ANL/CHM/CP--85031
Conf-950402--11

Preprint, to be submitted to the Petroleum Division for the "International Symposium on the Synthesis of Zeolites and Expanded Layered Compounds" at the 209th National ACS Meeting in Anaheim, CA on April 2-7, 1995.

SYNTHETIC POLYMER-LAYER SILICATE CLAY COMPOSITES*

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*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

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KEYWORDS: clays, composites, nanocomposites, polymers, hydrothermal synthesis

SUMMARY: Synthetic hectorites were hydrothermally crystallized with direct incorporation of water-soluble polyvinyl alcohol (PVA), a cationic polymer poly(dimethyl diallyl ammonium chloride) (PDDA), and two cellulosic polymers: hydroxypropyl methylcellulose (HPMC) and hydroxyethyl cellulose (HEC). The molecular weight of polyvinyl alcohols had little effect on the success of hydrothermal hectorite synthesis, d-spacing, or amount of polymer incorporated; the basal spacings range from 19.5 Å to 20.8 Å and the percent of polymer incorporated ranges from 20.4 wt% to 23.0 wt%. Synthetic PDDA-hectorite displays the lowest d-spacing at 15.8 Å, and less cationic PDDA is incorporated into hectorite (7.8 wt% organic) than the other neutral polymers (17.8-23.0 wt% organic). The basal spacing for synthetic HPMC-hectorite is the largest at 25.2 Å. Small angle neutron scattering was used to further examine the PVA-clay systems.

INTRODUCTION

Polymer-clay suspensions and composites have considerable commercial and technological importance (1). As a result of the current climate stressing the development of advanced materials, there are also recent reports of *in situ* intercalative polymerization processes (2) and of unique structural and electrical properties (2,3) of polymer-clay composites. Tomita and co-workers have shown that layered carbons can be produced by heating polyfurfuryl alcohol or polyacrylonitrile intercalated within clays such as montmorillonite (4). All studies to date involve modification of an existing clay mineral by such methods as ion-exchange, *in situ* intercalative polymerization, or simple adsorption from solution. We have undertaken the exploration of a new avenue of preparation: direct hydrothermal crystallization from a polymer-containing silicate gel. This approach may lead to unique polymer characteristics involving conformation and stability, and new composite materials not possible by natural clay modification.

We have previously reported a method for hydrothermally synthesizing hectorites with direct incorporation of organic or organometallic pillaring agents (5). This general technique of direct synthesis has been used to incorporate water-soluble porphyrins and metalloporphyrins (6), phthalocyanines (7), cationic dye molecules and organometallic complexes (8), and now (*see Figure 1*) polyvinyl alcohol (PVA), the hydroxypropyl methylcellulose (HPMC) and hydroxyethyl cellulose (HEC) polymers, and the cationic poly(dimethyl diallyl ammonium chloride) (PDDA) polymer. Neutral and cationic polymers were chosen to examine the effect of charge on crystallization and incorporation.

EXPERIMENTAL

The procedure for hydrothermal crystallization of hectorites has been explained in detail elsewhere (6). Reactants in the molar ratios of $LiF:MgO:SiO_2$ 0.266:1.00:1.52 were refluxed for 2 days as a 2 wt% aqueous slurry. In the purely inorganic synthetic hectorite lithium(I) is the exchangeable cation. A certain amount of this Li(I) can be replaced by organic or organometallic cations directly from a precursor organic-containing gel. The amount of polymer added was chosen such that, if all of the polymer was incorporated into the clay and assuming complete reaction, 10 wt% of the clay would be organic. Modification of clays was carried out for comparison with the synthetic clays. These 1 wt% clay slurries were charged with enough polymer to cause up to either 10 wt% or 20 wt% organic assuming full adsorption.

X-ray powder diffraction (XRD) analyses were carried out on a Scintag PAD-V instrument using Cu K_α radiation at a scan rate of 0.5° 2θ/min. Thermal gravimetric analysis (TGA) was performed on a Cahn 121X instrument under oxygen flow at a rate of 10°C/min. SANS measurements were made at the Intense Pulsed Neutron Source at Argonne National Laboratory, Ill. Experimental conditions are published elsewhere (6). Contrast-match conditions were attained by using a medium of 67% D_2O/H_2O in order to mask the contributions of silica to the signals.

RESULTS

The X-ray diffraction pattern of a synthetic hectorite with Li(I) exchangeable cations in the powder form is shown in Figure 2. This typical pattern of all the synthetic hectorites shows a basal or d(001) spacing of 14.3 Å (6.18° 2θ). The peaks at 4.30 Å (20.5° 2θ) and 2.56 Å (35.6° 2θ) represent the clay (110,020) and (130) reflections, respectively. For comparison, a natural hectorite is shown in Figure 2 as well. This demonstrates the similarity in peak widths and intensities of hk reflections for both natural and synthetic minerals. Even though the natural hectorite has been extensively purified, it still contains a $(Mg,Fe)SiO_3$ impurity as indicated by the asterisks. Figure 2 also contains XRD patterns for syntheic PDDA- and PVA-hectorites. Note the increase in basal spacing with polymer uptake.

The d(001) spacings, the amount of intercalant incorporated, and the synthetic polymer-clay yields are listed in Table I. The polymer loadings were calculated from the wt% C and the known molecular formulas (9). The loadings were also verified by TGA results. The molecular weight of polyvinyl alcohols had little effect on the d-spacing or amount of polymer incorporated, although some differences in the success of hydrothermal hectorite synthesis were observed (albeit in no clear trend). A comparison of the synthetic polymer-containing hectorites versus modified natural hectorites was also carried out. Table II contains pertinent information for cationic PDDA and neutral PVA (MW 50,000). Note that the basal spacings and polymer loadings are nearly identical for the two methods of loading.

DISCUSSION

Synthetic PDDA-hectorite has the smallest basal spacing of the group at 15.8 Å, which is similar to that of synthetic Li^+-hectorite at 16.0 Å. This is likely a result of the charge-compensating electrostatic interaction between the negatively charged smectite layer and the positively charged nitrogens along the polymer chain coiled between the clay sheets. PDDA has been shown to act as a template for the formation of a new metal silicate hydrate in the same way as is known for high silica zeolites (10), and it now appears to act in a similar fashion for the crystallization of smectite minerals.

Synthetic HPMC-hectorite has the largest basal spacing of the synthetic polymer-hectorites at 25.2 Å. Theng has discussed the general adsorption properties of various uncharged polysaccharides, including cellulosic polymers, as a function of several variables (11). The most important variable seems to simply be the degree to which the clay layers swell in solution, which is a factor ultimately controlled by the exchange cation of natural clays. The results reported here indicate quite reasonably that the synthetic clay layers are far apart as they crystallize from a gel, thus providing the polymer ample surface with which to interact.

The adsorption of PVA by natural montmorillonite has been found to be influenced by the nature of the exchangeable cation and by ionic strength (12). Exchangeable cations effect the degree to which a clay will swell in aqueous solution (13) which in turn is a factor regarding polymer adsorption in general. A complex with Na-montmorillonite, for example, at maximum adsorption (ca. 80 wt%) has a basal spacing of 30 Å (14). This corresponds to two flat extended monolayers of PVA within the gallery of average loop length 10 Å (12). Ca-smectites do not swell to as large a degree as the Na-analogs, however (13). This phenomenon is born out in the results of PVA-montmorillonite shown in Table II. The d-spacing is considerably less for the Ca-montmorillonite, although it increases slightly upon heating. This heating effect on d-spacing is not observed for the Na-hectorite. The coverages observed for the synthetic crystallized PVA-hectorite samples are at about 1/4 of the full-loading level reported above, with gallery heights of about 10 Å corresponding to a single flat extended monolayer of PVA.

There is some question regarding the exact physical structure of PVA-clay complexes. Lagaly reports that a PVA-sodium smectite yields a very broad basal reflection (15) in contrast to the result of Greenland of 30Å (14). Lagaly postulates that the silicate layers are no longer parallel but are embedded in a gel of PVA and water. Ege et al. support this scenario by electron spin resonance methods (16). While the results of Lagaly and Ege are consistent with each other, our results agree more with those of Greenland. There is no clear reason for the reported differences, leading one to speculate only that the method of preparation must be a critical factor.

The process of smectite clay layer formation from a gel has been probed in detail by small-angle neutron scattering (7), and results supported the generally accepted mechanism whereby tetrahedral silica layers are condensed on preexisting brucitic sheets. SANS experiments were also performed to monitor any changes in polymer conformation during synthetic PVA-hectorite crystallization. A PVA solution of MW 50,000 was well dispersed and did not agglomerate during heating. Contrast-matching methods revealed that PVA in a silica solution looked the same as PVA alone. Future SANS experiments are planned in order to better observe changes to the polymer during clay crystallization.

ACKNOWLEDGMENTS

This work benefited from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory. The financial support from the Division of Educational Programs at ANL is gratefully acknowledged by DLE. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Dept. of Energy, under contract number W-31-109-ENG-38.

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Table I. Physical Properties of Synthetic Polymer-Containing Hectorites.

Gallery Species	**XRD**[1] **d(001) Å**	**wt% organic**	**% yield**
Li	16.5	-	20
PDDA	15.8	7.8	70
HEC	19.6	17.8	78
HPMC	25.2	22.1	74
PVA (MW: 9-10,000)	20.7	22.6	20
PVA (MW: 13-23,000)	20.3	22.2	12
PVA (MW: 31-50,000)	19.5	20.4	38
PVA (MW: 50,000)	20.4	22.2	37
PVA (MW: 85-146,000)	19.8	20.6	47

[1] measured as thin films, results from powders nearly identical.

Table II. Comparison of Synthetic and Natural Polymer-Containing Clays.

Polymer-Clay Complex	**XRD[1] d(001) Å**	**wt% organic**
synthetic PDDA-hectorite	15.8	7.8
natural PDDA-hectorite	15.8	5.3
synthetic PVA-hectorite	20.4	22.2
natural PVA-hectorite	19.8	24.2
natural PVA-montmorillonite	15.5	8.0
natural PVA-montmorillonite (heated[2])	17.0	10.3

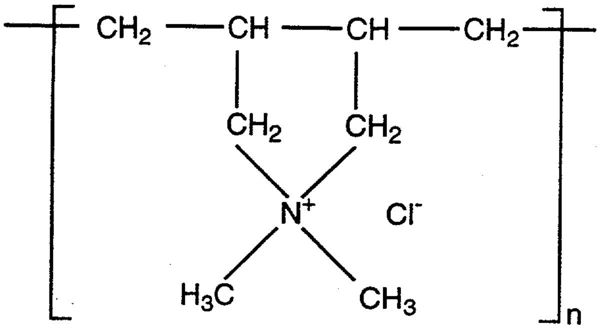
[1] measured as thin films, results from powders nearly identical.

[2] the ion-exchange took place under reflux conditions. PVAOH MW=50,000.

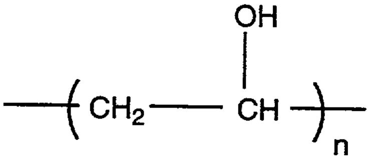
FIGURE CAPTIONS

1. Structures of the cationic and neutral polymers used in this study: PDDA = poly(dimethyl diallyl ammonium chloride), PVA = polyvinyl alcohol, HPMC = hydroxypropyl methyl cellulose, and HEC = hydroxyethyl cellulose.

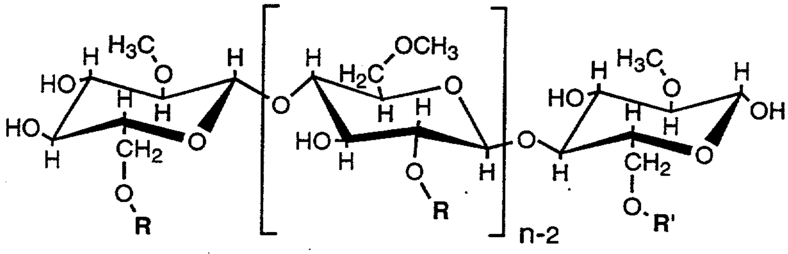
2. X-ray diffraction powder patterns of a purified natural Na-hectorite and synthetic hectorites containing Li(I), PDDA, and PVA within the interlayers; the peaks indicated with an asterisk (*) in the natural hectorite plot are due to residual $(Mg,Fe)SiO_3$ (JCPDS file#19-605).



PDDA

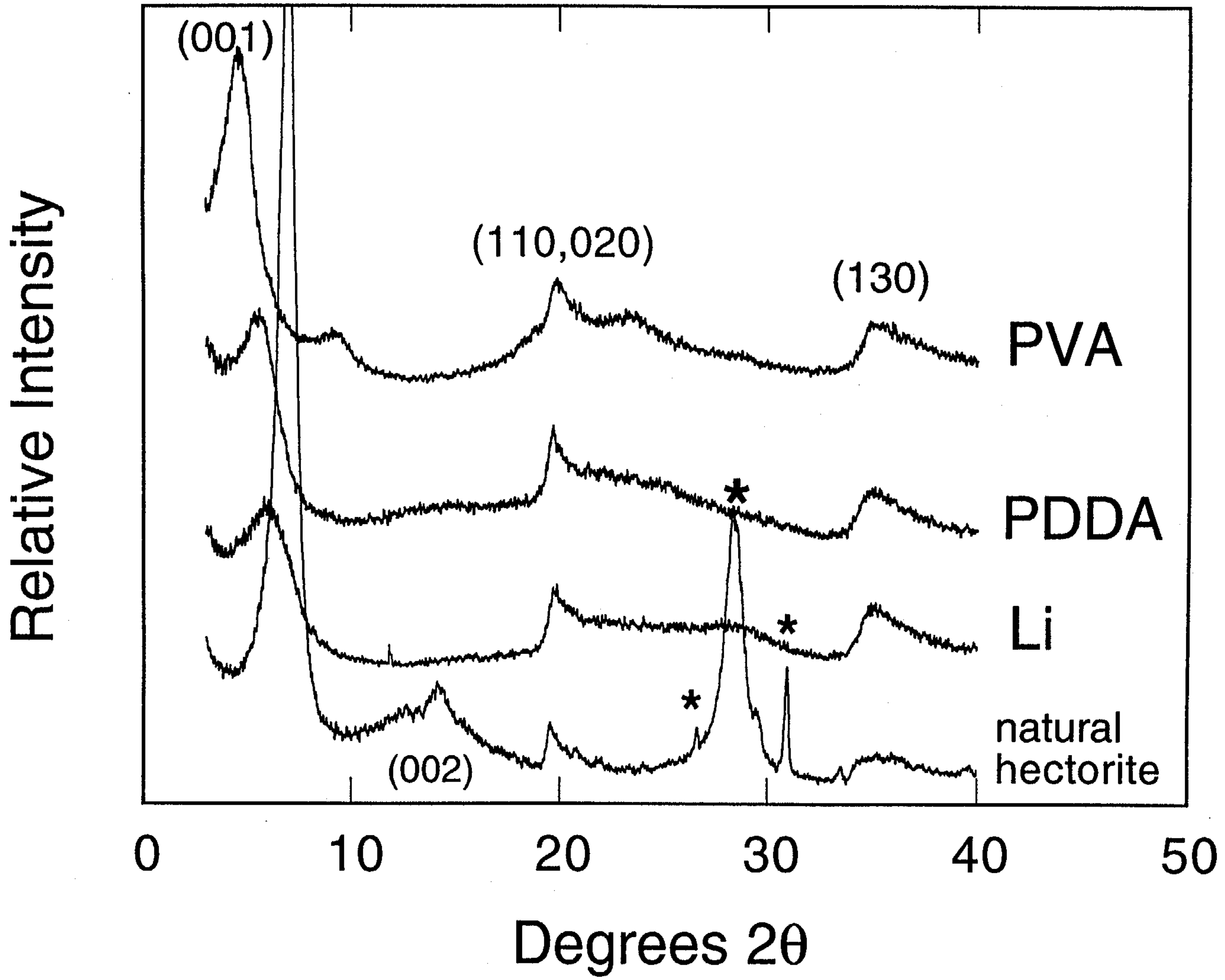

$-\left(CH_2-\overset{OH}{CH}\right)_n-$

PVA



HPMC: R = $CH_2CH(OH)CH_3$
R' = CH_3

HEC: R = $CH(OH)CH_3$
R' = H


(001)
(110,020)
(130)
(002)
PVA
PDDA
Li
natural hectorite
*
*
*
*
Relative Intensity
0
10
20
30
40
50
Degrees 2θ