Experimental report

28/12/2016

Proposal:	**9-12-473**	**Council:**	4/2016
Title:	Selective adsorption of biopolyelectrolytes onto Halloysite nanotubessurfaces		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: Al2Si2O5(OH)4

Instrument	Requested days	Allocated days	From	To
D11	2	2	25/11/2016	27/11/2016

Abstract:

We intend to study the selective adsorption of biopolyelectrolytes onto or into Halloysite nanotubes (HNT). Recently, the use of HNT as filler in polymer nanocomposites as well as for drug delivery in aqueous dispersion received an outburst in literature due to the improvement of the properties of the materials and the possibility to load and release active molecules. We recently succeeded in controlling the stability of HNT dispersions in water. The mesoscopic structure of these dispersions is of essential interest for the fundamental understanding and for potential applications of the dispersions themselves. The aim of this study is to correlate the molecular structure of the biopolyelectrolyte employed with its ability to disperse HNTs and the structure of the complexes formed by polymer adsorption and its dependence on the polymer type.

Introduction

Over the last few decades, clay nanoparticles have attracted large interest because their physico-chemical properties may be easily tuned endowing to obtain green nanostructures promising for several biological and industrial applications. Among the nanoclays, halloysite (HNT) represents a newly emerging clay because of its tunable surface chemistry, huge specific area and hollow tubular structure. The HNT size are quite polydisperse depending on their geological deposit. The length ranges between 0.5 and 5 microns, while the external and inner diameters are about 20-200 nm and 10-70 nm, respectively. The selective adsorption of biopolyelectrolytes onto or into HNT surfaces is a way to control the aqueous colloidal stability of the nanotubes, which is crucial for several applications within pharmaceutics and materials science. This study was aimed to investigate the structure of the complexes formed by polymer adsorption and its dependence on the polymer type. To this purpose, nonionic (hydroxylpropylcellulose), anionic (pectins and alginate) and cationic (chitosan) polymers were selected.

Experimental

SANS experiments were performed both in full contrast (D_2O as solvent) and in H_2O/D_2O mixtures, to match the silica scattering. As concerns the measurements in D_2O, the sample to detector (and in parenthesis collimation) distances were chosen as 1.5m (8m), 8m (8m), 34m (34m) and 39 m (40.5 m) in order to cover the 0.007 to 4.20 nm^{-1} range of the scattering vector (q). The experiments in H_2O/D_2O mixtures were conducted in three configurations (the sample to detector (and in parenthesis collimation) distances were chosen as 1.5m (8m), 8m (8m) and 34m in order to cover the 0.017 to 4.20 nm^{-1} range of the scattering vector (q). The wavelength of SANS measurements at very high q range was 13.0 Å, while all the other experiments were conducted at a wavelength of 6.0 Å. Absolute scale was obtained using the intensity of water; all corrected patterns being isotropic were radially averaged. All samples were prepared in D_2O and in some cases in H_2O/D_2O mixtures that match the HNT scattering length density. The experimental HNT scattering length density was determined by measuring the total scattered intensity of several HNT dispersions at variable D_2O/H_2O ratio. Some experiments were carried out in HNT contrast variation conditions.

Results and discussion

Figure 1 shows the scattering curves in full contrast for HNT provided from different geological deposits. The scattering intensity was normalized for the concentration of the scattering objects.

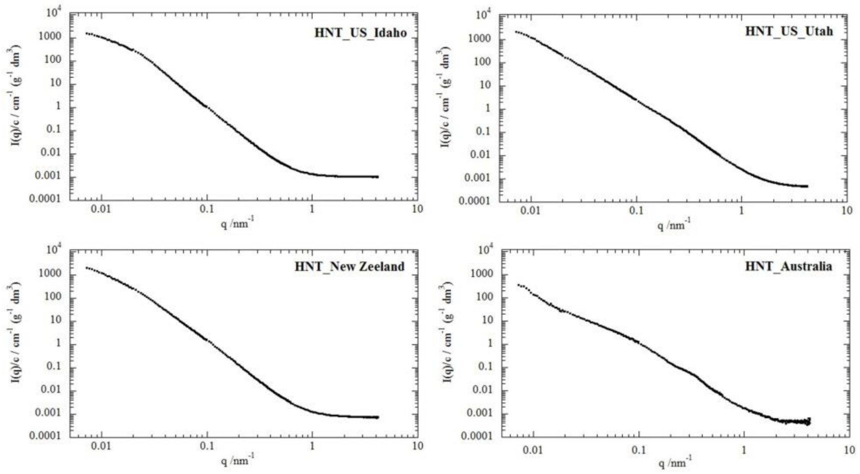

Figure 1. SANS intensity normalized for the concentration of the scattering objects as function of q, the magnitude of the scattering vector, for dispersions of functionalized HNT in D_2O.

The SANS curve for HNT from Australia (patch-HNT) shows interesting scattering features, which are not observed for the nanotubes provided from different sources. This peculiarity agrees with the lower size polydispersity of patch-HNT and a thinner shell. The absence of oscillations for the other HNT samples can be attributed to a larger polydispersity of their radii that smears out the scattering features expected for a hollow cylinder. SANS experiments on HNT/polymer dispersions were carried out in D_2O at variable weight composition. HNT from Australia and New Zeeland were selected to study the adsorption of the polymers onto halloysite surfaces. As example, Figure 2 shows the SANS curves for patch-HNT/chitosan mixtures.

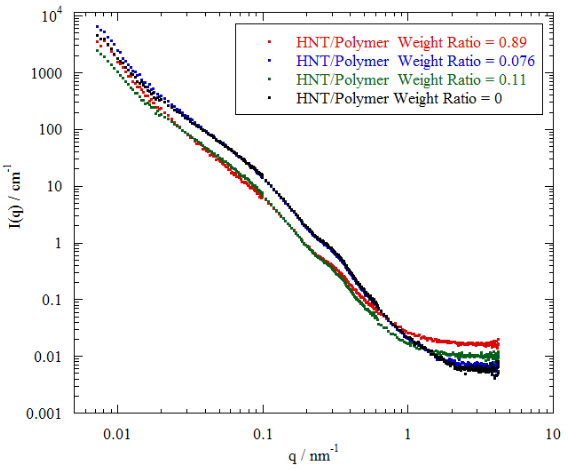

Figure 2. SANS intensity as function of q, the magnitude of the scattering vector, for the patch-HNT/chitosan dispersions in D_2O. The HNT concentration was 1.25 wt%.

The scattering features observed for pristine patch-HNT are still present for all dispersions. Therefore, SANS curves could be fitted by using a hollow cylinder as model providing insights on the specific interactions between the polymers and HNT. The experiments in HNT contrast matching were conducted in a mixed solvent (D_2O = 50.70 vol%). Although the halloysite scattering intensity was not completely matched, the experimental curves for patch-HNT showed a smaller intensity with respect to both the patch-HNT/chitosan and patch-HNT/Hydroxylpropylcellulose dispersions. On the contrary, the scattering intensity for HNT/alginate is close to that of patch-HNT.

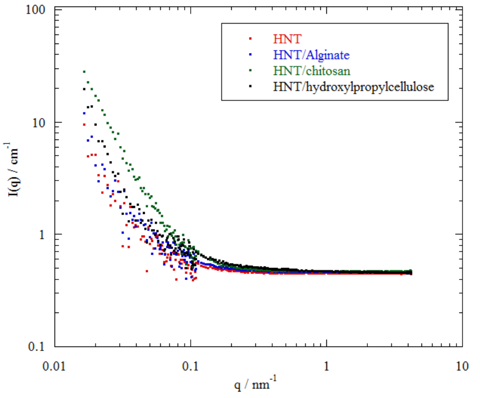

Figure 3. SANS intensity as function of q, the magnitude of the scattering vector, for the patch-HNT/polymer dispersions in D2O/H2O mixed solvent (51.70 vol% D_2O). The HNT/polymer ratio was 1.