factor of the Nielsen’s formula:

$$\tau = \xi(\phi) \left(1 + \frac{\alpha(\phi) \phi_i}{3} \left(0 + \frac{1}{2}\right)\right) \quad (19)$$

From the experimental point of view, it is rather difficult to highlight clearly the role played by the chain–segment mobility in nanocomposites. In our case, the analysis of the glass transition temperature, $T_g$, seems not appropriate for a discussion on the influence of the presence of nanoclays on the chain–segment mobility in the amorphous phase. Indeed, the glass transition temperature is affected by the presence of concomitant effects such as the plasticization effect of water, chain relaxation phenomena and the polymer crystallinity fraction. Furthermore, from our DSC results, the $T_g$ onset, at which the glass transition begins, seems unchanged with the filler content and the structure of the nanocomposites. The determination of the immobility factor $\zeta$ would require more investigations at the molecular scale. However, to have a first approach of the chain–segment mobility, the stiffness of the nanocomposite has been evaluated from tensile tests. The tensile modulus $E$ was determined and the values are gathered in Table 3. The increase of $E$ appears not to be linear as a function of nanofillers and depends on the structure of the material. Indeed, compared to partially intercalated structure, the stiffness of the nanocomposite is found higher with the partially exfoliated structure, especially for C30B volume fractions above ~2.5%. This result is consistent with the idea of a more homogeneous system for the partially exfoliated structure for which the nanofillers would be better dispersed, as revealed by TEM images (Fig. 3).

It is clear that the immobility parameter $\zeta$ is correlated to the stiffness of the sample but cannot be directly calculated from the Young’s modulus which is a macroscopic value. Nevertheless, it can be noted that the curves of the normalized $E$ (Fig. 10) clearly exhibit the threshold of $\phi \sim 2.5\%$, volume fraction above which the difference between the two structures becomes significant. The existence of such a content threshold is reminiscent of that observed, at $\phi \sim 2.5\%$, for the water barrier properties of these nanocomposites. Thus, in the fitting of the relative permeability, the variation of $\zeta$ with the volume fraction of C30B was attempted by using the ratio $E_\infty/E_{m}$. If the fitting using $E_\infty/E_{m}$ ratio is truly correct, it will give a trend in variation which allows us to introduce an adjustable exponent $b$:

$$\zeta(\phi) = \left(\frac{E_{m}}{E_\infty}\right)^{b} \quad (20)$$

3.4.4.3. Solubility factor $\beta$. The transport of small molecules through a nanocomposite depends not only on the size of the diffusing molecules but also on their chemical nature. For instance, specific interactions can occur during the permeation process such as interactions between water and clays, water and the polymeric matrix and some interactions at the polymer matrix/nanoclay interface. Some of these interactions can lead to a chain plasticization, associated to an increase in the free volume, but also to an aggregation of water molecules. In order to take into account these specific interactions in the modelling of the transport process, Waché et al. [60] proposed to consider a $\beta$ factor in the expression of the

<table>
<thead>
<tr>
<th>Volume fraction of C30B $\phi_{C30B}$ (%)</th>
<th>Partially intercalated</th>
<th>Partially exfoliated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81–0.83</td>
<td>13.5 1.1</td>
<td>14.2 1.1</td>
</tr>
<tr>
<td>1.31–1.13</td>
<td>13.5 1.1</td>
<td>13.2 1.1</td>
</tr>
<tr>
<td>2.35–2.71</td>
<td>15.5 1.2</td>
<td>14.1 1.2</td>
</tr>
<tr>
<td>4.03–4.06</td>
<td>13.3 1.2</td>
<td>14.3 1.2</td>
</tr>
<tr>
<td>4.68–4.52</td>
<td>13.7 1.6</td>
<td>13.3 1.4</td>
</tr>
</tbody>
</table>
solubility:

\[ S_n = S_{0n}(1 - \beta \phi) \]  

(21)

where the index \( n \) and \( m \) denote the nanocomposite and the matrix, respectively. By assuming that the crystallinity of the matrix can change with the nanofiller content, the solubility is then expressed by

\[ S_n = S_{0n}(1 - \beta \phi) \frac{1 - X_n^0}{1 - X_C^0} \]  

(22)

\( X_n^0 \) and \( X_C^0 \) being the crystallinity of PA12 in the filled and unfilled polymer, respectively. \( S_{0n} \) is the water solubility coefficient in the pristine PA12.

The \( \beta \) factor is deduced from Eq. (22), with the solubility calculated from the water equilibration concentration \( C_{eq} \) (Eq. (9)) and the crystallinity either from XRD or DSC data. As it can be seen from the \( \beta \) values in Table 6, the same behaviour is obtained for \( \beta \) from XRD or DSC results, when the clay volume fraction changes. The \( \beta \) parameter is not constant: an increase of \( \beta \) for low clay content followed by a decrease for clay volume fractions higher than 4% is observed. The variation of \( \beta \) for partially exfoliated structure is reduced compared with that of the partially intercalated one. It is observed. The variation of \( \gamma_{C_{eq}} \) for low clay content and is similar to that for the plasticization parameter by Nielsen[34] proposed another model based on the idea that a diffusing molecule can get through the filled system by going through the polymer and also diffusing along a path which consists of both the polymer and the interfacial zones. This model, schematized in Fig. 20[a], is given by the following equation:

\[ \frac{P_n}{P_m} = \frac{P_1}{P_m} + P_1 (1 - \phi m) \left( \frac{\phi \eta_1}{\eta}\right) + \left( \frac{\phi m + \phi_{lm}}{\eta m}\right) \]  

(24)

where \( \gamma = \langle D_o/D \rangle \) represents the plasticization effect, and \( \epsilon \) the adjustable parameter for this effect.

It can be further assumed that around each filler particle or filler aggregate, there is an interfacial layer whose properties differ from that of the bulk polymer saturated with liquid. Nielsen[34] proposed another model based on the idea that a diffusing molecule can get through the filled system by going through the polymer and also diffusing along a path which consists of both the polymer and the interfacial zones. This model, schematized in Fig. 20(a), is given by the following equation:

\[ \frac{P_n}{P_m} = \frac{k_1 k_2}{\phi n + k_1 (1 - \phi n)} \left( \frac{\phi \eta_1}{\epsilon} \right) + \left( \frac{P_n}{P_m} \right) \]  

(25)

\( k_1 = P_1/P_m \) and \( k_2 = \phi \eta_1/\phi n \) in Eq. (24) are the crystallinities of PA12 in the filled and unfilled polymer, respectively. \( P_n/P_m \) is the relative permeability calculated from Eq. (23).

More recently, Waché et al. have developed a polymer/nanofiller interaction modelling [60]. They supposed that the velocity of the diffusing molecules in the interface zone \( \left(V_i\right) \) can be different in the polymer matrix phase \( \left(V_m\right) \) (Fig. 20(b)). The tortuosity is then given

---

### Table 6

<table>
<thead>
<tr>
<th>Volume fraction of C30B</th>
<th>( \beta )</th>
<th>Partially intercalated XRD</th>
<th>( \beta )</th>
<th>Partially exfoliated XRD</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81–0.83</td>
<td>56.6</td>
<td>–43.3</td>
<td>26.3</td>
<td>–8.7</td>
<td></td>
</tr>
<tr>
<td>1.31–1.13</td>
<td>8.1</td>
<td>15.8</td>
<td>28.7</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>2.35–2.71</td>
<td>15.7</td>
<td>17.8</td>
<td>2.7</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>4.03–4.06</td>
<td>–3.9</td>
<td>–4.2</td>
<td>4.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>4.68–4.52</td>
<td>–39.3</td>
<td>–43.3</td>
<td>–4.9</td>
<td>–11.3</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 21. Relative permeability as a function of C30B volume fraction for partially intercalated nanocomposites. (○) experimental results and calculated values according to Eqs. (23), (25) and (27) in which \( \tau = 2 \), \( \varepsilon = 1 \), \( \tau^* = 1 \), \( k_1 = 50 \), \( k_2 = 0.5 \), \( \phi < 4\% \), \( n = 1 \) else \( n = 0.003 \) (a) \( \chi_c \) determined from DSC results and (b) \( \chi_c \) determined from XRD results.

Fig. 22. Relative permeability as a function of C30B volume fraction for partially exfoliated nanocomposites. (□) experimental results and calculated values according to Eqs. (23), (25) and (27) in which \( \tau = 1.1 \), \( \varepsilon = 0.5 \), \( \tau^* = 1 \), \( k_1 = 50 \), \( k_2 = 0.01 \), for \( \phi < 4\% \), \( n = 1 \) else \( n = 0.003 \) (a) \( \chi_c \) determined from DSC results and (b) \( \chi_c \) determined from XRD results.

\[
\tau = 1 + \phi \left( 1 + \frac{\alpha}{\frac{3}{2}} \frac{V_m}{V_i} - 1 \right)
\]

(26)

From previous considerations, such a tortuosity factor can be slightly modified by integrating the immobility factor and the new mean aspect ratio, leading to a new expression of the relative permeability:

\[
\frac{P_n}{P_m} = \frac{1 - \beta \phi_i}{\bar{\chi}(\phi)(1 + \phi_i(1 + (\alpha/\phi_i/3)(V_m/V_i) - 1)) \left[ \frac{1 - \chi_c^m}{1 - \chi_c^0} \right]^{2} \left[ \frac{y_n}{y_m} \right]^\varepsilon \tau^*}
\]

(27)

The modelling of the relative permeability of our nanocomposite systems for different volume fractions of clays were tested by using Eqs. (23), (25) and (27). Results of data fitting are shown in Figs. 21 and 22. The experimental curves were fitted by using the following values for the parameters: for partially intercalated nanocomposites \( \delta = 1.9 \), \( \varepsilon = 1 \), \( \tau^* = 1 \), \( k_1 = 50 \), \( k_2 = 0.4 \), for \( \phi < 4\% \), \( n = 1 \) else \( n = 0.009 \) and for partially exfoliated nanocomposites \( \delta = 1.05 \), \( \varepsilon = 0.5 \), \( \tau^* = 1 \), \( k_1 = 50 \), \( k_2 = 0.01 \), for \( \phi < 4\% \), \( n = 1 \) else \( n = 0.009 \). For both types of nanocomposite membranes, the crystallinity has been taken into account either from XRD or DSC results.

The values of \( \delta, \varepsilon, k_1, k_2, n \) used to fit the experimental data are arbitrary and thus the interpretation based on the comparison of these parameters for both structures can be erroneous. Nevertheless, it can be noticed that the values of \( \delta \) and \( \varepsilon \) are reduced by a factor of 2 for partially exfoliated nanocomposites compared to partially intercalated ones. The values of \( k_1 \) and \( k_2 \) are consistent with the fact that the permeability of the liquid in the interface, \( P_i \), is higher than \( P_m \) and the volume fraction of liquid in the inter-

![Fig. 23. Illustration of the diffusion of water through partially intercalated and exfoliated nanocomposites.](image-url)
facial region $\phi_{f}$ remains lower than $\phi_{m}$, the volume fraction of liquid dissolved in the polymer. The main interest of this model is that, in addition to the parameters proposed by other authors, it considers that a penetrate molecule can diffuse along paths which consist of both polymer and the interfacial region. Indeed, to explain such a re-increase in the relative permeability especially for partially intercalated nanocomposites, the variation of crystallinity and the increase in hydrophilic particle contents are not sufficient. The matrix/clay interface appears to play a key role in the transport properties. The percolation phenomenon, as illustrated in Fig. 23, would then contribute to the increase in the permeability and particularly with a material including aggregated particles, which is the situation for the highly filled nanocomposites with partially intercalated structure. In the latter case, for $\phi > 4\%$, $n$ was close to 0, which suggests interfacial regions form channels all the way through the film.

4. Conclusions

The water barrier properties of polyamide 12 incorporating organo-modified montmorillonite C30B were investigated by water permeation kinetics. The permeation results revealed limited water-barrier properties of the nanocomposite films and clearly showed a permeability transition at low silicate content, ~2.5%. Up to 2.5% of the C30B nanofiller, the water permeability decreases with the increase in the nanofiller volume fraction, in accordance with the tortuous path model. Indeed, for low nanoclay contents, the transport of water is mainly governed by the tortuosity and is evidenced by the decrease in the diffusivity ($D_1$, $D_2$, $D_3$). This tortuosity is a complex parameter, because it depends on several factors, like the aspect ratio, the stiffness and the crystallinity which are functions of the C30B volume fraction. Above 2.5%, the water barrier effect was not improved by further addition of clay particles and may even be cancelled in the case of partially intercalated nanocomposites. This loss of barrier properties was attributed to several concomitant effects: the possible change in polymer crystallite parameters (like morphology and fraction) of the matrix in presence of clay particles, the water-induced plasticization and the structure heterogeneity, particularly pronounced for highly filled and partially intercalated nanocomposites. In the latter case, the presence of more aggregate particles could lead to a percolation process. The lower performances of partially intercalated nanocomposites, compared to partially exfoliated ones, were not only observed with water permeation results but also with tensile measurements. Besides, it was interesting to note the existence of a same volume fraction threshold ($\phi \sim 2.5\%$), above which the difference between the two structures becomes significant for barrier and mechanical properties.

In terms of barrier properties, the analysis of the permeation fluxes allows a better understanding of the behaviour of nanocomposite membranes by considering that water molecules act as a probe inside the material at a nanoscale and that the nanocomposite properties highly depend on the interface between nanoclays and polymer matrix.

From the modelling data, we showed that the first Nielsen and Bharadwaj’s model, a geometrical approach more convenient for gas transport, was not sufficient to well describe the transport of water through the PA12-based nanocomposite films. Liquids often have appreciable solubility in the polymer, so that the polymer can be plasticized. In this work, the modelling of water permeation data was carried out in considering not only the volume-fraction-dependent factors that affect the tortuosity (the immobility factor, aspect ratio, recovery parameter, crystallinity) but also the plasticization factor and the solubility factor. All those parameters result from specific interactions between water molecules and the components of the nanocomposite (matrix and nanoclays). The modified Nielsen’s model which is based on the diffusion of a permeant through the polymer and along the interface region, was retained, because it is the only one capable to correctly model a relative water permeability characterized by a transition with the structure-dependent volume fraction of nanoclays in PA12.

Acknowledgments

RMPP “Réseau Matériaux Polymères Plasturgie” funding is gratefully acknowledged. Electron microscopy was done at the Centre commun de microscopie électronique de la Plate-forme de Recherche en Imagerie Cellulaire de Haute- Normandie – UMR 6037 CNRS- Université de Rouen – France. Thanks are due to L. Chevalier for her excellent technical assistance during all microscopy works.

References
