# Chapter 3

## Poly(vinyl sulfonate) intercalation into stearate intercalated layered double hydroxides

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## Abstract

Poly(vinyl sulfonate), PVS, was intercalated into a carbonate layered double hydroxide (LDH-$CO_3$), after an intercalative reaction with stearic acid in a one-pot reaction. The intercalated stearate ion exchanged with the PVS to form sodium stearate and LDH-PVS. Within an hour at 78 °C all the carbonate anions reacted. The PVS intercalated material had low crystallinity and features an interlayer distance of 13,91 Å attributed by Oriakhi *et al.* [1] to a bilayer intercalation.

*Keywords*: layered double hydroxides; carbonate hydrotalcite; intercalation; stearate; poly(vinyl sulfonate); ion exchange

## 3.1. Introduction

Intercalation of polymers into layered inorganic minerals has recently received a lot of attention [2]. The composites display physical properties, due to the molecular level interactions, that cannot be achieved by the polymer or filler alone. For instance, the polymer could be protected from UV degradation, the mineral could act as flame retardant or the thermal stability of the composite could be enhanced above that of the separate constituents [2,3].

Hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$] is an anionic clay. It is a member of the family of layered double hydroxides (LDH). LDHs have the same stacked sheet structure as brucite [$Mg(OH)_2$] but are distinguished by the partial replacement of $Mg^{2+}$ with $Al^{3+}$ ions in the sheets and the presence of charge balancing anions, for example $CO_3^{2-}$, $Cl^-$, $NO_3^-$ or stearate, in the interlayer [4]. The corresponding compounds are referred to as LDH-$CO_3$, LDH-Cl, LDH-$NO_3$ or LDH-SA.

Several methods have been employed [1,5,6,7] to intercalate polymers into LDHs and other layered minerals or clays. Anionic polymers such as poly(styrenesulfonate), poly(acrylic acid) and poly(vinylsulfonate) have been intercalated by synthesizing the LDH in the presence of the polymer [1,5]. The products obtained were amorphous but hydrothermal treatment improved the crystallinity [5]. The polymers only intercalated under $N_2$ atmosphere. When the procedure was attempted in air, the carbonate intercalated LDH (LDH-$CO_3$) was obtained [1]. Choy *et al.* [6] successfully intercalated DNA (deoxyribonucleic acid, an anionic polymer) into $Mg_2Al$-$NO_3$ LDH by ion exchange. The key to intercalation into layered species is usually to modify the interlayer region by surfactants with hydrophobic tails [2]. This surfactant-mediated method was successfully used by Kerr *et al.* [7] to intercalate poly(*p*-phenylene) into $MoO_3$. The polymer chains are preferentially adsorbed into the hydrophobic interlayer region from the polar solution.

Due to the strong electrostatic and hydrogen-bond interactions, the carbonate anions in the interlayer are difficult to ion exchange. When the LDH-$CO_3$ is dehydroxylated and decarbonated at 400 - 500°C to form a layered double oxide (LDO) and subsequently reconstructed in an aqueous solution of a carboxylic acid (or its salt) or anionic surfactant, intercalation of the acid or the surfactant can be achieved [8]. Fatty acids such as stearic acid, however, can be intercalated into uncalcined LDH-$CO_3$ (unpublished results). The stearate anions intercalate as a bilayer into the interlayer of the LDH (Fig. 3-1) with an interlayer distance in the region of 50 Å. The aim of this study was to intercalate stearate anions into the interlayer region of $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ (LDH-$CO_3$) by using molten stearic acid (SA) emulsified by poly(vinyl sulfonate) in a water-ethanol medium. Possibly the stearate bilayer would facilitate the intercalation of the PVS. This would represent an easy and environmentally friendly method of intercalating an anionic polymer into the cheap LDH-$CO_3$, without the need for energy intensive calcination.

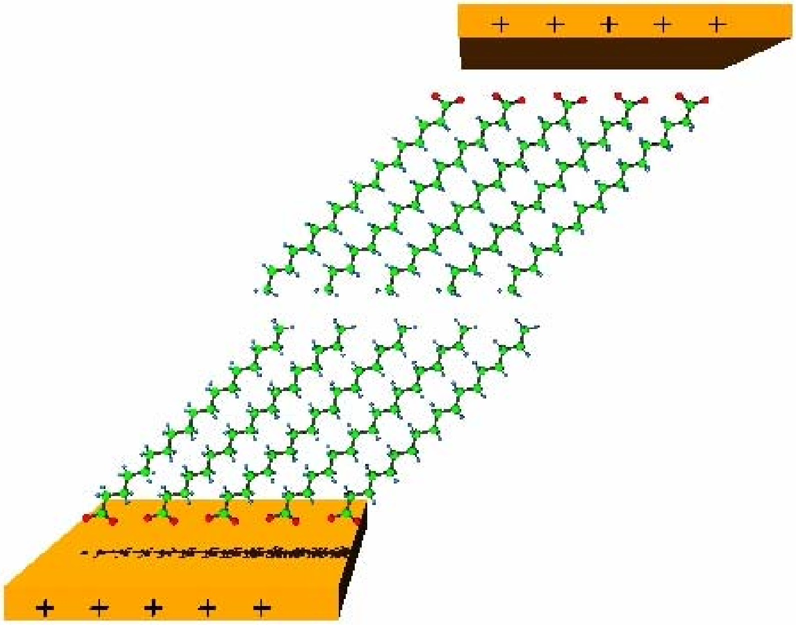

*Figure 3-1* Bilayer arrangement of stearate intercalated LDH (LDH-SA).

## 3.2. Materials and methods

### 3.2.1. Materials

The layered double hydroxide used in this study had the chemical composition $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$. The mole ratio of Mg:Al was determined from XRF analysis as 2.01:1 (Appendix B). The LDH was received from the local manufacturer Chamotte Holdings (Pty) Ltd. The particle size distribution as determined by a Mastersizer 2000 (Malvern Instruments) was d(0,1): 0,694 μm; d(0,5): 5,062 μm and d(0,9): 23,925 μm. The theoretical anionic exchange capacity of this LDH-$CO_3$ was calculated to be 213 meq/100 g.

25% m/m poly(vinyl sulfonate, sodium salt) solution in water (PVS, Mw 70 000, Sigma-Aldrich), stearic acid ($C_{18}H_{36}O_2$, Merck, 85% pure) and ethanol (96% rectified, Dana Chemicals) were used. Reactions were carried out in deionized water. Deionized water, tap water or solutions of $CaCl_2.2H_2O$ (UNIVAR®, Saarchem) in deionized water (20 volume equivalents) were used to dilute the reacted mixtures (1 volume equivalent).

### 3.2.2. Intercalation method

8 g of the 25% m/m sodium-PVS solution in water was added to 57 ml deionised water to obtain a solution consisting of approximately 2 g of PVS in 60 ml water. This solution was heated to 78 °C. 0,7 g stearic acid (SA) was dissolved in 30 ml ethanol and heated to approximately 60 °C. The SA solution was slowly added to the PVS solution and the temperature allowed to reach 78 °C. 0,34 g of the LDH powder was added to the solution and stirred for 1 h. Itoh *et al.* [9] found that stearate is capable of intercalating up to about 225% of the anionic exchange capacity (AEC) of the LDH and therefore a level of 200% SA in relation to the AEC was used. The reaction mixture will be referred to as the PVS-SA-LDH mixture.

### 3.2.3. Characterization

#### 3.2.3.1. *Fourier Transform Infrared spectroscopy (FTIR)*

A Perkin Elmer Spectrum RX I FT-IR System was used to scan the infrared transmittance through a KBr (Uvasol, potassium bromide, Merck) pellet 32 times at a resolution of 2 $cm^{-1}$. The averaged spectrum was background-corrected using a pure KBr pellet run under similar conditions. The pellets were prepared with approximately 2 mg of sample and 100 mg of KBr. The 2 mg powder samples were obtained by diluting the cooled down reaction mixture with a 20-fold excess of deionised or tap water or $CaCl_2$ solution, in order to release (flocculate) the insoluble reaction products, which were subsequently centrifuged off, washed again (to remove any unreacted PVS or salts), dried and ground.

#### 3.2.3.2. *Powder X-ray Diffraction (XRD)*

The XRD analyses were performed on a Siemens D500 X-ray system equipped with a 2.2 kW Cu long fine focus tube, variable slit and secondary graphite monochromator (to eliminate $K_\beta$ radiation and reduce fluorescent radiation). The system is computer controlled using SIEMENS DIFFRAC $^{Plus}$ software. The goniometer was set to reflection mode. Samples were scanned from 1 to 35° $2\theta$ with Cu $K_\alpha$ radiation (1,5418 Å) at a speed of 0.02° $2\theta$, with a recording time of 2 s per step and generator settings of 40 kV and 30 mA. Part of the reacted mixture was cast onto an aluminium sample holder and the solvent was allowed to evaporate. This was repeated a few times to obtain enough material to mask the aluminium. One would expect the intercalated LDH phases to be highly oriented within these holders and the interlayer distances to be preferentially enhanced [10].

#### 3.2.3.3. *Scanning Electron Microscopy (SEM)*

A small disc of the clear and white parts of the gel was placed onto carbon stubs of approximately 5 mm diameter. It was frozen in a Reichert KF80 plunge freezer (Vienna, Austria). A drop of the gel that was diluted with deionized water was also placed on a stub and was frozen in the same way. The frozen samples were dried in a custom-built high vacuum freeze drier (Pretoria Technicon, South Africa). A drop of the gel that was diluted with deionized water was also allowed to air dry on a stub. These were coated by chromium in a high resolution ion beam coater, Gatan model 681 (Warrendale, PA, USA) and studied with a JSM-6000F field emission scanning electron microscope (JEOL, Tokyo, Japan).

#### 3.2.3.4. *Transmission Electron Microscopy (TEM)*

The mixture (before onset of gelling) was diluted with deionised or tap water. A droplet of the solution containing white suspended particles was placed onto a carbon coated formvar grid, the excess water was removed by the capillary action of filter paper and it was allowed to dry in air. The Philips EM301 (Eindhoven, Netherlands) Transmission electron microscope was used.

## 3.3. Results and discussion

### 3.3.1. General

After the addition of the LDH-$CO_3$ to the SA-PVS emulsion, $CO_2$ gas was released. Some particles settled to the bottom after the reaction, but most of the particles were suspended. In time a small amount of clear solution collected at the top. Within a few days both the clear phase and the reaction mixture as a whole had gelled. Upon shaking, the gel broke but reformed in time. Experiments showed that the sodium PVS solutions did not gel in the presence of $Mg^{2+}$, $Al^{3+}$, $Ca^{2+}$ or $H^+$ ions as some other anionic polymers do. The gelling mechanism is, therefore, unknown.

Before the onset of the gelling, some of the mixture was diluted with water. Upon addition of 20 volumes of deionized water, a suspension of white fluffy particles (> 10-20 μm, Fig. 3-7E) formed. After centrifuging, the sediment particles went back into suspension upon the least disturbance, probably due to electrostatic repulsion. The white particles have been unchanged and in suspension for more than a year at the time of writing. Upon dilution with tap water, however, the suspension became unstable and the fluffy particles collected at the top. With time the particles formed heavy white globules, which settled to the bottom. After 2 to 3 months the solution and the sediment became yellow due to oxidation of the PVS (Fig. 3-2).

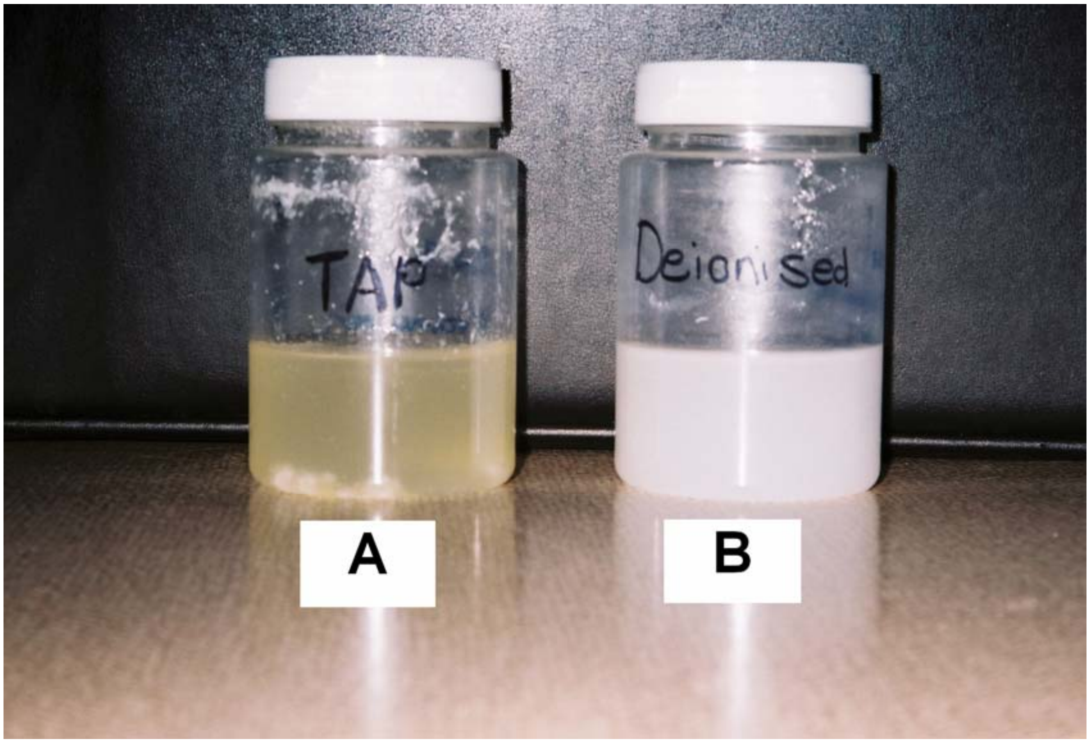

*Figure 3-2* The reaction mixture diluted with tap water (A) and deionized water (B), showing that the suspension is destabilized by the divalent cations in tap water, leading to PVS release and decomposition.

### 3.3.2. FTIR results

When PVS was not present in the system, the reaction between LDH-$CO_3$ and SA could not proceed to completion under the conditions employed (78 °C, 1 h) as evidenced by the presence of unreacted carbonate (1367 $cm^{-1}$) and unreacted carboxylic acid (1703 $cm^{-1}$) in Fig. 3-3A. In the presence of other surfactants, such as sodium dodecyl sulfate (SDS), the reaction also does not go to completion, even in 24 hours. In the presence of PVS, however, the reaction proceeded to completion under the same conditions (only 1 hour). Only a small carbonate vibration peak remained at 1383 $cm^{-1}$ (Fig. 3-3B). The LDH platelets were still intact, because the OH stretching vibration (3440 $cm^{-1}$) and the O-M-O bending vibration (446 $cm^{-1}$) were present (Fig. 3-4) [11]. If the hydroxide layers had reacted to form an Mg/Al type stearate salt, these vibrations would no longer be present. The PVS is intercalated (refer to Section 3.3.3): In spite of extensive washing, the sulfonate peak around 1176-1181 $cm^{-1}$ remains (Figs. 3 and 4B).

When heating and melting SA in the presence of PVS, no acid-base reaction can occur because sodium PVS is a weak conjugated base of the strong polyvinyl sulfonic acid. Therefore, one does not expect sodium stearate and polyvinyl sulfonic acid to form. Upon cooling, the SA crystallizes out of the emulsion. When the PVS-SA-LDH reaction product was diluted with tap water or $CaCl_2$ solution, the observable peaks in the carboxylate asymmetric stretching region were different from when it was diluted with deionized water. The peak at 1558 $cm^{-1}$, which corresponds to that of sodium stearate, decreased in intensity and peaks at 1572 and 1539 $cm^{-1}$, which corresponds to that of calcium stearate, appeared (Figs. 3B and C). Therefore, sodium stearate formed during the PVS-SA-LDH-$CO_3$ reaction. In comparison, when PVS is absent, the vibration peaks in the carboxylate asymmetric stretching region were typical of stearate intercalated LDHs (Fig. 3-3A and [12]).

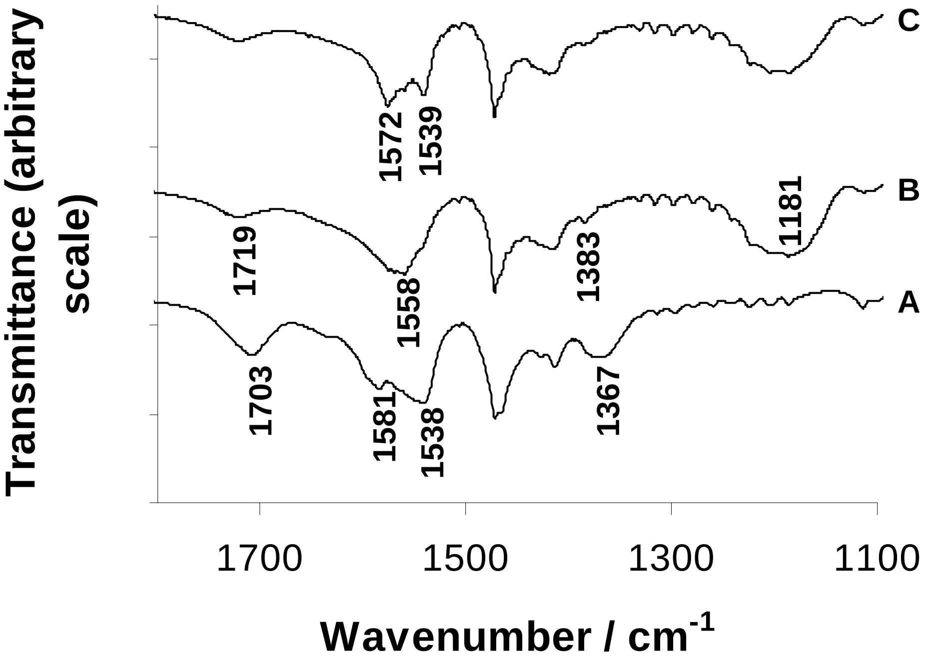

*Figure 3-3* FTIR spectra of the LDH-SA (A), PVS-SA-LDH product (B) and the PVS-SA-LDH product isolated from tap water (C), showing that sodium stearate (1558 cm$^{-1}$) formed, which changed to calcium stearate (1572 cm$^{-1}$, 1539 cm$^{-1}$) in tap water in contrast to the typical LDH-SA bands at 1538 cm$^{-1}$ and 1581 cm$^{-1}$ (A).

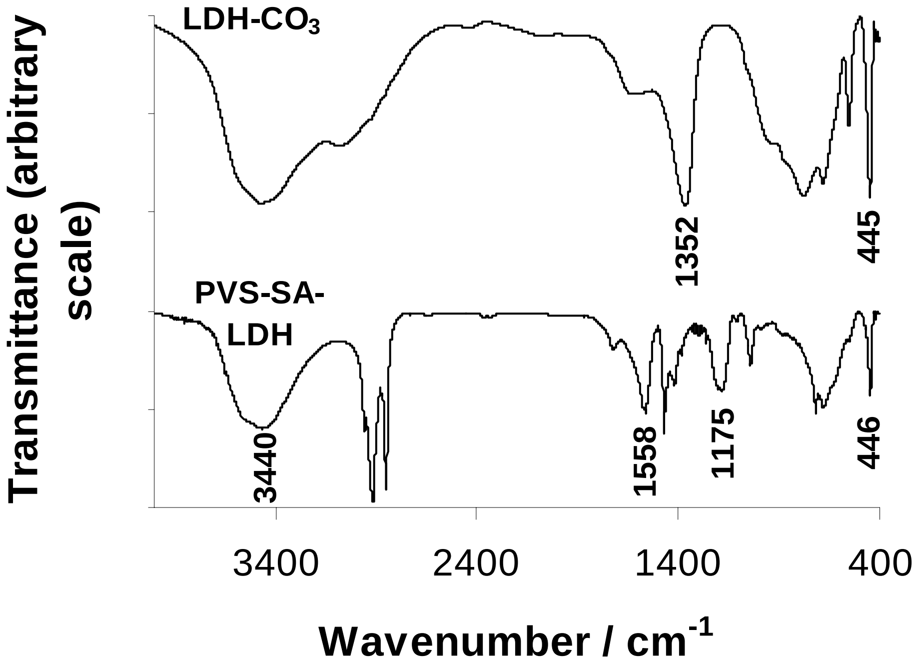

*Figure 3-4* FTIR spectra of the PVS-SA-LDH reaction mixture (bottom) and the LDH-$CO_3$ (top), showing that the PVS intercalated and that the LDH platelets were intact (O-M-O bending vibration at 445 cm$^{-1}$).

It is supposed that the mechanism of intercalation of the PVS into the LDH consists of two steps. First, the acid-base reaction between SA and the interlayer carbonate anions takes place, releasing $H_2CO_3$ and eventually $CO_2$, with the stearate anions being intercalated as bilayers. Second, the sodium PVS ion exchange with the stearate ions, releasing sodium stearate and the PVS intercalates. The entropy gain due to the release of the bilayer-intercalated stearates is probably larger than the entropy loss due to the intercalation of the PVS. The sodium stearate probably stabilized the suspended particles through electrostatic repulsion, but in tap water calcium stearate formed, which precipitated and, hence, could not stabilize the suspension.

### 3.3.3. XRD results

The X-ray diffractogram (Fig. 3-5) of the reaction product obtained in the absence of PVS showed the presence unreacted SA (39,20 Å, 13,17 Å, 4,12 Å and 3,11 Å), unreacted LDH-$CO_3$ (7,60 Å, 3,79 Å and 2,57 Å) and bilayer intercalated LDH-SA (49,52 Å, 25,43 Å, 17,11 Å, 10,29 Å). The product obtained in the presence of PVS was amorphous (broad, low intensity reflections, Fig. 3-6). The reflections at 13,91 Å (and 6,94 Å, second order) are due to intercalation of a bilayer of PVS [1] and it correlates well with the value of 13,1 Å observed by Oriakhi *et al.* [1]. The reflection at 45,17 Å is probably the remnant of bilayer intercalated LDH-SA which was too stable to allow for exchange with PVS chains because of the high degree of interpenetration of the two stearate layers. There was only a small reflection left at 7,81 Å, indicating that most of the LDH-$CO_3$ reacted. When stirring the LDH-$CO_3$ and PVS together under the same conditions but in the absence of SA, the diffractogram of the LDH-$CO_3$ was unchanged (not shown). This is due to the stability of the LDH-$CO_3$ and the slow diffusion of the polymer chains [1]. The intercalated stearate anions destabilize the layered structure and allows for the PVS chains to intercalate.

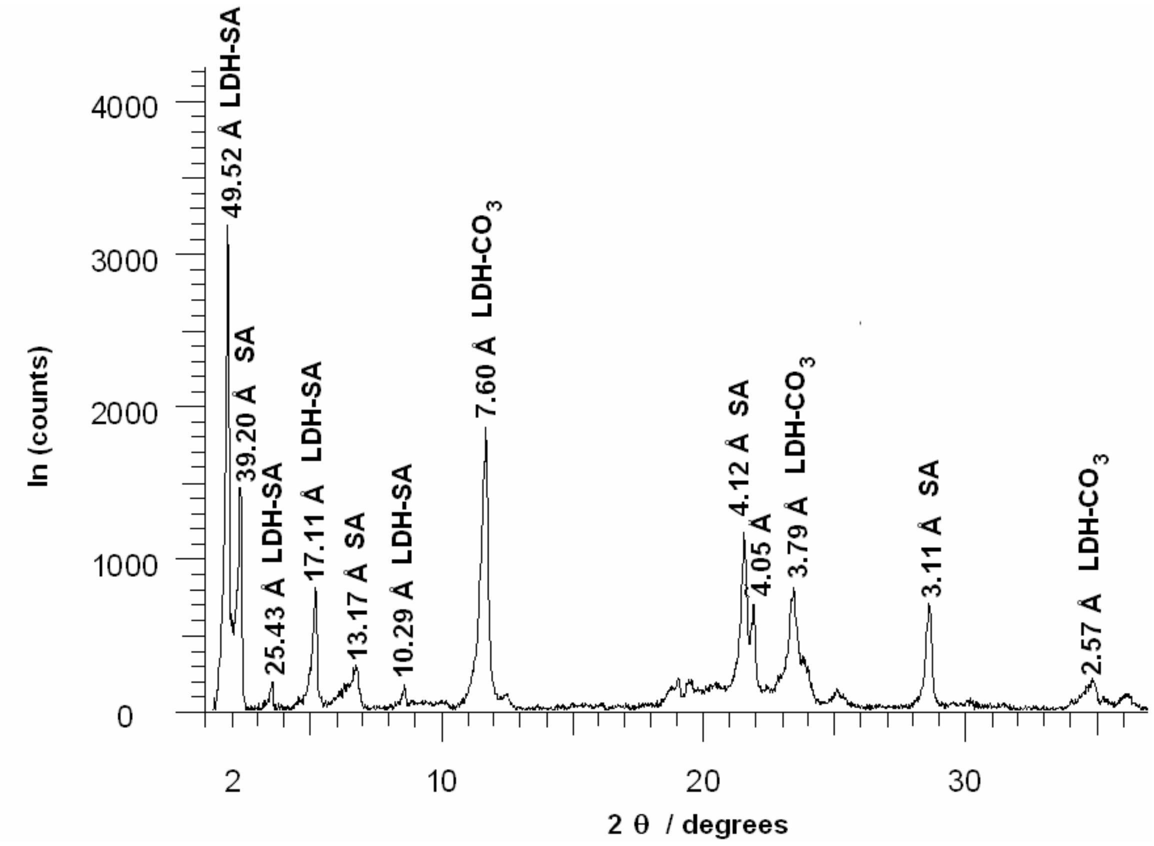

*Figure 3-5* X-ray diffractogram of the LDH-SA product formed in the absence of PVS, showing that it is highly crystalline.

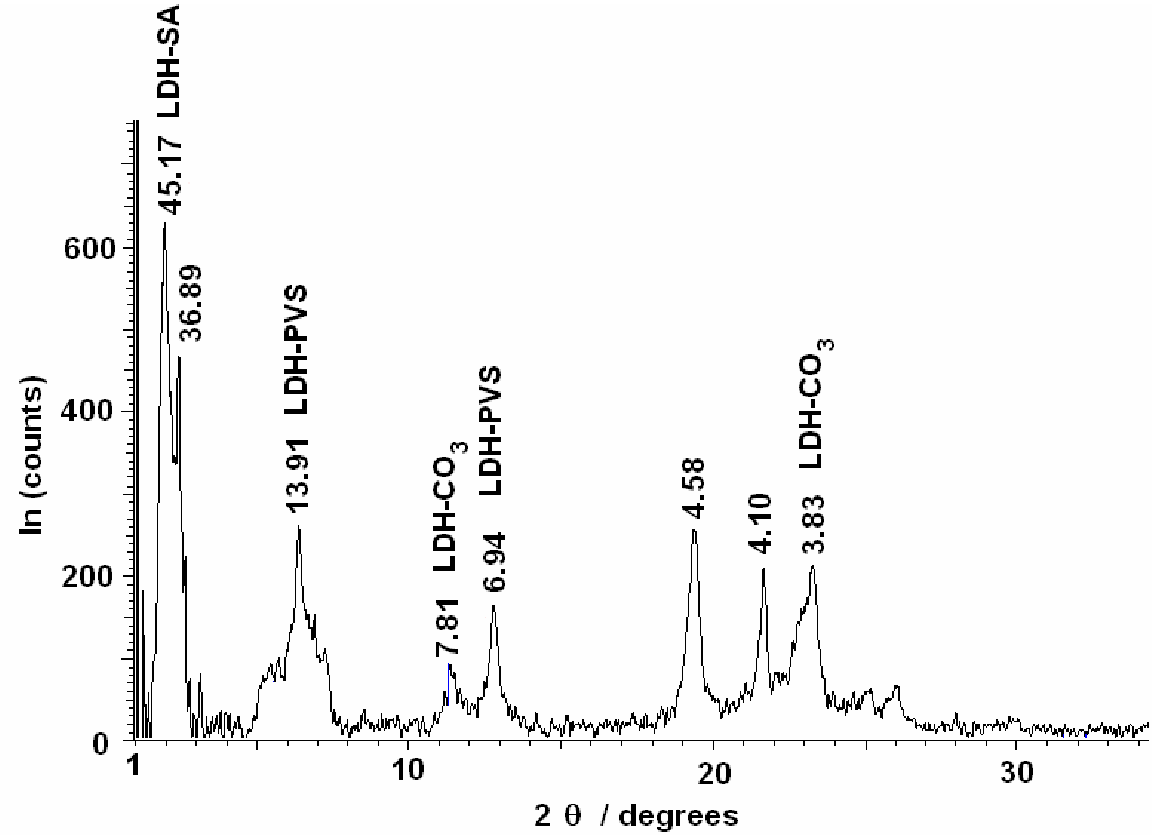

*Figure 3-6* X-ray diffractogram of the dried PVS-SA-LDH reaction mixture, showing that the LDH-SA reflections diminished and LDH-PVS appeared at around 13,91 Å. The peaks are broad and of low intensity, attesting that the products are less crystalline.

### 3.3.4. SEM results

The FTIR results showed that sodium stearate had formed. It was originally thought that the gelling was caused by formation of sodium stearate within the PVS-SA-LDH mixture. When the microstructures of sodium stearate (Fig. 3-7A) and the clear part of the gel (Fig. 3-7B) are compared, this is clearly not the case. The latter shows a spaghetti-like structure approximately 200 nm in diameter and several micrometers in length. Fig. 3-7C is the SEM micrograph of the white part of the gel, which shows large plate-like structures of the LDH (> 10 μm diameter), which are similar to the structures obtained by Itoh *et al*. [9] for stearate intercalated LDHs. The SA and PVS stabilize this plate-like structure above the usual sand-rose – intergrown particulates – structure of LDH-$CO_3$ (Fig. 3-7D) [13]. The SEM micrograph (Fig. 3-7E) of the freeze-dried suspension of the mixture diluted with deionized water consisted of large thin plate-like structures (> 20 μm diameter). When the diluted mixture was allowed to air dry, the plate-like structures seemed to role up into tubes of diameter 0,5 – 1 μm (Fig. 3-7F). When freeze-dried, the rolling up could not take place and the large, thin plates remained in their original state. Dispersing these plate-like structures, of which the thickness is in the sub-micrometre region, into polymer matrices could lead to the formation of nanocomposites.

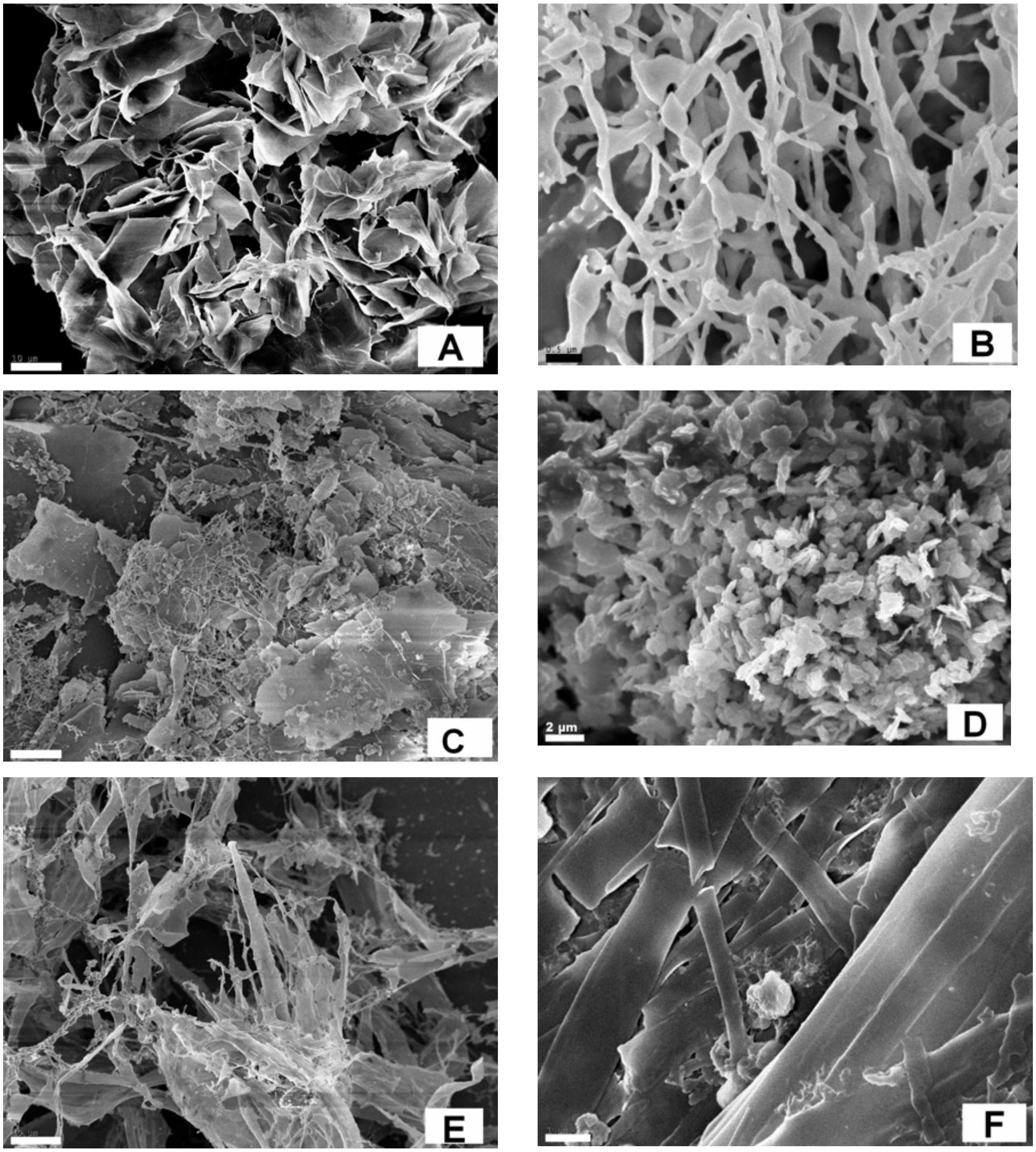

*Figure 3-7* Scanning electron micrographs of

(A) Freeze-dried sodium stearate gel, bar is 10 μm.
(B) Freeze-dried clear part of the gel of the PVS-SA-LDH reaction mixture, bar is 500 nm.
(C) Freeze-dried white part of the gel of the PVS-SA-LDH reaction mixture, bar is 5 μm.
(D) The sand-rose microscopic structure of the LDH-$CO_3$, bar is 2 μm.
(E) Freeze-dried sample of the diluted PVS-SA-LDH suspension, bar is 10 μm.
(F) Air-dried sample of the diluted PVS-SA-LDH suspension, bar is 1 μm.
(G)

### 3.3.5. TEM results

The TEM images of the tap and deionized water diluted air-dried samples showed the presence of long fibers or tubes (Figs. 8A and B, > 10 μm long and 1 μm wide, possibly the same as was seen in Fig. 3-7F), small unreacted particulates (black, less than 1 μm in size) and large plate-like structures (approximately 10 μm diameter, Figs. 8C and D). In the case of diluting with tap water, the fibers looked more etched, as if it reacted (Fig. 3-8B). Upon drying, the plate-like structures seemed to crack (Fig. 3-8C). It might be that this cracking phenomenon led to the formation of the fiber- or tube-like structures; or perhaps the large plates rolled up to form long, thin tubes. The fibers seem to be of the same length as the diameter of the flat layers (10-20 μm, Figs. 7C, 7E and 8D). Tube-like and fiber-like features were reported by Leontidis *et al.* [14,15] for PEO-SDS-acetate-Pb-sulfide containing systems as well as by Ogata *et al.* [16] for $Zn(OH)_2$-carboxylic acid systems, which are both similar to the current system (layered inorganic substances in combination with carboxylic acids). The fact that the plates are so thin attests to the fact that the sand-rose morphology was broken down to a large extent and that the stearate and PVS stabilized the structure at a few layers. It is possible that exfoliation took place some extent as well. Moujahid *et al.* [5] found that LDH-Cl exfoliated in excess polystyrene sulfonate and possibly the same happened for LDH-SA in excess PVS, which also explains the almost featureless X-ray diffractogram (Fig. 3-6).

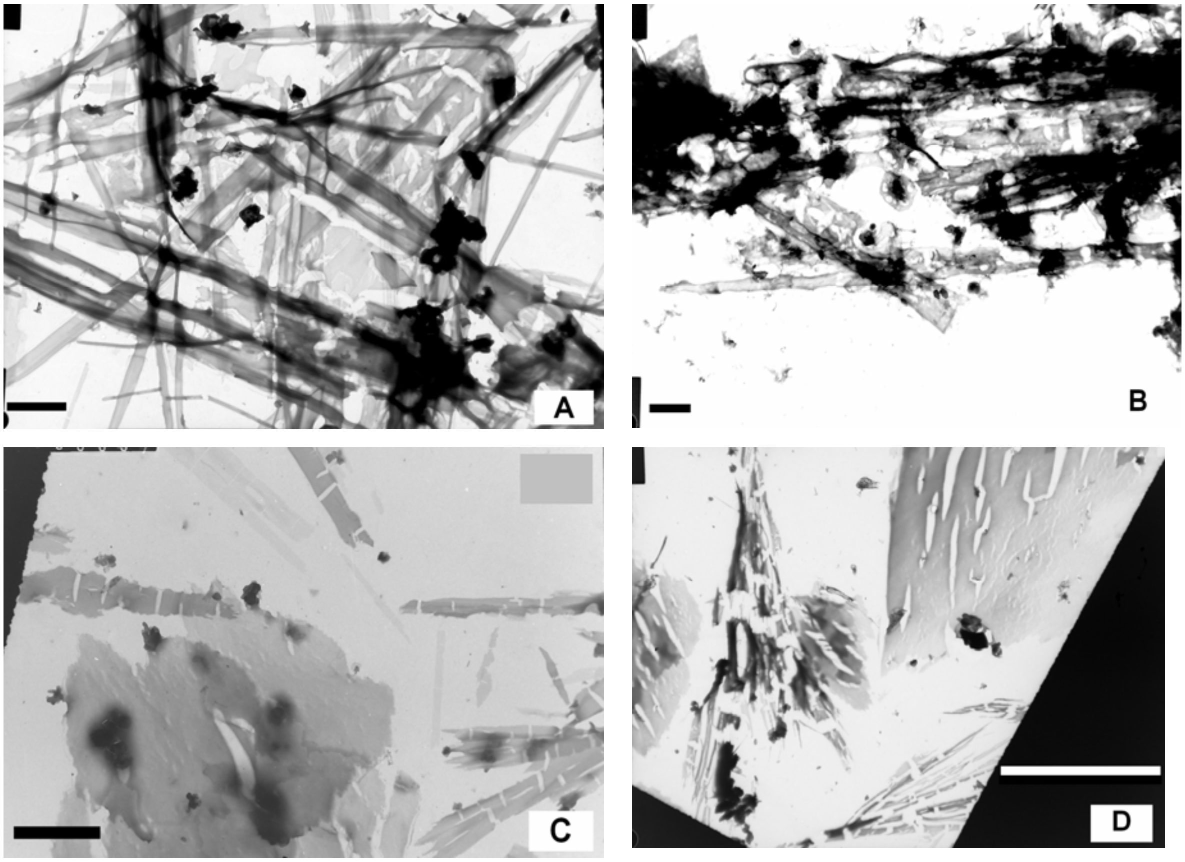

*Figure 3-8* Transmission electron micrographs of

(A) Deionized water diluted PVS-SA-LDH reaction mixture dried in air, showing smooth fibers or tubes. Bar is 2 μm.

(B) Tap water diluted PVS-SA-LDH reaction mixture dried in air, showing etched (reacted) fibers or tubes. Bar is 2 μm.

(C) Deionized water diluted PVS-SA-LDH reaction mixture dried in air, showing large, plate-like structures. Bar is 3 μm.

(D) Deionized water diluted PVS-SA-LDH reaction mixture dried in air, showing cracked plate-like structures. Bar is 10 μm.

## 3.4. Conclusions

The stearic acid reacted with all of the carbonate in the interlayer (FTIR results). XRD showed that the PVS had intercalated and the amount of LDH-SA had diminished. The stearate and PVS anions exchanged to form sodium stearate. The process might be driven by the increase in entropy due to the disassembly of the stearate bilayer. Calcination was not necessary to successfully intercalate the stearate and PVS into the LDH-$CO_3$; therefore the LDH platelets could keep their original crystallinity. No $N_2$ atmosphere was needed, probably because the LDH-SA is of similar stability than the LDH-$CO_3$. The layered mineral or clay is sometimes modified by a surfactant in a separate step before introducing the polymer [2], but in the current system the surfactant modification and polymer incorporation takes place in one pot. In most other instances the polymer intercalated LDHs is prepared by synthesizing (coprecipitating) the LDH in the presence of the polymer; a procedure which requires a $N_2$ atmosphere. The current process is more environmentally friendly (no calcination, single batch), cheap (LDH-$CO_3$ starting reagent) and upscalable (no $N_2$ atmosphere).

The intercalated PVS appears to be stabilized and protected from oxidative or UV degradation (Fig. 3-2). This reaction could possibly be carried out simultaneously with emulsion polymerization of polymers in order to ensure good dispersion of the LDH into the polymers, which could lead to the formation of nanocomposites. The PVS intercalation could also be a model for intercalation of other anionic polymers, like DNA, by the same method.

## References

1 C.O. ORIAKHI, I.V. FARR, M.M. LERNER, *J. Mater. Chem.* **6** (1996) 103.

2 F. LEROUX, J.-P. BESSE, *Chem. Mater.* **13** (2001) 3507.

3 P.B. MESSERSMITH, S.I. STUPP, *Chem. Mater.* **7** (1995) 454.

4 S. MIYATA and T. KUMURA, *Chem. Lett.* (1973) 843.

5 E.M. MOUJAHID, J.-P. BESSE, F. LEROUX, *J. Mater. Chem.* **12** (2002) 3324.

6 J.-H. CHOY, S.-Y. KWAK, J.-S. PARK, Y.-J. JEONG, J. PORTIER, *J. Am. Chem. Soc.* **121** (1999) 1399.

7 T.A. KERR, F. LEROUX, L.F. NAZAR, *Chem. Mater.* **10** (1998) 2588.

8 E.L. CREPALDI, J. TRONTO, L.P. CARDOSO, J.B. VALIM, *Colloids Surf. A* **211** (2002) 103.

9 T. ITOH, N. OHTA, T. SHICHI, T. YUI, K. TAKAGI, *Langmuir* **19** (2003) 9120.

10 G.T.D. SHOULDICE, P.Y. CHOI, B.E. KOENE, L.F. NAZAR, A. RUDIN, *J. Polym. Sci.* Part A: Polym. Chem. **33** (1995) 1409.

11 J.T. KLOPROGGE, L. HICKEY, R.L. FROST, *J. Mater. Sci. Lett.* **21** (2002) 603.

12 M. BORJA, P.K. DUTTA, *J. Phys. Chem.* **96** (1992) 5434.

13 M. ADACHI-PAGANO, C. FORANO, J.-P. BESSE, *Chem. Commun.* (2000) 91.

14 E. LEONTIDIS, T. KYPRIANIDOU-LEODIDOU, W. CASERI, K.C. KYRIACOU, *Langmuir* **15** (1999) 3381.

15 E. LEONTIDIS, T. KYPRIANIDOU-LEODIDOU, W. CASERI, P. ROBYR, F. KRUMEICH, K.C. KYRIACOU, *J. Phys. Chem. B* **105** (2001) 4233.

16 S. OGATA, H. TAGAYA, M. KARASU, J. KADOKAWA, *J. Mater. Chem.* **10** (2000) 321.