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The impact of PEG bulk volume fraction on the interlayer distance of clay-PEG hybrids: Experimental and theoretical study

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Abstract

The intercalation of polyethylene glycol (PEG) chains, in the inter-layer environment of the clay from Meknes, was performed using the direct intercalation method in the presence of water as a solvent. X-ray diffraction (XRD) technique was applied to follow the evolution of interlayer distances as a function of PEG bulk volume fraction. The XRD data assert the formation of an intercalated structure through the displacement of the peaks, which characterize the clay minerals towards the small and large angles. The evolution of the \( d_{001} \)-spacings for the three classes of clays was similar. Indeed, as \( \varphi \) increases, the \( d_{001} \) variation is marked by two depletion phenomena due to the magnitude of the gyration radius compared to the inter-layer distance of the clay minerals. The plateau regime, characterized by the weak insertion of the chains, appears after each depletion/expansion cycle, which reveals a succession of the depletion-adsorption-plateau phenomenon. Based on the results of the XRD method, we proposed a model for the insertion of PEG chains in monolayer and bilayer forms into the interlayer environment of clay minerals. Finally, the scaling theory reveals a good agreement with the experimental findings and perfectly illustrates the succession of three regimes: dilute, bidimensional semi-dilute, and plateau.

Keywords

Clay-polymer hybrids, polyethylene glycol, scaling theory, plateau regime, bulk volume fraction

1. Introduction

Concerns about the question of climate change and sustainable development have steadily increased in the international community, especially in the field of construction. Thus, the issue today is to respond urgently, while thinking about the future, to these two challenges of the 21st century, to limit greenhouse gas emissions (Kurekci, 2016; Islam and Bhat, 2019; Ozturk et al., 2019; Santamouris et al., 2020; Abden et al., 2022; Wang et al., 2022). It is therefore mandatory to look for renewable energy sources able to replace coal and oil, especially in buildings that consume about 30-40% of the world’s energy to ensure a healthy and comfortable space. Similarly, the energy efficiency of buildings has started to gain enormous significance in order to contribute to the reduction of the pressure on the environment by inserting ecological and recyclable thermal insulation throughout their life cycle (Adamczyk and Dylewski, 2017; Philip and Rakendu, 2020; Pal et al., 2021; Füchsl et al., 2022). Currently, the thermal insulation of buildings is ensured by non-renewable synthetic inorganic materials such as glass and rock fiber, mineral wool, and so on (Pataiok et al., 2015). The high thermal conductivity and the impact on human health are the main drawbacks of these materials. Subsequently, various substances with extremely low thermal conductivity are constantly coming on the market for thermal insulation of buildings, namely aerogels, phase change materials, and vacuum insulation panels (Jelle, 2011; Hung Anh and Pásztory, 2021). The disadvantage of these substances is their poor mechanical properties, low fire resistance and insufficient durability (Bouchattem et al., 2017; Jia et al., 2018; Pedroso et al., 2020). In order to overcome these weaknesses, researchers have started to test the combination of the two organic and inorganic worlds, as innovative and promising hybrids for the thermal insulation of buildings (S Zhu et al., 2013; Villabona-Estupiñán et al., 2017; Kenane et al., 2020; Dede et al., 2021).

Among the most promising and suitable inorganic materials to guarantee energy efficiency, we mention the clays that present remarkable physical properties that make these fabulous materials good candidates in thermal transmission (Ashour et al., 2010; Belghazdis and Hachem, 2022a). This interest is mainly due to their abundance, ecological properties, and single-sheet structure (Fig.1) (Belghazdis et al., 2022a). Due to the low conductivity of polymers (Wang et al., 2019), clay-polymer hybrids have received a lot of attention in recent years and can be a new class of adorable and highly efficient thermal insulation material. This encourages academics to develop theoretical models close to reality that can explain the adsorption mechanisms and describe the various phenomena that appear in confined spaces. The most inserted polymers in the interlayer environment of clays are polyethylene oxide (PEO) and polyethylene glycol (PEG) because they are water-soluble, biodegradable, and easily adsorbed onto the clay mineral sheets (Tunç and Duman, 2008; Ebagninin et al., 2009; Majumdar et al., 2010; Sarier and Onder, 2010; Xie et al., 2012; S. Zhu et al., 2013; Hom and Bhatia, 2017). In a theoretical study of previously published experimental results of clay-PEG hybrids (Ghyati et al., 2021), the authors found good agreement between theory and experiment. They concluded that the adsorption scaling theory, used to track the evolution of the \( d_{001} \)-spacings, is more general and powerful than the classical adsorption theory based on the mean-field theory. The effect of PEG4000 insertion on the interlayer distances of the three clay minerals (Illite, kaolinite, and chlorite) has been reported in another study (Ghyati et al., 2020). The adsorption theory developed from De Gennes scaling laws follows almost the same evolution as the results obtained from the experiment when measuring the interlayer distance as a function of the initial PEG concentration.
This work investigates the effect of the bulk volume fraction of PEG on the variation of the interlayer space of clay minerals in the case of the two clay-PEG2000 (HPEG2000) and clay-PEG6000 (HPEG6000) hybrids. These hybrids were elaborated by the direct intercalation method in the presence of water as solvent. The interlayer distance was evaluated by the X-ray diffraction (XRD) technique. Finally, a theoretical model based on De Gennes scaling theory has been introduced to follow the evolution of the \( d_{001} \)-spacing of the three clay minerals constituting the studied clay. Theoretical results will be compared with experimental data.

The rest of the study is organized as follows: the materials and methods used in the elaboration of the purified clay and the composites will be exposed in the second part. Then, the third part will be devoted to the description of the characterization techniques. We will dedicate the fourth part to the presentation and discussion of the results obtained for both HPEG2000 and HPEG6000 hybrids. The fifth section will be reserved for the introduction of the adsorption scaling theory to explain the experimental results. Finally, we will end with a conclusion in the last section.

Fig. 1 Illustration of the TOT (Tetra: Octa: Tetra) clay structure (Schoonheydt et al., 2018).

2. Experimental and method

2.1. Materials

The clay deposit investigated is located in the north of Meknes in north central Morocco. The quantification of this clay shows the dominance of quartz (66.83%), then an important quantity of illite (15.8%) and finally smectite (8.26%) (Belghazdis et al., 2022b). However, the X-ray fluorescence technique (XRF) reveals that its composition in terms of mass % of oxides is as follows: \( SiO_2 \) (49.94%), \( Al_2O_3 \) (20.31%), \( Fe_2O_3 \) (9.31%), \( K_2O \) (3.04%), \( MgO \) (2.65%), \( CaO \) (1.21%), \( TiO_2 \) (0.90%), \( Na_2O \) (0.43%) and \( P_2O_5 \) (0.37%). Other oxides such as \( SO_3 \), \( Cr_2O_3 \), \( ZnO \), \( SrO \) are present in small quantities and sometimes in trace amounts. PEG with weight-average molecular weight \( M_w = 2000 \ g/mol \) and \( M_w = 6000 \ g/mol \), were obtained from SIGMA-ALDRICH of Germany.

2.2. Purification of natural clay and preparation of hybrid

The reduction of the influence of impurities, concentration and release of the clay minerals present, requires the purification of the natural clay. In this context, the clay powder (< 63\( \mu m \)) was attacked by acetic acid to remove calcite. Then, the clay fraction was recovered by sedimentation which allows decreasing considerably the quantities of quartz (Boylu et al., 2010; Gong et al., 2016).

The purified clay powder thus obtained was combined with PEG in the following form: (S Zhu et al., 2013; Ghyati et al., 2020) (5g) of purified clay was added to a beaker containing 400 ml of distilled water. After shaking, a quantity of PEG2000 corresponding to a given volume fraction phi was added to the clay suspension (Fig. 2). The PEG bulk volume fractions used are 0.014, 0.029, 0.041, 0.056, 0.062, 0.068, 0.086, 0.1. Then the mixture was stirred at 67°C for 6 hours and heated for 12 hours at 67°C. After centrifugation and washing with water, the hybrids named HPEG2000 were recovered. HPEG6000 hybrids were prepared in a similar manner.

Fig. 2 Schematic illustration of the elaboration of clay-polymer composites
2.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) measurements were performed with XRD-6100 Shimadzu Diffractometer, using Cu-Kα radiation ($\lambda = 1.5418 \text{ Å}$), step scan of 0.05°, 10 s per step in the $3 - 40 \theta$-range. The $d_{hkl}$-value was determined according to Bragg’s Law: $dhkl = \lambda/(2\sin\theta)$.

3. Results and discussions

3.1. XRD-analysis

Figure 3 shows typical reflections of the aluminosilicates illite, kaolinite, and smectite in the diagram of the purified clay. Other reflections related to quartz were also detected. Indeed, the intense peak at about $2\theta = 6.11^\circ$, which corresponds to $d_{001} = 14.45 \text{ Å}$, is assigned to smectite. However, illite was detected from both reflections at $2\theta = 8.62^\circ$ and $2\theta = 17.72^\circ$, suggesting that the interlayer distances are $d_{001} = 10.24 \text{ Å}$ and $d_{002} = 5 \text{ Å}$, respectively. As for kaolinite, two reflections are assigned to this phase and that were detected at $2\theta = 12.28^\circ$ and $2\theta = 25.42^\circ$, which correspond to $d_{001} = 7.20 \text{ Å}$ and $d_{002} = 3.5 \text{ Å}$, respectively. The associated mineral (quartz) was identified by both peaks at $2\theta = 20.83^\circ$ and $2\theta = 26.74^\circ$. The inter-layer distances of these two reflections are, respectively, 4.26 Å and 3.33 Å. Thus, the purified clay from Meknes contains the three categories of illite, smectite, and kaolinite, together with quartz.

In order to evaluate the effect of PEG volume fraction on the interlayer space of the three classes of clays, a comparison between the diagrams of the purified clay and the different prepared hybrids was shown in Figures 3 and 5. Figure 3, compares the diagrams of the purified clay with those of HPEG2000 at different bulk volume fractions of PEG2000. While Figure 5, compares the diagrams of purified clay with those of HPEG6000 at different volume fractions of PEG6000. To properly judge the displacements recorded in the structures, we focused on the $d_{001}$ reflections of each clay mineral for both hybrids in the $2\theta = 5^\circ:14^\circ$ zone (Fig. 4 and Fig. 6). The two developed hybrids HPEG2000 and HPEG6000 show shifts to small and large angles indicating an increase and decrease in the interlayer distance, respectively. In the first stage, the hybrids reveal a decrease of $d_{001}$ due to the depletion phenomenon, which appears when the gyration radius of the PEG-chain is higher than the initial distance $d_{001}$ of the clay. Next, all three clay categories in both hybrids show an increase in $d_{001}$, indicating the insertion of PEG2000 and PEG6000 chains into the interlayer environment of these minerals as the volume fraction increases. By further increasing the polymer volume fraction, the $d_{001}$-spacing of the clay minerals remain almost invariant indicating that a plateau regime is established. The increase of the PEG bulk volume fraction in the case of the plateau regime obliges the chains to stay in the volume, which again produces the depletion phenomenon decreasing the inter-layer distance of the three clays. The depletion phenomenon was more important in the case of HPEG6000 hybrids because of the large size of the gyration radius ($R \sim aN^{3/5}$) of the PEG6000 chain ($R_P(\text{PEG6000}) = 66.8 \text{ Å}$) compared to the PEG2000 gyration radius ($R_P(\text{PEG2000}) = 34.5 \text{ Å}$). The intercalation of a second PEG layer gives a further expansion of the interlayer environment for the different hybrids.

![Fig. 3 XRD patterns of purified clay and HPEG2000 composites prepared for different bulk volume fractions.](image-url)
Fig. 4 XRD models of purified clay and HPEG2000 composites for different bulk volume fractions for $2\theta: 5 - 15^\circ$.

Fig. 5 XRD patterns of purified clay and HPEG6000 composites prepared for different volume fractions.
Fig. 6 XRD models of purified clay and HPEG6000 composites for different bulk volume fractions for \(2\theta: 5 - 15^\circ\).

4. Comparison between theory and experiment

Generally, the adsorption of a polymer is dictated by its affinity with the clay sheet surface resulting from the balance of energy variations. The most important factors in this phenomenon are the initial bulk volume fraction of the polymer and the surface coverage rate, \(\Gamma\). Indeed, these two factors affect the affinity between the polymer chains and the surface and allow the distinction of several adsorption regimes near the surface. On the other hand, the presence of polymers near an interface has generated considerable interest in a number of applications such as colloidal stabilization, wastewater purification, paint and ink manufacture, ceramic powder manufacture, mineral separation, and paper production. These advantages of use have motivated the search for more realistic theoretical approaches and models to describe the experimental results.

In our case, we focus on the situation of reversible adsorption of PEG, on a flat, attractive, and impenetrable surface of the clay by introducing the De Gennes scaling theory, which allows following the evolution of the interlayer distance versus the PEG volume fraction.

We have previously used De Gennes scaling theory to estimate the evolution of the surface coverage, \(\Gamma\), (Hachem et al., 2022) which represents the number of monomers adsorbed on the solid surface per unit area, for all surface regimes (dilute, bidimensional semi-dilute, plateau).

The surface coverage varies as:

\[
\Gamma(\varphi) = \begin{cases} 
\frac{1}{2} \delta^{-1} \varphi \exp\left(\frac{M}{M_0} \delta^5\right) & \text{for } 0 < \varphi < \varphi_1 \\
\frac{1}{2} \delta^{-1} \varphi \exp\left(\frac{M}{M_0} \delta^5\right) & \text{for } \varphi_1 < \varphi < \varphi_2 \\
\delta^{1/3} \left[1 + \frac{M_0}{2M\delta^{5/3}} \ln(\varphi^{4/3})\right] & \text{for } \varphi_2 < \varphi < \varphi_3
\end{cases} \tag{1.1}
\]

With, \(\varphi_1, \varphi_2, \varphi_3\) are typical bulk volume fractions of PEG that separate the three regimes of the surface (dilute, two-dimensional semi-dilute, plateau). These quantities scale as follows:

\[
\begin{align*}
\varphi_1 &\sim N^{-1/2} \delta^{1/2} \exp\left(-\frac{M}{M_0} \delta^3\right) \tag{2.1} \\
\varphi_2 &\sim \delta^{3} \exp\left(-\frac{M}{M_0} \delta^3\right) \tag{2.2} \\
\varphi_3 &\sim \delta^{3} \tag{2.3}
\end{align*}
\]

Where, \(M\) is the molecular weight of the polymer; \(M_0\) is the molecular weight of the monomer, and \(\delta\), is the attraction energy or surface coupling. The transition from the surface coverage, \(\Gamma\), to the interlayer distance \(d_{hk}\) is ensured by the relationship: (Ghyati et al., 2020)

\[
d(\varphi) = d_0 \mp a \Gamma(\varphi) \tag{3}
\]
Where a is the monomer size and
\[ d_0 = \begin{cases} 
7.20\text{Å} & \text{for Kaolinite} \\
10.24\text{Å} & \text{for Illite} \\
14.45\text{Å} & \text{for Smectite} 
\end{cases} \]

We chose to follow the evolution of \( d_{001} \) of the three minerals, illite, kaolinite, and smectite for HPEG2000 and HPEG6000 using the XRD method.

The results are illustrated in figures 7 and 8 and show the presence of a succession of cycles containing the three regimes diluted, semi-diluted, and plateau. Each cycle characterizes the adsorption of a PEG layer on the opposite surfaces of the sheets. Furthermore, the depletion phenomenon at the beginning of each cycle is a function of the molecular weight and the type of clay mineral. Let us now discuss the evolution of the theoretical interlayer distance in the three possible regimes.

**Regime I**: We record a decrease in the \( d_{001} \) distance of the three clay categories in the case of the two HPEG2000 and HPEG6000 hybrids for very small volume fractions \( \varphi < \varphi_1 \). This behavior indicates the occurrence of a depletion phenomenon that forces the PEG chains to remain in the volume because the inter-layer distances \( d_0 \) are smaller than the gyration radius \( R \sim aN^{3/5} \) of the PEG chains \( (R_p(PEG2000) = 34.5 \text{ Å}) \) and \( (R_p(PEG6000)) = 66.8 \text{ Å} \).

Introducing equation (1.a) into equation (3), the theoretical distance \( d_{001} \) of the diluted regime is written as:
\[ d(\varphi) = d_0 - \frac{1}{2}AAa\delta^{-1} \varphi \exp\left(\frac{M}{M_0}\delta^3\right) \]  
(4)

A is a positive constant determined from the experimental data. The experimental results show that the interlayer distance \( d \) is a straight line of the form:
\[ d(\varphi) = a_1 - b_1 \varphi \]  
(5)

Thus, \( \frac{1}{2}AAa\delta^{-1} \exp\left(\frac{M}{M_0}\delta^3\right) = b_1 \) et \( a_1 = d_0 \)

So,
\[ A = \frac{2b_1}{a} \exp\left(-\frac{M}{M_0}\delta^3\right) \]  
(6)

The constants \( a_1, b_1 \) and \( A \) for each clay category will be illustrated in Table 1 below.

Let us also note \( \delta_j \), with \( j = ill, kao, sme \), the attraction energy of illite, kaolinite, and smectite, respectively. The values of \( \delta_j \) will also be shown in Table 1.

**Regime II**: Above \( \varphi_1 \) and up to \( \varphi_2 \), we notice a linear increase of the interlayer distance in the different clay minerals for HPEG2000 and HPEG6000. This volume fraction range is marked by the presence of the bidimensional semi-diluted surface regime. The theoretical distance \( d_{001} \) of this regime is the same as that of the diluted regime and takes the form:
\[ d(\varphi) = d_0 + \frac{1}{2}AAa\delta^{-1} \varphi \exp\left(\frac{M}{M_0}\delta^3\right) \]  
(7)

A is the same constant calculated in regime I. Moreover, the experimental results reveal a linear evolution of the same form as regime I.
\[ d(\varphi) = a_1 + b_1 \varphi \]  
(8)

**Regime III**: As the volume fraction exceeds \( \varphi_2 \), the evolution of the interlayer distance becomes logarithmic indicating that the adsorption in this regime is very low. This plateau regime persists until the volume fraction \( \varphi_3 \). Introducing the equation (1.c) in the relation (3), the theoretical distance \( d_{001} \) of the plateau regime takes the form:
\[ d(\varphi) = d_1 + B\delta^{1/3}\left[1 + \frac{M_0}{2M\delta^{5/3}}\ln(\varphi\delta^{-4/3})\right] \]  
(9)

B is a constant calculated from experimental data. The evolution of the experimental interlayer distance follows the form:
\[ d(\varphi) = a_2 + b_2 \ln(\varphi) \]  
(10)

The constants \( a_2 \) and \( b_2 \) of the plateau regime for the three categories of clay (illite, kaolinite, smectite) will be illustrated in Table 1.

From equations (9) and (10), the constant B can be deduced by the relation:
\[ B = \frac{2M\delta^{1/3}b_2}{M_0} \]

While the constant \( d_1 \) is given by the relation:
\[ d_1 = a_2 - B \delta^{1/3} \left[ 1 + \frac{M_0}{2M\delta^{5/3}} \ln(\delta^{-4/3}) \right] \]

The values of the constants \( B \) and \( d_1 \) for the different categories of clay minerals and in the case of two hybrids HPEG2000 and HPEG6000 will also be listed in Table 1.

Fig. 7 Comparison between experimental and theoretical results of interlayer space of illite (a), kaolinite (b), and smectite (c) versus bulk volume fraction (\( \varphi \)) for clay-PEG2000 hybrids.

It is clear, from Table 1, that the \( \varphi_1, \varphi_2, \) and \( \varphi_3 \) bulk volume fractions vary with the PEG molecular weight. For example, the \( \varphi_1 \) of illite and smectite increases as the molecular weight of PEG increases due to the larger gyration radius of PEG6000 which requires more osmotic pressure to force the insertion of the chains into the confined spaces of illite and smectite. On the other hand, in the case of kaolinite, this critical volume fraction (\( \varphi_1 \)) decreases for HPEG6000 indicating the strong affinity of PEG6000 chains compared to PEG2000 chains towards the kaolinite surface. Similarly, for \( \varphi_2 \), it shows an increase for smectite, decrease for kaolinite, and remains stable in the case of illite. As for the critical fraction \( \varphi_3 \), we observe an increase in the case of illite, diminution in the case of kaolinite, and a stability for smectite. Regarding the surface coupling (\( \delta \)), we notice that the smectite surface strongly attracts the PEG chains followed by the illite sheet surface and finally the kaolinite surface with less weak attraction energy.

The comparison between theory and experiment shows a very good agreement between the two approaches for the different categories of clay minerals in the case of the two hybrids HPEG2000 and HPEG6000. Thus, the DE Gennes scaling theory remains the most powerful and suitable theory to interpret and study the adsorption phenomena of polymer chains on a substrate in a confined environment. On the other hand, the effect of the molecular weight is very important in the adsorption process, especially on the depletion phenomenon and the critical bulk volume fractions that separate the different regimes.

Based on the results of the XRD method, we can propose a model of PEG chain intercalation in the confined space of clay minerals. Figure 9, illustrates the conformation of PEG chains in the interlayer environment in the form of monolayers and bilayers. During modeling, we retained the form of loops, trains, and tails. (Belghazdis and Hachem, 2022b)
Fig. 8 Comparison between experimental and theoretical results of interlayer space of illite (a), kaolinite (b), and smectite (c) versus bulk volume fraction ($\phi$) for clay-PEG6000 hybrids.

Fig. 9 Modeling of PEG intercalation in the interlayer environment of clay minerals

TABLE 1 Experimental values of the different parameters discussed in the theoretical part.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Polymer</th>
<th>Diluted and bidimensional semi-diluted regime</th>
<th>Plateau regime</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a_1$  $b_1$  $A$  $\varphi_1$  $\varphi_2$</td>
<td>$a_2$  $b_2$  $B$  $\varphi_3$  $d_1$</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>PEG2000</td>
<td>10.24  4.951  0.115  0.019  0.029</td>
<td>10.37  0.054  0.252  0.052  10.09</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>PEG6000</td>
<td>10.24  8.117  0.097  0.021  0.029</td>
<td>10.20  0.019  0.284  0.056  10.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>PEG2000</td>
<td>7.20  1.143  0.027  0.023  0.044</td>
<td>7.21  0.003  0.017  0.068  7.193</td>
</tr>
<tr>
<td></td>
<td>PEG6000</td>
<td>7.20  1.867  0.022  0.017  0.032</td>
<td>7.33  0.039  0.594  0.056  6.928</td>
<td></td>
</tr>
<tr>
<td>Smectite</td>
<td>PEG2000</td>
<td>14.45  33.64  0.712  0.007  0.021</td>
<td>14.75  0.046  0.232  0.056  14.50</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td>PEG6000</td>
<td>14.45  10.45  0.124  0.011  0.029</td>
<td>14.77  0.072  1.092  0.056  14.02</td>
<td></td>
</tr>
</tbody>
</table>
5. Conclusion

In order to continue the research on the use of renewable and ecological resources in the development of new intelligent materials for the construction industry, two types of hydrophilic PEGs (PEG20000, PEG60000) were favorably intercalated in the inter-layer environment of clay minerals using various PEG volume fractions and in the presence of water as a solvent. The structure and performance of the composite formulations developed by the direct intercalation method were examined by X-ray diffraction (XRD). The objective of this investigation was to study the effect of the PEG bulk volume fraction, for a fixed molecular weight, on the inter-layer distance of the clay minerals constituting the natural clay for a future valorization of the new hybrids in the thermal insulation of buildings.

The XRD results affirm the formation of an intercalated structure thanks to the displacement of the peaks, which characterize the clay minerals towards the small and large angles. In addition, the XRD technique has made it possible to experimentally follow the evolution of $d_{001}$ as a function of the PEG volume fraction for the three mineralogical groups: kaolinite, illite, and smectite, and to distinguish the different regimes near the surface. The variation of the interlayer environment for the three categories was similar, as $\varphi$ increased. It is marked by two depletion phenomena due to the magnitude of the gyration radius versus the interlayer distance of the clay minerals. The plateau regime, characterized by the weak insertion of the chains in the interlayer environment, appears after each depletion/expansion cycle, which reveals a succession of the depletion-adsorption-plateau phenomenon. Each cycle was assigned to the fixation of a PEG layer on the opposite surfaces of the clay sheets. Finally, based on the XRD findings, we proposed a model for PEG chain insertion in monolayer and bilayer forms within the interlayer environment of clay minerals. To further understand the processes by which polyethylene glycols adhere to opposing sheet surfaces, experimental results obtained from XRD data ($d_{001}$ measurement) were combined with a theoretical study developed from De Gennes' scaling laws. This theory shows a very good agreement with the experimental results and illustrates perfectly the succession of three regimes: diluted, bidimensional semi-diluted, and plateau. Thus, De Gennes' scaling theory remains very strong and gives results that are closer to reality than the classical Langmuir adsorption theory, because the scaling theory allows describing all solvent conditions, distinguishing between the layer and the solution, and assumes the chain adsorption in the form of loops, trains, and tails. Therefore, we join our opinion to the rest of the works that recommend the use of scaling laws in modeling the phenomenon of polymer chain adsorption on an impenetrable substrate.

Finally, the more realistic description of the adsorption process of PEG chains on the opposite surfaces of the clay mineral sheets requires the exploration of the limits of the approximation made on the clay sheet surface assumed heterogeneous, flat, and impenetrable. Indeed, it is legitimate to examine the defects (curvature effects) and the heterogeneity of the surface. Without forgetting the parameters related to the polymer and the solution such as the effect of the molecular weight (chain size) of the polymer, the solvent effect, the pH effect, and the temperature effect.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

References
