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Synergistic and Competitive Aspects of the Adsorption of Poly(ethylene glycol) and Poly(vinyl alcohol) onto Na-Bentonite

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Abstract

The competitive adsorption of poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVOH) onto Na-bentonite has been assessed quantitatively. Particular emphasis was focused on the amount of organic located within the bentonite interlayer and any subsequent effects on the extent of layer expansion. The individual isotherms showed strong adsorption for both PVOH and PEG at amounts lower than the quantities required to produce fully loaded bilayer (0.33 g of PVOH/g of clay) and single layered structures (0.10 g of PEG/g of clay), respectively. Above these concentrations the incremental amounts adsorbed were smaller, and the concentration of adsorbates in solution gradually increased. Na-bentonite adsorbed more PVOH than PEG at any given concentration. In the competitive study the amount of PVOH adsorbed was enhanced in the presence of PEG (0.10 and 0.30 g/g clay), but less PEG was adsorbed. At low loadings of PVOH (0.02-0.10 g/g clay) the amount of adsorbed PEG was increased but at higher PVOH levels PEG adsorption was reduced. The XRD data showed stepped changes in the d-spacing as the adsorbed amounts of both PEG and PVOH increased. The PEG-bentonite samples did not expand beyond a bilayer structure (18 Å), but the XRD data for PVOH-treated samples indicated the formation of multilayer structures ($d \geq 44$ Å).

Keywords (4-6 keywords)

Competitive adsorption, adsorption isotherms, poly(vinyl alcohol), poly(ethylene glycol), x-ray diffraction, clay-polymer nanocomposites.

Introduction

The adsorption of organic molecules, oligomers and polymers onto the surface of clay minerals has been studied in great depth within numerous scientific fields; those pertinent to poly(vinyl alcohol) (PVOH) and poly(ethylene glycol) (PEG) include; drilling muds and treatment fluids within the petroleum industry,¹ soil structure stabilisation,² water clarification, mineral separation in mining, membrane technology in pervaporation,³ polymer-clay nanocomposites,⁴⁻⁸ and biomedical hydrogels.⁹ Central to these studies is the need to stabilize or destabilize dispersed clay minerals in colloidal systems in order to control the formulation viscosity or improve the mechanical or barrier properties of the final products/constructs. This is because the adsorption of polymers at the particle-solution interface has profound effects on the surface energies of clay minerals and thus their flocculation and stabilization behavior in colloidal suspensions.¹⁰

Both PVOH and PEG are polar and miscible in water; they are compatible with aqueous clay mineral suspensions and interact at the molecular level. The hydroxyl groups present on edge sites of montmorillonite and the water bound to the exchangeable cations readily form hydrogen bonds with the hydroxyl groups along the PVOH chains or those terminating the PEG chains. Hydrogen-bonding and van der Waals interactions are also possible between PVOH or PEG with the comparatively hydrophobic basal Si-O groups on the montmorillonite in the regions between exchangeable cations. The distance between hydroxyl groups on PVOH (2.52 Å) is similar to that between oxygen atoms in the montmorillonite structure (2.56 Å) facilitating strong interactions between the two groups when adjacent to each other. The PEG molecules may also interact with the Si-O groups through their ether oxygens. Direct coordination of polar organic species with exchangeable

cations via ion-dipole interactions is possible, but the polarizing power of the exchangeable cations usually means that the interaction between montmorillonites and organic material is achieved via water bridges. For instance, Parfitt and Greenland¹¹ showed that PEGs of different molecular weight (200 – 20000) were strongly adsorbed on Cs, Na, Ca and Al-montmorillonites from aqueous solution and suggested the cation retained its hydration shell which precluded the formation of a direct, inner-sphere association. However, Lu *et al.*¹² intimated that polyether polyols, like PEG, interact with exchangeable cations via crown-ether type complexes without water bridging molecules. Interactions between organic molecules (polymer-polymer or polymer-oligomer) also need to be considered when probing clay mineral-organic interactions, especially when two or more organic species are in direct competition.

The adsorption of uncharged polymers on clay minerals is generally considered to be entropy driven,¹³ but several factors can influence the extent of adsorption. Increasing the suspension pH reduced the amount of PVOH adsorbed on Ca²⁺ - but not on Na-montmorillonite. Bajpai and Vishwakarma¹⁴ showed that the adsorption of PVOH on Fullers' earth decreased as the number of carbon atoms (C1 to C4) on the competing aliphatic alcohols increased. Chen and Evans¹⁵ demonstrated that higher molecular weight PEG (35,000 over 4,000) was preferentially adsorbed on Na montmorillonite, from a polydisperse mixture. This may have significant repercussions for polymer-clay nanocomposites, since the unadsorbed, lower molecular weight PEG remaining in the aqueous phase could reduce properties such as tensile strength.

Preferential adsorption of individual components can have disastrous outcomes. Treatment fluids, used in the recovery of oil, may fail when arriving at the target location because

function-critical components have been sequestered by clay minerals en route. Preferential adsorption of a plasticizer onto the clay mineral incorporated in nanocomposite coatings can lead to more brittle films or poorer barrier properties; particularly if the plasticizer exerts a negative influence by agglomerating clay mineral platelets. Up to 10 wt% of clay mineral can be exceptionally well dispersed in a PVOH matrix such that the initial registry between the platelets is completely lost^{4,5} whereas PEG is known to limit the expansion and create only intercalated species irrespective of the amount of PEG offered. Selective adsorption of PEG when present in PVOH-clay composites and coatings could therefore limit clay mineral dispersion and subsequently compromise the resulting property profile.

The recent development of sustainable barrier coatings using clay-starch-plasticizer formulations has demonstrated the need to select the most appropriate plasticizer type when optimizing the associated water vapor barrier properties.¹⁶ Further refinement and improvement of these novel coatings is critically dependent upon a deeper understanding of the competitive nature of the adsorption of starch and plasticizer on the clay. A similar understanding is also required for thermoplastic starch/PVOH/clay nanocomposites; where an optimized dispersion of clay platelets is essential to maximize the mechanical properties of starch.¹⁷ Unfortunately, the addition of small amounts of PVOH decreased clay dispersion and agglomerated particles in the composites but the complex interfacial interactions together with the competitive sorption of PVOH and starch on clay still delivered significant increases in tensile strength and modulus. Clearly, a more detailed understanding of the extent, and nature of, PVOH and starch adsorption and their interaction with clay would facilitate further optimization of this system and contribute to a greater understanding of other similar systems.

This study investigates how adding plasticizer (PEG) to an aqueous PVOH-clay coating affects the adsorption of both components and the subsequent proximity of the clay layers in the final dry coating. Whilst the adsorption of PVOH and PEG onto montmorillonite from low to medium loadings has been studied extensively their competitive adsorption has not. This work also investigates a much wider concentration matrix both as individual components and also in combination during the competitive adsorption of PVOH and PEG onto montmorillonite. Although water is effectively a competitor for the adsorption sites in the presence of PVOH and/or PEG, the adsorption systems herein that combine the two are described as binary systems, i.e. the competitive adsorption of PEG and PVOH would result in a binary sorption isotherm. X-ray diffraction (XRD) analysis is used to support the information from the adsorption data and the resulting interlayer distance of the organo-clay samples formed is discussed in terms of the amounts adsorbed.

Experimental

Materials

Sodium bentonite (Cloisite Na⁺, Southern Clay Products, USA) is referred to as NaMt.

Extensive characterization of this bentonite has confirmed the suppliers claims that it contains more than 95 weight percent montmorillonite [Supplementary data]. PVOH (98-99% hydrolyzed) and PEG with molecular weights of 31,000-50,000 and 600, respectively, were obtained from Sigma-Aldrich, UK. All materials were used without further purification.

PVOH, PEG and Clay Mineral Mixtures

In a typical experiment the required amounts of PEG and PVOH were mixed and stirred for 4 hours at 90 °C (in 6 ml deionized water) before the clay mineral suspension was added (1g /14ml) and then mixed for 18 hours at 90 °C.

With higher organic concentrations (> 49 parts per hundred, pph) in the single adsorption systems the amount of clay mineral in suspension was reduced in order to lower the viscosity of the suspensions and allow sufficient mixing. This was achieved by using the same volume of water (20 ml) and ensuring that the total solid content (PVOH or PEG + clay) always equaled 1 g. For example, the clay sample treated with 90 wt% PVOH contained 0.9 g PVOH and 0.1 g NaMt.

PVOH and NaMt or PEG and NaMt mixtures (each loaded with 20 pph organic) were subjected to 10 repeated washing steps (at room temperature) by dispersing the mixtures in deionized water (30 ml), centrifugation and decanting the supernatant. The amount of organic present in each supernatant was quantified gravimetrically [supplementary information].

Adsorption Isotherms

The amount of PVOH or PEG adsorbed onto NaMt in the individual isotherms was calculated gravimetrically by weighing the residue remaining after evaporation of the water from the supernatant after centrifugation (Sorvall RC6, 15,000 rpm for 90 minutes). The supernatant was clear and decanted into a Petri dish where the water was removed by evaporation at 50 °C.

A TGA method was developed to quantify the amounts of PVOH and/or PEG adsorbed on NaMt in the binary isotherms [see supplementary data].¹⁸ The residue from the

supernatant, which was obtained in the same way as for the individual isotherms, was analyzed by TGA measurements performed on a Mettler Toledo TG50 thermogravimetric analyzer. Samples were heated from 35 to 800 °C using a heating rate of 20 °C/min under nitrogen at a flow rate of 40 ml/min (see Supplementary data for further details).

X-ray Diffraction

XRD traces were recorded using a Philips X'Pert Pro diffraction system utilizing a Cu-tube ($\lambda = 1.542 \text{ \AA}$), operating at 40 kV and 40 mA. Two different families of x-ray diffraction data were collected. The first set of samples was prepared using the sediment remaining after centrifugation and removal of the supernatant (designated AC). The sediments were cast onto glass microscope slides and dried at 50 °C. The second set of samples was prepared by casting an aliquot of the suspension before it was centrifuged (designated BC), onto a glass microscope slide and dried at 50 °C. The resulting x-ray traces would provide information about the interlayer expansion in the absence or presence of excess organic material, respectively.

Parts Per Hundred (pph) Units used

The information within the text and Figures (including the supplementary data) reports the aqueous concentrations of PVOH and PEG offered to NaMt in units of parts per hundred (pph) to avoid the confusion associated with wt% units when discussing the binary adsorption isotherms. The number of pph of organic added are presented relative to the clay portion (100 pph). Consequently, a mixture of 1g clay and 1g PVOH would constitute 100 pph PVOH whereas a mixture containing 1g clay plus 0.30 g PEG plus 0.90 g PVOH would be represented as 30 pph PEG and 90 pph PVOH.

Results and Discussion

The steep increase at the start of the individual adsorption isotherms for PEG or PVOH with NaMt (Figure 1a) demonstrated that they were both strongly adsorbed at low loadings (solution concentrations <1 g/L). When the amount of PEG or PVOH offered was further increased the amounts remaining in solution gradually increased. The transition to significant amounts of free organic in solution occurred when 0.088 g PEG /g NaMt was adsorbed (0.945 g PEG/L in solution) and 0.325 g PVOH/g NaMt was adsorbed (0.730 g PVOH/L in solution). The use of pph in addition to g/L at equilibrium in Figure 1 helps to distinguish the initial conditions used to prepare the various samples and identify the data points arising from them. The transitions noted in Figure 1a relate to those in Figures 1b and c when the NaMt present had been offered 10 pph (9 wt%) and 33 pph (25 wt%) PEG and PVOH, respectively, and underline the greater capacity of NaMt for PVOH, compared to PEG.

Individual Adsorption Isotherm - PEG

The adsorption data for PEG (Figure 1a) approached that of the Langmuir isotherm, L-class, subgroup 2 in that initial strong adsorption occurred at low loadings (< 1 g/L) but the continued uptake, rather than a monolayer plateau, made it an L-class, subgroup 3-type isotherm.^{19,20} The PEG adsorption data returned a relatively poor fit to the linear form of the Langmuir equation ($R^2 = 0.9608$ for the low loading range with constant clay:solvent ratio, i.e. the first six data points and reducing to 0.9059 for the entire concentration range). Chen and Evans²¹ reported a L-type adsorption isotherm for PEG1500 on Na-montmorillonite (PEG:clay ratios from 0.2 to 0.7) with a plateau at ~0.24 g PEG/g clay. The broader range of PEG:clay ratios studied herein, which incorporates lower concentrations,

emphasized the strong adsorption at low loadings, and the gradual increase of free PEG in solution as the amount of PEG offered was increased (Figure 1b). Parfitt and Greenland¹¹ reported that the adsorption of PEG300, PEG600 and PEG20000 on Ca-montmorillonite resulted in types C, type L and type H isotherms.

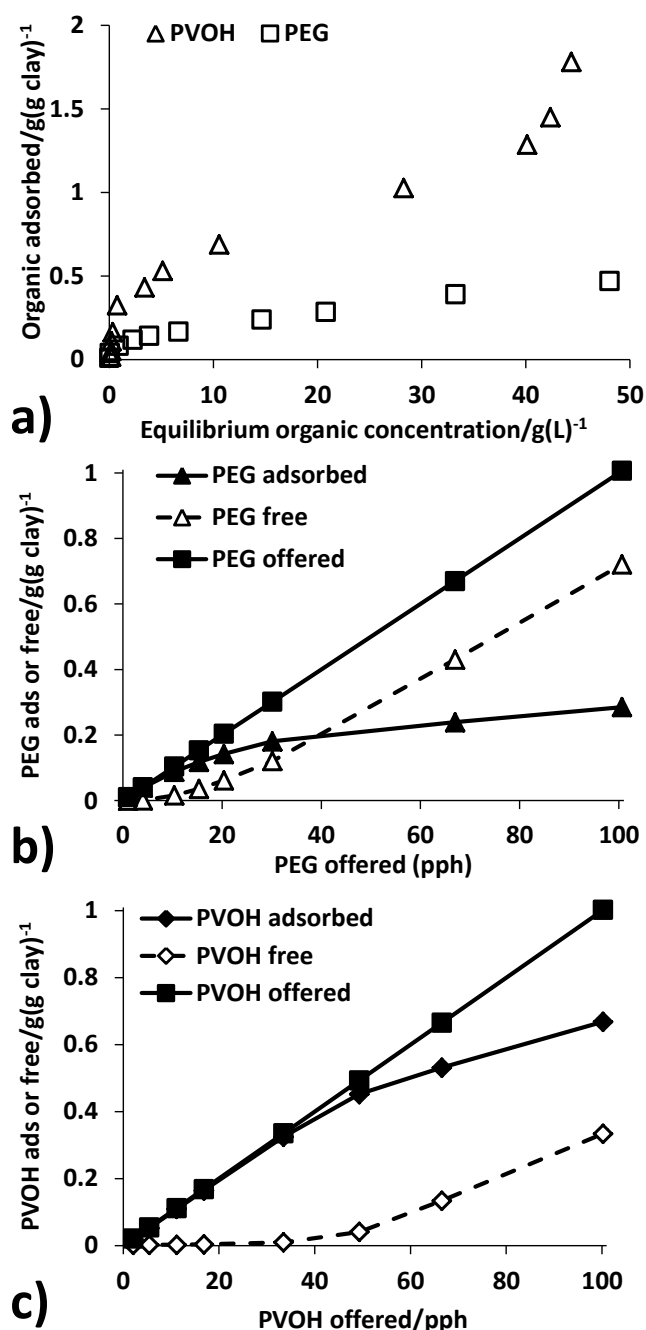


Figure 1: Adsorption isotherms for the PVOH and PEG on NaMt; a) complete data set and for the lower concentration range for (b) PEG and (c) PVOH.

Individual Adsorption Isotherm - PVOH

Adsorption of polymer on clay minerals is considered to be a slow and irreversible process. Greenland² showed that the adsorption of PVOH on Na-montmorillonite at 23 °C reached a maximum after 24 hours, but equilibration with Ca and Cs – montmorillonites required 7 days because the lower platelet-platelet separation in suspension hindered access to the interlamellar clay mineral surfaces. Chang *et al.*²² stated that equilibrium adsorption of PVOH on montmorillonite required 8 hours at 25 °C, whereas others¹⁴ considered that only 1 hour was necessary. Preliminary work here demonstrated that the 18 hour mixing was sufficient to reach equilibrium because mixing for up to two days did not result in further adsorption. The temperature of 90 °C was chosen to match that used in the preparation and mixing of coating suspensions in industry. Chiellini *et al.*²³ demonstrated that the amount of PVOH adsorbed on montmorillonite increased from 35 to 41 mg/g at suspension temperatures of 20 and 50 °C, respectively. Equilibrium was reached in 5 hours at 50 °C but took 300 hours at 20 °C.

The steep increase in adsorption at the higher PVOH loadings (solution concentration > 40 g/L) coincided with the lower clay:water ratios used to achieve this concentration range (Figure 1a). Greenland² showed that increasing the amount of clay in suspension (2.5 to 40 g/L) reduced the amount of PVOH adsorbed because the poorer clay dispersion prevented full access to the clay surface. However, the effect is considerably reduced at clay concentrations < 1 wt% (10 g/L). Given that all the high PVOH systems prepared here contained 0.5 g/L clay this factor is not expected to contribute significantly to the increasing amounts of PVOH adsorbed. The upturn in the isotherm more likely reflects the transition

to a clay-crosslinked PVOH hydrogel in which the network active PVOH chains only experience a minimum number of significant interactions with the clay mineral surface.²⁴

The adsorption isotherm for PVOH was described by L-class, subgroup 3 due to the increasing amounts of PVOH adsorbed beyond the knee of the isotherm and the further increase at higher concentrations.^{19,20} Bussetti and Ferreiro²⁵ described the adsorption of PVOH (MW= 14,000) on Na-montmorillonite at 28 °C as an H-class, subgroup 2 isotherm and calculated the adsorption maximum to be 0.496 g PVOH/g clay, which is close to the value at which free PVOH is observed here (between 0.33 g PVOH/g NaMt). Greenland² reported an L-class, subgroup 2 isotherm for the adsorption of PVOH (MW = 25000) at 23 °C with a monolayer coverage of 0.8 g PVOH/g clay (solution concentration range < 16 g/L). The higher molecular weight (MW 25,000) is likely to contribute to the higher coverage compared to that of Bussetti and Ferreiro.²⁵ Bajpai and Vishwakarma¹⁴ observed an upturn, similar to that presented here, in the amount of PVOH (MW = 37,500) adsorbed onto Fuller's earth at higher loadings after an initial monolayer coverage was complete (L-class subgroup 3 isotherm). Clearly, the strong hydrogen-bonding that occurs between PVOH molecules appears to encourage the formation of multiple-layer adsorption.

Binary Adsorption Isotherms

When a coating formulation is deposited onto a substrate the film formation occurs as the volatile solvent evaporates. In a coating which contains a swelling clay mineral, such as NaMt, a significant proportion of the organic, film forming species is considered to be present in the interlayer space between adjacent clay mineral layers, although some will also be attached to the outer surfaces of a stack of aggregated clay mineral layers and the edges of particles. Once dried, any PVOH or PEG which is not adsorbed in the interlayer or

directly attached to the outer surfaces, or the edges, becomes the coating matrix. While it is unlikely that unadsorbed PEG600 alone would contribute substantially to the structure of the dried coating, the same may not be true of any unadsorbed PVOH, which would be able to form bonds with PVOH on the accessible outer surfaces of clay mineral layers, stacks or particles.

A central requirement of this study was to evaluate the distribution of PVOH and PEG between the clay mineral and the surrounding medium in dried films/coatings; i.e. to determine the composition of the coating matrix and appreciate how it changes as the relative quantities of the different components in the formulation are altered. In the following description of the binary uptake curves (Figure 2) it is accepted that (1) the total amount offered (filled squares) is the amount of PVOH and PEG available in the initial coating formulation, (2) the quantities of PVOH free and PEG free (which are determined in the supernatant after centrifugation (open diamonds and triangles, respectively) and represent the amounts of PVOH and PEG that are not adsorbed in the clay mineral interlayer, or on the edge and/or outer surfaces) would form the coating matrix upon drying and (3) the composition of the adsorbed organic on clay mineral can be determined using the amounts of adsorbed PEG (closed triangles) and PVOH (closed diamonds) present. Furthermore, the combined amounts of adsorbed PVOH and PEG (open squares) when compared with the amount offered (filled squares) provides a clear indication of the amount of unadsorbed organic available to form the coating matrix.

The effect of adding PEG at 1, 10 and 30 pph on the amount of PVOH adsorbed on NaMt at 90 °C is shown in Figure 3. Except for the samples prepared using 50 or 90 pph of PVOH (Figure 2e and 2f), the NaMt adsorbed nearly all the PVOH offered. In addition, NaMt was

also able to accommodate relatively large quantities of PEG alongside PVOH, presumably in the interlayer region and especially when 30 pph PEG was offered.

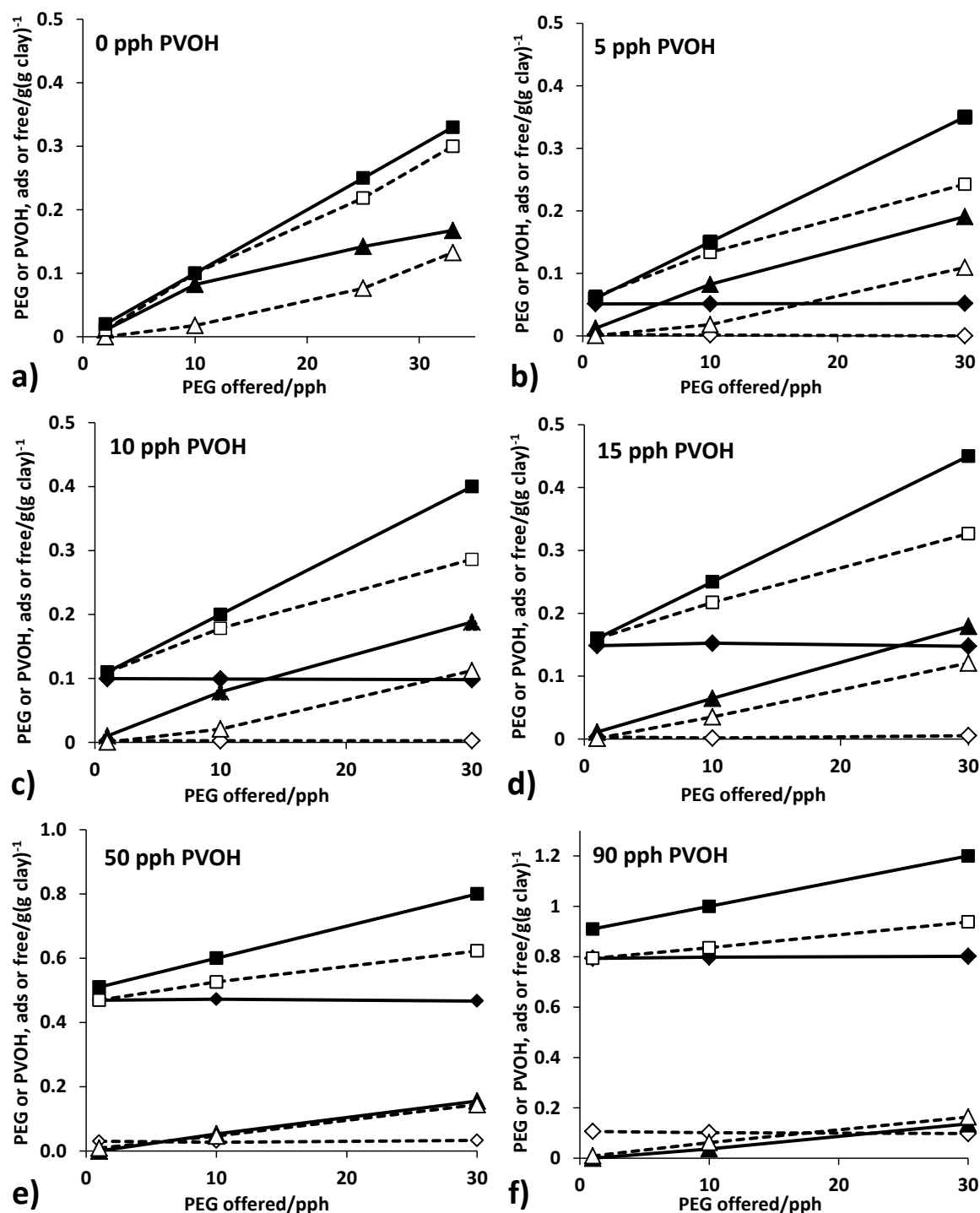


Figure 2: Uptake curves for the adsorption of (a) 0 pph, (b) 5 pph, (c) 10 pph, (d) 15 pph, (e) 50 pph and (f) 90 pph of PVOH on NaMt in the presence of 0, 1, 10 and 30 pph PEG.

When ≤ 15 pph PVOH was offered the addition of PEG did not prevent the NaMt from adsorbing all the available PVOH (Figures 2a-d). The amount of PEG600 adsorbed always increased with the amount of PEG offered, but a significant proportion of the available PEG was not adsorbed by the clay mineral and thus, in the corresponding dried samples, the coating matrix would contain only PEG600. The details of the competitive adsorption of PEG in the presence of PVOH were complex (Figure 3) and will be described in more detail below. When offered 50 and 90 pph PVOH the addition of any quantity of PEG600, even 1 pph, resulted in a fixed increase in the amount of PVOH adsorbed on the clay mineral. At 50 pph the increase was only 4% (0.45 to 0.47 g/g clay) whereas at 90 pph the amount of PVOH adsorbed increased from 0.67 to 0.79 ± 0.01 g/g clay; an increase of 18%. Even though PEG enhanced the amount of PVOH adsorbed not all the available PVOH was taken up by the clay mineral. Hence, in a dry coating, prepared using either 50 or 90 pph PVOH, the coating matrix would contain both PVOH and PEG. For example, in the sample prepared using 90 pph PVOH and 30 pph PEG (Figure 2f), the symbols Δ and \diamond indicate that the coating matrix would contain essentially equal amounts of PVOH and PEG. In contrast, the ratio of PEG:PVOH in a coating matrix produced using an initial mixture of 50 pph PVOH and 30 pph PEG would be approximately 4.5:1 (Figure 2e).

Figure 3 illustrates how the affinity between clay mineral and PVOH influenced the amount of PEG adsorbed. At 30 pph PEG the clay mineral adsorbed 0.18 g PEG/g clay in the absence of PVOH. Small additions of PVOH, 2 - 10 pph, resulted in an increase in PEG adsorption to ca. 0.19 g PEG/g clay. Further increases in the amount of PVOH available caused significant reductions in the amount of PEG adsorbed, suggesting that the amount of interlayer space available alongside PVOH was much reduced. The initial increase in PEG adsorbed in the

presence of low levels of PVOH, 1 pph, was not apparent when only 10 pph PEG was available. The amount of PEG adsorbed in the presence of 90 pph PVOH was reduced by 57% from 0.87 to 0.037 g PEG/g clay. At 1 pph PEG approximately, 0.01 g PEG/g clay was consistently adsorbed until the amount of PVOH exceeded 20 pph after which the adsorption of PEG was completely suppressed.

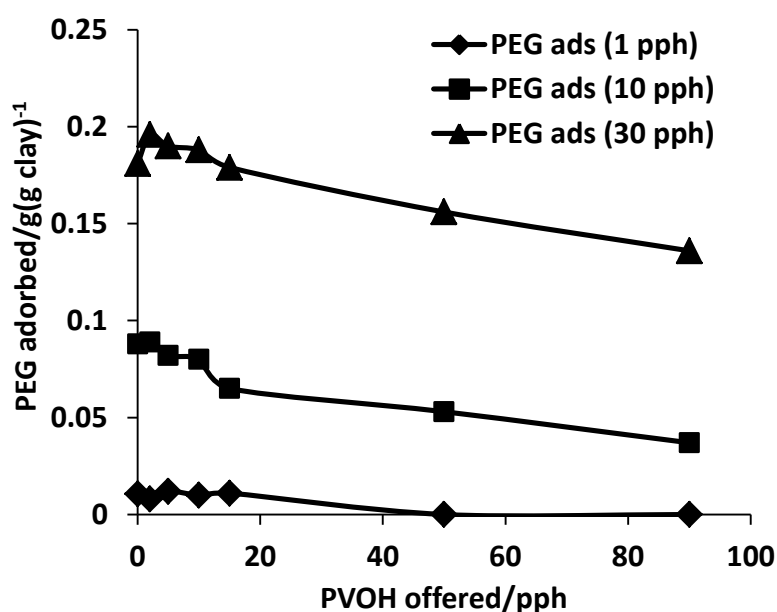


Figure 3: Uptake curves for the adsorption of fixed amounts (1, 10 and 30 pph) of PEG on NaMt in the presence of increasing quantities of PVOH.

Clearly, the PVOH and PEG interact on the surface, and in the interlayer of clay mineral, resulting in changes in the total amount of adsorbed organic and the ratio of PVOH and PEG adsorbed. When NaMt was offered 90 pph PVOH, in the absence of PEG (Figure 1c), the clay mineral retained 0.67 g PVOH/g clay. In the presence of just 1 pph PEG the amount of PVOH adsorbed increased, by 18%, to 0.79 g PVOH/g clay (Figure 2f). When the amount of PEG, made available to 90 pph PVOH, was increased to 30 pph (Figure 2f) the amount of adsorbed PVOH remained unchanged but the amount of PEG adsorbed was 0.14 g/g clay

making the total amount of organic adsorbed equal to 0.94 g/g clay; an increase of 40% of adsorbed organic compared with when the clay mineral was offered 90 pph of PVOH alone.

The relative amounts of PVOH and PEG, adsorbed by NaMt, reflects the balance between the amount of each molecule made available to the clay mineral and the demonstrated affinity between the clay mineral and PVOH. In the presence of 30 pph PEG the percentage of adsorbed PVOH changed as 21%, 75% and 85% when the clay mineral was offered 5, 50 and 90 pph PVOH. The corresponding percentage of adsorbed PVOH in the presence of 10 pph PEG were 40%, 90% and 95%. The increased amount of PVOH adsorbed in the presence of 10 pph PEG is considered to reflect the reduced amount of PEG available.

An explanation which is consistent with the observed behavior is that the smaller PEG molecules are more mobile and adsorb rapidly to the clay mineral surface. Nelson and Cosgrove²⁶ have shown that PEG is able to decorate the surface of hectorite particles, encourage their dispersion in water and resist changes that would normally result in aggregation. Therefore, it seems realistic that the PEG adsorbs on the clay mineral surface and promotes an enhanced degree of dispersion of the clay platelets (either a reduction in the number of layers per stack and/or a larger number of individual platelets) enabling the PVOH to access a greater proportion of the available clay mineral surface. The fact that just 1 pph PEG caused an abrupt increase in the amount of PVOH adsorbed (4 % and 20 % in the presence of 50 and 90 pph PVOH, respectively) was remarkable since this is equivalent to just one PEG molecule for every 60 cation exchange sites on the clay mineral surface. However, the PEG is most likely 'recycled' during the equilibration period in that it is displaced by the much preferred PVOH molecules thus freeing PEG to move to other clay mineral surfaces to begin the facilitation of PVOH adsorption anew. The XRD results

reported below will demonstrate that the final population of the clay mineral interlayers (enhanced basal spacing related to the amount of each adsorbate retained) reflected the greater affinity between clay minerals and PVOH.

X-ray Diffraction Analysis of PEG-NaMt Samples

The XRD traces collected from dry PEG-NaMt films prepared from sediment after centrifugation and removal of supernatant (AC) showed that the d-spacing exhibited a step change as the loading increased from 1 to 1900 pph (1 to 95 wt%) (Figures 4 and 5a). At low PEG loadings (1 - 10 pph; i.e. PEG adsorbed is 0.01 - 0.8 g/g) single layer structures (13.1 - 13.8 Å) are formed, at medium loadings (15 to 30 pph; 0.12 - 0.18 g/g - shaded area in Figure 5a) a mixture of single and bilayer structures (17.9 Å) coexist, and bilayers dominate at high loadings (> 30 pph; >0.18 g/g). Even when large amounts of PEG were available no more than 2 layers were present within the interlayer space confirming that PEG does not form multilayer structures and limits clay layer disassociation in a dry film. Basal-spacings near or equal to the bilayer spacing of 17.9 Å are regularly reported and are independent of loading, MW (300-20,000) or whether samples are produced from solution or by melt compounding.^{21,27,28}

The increase in intensity and decrease in full-width at half-height for the 001 peak together with the presence of higher order 00l reflections for PEG loadings of 10 and 100 pph (0.08 and 0.28 g/g) indicated a greater number of regularly ordered stacks of clay layers and reflects the formation of full single and bilayer structures, respectively. The highly ordered structure is typical of PEG-clay samples.²⁹ Subtraction of the clay layer thickness (9.6 Å) from the spacings of a full single layer and full bi-layer structure provides internal dimensions of 4.2 and 8.3 Å, respectively, which is commensurate with the thickness of the PEG molecules.

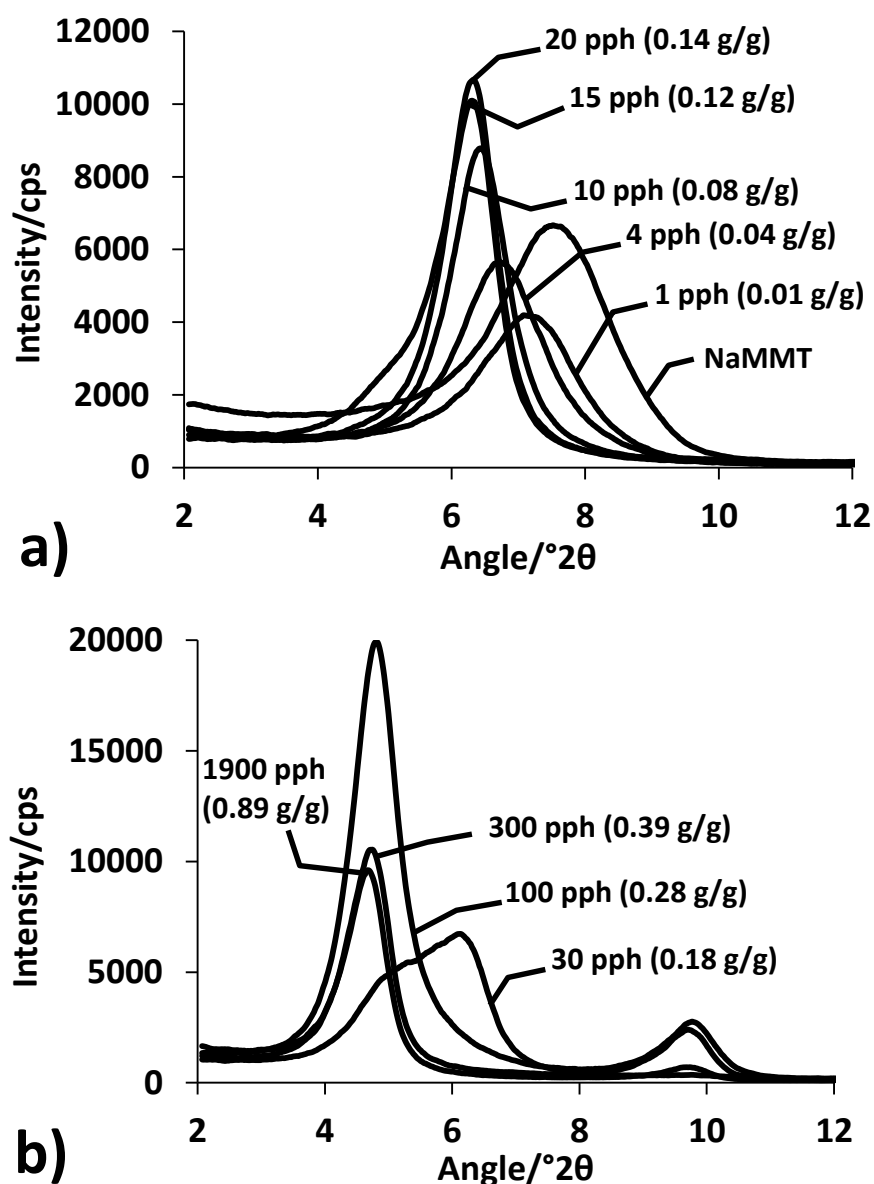


Figure 4: XRD traces collected from PEG-NaMt films prepared from sediment after centrifugation and removal of supernatant (AC). Numbers on individual traces represent the amount of PVOH offered in pph with respect to 100 pph NaMt. Numbers in parentheses represent the amount of PEG adsorbed.

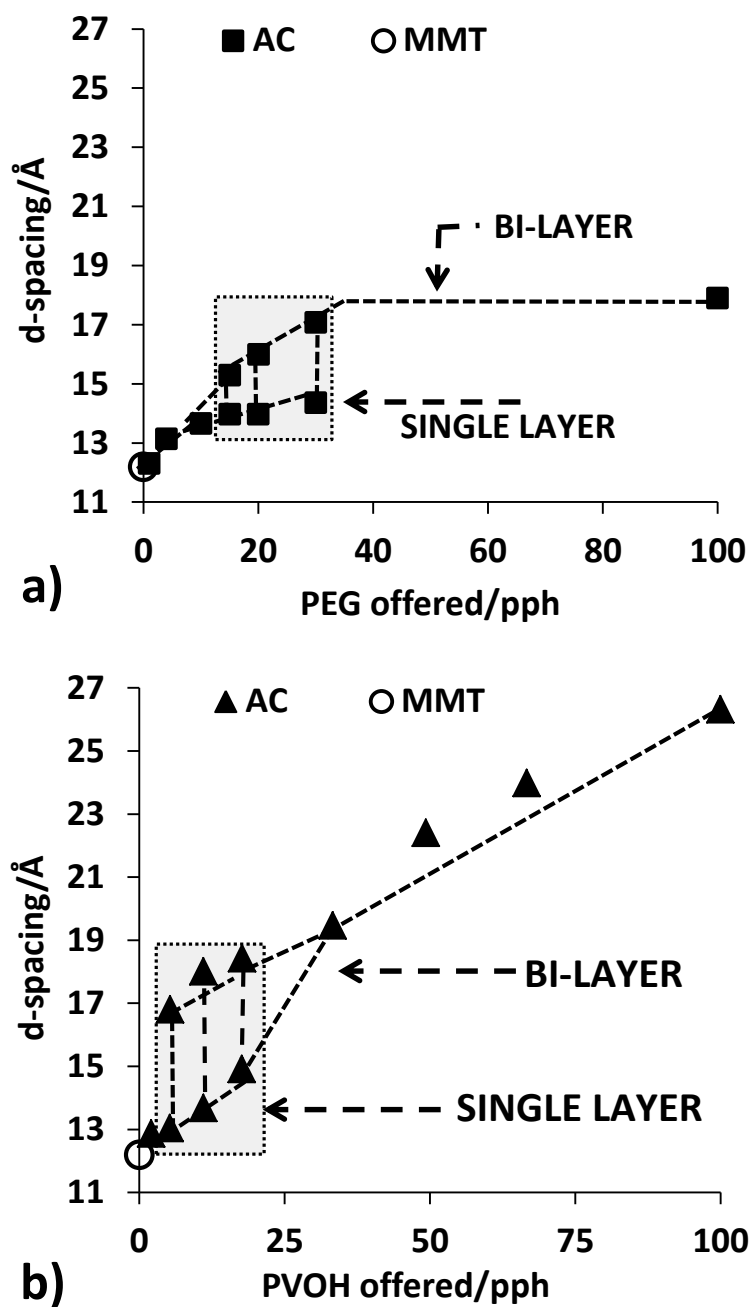


Figure 5: a) d-spacings of PEG600-NaMt mixtures (AC) and b) d-spacings of PVOH-NaMt (AC).

Mixed single and bilayer structures are indicated by the presence of two data points at a single PVOH loading (shaded areas). The dashed lines are to guide the eye.

X-ray Diffraction Analysis of PVOH-NaMt Samples

XRD patterns collected from dried films prepared from PVOH and NaMt suspensions after centrifugation and removal of supernatant (AC) showed that, as the loading of PVOH increased from 2 to 300 pph (i.e. PVOH adsorbed is 0.02 - 1.02 g/g), systematic increases in d-spacing were observed (Figure 6 and 5b). Greenland² reported a linear increase in basal spacing from 17 to 30 Å as the PVOH offered to the clay mineral increased from 15 to 69 pph. At low loadings, PVOH molecules were adsorbed as a single layer in the clay interlayer (Figure 6a, 2-5 pph; $6.3^\circ 2\theta$, ~ 13.9 Å). At 18 pph (0.16 g/g) the XRD data indicated that most PVOH was present as a bilayer (18.1 Å), whereas at 11 pph (0.11 g/g) the two overlapping peaks showed that a combination of 1 and 2 layer intercalates was clearly present. The two symbols at a single value of PVOH offered (Figure 5b, shaded area) indicate that two discrete spacings (a single layer and a bilayer) were present.

Although the single and bilayer terminology used for the PEG-NaMt system may seem a rather simplistic representation for the arrangement of polymer molecules within the clay gallery, it is not uncommon in the literature. Its simplicity does not account for PVOH or PEG molecules adopting conformations (trains, loops, tails) that do not maximize coverage of the clay mineral surface. Indeed, small portions of the molecules may be adsorbed in the interlayer space whilst a long tail or loop remains unattached or interacts with the edges.²⁶

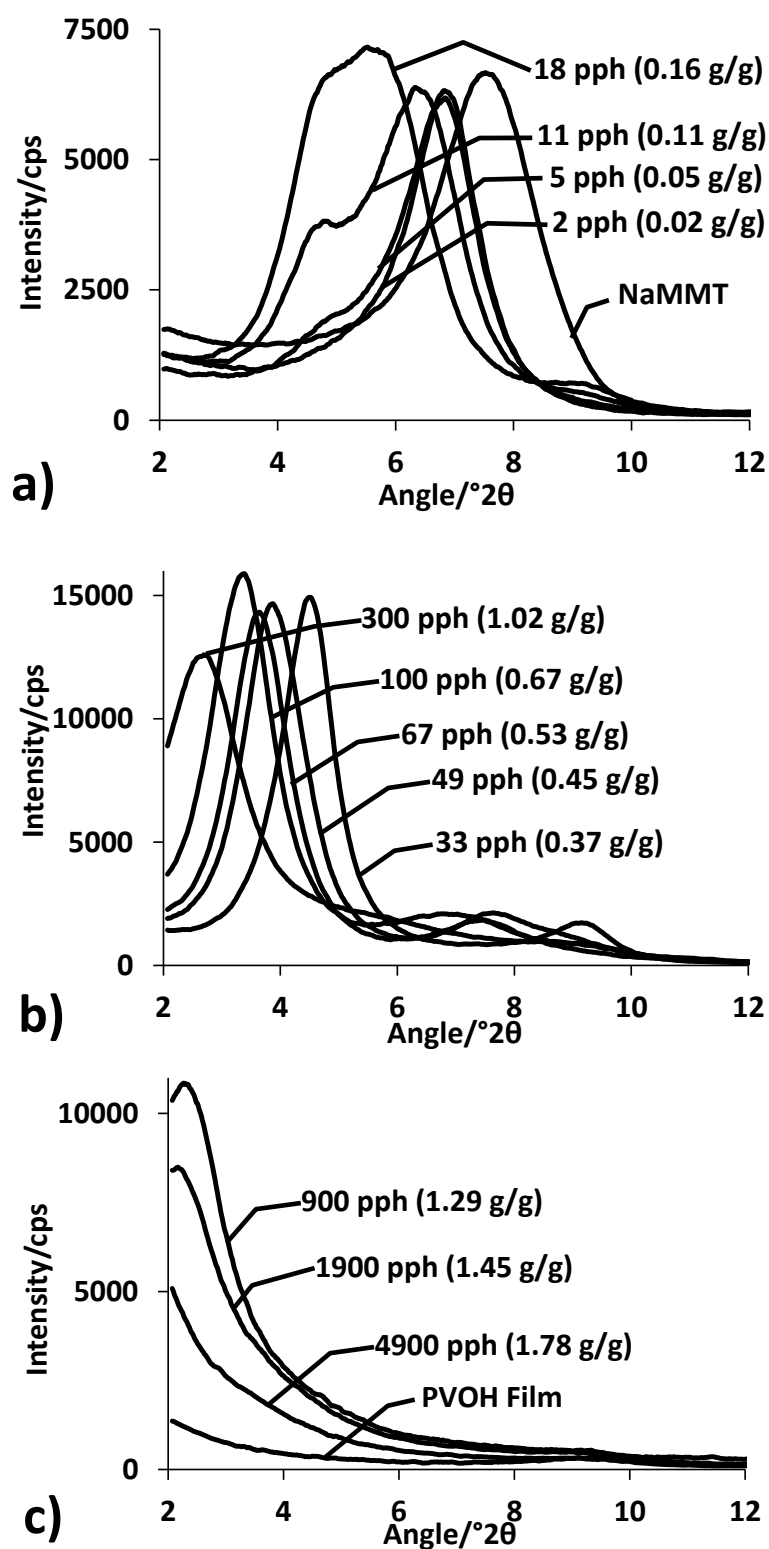


Figure 6: XRD traces collected from PVOH-NaMt films prepared from sediment after centrifugation and removal of supernatant (AC). Numbers on individual traces represent the amount of PVOH offered in pph with respect to 100 pph NaMt. Numbers in parentheses represent the amount of PVOH adsorbed.

The single layer of PVOH chains (approximately 5 Å thick)² is envisaged to lie parallel to the plane of the clay layer and for a bilayer structure the chains are stacked upon each other, which requires overlapping or folding of the chains in order to accommodate all the molecules at higher loadings both within the interlayer and on exposed basal surfaces. The interlayer spacings, determined by XRD, increased in increments closely matching simple multiples of the molecular diameter of the PVOH chains. Thus, at loadings ≤ 33 pph (0.37 g/g) the use of the single and bilayer terminology is considered acceptable.

With medium PVOH loadings (33 - 300 pph; 0.37 - 1.02 g/g, ~ 20.3 - 35.3 Å) multiple layers exist, the peak position at $2.5^\circ 2\theta$ (35.3 Å) for the clay mineral treated with 300 pph (ca. 1.02 g PVOH adsorbed/g clay) could contain as many as 4-5 'layers'. However, as more PVOH enters the interlayer the normals to the clay platelets would need to adopt a greater angular variation in order to accommodate all the PVOH³⁰ thus diminishing the intensity and broadening the d001 peak. At high loadings > 900 pph (> 1.29 g/g) the PVOH-NaMt systems exhibited expanded layers with a d-spacing close to 40 Å. At 4900 pph (1.78 g/g) the increasing baseline towards lower angles strongly suggested that the layers were very well dispersed, were no longer in register with each other and had little order.^{31,32} This enhanced dispersion, together with the marked increase in PVOH adsorption at higher loadings (Figure 1a, > 40 g/L), reflects a change in the structure of the fully wetted system towards that of a hydrogel in which very well dispersed clay platelets act as physical crosslinks between the PVOH chains.

X-ray Diffraction Analysis of PVOH-PEG-NaMt Samples

The x-ray diffraction analysis of the cast films prepared from binary mixtures of PVOH and PEG focused on the samples in Figure 2; particularly the addition of 10 and 30 pph PEG

which provided a stable monolayer and bilayer, respectively (Figure 5a). The XRD patterns in Figure 7 illustrate how each incremental addition of PEG to samples of PVOH-NaMt moved the d_{001} peak to smaller angles (higher spacing). This XRD data is summarized in Figure 8, where for ease of comparison, the data from the PVOH plus NaMt system are linked by the dotted line. The shaded areas in Figure 8 serve to illustrate how the addition of PEG (especially at the 30 pph level) resulted in the transformation from a single layer to a bilayer at lower values of PVOH offered. Figure 8c shows that when 30 pph PEG600 was offered in addition to 50 pph PVOH the d-spacing increased from 22.4 Å to 27.5 Å. The corresponding adsorption data shows that the amount of PVOH in the sample increased from 0.45 to 0.47 g/g NaMt and the amount of 'co-adsorbed' PEG was 0.16 g/g NaMt. Combining 30 pph of PEG with 90 pph PVOH increased the d-spacing from 26 to 30 Å reflecting the fact that the amount of PVOH increased from 0.67 g/g to 0.79 g/g and the amount of PEG retained by the clay mineral was 0.14 g/g. Clearly, significant increases in d-spacing only occurred when 10 and 30 pph PEG were offered together with PVOH. The XRD traces of the NaMt treated with both PVOH and PEG generally reported higher d-spacings than those associated with the adsorption of PVOH or PEG alone providing further strong evidence that both components were located in the same gallery.

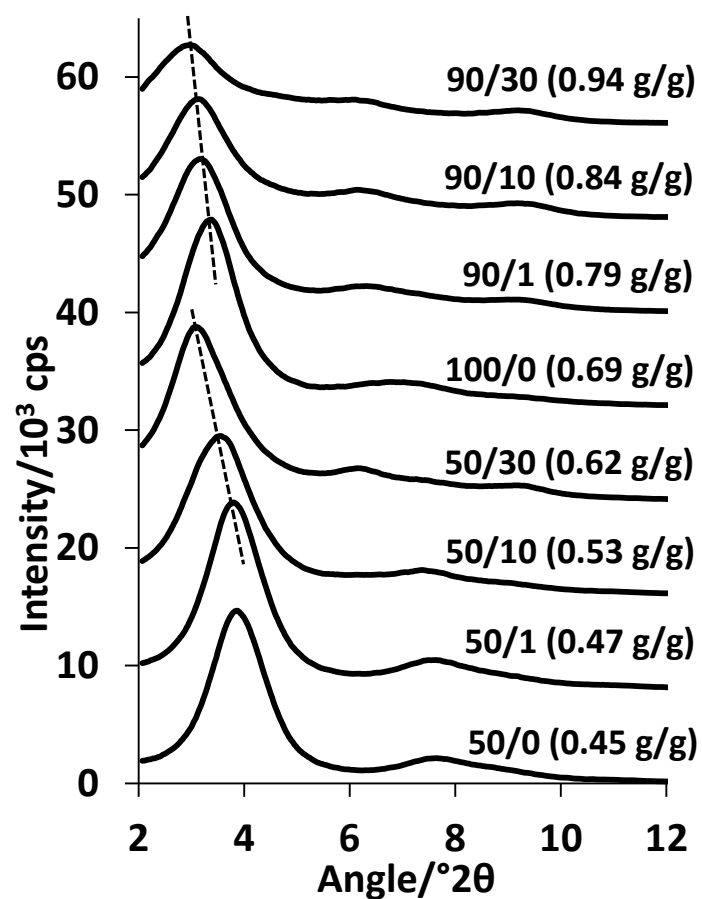


Figure 7: Diffraction traces from PVOH-PEG-NaMt composites prepared from the sediment after centrifugation and removal of supernatant (AC). Numbers on individual traces represent loading of PVOH/PEG in pph with respect to 100 pph NaMt. Numbers in parentheses represent combined amount of PVOH and PEG adsorbed.

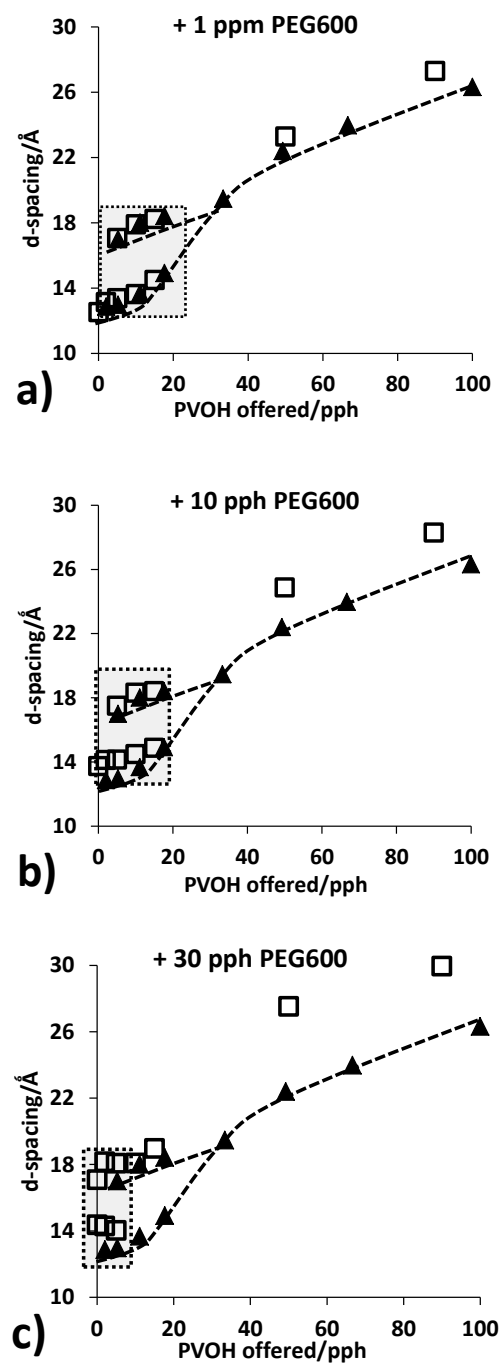


Figure 8: The d-spacings of dried PVOH-PEG-NaMt composites prepared from the sediment after centrifugation and removal of supernatant (AC). Displayed as a function of a) low (1 pph), b) medium (10 pph) and c) high (30 pph) PEG loading. Mixed single and bilayer structures are indicated by the presence of two data points at a single PVOH loading. Data marked with closed triangles represents the d-spacings of PVOH-NaMt (AC). The lines are to guide the eye.

The results in Figures 7 and 8 show that the formation of multi-layers was possible using the binary mixtures because d-spacings greater than $\sim 21 \text{ \AA}$ were observed. Recalling that adding PEG at 100 pph produced a bilayer structure (Figure 4a) that did not expand further upon addition of more PEG, the $> 21 \text{ \AA}$ d-spacings demonstrate that PVOH was able to enter the interlayer and that PEG was unable to 'control' the d-spacing by limiting the swelling. Furthermore, an XRD silent trace (not shown) was still evident in samples prepared using 700 pph PVOH plus 200 pph PEG showing that high clay mineral dispersion (in the dried, solid samples) was still possible in the presence of relatively high amounts of PEG; the PEG was therefore unable to cause agglomeration or flocculation of the clay layers.

X-ray Diffraction Analysis of Non-Centrifuged Samples

The foregoing discussion has rightly focused on the behavior of samples which have undergone centrifugation to remove unadsorbed organic material. However, in a coating operation the total amount of organic contained in the suspension is retained in the coating layer and any unadsorbed organic remains and must to be accommodated in the final product because only the water is removed during the drying process. The XRD traces in Figure 9 illustrate how this excess organic, clearly identified in Figure 2, influenced the presence, position and intensity of the d_{001} peaks for the dry coating. Only small amounts of unadsorbed PEG were present, at loadings $< 15 \text{ pph PEG}$ (Figure 1b), and these exerted little influence on the position of the diffraction peak which confirmed a single layer of PEG in the interlayer (Figure 9a and b). The diffraction traces of the centrifuged samples, prepared using 20 and 30 pph PEG (Figure 9b), also reflected a majority of single layer PEG molecules in the interlayer. In contrast, the XRD traces obtained from the corresponding dried suspensions confirmed the presence of PEG bilayers in the interlamellar space. At PEG

loadings of > 30 pph the d-spacings were almost identical, because the amount of PEG offered exceeded that required to maintain a stable bilayer and any unadsorbed PEG must have been accommodated outside the gallery. These results indicate that the increased spacing (in the BC samples) reflected the fact that the film dried in equilibration with a larger amount of adsorbate.

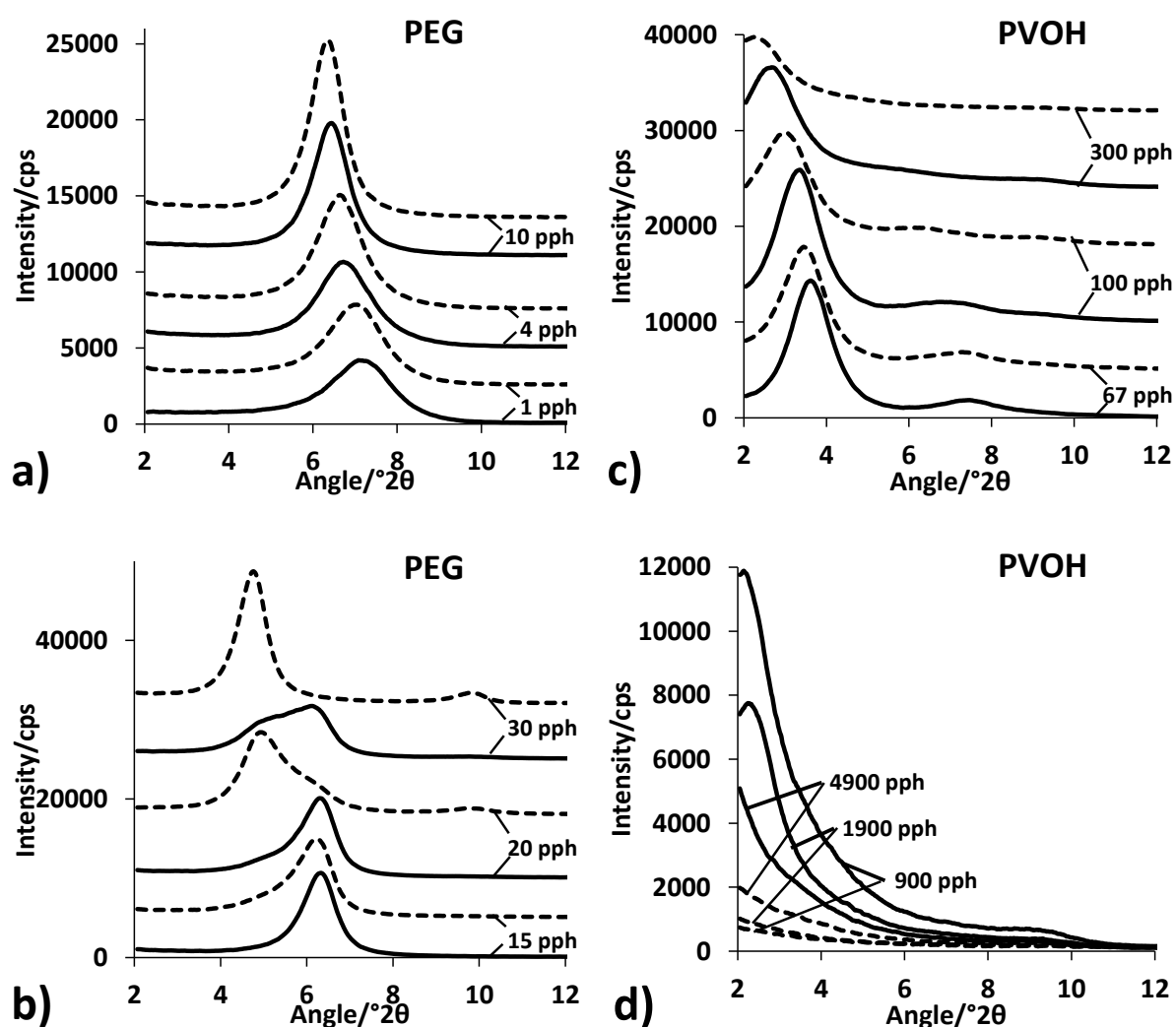


Figure 9: Diffraction data collected from sediment after centrifugation and removal of supernatant (AC - full lines) compared to those collected from dried suspension (BC - dashed lines), a) and b) show PEG-NaMt mixtures whereas c) and d) show PVOH-NaMt mixtures.

The d-spacings observed in the PVOH-NaMt films prepared from suspension (BC) with loadings ≤ 33 pph (data not shown) were very similar to those observed in the films prepared from the sediment after centrifugation (AC) (Figure 6a). However, higher d-spacings were observed in those samples prepared from suspensions in which the PVOH loadings were >33 pph (Figure 8c). These observations imply that a completely formed bilayer-structure was produced at a loading of 33 pph. This was also the loading at which free PVOH is first observed in solution (Figure 1).

The d_{001} spacing for the centrifuged samples, prepared using PVOH aliquots of 67 to 300 pph, were always lower in the centrifuged samples (Figure 9c) for the same reasons as the PEG treated samples. With PVOH loadings >900 pph the non-centrifuged samples did not exhibit a d_{001} peak indicating that the spacing was > 44 Å. Following centrifugation the samples prepared using 900, 1900 and 4900 pph PVOH exhibited increasingly intense peaks with a spacing close to 40 Å. It is important to reinforce that, at high loadings, the PVOH was not simply occluded in the sample but continued to enter the interlayer and increased the d-spacing, unlike PEG which was unable to expand the clay mineral above 18 Å.

The apparent discrepancy in basal spacings (as a function of amount of organic offered), between the samples obtained before centrifugation (BC) and after centrifugation (AC) (Supplementary data) is readily explained. In the AC samples a portion of the PVOH or PEG available to the clay mineral was removed with the supernatant. Therefore, there was less PVOH or PEG to equilibrate with the clay mineral as the sample dried. Consequently, the actual amount of organic present was less than that originally offered whereas in the BC samples the actual amount present was identical to the amount offered. Therefore, the

data points associated with the AC samples (▲) would all be transposed along the x-axis towards the origin making both sets the symbols (▲, X) lie on the dotted line.

Mixing Sequence

Having established that NaMt has a higher capacity for PVOH than for PEG (Figure 1) and that offering 90 pph PVOH and 30 pph PEG simultaneously resulted in the uptake of 0.13 g/g of PEG, an enhancement in the adsorption of PVOH (from 0.67 to 0.80 g/g) and an increased basal spacing (from 26 to 30 Å) (Figure 6 and 7) it was decided to briefly consider how the sample characteristics were affected by altering the mixing sequence.

When PEG was mixed with NaMt before adding PVOH the d-spacings of all samples over the whole PVOH/PEG/NaMt concentration range and when prepared from suspension (BC) were always slightly higher ($\sim 1\text{-}2$ Å). The respective spacings also remained higher when the samples were heated to 80 or 150 °C indicating that they had not been increased due to the presence of higher amounts of water. Correspondingly, when PVOH was mixed with the NaMt before adding PEG the d-spacings were the same as when PVOH and PEG were added simultaneously to the NaMt.

The d-spacings of all samples prepared from sediment (AC) and from all three different mixing sequences were all very similar. This observation combined with the fact that the amounts of PVOH and PEG adsorbed by NaMt when prepared via the three different sequences of addition displayed no significant differences suggested that the higher d-spacings in the films prepared by adding PEG first were not due to increased adsorption (of either PEG or PVOH) but rather the different molecular arrangements in which the free PVOH or PEG molecules were organized or associated with clay mineral upon drying.

The current hypothesis for this behavior is that when PVOH was allowed to adsorb on the clay mineral surface first, the smaller PEG600 molecules were able to neatly fill any remaining space thus optimizing the packing density resulting in lower d-spacings. Conversely, when PEG was allowed to adsorb on the clay mineral surface first, PVOH's strong interaction with the clay mineral and its tenacity when adsorbed (as demonstrated in the desorption experiments, see Supplementary data for further details) led to an alternative packing arrangement of the bulkier PVOH molecules. Consequently, when the PVOH or PEG free in solution entered the interlayer upon drying it led to a lower packing density and a higher d_{001} -spacing.

It is believed that the PEG contributing to the single layer structure, which was more strongly adsorbed, would contribute to the alternative packing of subsequently added PVOH molecules, rather than those contributing to the bi-layer structure. Their immobility when adsorbed onto the clay mineral therefore contributed to the enhanced d_{001} -spacing when PEG was added to clay mineral before PVOH.

Conclusions

This study describes the competitive adsorption of PEG and PVOH onto the surface of clay minerals at 90 °C and how the relative amounts of each adsorbate varied in both the adsorbed phase and the sample matrix - in uncentrifuged samples. As anticipated, both adsorbed strongly to the clay mineral, but the higher molecular weight and greater hydrogen-bonding capability of the PVOH resulted in the stronger adsorption of PVOH over PEG. Relatively small amounts of PEG caused a step change in the amount of PVOH

adsorbed at high loadings (4% increase in the presence of 10 pph PEG and 20 % increase when 30 pph PEG was used). PEG did not influence the PVOH uptake at $\text{PVOH} \leq 30$ pph. At a particular PVOH loading the amount of PEG adsorbed increased with the amount offered. At PVOH levels ≤ 5 pph the adsorption of PEG could be enhanced, but when the amount of PVOH offered was high (≥ 10 pph) the amount of PEG adsorbed was reduced. These studies have also shown that the d-spacing of PVOH and NaMt increased systematically, with the amount of PVOH offered, to produce multi-layered structures, whereas even when high levels of PEG were offered to NaMt only a bilayer of PEG could be accommodated in the clay interlayer. When PVOH and PEG were offered to NaMt in a binary system both were able to enter the interlayer concurrently and whilst the PEG alone was unable to produce more than a bilayer structure, it did not limit further expansion when used in combination with PVOH.

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Supporting Information Available

The supporting information provides a more detailed description of the quantitative thermogravimetric method developed to determine the amounts of PEG and PVOH adsorbed on the clay mineral for the binary systems. The supporting information also shows a diagram of the d-spacings of dried PVOH-PEG-NaMt composites prepared from the sediment after centrifugation and removal of supernatant (AC) together with the respective

samples prepared from dried suspensions (BC). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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