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Polymer nanocomposites from natural clay: Understanding clay-PEG interaction and their effect on spacing between clay-plates

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Abstract : The interactions between clay-plates and hydrophilic polymer are investigated assuming that the polyethylene glycol chains are grafted onto face-to-face clay-plates. Besides the usual van der Waals attractive interaction, the clay-plates experience a repulsive effective interaction, due to the excluded volume force between monomers along the grafted PEG chains. The face-to-face clay-plates then play the role of polymer brushes. The free energy (per unit area) of a clay-plate pair is the sum of these interactions, and from its expression, we determine the minimal inter-sheet distance, after intercalation, which corresponds to a critical percentage of PEG. Finally, our results are found to be in good agreement with some recent experimental work.

Keywords : NANOCOMPOSITES, CLAY, POLYETHYLENE GLYCOL, INTERACTIONS.

Introduction

Properties emerging from nanocomposites based on clay have been extensively studied and explored as powerful tools in a series of applications, such as adsorbents of organic pollutants in soil, water and air, rheological control agents, paints, medicine [1-4]. Owing to hydrophilic nature of clay, the intercalation by water-soluble polymers is expected to be relatively simple. However, early attempts to intercalate PVAL, P4VP or PEG between face-to-face clay-plates were not successful, as shown by XRD experiment [5]. In fact, that is due to many factors, as the solvent quality and the elaboration methods.

The main role of the polymer intercalation is to expand the interlayer-spacing and to reduce the effective interaction between the clay-platelets. The first goal has been achieved by making use of the anionic charge within the interlamellar galleries. Since the van der Waals interactions between solid surfaces decrease with the square of the separation-distance, the insertion of the organic or inorganic molecules into the interlamellar space greatly helps to achieve the second aim [6-7].

The used poly(ethylene oxide) (PEO) is a nonionic and water-soluble polymer with many applications, due to its flocculent, thickening, lubrication, dispersing, and water-retention properties [8]. Recently, PEO/Clay nanocomposites are

promising materials and showing a great potential for various applications. PEO and its low-molecular-weight PEG can intercalate between clay-plates giving rise to a limited increase of the basal spacing (about 0.8 nm) [9].
Many studies have further more focused on the structure and the conformation of the PEO chains in the confined space of clays [10]-[11].
The purpose of this work is to contribute to the understanding of how hydrophilic PEG6000 chains interact with clay-plates and to obtain further information regarding the interplate separation profile, as a function of the polymer-density. For this we assume that the PEG chains are grafted onto face-to-face clay-plates.
This paper is organized as follows. In the next section, we summarize our theoretical framework about the face-to-face effective interactions. A comparison between the theory and some experimentis given in the third section. Finally, some concluding remarks are drawn in the last section.

Theoretical framework

Consider a given clay-plate pair confining end-grafted polymer chains (figure 1). Each consists of N monomers of common size, b. In addition, we assume that the confined host medium is a good solvent

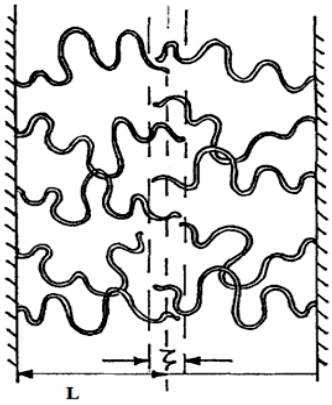

Figure 1: Two interacting layers of grafted PEG chains.

To describe physics, we need the expression of the free energy (per unit area), F_{tot}. In fact, the latter is the sum of two contributions

$$F_{tot} = F_{vdw} + F_p \ . \qquad (1)$$

The first term accounts for the contribution of the van der Waals forces between the adjacent clay-plates [12],

$$F_{vdw} = -\frac{A_H}{12\pi d^2} \ , \qquad (2)$$

where d is the separation between the considered clay-plates and A_H is the Hamaker constant. The second term in equality (1) is that of the steric forces [13],

$$F_p = \alpha k_B T b^3 N^2 \Gamma^2 \left(\frac{1}{d}\right). \qquad (3)$$

Here α is a numerical coefficient of the order of *unity*, $\Gamma = 1/s^2$ is the surface coverage (number of grafted polymer chains per *unit area*), where s is the mean-distance between the grafted chains, and $\Gamma^* = R_G^{-2}$ denotes some threshold that indicates the passage from the mushroom to brush regimes, with the gyration-radius of a single swollen polymer chain, $R_G \sim bN^{3/5}$. There, T is the absolute temperatura and k_B is the Boltmann's constant. In this work, we are interested rather in the brush-regime, with $\Gamma > \Gamma^*$. The mushroom regime corresponds to the condition $\Gamma < \Gamma^*$. Then, there is a competition between the attractive interaction that exists even in the absence of the polymer and the repulsive one that results from the excluded volume forces.
Notice that the surface coverage is simply proportional to the volume fraction of the intercalated polymer between the clay-sheets. It is then natural to consider the phase-diagram in (Γ, d)-plane.
Now, equating the first derivative of the total free energy (1), with respect to the inter-sheet distance, d, at fixed surface coverage, gives the equilibrium relationship

$$\frac{d}{b} = \frac{A_H}{6\pi\alpha N^2 k_B T} \times \frac{1}{(\Gamma b^2)^2} \qquad (4)$$

Then the equilibrium distance decreases as the inverse of the squared surface coverage. Indeed, as the polymer-concentration is increased, the excluded volume force between monomers belonging to the grafted polymer chains is screened out.
In figure 2, we report the renormalized inter-sheet distance d/b, upon the dimensionless surface coverage, Γb^2.

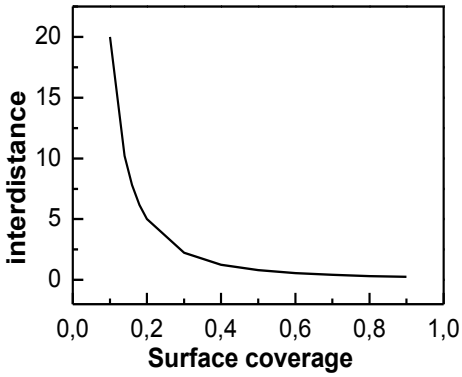

Figure 2: Renormalized inter-sheet distance, d/b, upon the dimensionless surface coverage, Γb^2.

Comparison between experiment and theory

In this section, we compare the predictions of the theoretical model described above with some recent measurements of the interplate separation-values, d_{001}, obtained from five samples using XRD analysis [14]. These results have been investigated by experiments on a three-component clay-polymer-water system. At fixed amount of clay $(m = 6g)$, figure 3 shows the plot of d_{001}-values for Kaolinite, as a function of PEG6000 percentage.

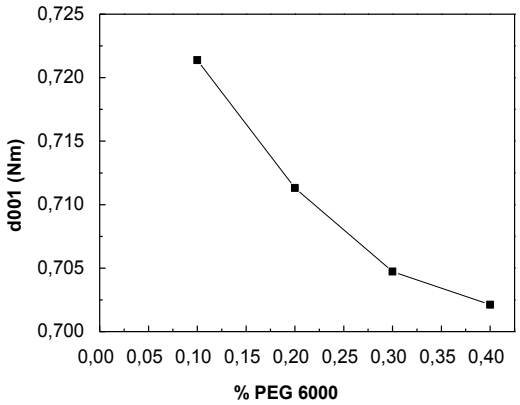

Figure 3: Interplate separation as a function of PEG6000 percentage.

As shown in this figure, there is a remarkable agreement between the experimental results and the theoretical predictions (figure 2). In fact, the inter-sheet distance decreases with the polymer-density, because of the screening effect caused by the PEG brushes leading to a significant decrease in the layer thickness, and therefore, strengthening the van der Waals attraction.

Conclusion

In this paper, we present a comparative analysis between recent experimental results giving the evolution of the inter-sheet distance, as a function of the PEG6000 percentage, and some theoretical model we recently developed. The latter is based on a balance between a van der Waals attractive interaction which tends to bring the clay-plates close to each other and a repulsive energy induced by the end-adsorbed chains.

The main outcome of this study confirmed the decrease of the separation between clay-platelets with the polymer-density and to understand how small densities of PEG6000 chains interact with the clay-plates.

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