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Polymer 44 (2003) 2271–2279

polymer

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Vapor barrier properties of polycaprolactone montmorillonite nanocomposites: effect of clay dispersion

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Received 30 July 2002; received in revised form 10 December 2002; accepted 27 January 2003

Abstract

Different compositions of poly(ε-caprolactone) (PCL) and (organo-modified) montmorillonite were prepared by melt blending or catalyzed ring opening polymerization of ε-caprolactone. Microphase composites were obtained by direct melt blending of PCL and sodium montmorillonite (MMT-Na^+). Exfoliated nanocomposites were obtained by in situ ring opening polymerization of ε-caprolactone with an organo-modified montmorillonite (MMT-$(OH)_2$) by using dibutyltin dimethoxide as an initiator/catalyst. Intercalated nanocomposites were formed either by melt blending with organo-modified montmorillonite or in situ polymerization within sodium montmorillonite. The barrier properties were studied for water vapor and dichloromethane as an organic solvent. The sorption (S) and the zero concentration diffusion coefficient (D_0) were evaluated for both vapors. The water sorption increases with increasing the MMT content, particularly for the microcomposites containing the unmodified MMT-Na^+. The thermodynamic diffusion parameters, D_0, were compared to the value of the parent PCL: both microcomposites and intercalated nanocomposites show diffusion parameters very near to PCL. At variance exfoliated nanocomposites show much lower values, even for small montmorillonite content. In the case of the organic vapor, the value of sorption at low relative pressure is mainly dominated by the amorphous fraction present in the samples, not showing any preferential adsorption on the inorganic component. At high relative pressure the isotherms showed an exponential increase of sorption, due to plasticization of the polyester matrix. The D_0 parameters were also compared to those of the unfilled PCL; in this case, both the exfoliated and the intercalated samples showed lower values, due to a more tortuous path for the penetrant molecules.

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Keywords: Nanocomposites; Sorption; Diffusion

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1. Introduction

In the development of engineering polymers an important objective is to reinforce the polymer matrix and to improve mechanical and thermal properties without spoiling processability, optical properties and toughness. Inorganic additives are introduced into polymer systems as fine solids to act either as fillers or as reinforcing agents. Among the inorganic materials, the smectite clays receive considerable interest because their structure exhibit stiffness, strength and dimensional stability in two dimensions, rather than one [1,2]. The efficiency of montmorillonite to modify the properties of the polymer is primarily determined by the degree of its dispersion in the polymeric matrix. The hydrophilic nature of the mineral hinders homogeneous dispersion of the montmorillonite in the polymer; however, due to their rich intercalation chemistry, the clays can be organically modified and made compatible with the organic matrix. By replacing the hydrophilic Na^+ cations with a more hydrophobic onium ion, such as ammonium cations with long alkyl chains, the miscibility between the silicate layers and the polymer matrix can be enhanced, and a concomitant increase of the interlayer distance is observed. In this way, nanocomposites are obtained in which the nanoparticles dispersed in the organic matrix are either intercalated by the polymer or exfoliated into individual silicate layers of 1 nm thick [3–5]. Because of their nanometer size features, these nanocomposites possess

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doi:10.1016/S0032-3861(03)00108-3

unique properties typically not shared by the conventional microcomposites.

The preparation of a polymer/clay nanocomposite can be achieved by intercalation of a suitable monomer into the swelling clay mineral, followed by in situ polymerization [2,6]. Alternatively, a direct polymer intercalation of molten polymer can be used [2,4,7,8]. In either case the nanoparticles can be intercalated by the macromolecules or exfoliated.

As shown in previous papers [9,10], microcomposite systems are obtained by melt blending a commercial poly(ε-caprolactone) (PCL) with a non-modified montmorillonite (MMT-Na^+), whereas intercalated samples can be obtained by melt blending the montmorillonite modified by various alkylammonium cations. Moreover ε-caprolactone (CL) can be mixed with MMT and polymerized at room temperature by activating the polymerization with dibutyltin dimethoxide [11]. Several MMT were studied, modified by alkylammonium cations either non-functionalized or bearing hydroxyl groups. Depending on the surface modification of MMT, intercalated or exfoliated clay minerals were obtained. In particular, an exfoliated system was obtained with a MMT modified with an alkylammonium cation bearing two primary hydroxyl groups (MMT-$(OH)_2$) [9–11].

In this paper we investigated the transport properties, sorption and diffusion, of a series of microcomposites and nanocomposites, either intercalated or exfoliated, based on poly(ε-caprolactone) and montmorillonite. In the composites the clay content was varied from 1 to 10% by weight. The aim was to determine the influence of either the inorganic content or the morphological texture on the sorption and diffusion of water vapor and of dichloromethane as an organic vapor.

2. Experimental part

2.1. Materials

ε-Caprolactone (Fluka) was dried over CaH_2 and distilled under reduced pressure prior to use. Dibutyltin dimethoxide ($Bu_2Sn(OMe)_2$) was purchased from Aldrich and diluted with dry toluene. Commercial grade poly(ε-caprolactone) (CAPA®650) was supplied by Solvay Chemicals sector-SBU. The number average molar mass was 49,000 with a polydispersity of 1.4, as determined by size exclusion chromatography. The clays were supplied by Southern Clay Products (Texas, USA). Cloisite® Na^+ (MMT-Na^+) is a natural unmodified montmorillonite with a cation exchange capacity (CEC) of 92 meq/100 g and with an interlayer distance of 1.2 nm (evaluated by X-ray diffraction measurement on the powder dried in vacuo at 80 °C). Cloisite® 30B (MMT-$(OH)_2$) is a montmorillonite modified by (hydrogenated tallow alkyl)methyl bis(2-hydroxyethyl) ammonium ions. The organic content of the organo-modified montmorillonite (MMT-$(OH)_2$) was 20.5 wt%, as determined by thermogravimetric analysis (TGA).

2.2. Preparation of microcomposites by melt blending

The microcomposites were obtained by melt-blending commercial PCL (M_n 49,000) with unmodified montmorillonite (MMT-Na^+). These PCL silicate microcomposites were prepared by mechanical kneading on an Agila two-roll mill at 130 °C for 10 min. The collected molten materials were compression-molded into 3 mm-thick plates by hot-pressing at 100 °C under 150 bars for 10 s, then under 30 bars for 10 additional seconds, followed by cold pressing at 15 °C under 30 bars for 5 min. Composites containing 1, 3, 5 and 10 wt% of MMT-Na^+ were prepared. The inorganic content of each composite was checked by TGA.

2.3. Preparation of intercalated nanocomposites

Intercalated nanocomposites were obtained either by melt blending PCL with the organo-modified montmorillonite (MMT-$(OH)_2$ in this case) or by in situ intercalative polymerization of CL with unmodified montmorillonite (MMT-Na^+). These samples were prepared as aforementioned for the microcompositions. It is worth pointing out that perfectly intercalated nano-structures without any trace of MMT delamination/exfoliation, were generated by in situ intercalative polymerization of CL with MMT-Na^+. On the other hand, intercalated nanocomposites with some extent of clay delamination were obtained by melt blending PCL with MMT-$(OH)_2$ [9–11].

2.4. Preparation of exfoliated nanocomposites by in situ polymerization

Exfoliated nanocomposites were obtained by in situ intercalative polymerization of ε-caprolactone (CL) with montmorillonite modified by alkylammonium cations bearing two hydroxyl groups. Before polymerization, this organo-modified montmorillonite (MMT-$(OH)_2$) was dried in a ventilated oven at 70 °C for one night. The desired amount of clay was added into a polymerization tube and dried under vacuum at 70 °C for 3 h. A known amount of ε-caprolactone (CL) was then added under nitrogen, and the reaction medium was stirred at room temperature for 1 h. A solution of $Bu_2Sn(OMe)_2$ in dry toluene was finally added, such that the $[monomer]_0/[Sn]$ molar ratio was 300. The polymerization was allowed to proceed at room temperature for 24 h. Nanocomposites containing 1, 3, 5 or 10 wt% of inorganics were targeted. The clay content within each composite was assessed by TGA.

2.5. Film preparation

Films were obtained by molding the samples in a Carver laboratory press, at the temperature of 100 °C, followed by a quick quenching in a ice-water bath. Sample are coded as: (Type of montmorillonite) PCLXY where $X = 1, 3, 5, 10$ for samples containing 1, 3, 5, 10 wt% of MMT; and $Y = $ M, E, I is M for melt blended microcomposites, E for in situ polymerized exfoliated nanocomposites, I for intercalated nanocomposites either by melt blending or by in situ polymerization.

2.6. Measurements of transport properties

Sorption and diffusion were measured by a microgravimetric method, using a quartz spring balance having an extension of 1.62 cm/mg. The vapor permeants were dichloromethane at 25 °C and water vapor at 30 °C. Sorption was measured as a function of the relative pressure, $a = P/P_0$, where P is the actual pressure (in atm) of the experiment, and P_0 the saturation pressure at 25 °C for dichloromethane (0.54 atm) and at 30 °C for water (0.042 atm).

3. Results and discussion

In semi-crystalline polymers the crystalline regions are considered to be impermeable to the vapor molecules. The amorphous phase is supposed to have the same specific permeability irrespective of the extent of crystallinity. Therefore, by increasing the crystallinity, there is a decrease in sorption due to a reduced amorphous volume and a decrease in diffusion due to a more tortuous path for the diffusing molecules [12–14]. It was found for polyethylene and polypropylene that the sorption was proportional to the amorphous fraction; at variance the thermodynamic diffusion parameter was constant in a wide range of crystallinities and decreased for values higher than 60% [15,16]. In polymeric systems containing a mesophase, at low penetrant pressure the sorption was found related to the amorphous phase, the mesophase being impermeable like the crystalline phase [17–21].

Composites and nanocomposites are multiphase systems in which the coexistence of phases with different permeabilities can cause complex transport phenomena [22]. When only one phase is permeable to the penetrant, or shows a much higher permeability than the other phases, one can assume that transport only occurs in the permeable phase. This phase is presumed to have the same specific sorption capability, irrespective of the extent of the impermeable phases.

In the case of PCL composite samples, the system comprises a semi-crystalline polymer, poly(ε-caprolactone), and large aggregates of montmorillonite (microcomposites) or dispersed domains of the organically modified montmorillonite (exfoliated and intercalated nanocomposites). Morphology and microstructure of this multi-phase system are expected to play a very important role in determining the transport phenomena [22]. On one hand, the presence of the montmorillonite layers can introduce specific sites in which hydrophilic molecules can be adsorbed and, in some cases, immobilized [23]. On the other hand, the presence of highly dispersed clay platelets ought to increase to a large extent the tortuosity of the system, leading to an expected large decrease in the value of the diffusion coefficient. As far as sorption is concerned, the value will be mainly influenced by the amount of the amorphous fraction of PCL as well as the chemical nature of the permeant vapor. In addition, sorption on specific sites of the inorganic component can contribute to the overall sorption.

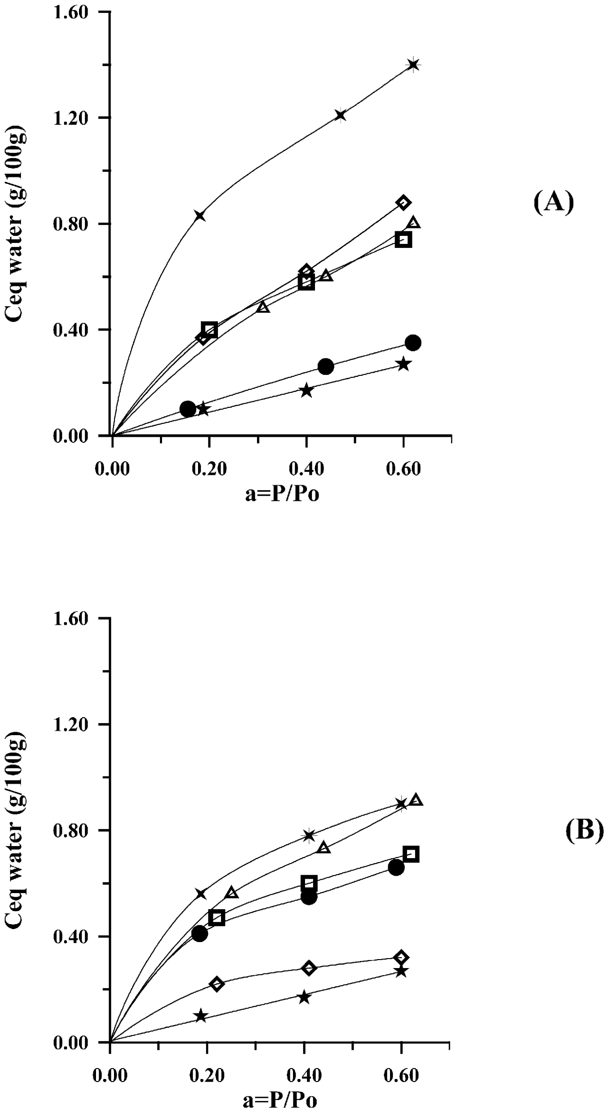

Fig. 1. Sorption isotherm of water vapor for (A): (★) PCL, (●) (MMT-Na$^+$)PCL1M, (◻) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)-PCL5M, (◇) (MMT-Na$^+$)PCL10M, (✳) MMT-Na$^+$. (B): (★) PCL, (●) (MMT-(OH)$_2$)PCL1E, (◻) (MMT-(OH)$_2$)PCL3E, (△) (MMT-(OH)$_2$)-PCL5E, (◇) (MMT-(OH)$_2$)PCL10E, (✳) MMT-(OH)$_2$.

3.1. Water vapor

Fig. 1 shows the equilibrium concentration, C_{eq} (g/100 g), of water vapor as a function of the activity, $a = P/P_0$, for the microcomposites (A) and exfoliated nanocomposites (B). For comparison, the isotherms of the unfilled PCL sample and of the two different montmorillonites used are also displayed. The sorption curve of the inorganic component follows the dual-sorption behavior [23]: at low activity (up to $a \approx 0.2$), a rapid increase of vapor concentration indicates that, besides the normal dissolution process, the sorption of the polar solvent also occurs on preferential sites, in which the molecules are adsorbed and/or immobilized. It is assumed that these specific sites on the matrix have a finite capacity. When the preferential sites are occupied the isotherm becomes linear due to the normal vapor dissolution. At each activity, the sorption of MMT-Na$^+$ (Fig. 1A) is larger than that of MMT-(OH)$_2$ (Fig. 1B), due to a more hydrophilic character of MMT-Na$^+$.

Pure PCL polymer does not show the dual-sorption; in this case the equilibrium concentration of water vapor increases linearly with the activity in the investigated range. At variance, all the composite systems show the dual sorption behavior. Moreover in both micro- and nanocomposites the amount of sorbed water increases with MMT content, indicating that the clay mineral is responsible of the enhanced sorption. However, it seems that the dispersed montmorillonite sorbs more than expected from its weight fraction in the composite samples. Actually the dispersion of the inorganic component into the polymer matrix, opening the layered structure, could make more and more sites available to the water molecules.

From the second part of the isotherms, where the specific sites are occupied and C_{eq} increases linearly with P/P_0, we derived a sorption parameter (S) [22]:

$$S = \mathrm{d}C_{eq}/\mathrm{d}P \qquad (1)$$

where P is the partial pressure of the water vapor.

The numerical values of S agree with the previous observations: also in the second part of the curve the sorption increases with increasing montmorillonite content. It is worth noting that the crystallinity values, derived by calorimetric measurements not reported here, are very similar for all the composite samples, ranging between 45 and 50%. In this sense, sorption of water in nanocomposite systems is not simply related to the amorphous fraction present in the samples but depends on the inorganic content and on its texture.

The exfoliated nanocomposite sample containing 10 wt% of montmorillonite (MMT-(OH)$_2$) shows an anomalous behavior, being its sorption coefficient the lowest. This may be related to a different morphological organization of the clay mineral particles in this sample. For example, a more 'closed' structure, in which the hydrophilic residues are shielded or appear less available to the sorption of the water molecules, could explain the lower sorption. This aspect needs a further investigation.

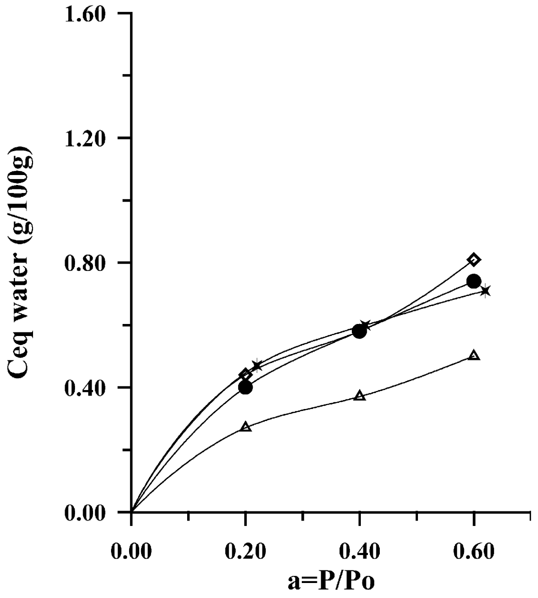

Fig. 2. Sorption isotherm of water vapor for (★) (MMT-(OH)$_2$)PCL3E, (●) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL3I, (◇) (MMT-(OH)$_2$)PCL3I.

In Fig. 2 we compare the sorption properties of the microcomposite, of the intercalated and of the exfoliated nanocomposite containing 3 wt% of montmorillonite. Compared to the microcomposites and exfoliated nanocomposites, the intercalated (MMT-Na$^+$)PCL3I sample shows a lower sorption on the specific montmorillonite sites. Also in this case a different morphological organization may be assumed. Moreover Table 1 shows that the sorption of the intercalated systems depends on the type of montmorillonite, too. The nanocomposites of intercalated organomontmorillonite have higher sorption compared to exfoliated nanostructures. In conclusion, sorption at low activity is mainly determined by the presence of the inorganic component and depends on its concentration and texture. Morphological studies are in progress to clarify this aspect of the composite systems.

Table 1
Sorption coefficients, S (wt%/mm Hg), and zero concentration diffusion coefficients, D_0 (cm^2/s), of water vapor

Sample	S (wt%/atm)	D_0 (cm^2/s)
PCL	10.336	9.76×10^{-8}
(MMT-Na$^+$)PCL1M	11.856	1.99×10^{-7}
(MMT-Na$^+$)PCL3M	21.280	1.29×10^{-7}
(MMT-Na$^+$)PCL5M	22.040	1.09×10^{-7}
(MMT-Na$^+$)PCL10M	28.120	3.72×10^{-8}
(MMT-(OH)$_2$)PCL1E	14.440	3.27×10^{-9}
(MMT-(OH)$_2$)PCL3E	15.960	2.12×10^{-9}
(MMT-(OH)$_2$)PCL5E	22.040	6.59×10^{-10}
(MMT-(OH)$_2$)PCL10E	0.0760	2.89×10^{-10}
(MMT-Na$^+$)PCL3I	13.680	6.77×10^{-8}
(MMT-(OH)$_2$)PCL3I	22.040	2.21×10^{-7}

For all the composite systems the diffusion coefficient, at different vapor activities, was obtained from a plot of the reduced sorption:

$$C_t/C_{eq} = 4d(Dt/\pi)^{1/2} \qquad (2)$$

where d (cm) is the thickness of the sample, C_t is the water concentration at time t, and C_{eq} is the water concentration at the equilibrium value.

In the case of Fickian behavior, the reduced sorption curve presents an initial linear behavior followed by a plateau indicating the equilibrium sorption; from the first linear part the mean diffusion coefficient, D (cm^2/s), for each vapor activity, is obtained.

For polymer–solvent systems, the diffusion parameter is usually not constant, but depends on the vapor activity, according to the empirical equation:

$$D = D_0 \exp(\gamma C_{eq}) \qquad (3)$$

where D_0 (cm^2/s) is the zero concentration diffusion coefficient (related to the fractional free volume and to the microstructure of the polymer); γ is a coefficient, which depends on the fractional free volume and on the effectiveness of the penetrant to plasticize the matrix.

In Fig. 3 we show the diffusion parameter, D (cm^2/s), as a function of the concentration of sorbed water, C_{eq}, for the microcomposites (A) and for the exfoliated nanocomposites (B). All the samples show a linear behavior, following Eq. (3); therefore D_0 was obtained by extrapolation to zero vapor concentration. The obtained values are reported in Table 1.

The extrapolated diffusion parameters of the microcomposite samples are very near or even higher than those of the PCL, and only the sample with the highest montmorillonite content (MMT-Na$^+$)PCL10M shows a slightly lower diffusion. At variance, in the case of the exfoliated nanocomposites even a very small quantity of clay (as in sample (MMT(OH)$_2$)PCL1E) decreases the diffusion coefficient of, at least, one order of magnitude. Sample (MMT(OH)$_2$)PCL10E shows a decrease of almost three orders of magnitude.

The diffusion parameters of the samples containing 3 wt% of montmorilloniles, reported in Fig. 4, vary in a narrow range very near or even higher than for the pure PCL value.

To illustrate the influence of the texture on the diffusion parameter, Fig. 5 shows log D_0 as a function of the montmorillonite content for the microcomposites (M), the exfoliated nanocomposites (E), and the 3 wt% intercalated composites (I). The horizontal straight line represents the D_0 of the pure unfilled PCL. Taking into account the logarithmic scale, the values for the microcomposites and intercalated nanocomposites are distributed around the PCL value, while the exfoliated nanocomposites strongly deviate, even at low montmorillonite content. The exfoliation of the inorganic component in the continuous polymeric phase is therefore a pre-requisite to improve the barrier properties of the material to the water vapor. Similar results were reported for PCL samples containing a different type of

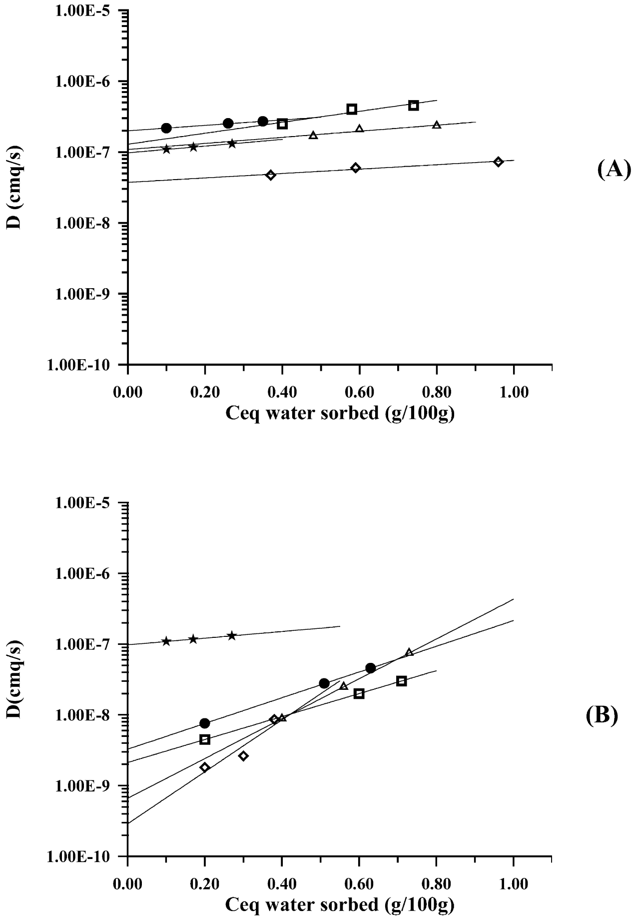

Fig. 3. Diffusion coefficients, D (cm^2/s), as function of C_{eq} (g/100 g) of water vapor for (A): (★) PCL, (●) (MMT-Na$^+$)PCL1M, (◻) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL5M, (◇) (MMT-Na$^+$)PCL10M. (B): (★) PCL, (●) (MMT-(OH)$_2$)PCL1E, (◻) (MMT-(OH)$_2$)PCL3E, (△) (MMT-(OH)$_2$)PCL5E, (◇) (MMT-(OH)$_2$)PCL10E.

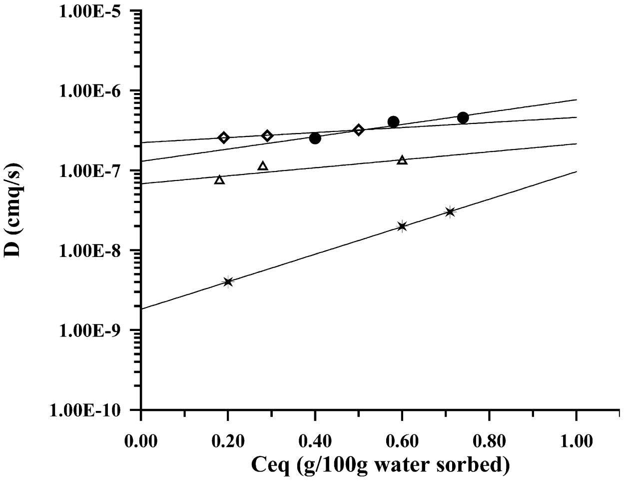

Fig. 4. Diffusion coefficients, D (cm^2/s), as function of C_{eq} (g/100 g) of water vapor for (★) (MMT-(OH)$_2$)PCL3E, (●) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL3I, (◇) (MMT-(OH)$_2$)PCL3I.

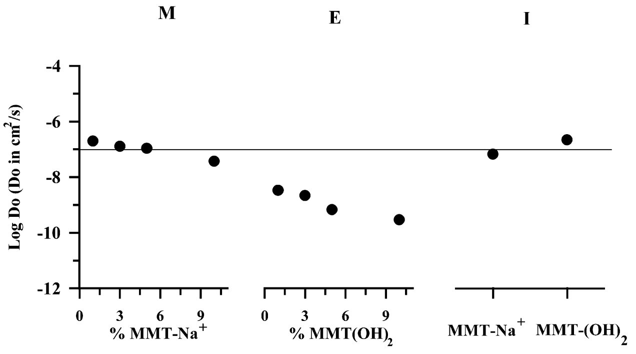

Fig. 5. log D_0 (D_0 in cm^2/s) to water vapor, as function of clay content for the microcomposite (M), the exfoliated nanocomposites (E) and the 3 wt% intercalated nanocomposites (I).

modified montmorillonite [24]. We can suggest that in the microcomposite or in the intercalated samples, the ordered structure of the inorganic component do not constitute a barrier to the diffusion of the water molecules that can jump from one specific site to another. This diffusion mechanism is not possible when the structure is exfoliated, since there is no continuity in the inorganic phase. In the last case the inorganic platelets really do act as a barrier to the diffusion path.

3.2. Dichloromethane vapor

With the purpose to investigate the transport properties of an organic vapor, we chose dichloromethane, because it is absorbed by PCL due to its slightly polar character. Non-polar molecules, such as hexane or benzene, are not soluble in PCL, whereas more polar molecules completely dissolve the polymer, even in the vapor phase.

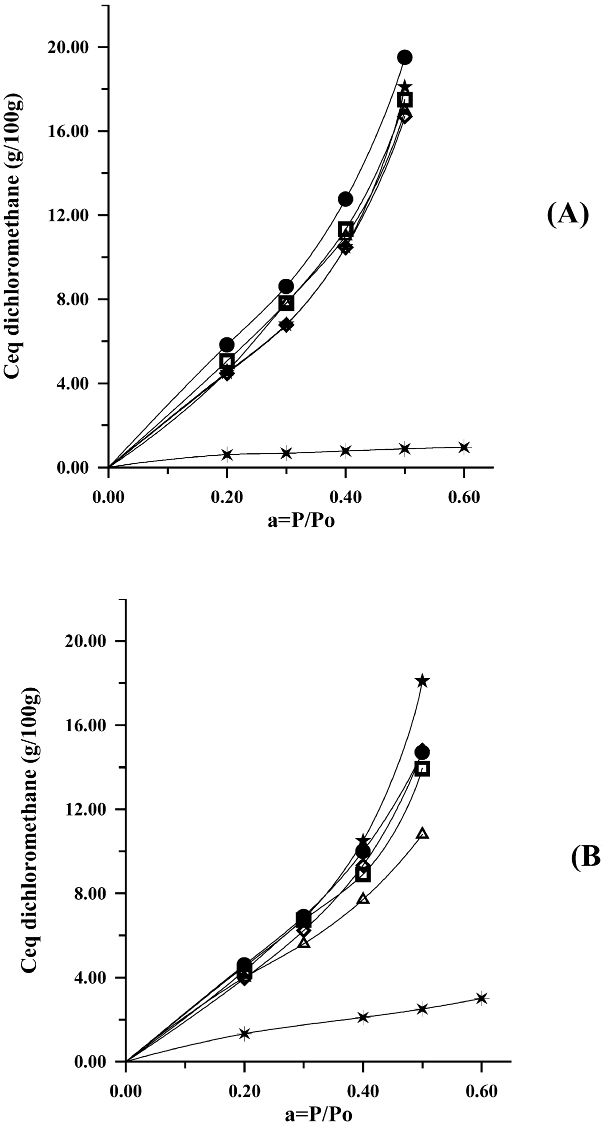

Fig. 6. Sorption isotherm of dichloromethane vapor for (A): (★) PCL, (●) (MMT-Na$^+$)PCL1M, (□) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL5M, (◇) (MMT-Na$^+$)PCL10M, (✱) MMT-Na$^+$. (B): (★) PCL, (●) (MMT-(OH)$_2$)PCL1E, (□) (MMT-(OH)$_2$)PCL3E, (△) (MMT-(OH)$_2$)PCL5E, (◇) (MMT-(OH)$_2$)PCL10E, (✱) MMT-(OH)$_2$.

Fig. 6 displays the equilibrium concentration of sorbed dichloromethane, C_{eq} (g/100 g), as a function of vapor activity for the microcomposites (A) and exfoliated nanocomposites (B), at 25 °C. The isotherms of the pure polymer and of the montmorillonites are reported for comparison. As expected, MMT-(OH)$_2$ shows higher values of sorbed solvent than MMT-Na$^+$, due to the better interaction of dichloromethane with the organic modifier, linked to the inorganic component. The sorption curves of the two clays are almost linear, with a slight dual-sorption behavior, due to a small adsorption on specific sites of the clay mineral. At low vapor activity the isotherms of all the hybrid samples are linear, following the Henry' distribution, whereas exponential increase is observed at higher activities ($a > 0.3$), indicating a Flory–Huggins behavior [23]. This behavior represents a preference for the formation of penetrant–penetrant pairs, so the solubility coefficient continuously increases with the activity. The first molecules sorbed tend to locally loosen the polymer structure and make it easier for following molecules to enter. These isotherms are observed when the penetrant effectively plasticizes the polymer, being a strong solvent or swelling agent for the polymer. Actually, this is the case of dichloromethane which, at $a = 1$, i.e. in the liquid phase, completely dissolves PCL samples.

The equilibrium concentrations at an activity around 0.2, derived from the sorption isotherms, are reported in Table 2. There is a decrement of values of solvent adsorbed increasing the clay content for the exfoliated nanocomposites, while an increase of such values is observed for the microcomposites.

The equilibrium concentrations of dichloromethane, C_{eq} (g/100 g), as a function of vapor activity, for the samples containing 3 wt% of the different montmorillonite are reported in Fig. 7. The sorption behavior of the intercalated composites is very similar to the previous ones, shown in

Table 2
Equilibrium concentration at activity 0.2, C_{eq} (g/100 g), and zero concentration diffusion coefficients, D_0 (cm^2/s), of dichloromethane vapor

Sample	C_{eq} (g/100 g)	D_0 (cm^2/s)
PCL	4.52	3.17×10^{-8}
(MMT-Na$^+$)PCL1M	5.82	1.70×10^{-8}
(MMT-Na$^+$)PCL3M	5.06	9.56×10^{-9}
(MMT-Na$^+$)PCL5M	4.57	3.48×10^{-8}
(MMT-Na$^+$)PCL10M	4.47	1.64×10^{-8}
(MMT-(OH)$_2$)PCL1E	4.60	1.21×10^{-8}
(MMT-(OH)$_2$)PCL3E	4.32	9.29×10^{-9}
(MMT-(OH)$_2$)PCL5E	4.00	5.08×10^{-9}
(MMT-(OH)$_2$)PCL10E	3.95	7.58×10^{-10}
(MMT-Na$^+$)PCL3I	4.54	1.26×10^{-8}
(MMT-(OH)$_2$)PCL3I	5.41	2.57×10^{-9}

Fig. 6. The values of C_{eq} for micro- and intercalated composites are very similar to pure PCL, whereas the exfoliated samples show lower values.

As in the case of water vapor, the diffusion coefficients were derived from Eq. (2) and are reported in Fig. 8 as a function of the equilibrium concentration.

Two regions of the curves are clearly recognizable: at low vapor concentration, the diffusion coefficient increases steeply and linearly with C_{eq}, whereas at high concentration (>5 g/100 g) a still linear but smoother dependence is shown by all the samples. The transition is observed for concentrations of sorbed vapor higher than 5%. As we observed from the sorption curve in Fig. 6, a strong interaction was evident at high activities for amounts adsorbed higher than 5%. The strong interaction with the penetrating molecules, leading to a high mobility of polymer chains, can induce structural transformations, as clustering of solvent molecules, crazing or partial dissolution. The systems loose their compactness and diffusion becomes less dependent or even independent of the amount of vapor adsorbed, as we can observe by the second part of the curves. At even higher concentrations the films dissolve completely in the vapor.

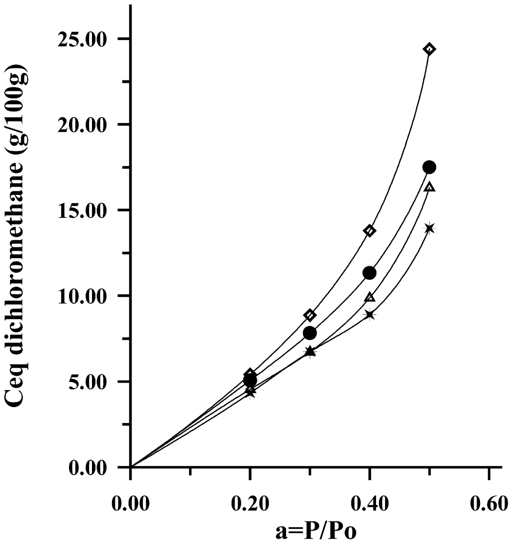

Fig. 7. Sorption isotherm of dichloromethane vapor for (★) (MMT-(OH)$_2$)PCL3E, (●) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL3I, (◇) (MMT-(OH)$_2$)PCL3I.

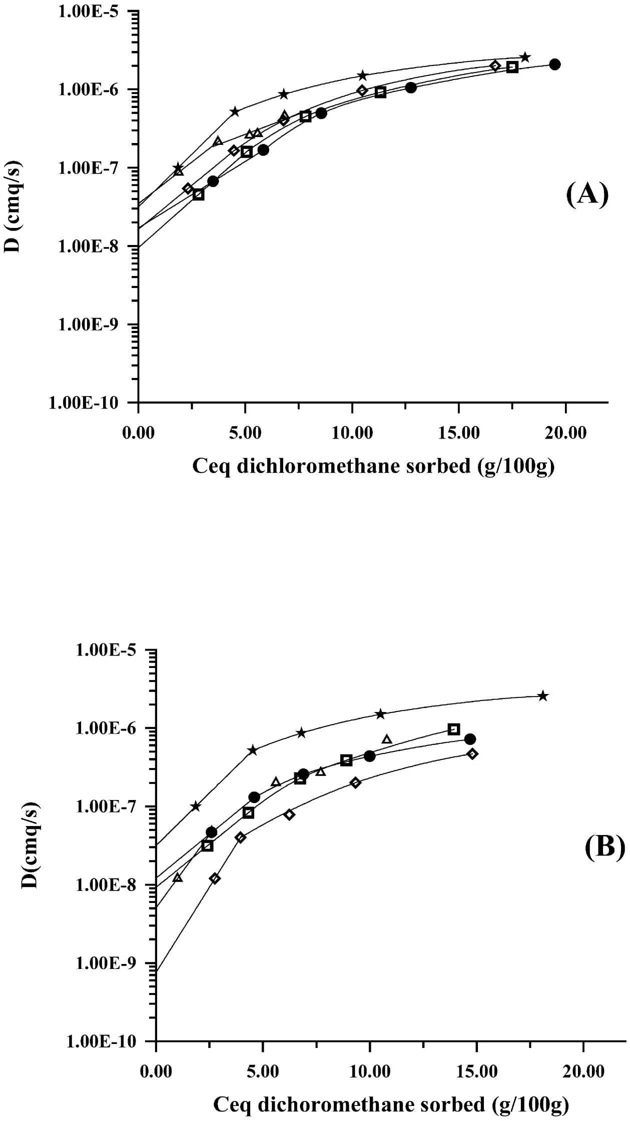

Fig. 8. Diffusion coefficients, D (cm^2/s), as function of C_{eq} (g/100 g) of dichloromethane vapor for (A): (★) PCL, (●) (MMT-Na$^+$)PCL1M, (◻) (MMT-Na$^+$)PCL3M, (△) (MMT-Na$^+$)PCL5M, (◇) (MMT-Na$^+$)-PCL10M. (B): (★) PCL, (●) (MMT-(OH)$_2$)PCL1E, (◻) (MMT-(OH)$_2$)-PCL3E, (△) (MMT-(OH)$_2$)PCL5E, (◇) (MMT-(OH)$_2$)PCL10E.

From the first part of the curves we derived the zero concentration diffusion coefficients, reported in Table 2. In the microcomposites the zero concentration diffusion parameter is weakly influenced by the clay, whereas a strong effect, even for small clay contents, is observed for the exfoliated nanocomposites.

In Fig. 9 the diffusion coefficients as a function of the equilibrium concentration of dichloromethane absorbed are reported for samples by the samples containing 3 wt% montmorillonites. Again two zones are recognized, with the transition between the steeper and the

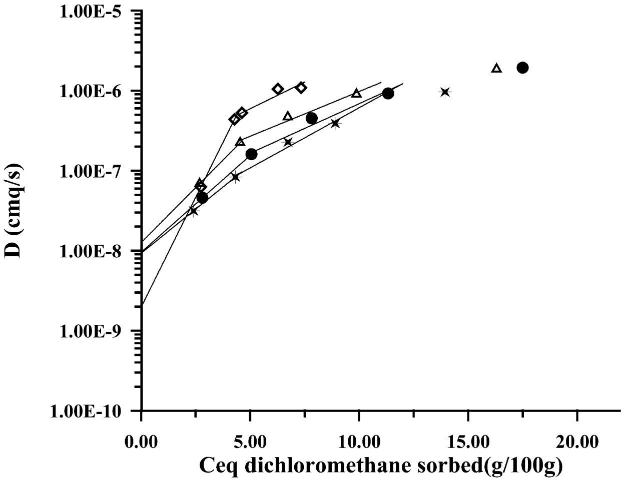

Fig. 9. Diffusion coefficients, D (cm^2/s),as function of C_{eq} (g/100 g) of dichloromethane vapor for (★) (MMT-(OH)$_2$)PCL3E, (●) (MMT-Na$^+$)-PCL3M, (△) (MMT-Na$^+$)PCL3I, (◇) (MMT-(OH)$_2$)PCL3I.

smoother dependence of diffusion on C_{eq} occurring at about 5% of dichloromethane. After the transition all the samples tend to follow the same straight line. The system is highly plasticized, and the penetrating molecules do not meet many obstacles to their passage.

The values of $\log D_0$ as a function of the montmorillonite content for the microcomposites (M), the exfoliated nanocomposites (E), and for the 3 wt% intercalated nanocomposites (I), are reported in Fig. 10. Also in this case the straight line gives the D_0 value of the pure PCL. The diffusion coefficients of the microcomposites are very close to such a line, while the exfoliated nanocomposites strongly deviate especially for 5 and 10 wt% of MMT.

It is interesting to note that, at variance with water vapor, in the case of dichloromethane also the intercalated samples show lower values of diffusion respect to the parent PCL. In the first case we suggested that in the ordered structure the water molecules could jump from one site to the other of the inorganic platelets, whereas this is not possible for the organic molecules that are not absorbed on specific sites, as shown by the sorption curve.

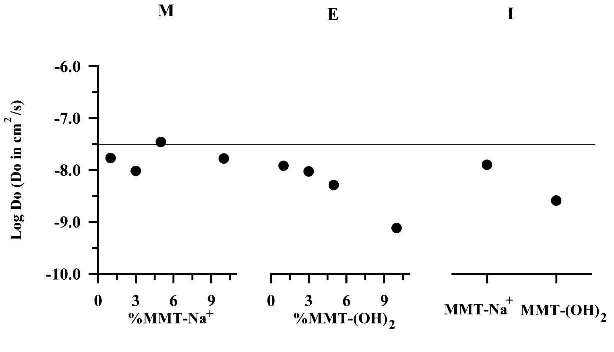

Fig. 10. log D_0 (D_0 in cm^2/s) to dichloromethane vapor, as function of clay content for the microcomposite (M), the exfoliated nanocomposites (E) and the 3 wt% intercalated nanocomposites (I).

4. Conclusions

Microcomposites of polycaprolactone with MMT-Na$^+$ were prepared by melt blending; exfoliated nanocomposites were obtained by in situ polymerization of ε-caprolactone with organo monmorillonite; intercalated nanocomposites were obtained either by melt blending or by in situ intercalative polymerization. Transport properties of water vapor and dichloromethane were measured.

The sorption curves of water vapor in all the composite samples follow the dual-sorption behavior. Montmorillonite presents specific sites on which the water molecules are adsorbed. The amount of solvent absorbed derived from the linear part of the curve, increases on increasing the MMT content, particularly for the microcomposites obtained from the unmodified MMT-Na$^+$.

The diffusion parameters depend on the amount of vapor sorbed; therefore the diffusion parameter D_0 were derived by extrapolation to zero vapor concentration and compared to the value of the pure PCL. The microcomposites as well as the intercalated nanocomposites have diffusion parameters very near to PCL, while the exfoliated nanocomposites show much lower values, even at low montmorillonite content. This is an indication that the water molecules on specific sites are not immobilized but can jump from one site to another. Only in the case of the exfoliated samples the inorganic platelets, dispersed in a not ordered distribution, can constitute a barrier to the path of the hydrophilic molecules.

The sorption curves of dichloromethane are similar to the pure PCL, showing that no specific sites of MMT are occupied by dichloromethane. In this case the value of sorbed solvent at low activity is mainly dominated by the amorphous fraction present in PCL. At high vapor activity all curves show an exponential increase, due to plasticization of the polymer. The diffusion parameters of the microcomposites are very close to PCL, while the exfoliated nanocomposites also in this case show much lower values. For the organic solvent also the intercalated samples show lower diffusion parameters confirming that it is not the content of clay alone but the type of dispersion of the inorganic component in the polymer phase that is important for improving the barrier properties of the samples.

Acknowledgements

SMPC is much indebted to the Région Wallonne and the Fonds Social Européen for support in the frame of Objectif 1-Hainaut/Phasing Out: Materia Nova. SMPC is grateful to the Région Wallonne for support in the frame of the W.D.U. program: TECMAVER including a grant to E.P. and B.L.

The Italian authors thank the FISR Project, from the Italian Ministry of the University and Scientific Research, for the financial support.

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