PMSE 193-Halloysite clay nanotubes as a reservoir for corrosion inhibitors and template for layer-by-layer encapsulation

Halloysite Clay Nanotubes as a Reservoir for Corrosion Inhibitors and Template for Layer-by-Layer Encapsulation

Elshad Abdullayev[1], Dmitry Shchukin[2], Yuri Lvov[1]

[1]*Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana-71272, USA*

[2]*Max Planck Institute for Colloids and Interfaces, Golm, Germany - 14424*

INTRODUCTION

Corrosion of the metals is a serious technological problem. Benzotriazole and its derivatives are widely used for protection of variety of metals, especially copper and copper containing alloys[1, - 4]. In highly corrosive environments, such as chloride containing aggressive media, inhibitive performance of anticorrosion agents alone may not be sufficient for metal protection. Therefore combination of metal corrosion inhibition with passive corrosion protection methods, such as painting, is required in most of the cases. Direct addition of benzotriazole into the paint is not effective since it is easily washed away with water. On the other hand, introduction of benzotriazole into paint with encapsulation seems to be the best solution. Different microcapsule designs were introduced, such as polyelectrolyte and polymer microcapsules, sol-gel nanoparticles, nanotubes, etc[3, 5, 6]. Herein we report the usage of naturally available halloysite clay nanotubes as reservoirs for the loading, storage and controlled release of the corrosion inhibitor benzotriazole. Anticorrosive properties of coatings can be improved by addition of loaded tubules into paints. Such kind of coatings will act as a self healing system for metals when the scratch is occurred.

EXPERIMENTAL

Reagents. Halloysite samples were obtained from Atlas Mining Corporation, Utah and Imerys Corporation, New Zealand. Polyethylenimine (typical MW 2000) was purchased from Sigma-Aldrich, USA as 50 wt% solution in water. Polyacrylic acid (typical MW 5100) was purchased from Fluka Chemika, Switzerland as a powder. Benzotriazole was purchased from Sigma-Aldrich, USA.

Instrumentation. Scanning Electron Microscope (Hitachi S 4800 FE-SEM), Cressington Sputter coater (208HR), UV spectrophotometer (Agilent 8453), Zeta Potential Analyzer (Brookhaven Instruments Corporation) and Eppendorf 5804R Centrifuge.

Methodology. Halloysite samples were characterized by using scanning electron microscope (after 1.6nm thickness coating with Platinum by sputter coater) and zeta potential analyzer to measure surface charges and average particle sizes. Elemental composition of halloysite was determined by using SEM EDX elemental analysis.

Nanotubule Loading Procedure. To entrap benzotriazole, the halloysite was mixed as a dry powder with a saturated solution of the compound in acetone (80 mg/mL). A beaker containing benzotriazole and halloysite suspension was transferred to a vacuum jar, which was then evacuated using a mechanical vacuum pump. Suspension was kept under vacuum for approximately 20 min, and then removed to atmospheric pressure. This process was repeated 3 times in order to increase loading efficiency. In addition, halloysite particles were kept in the solution overnight, which is believed to further increase loading efficiency. Finally, halloysite nanotubes were separated from solution by centrifugation and washed with water. Loading of benzotriazole from its melt was also performed.

A Study of Benzotriazole Release Profile. Benzotriazole release study was performed in water at room temperature. Suspension of halloysite nanotubes was constantly stirred with magnetic stirrer during entire release process in order to establish equilibrium condition. Samples for analysis were taken from suspension by centrifugation. Concentration of benzotriazole was determined by UV spectrophotometer. Complete release was achieved by sonication of halloysite samples in the end of each release study.

Layer-by-Layer Nanoassembly. Polyethylenimine (PEI) and Polyacrylic acid (PAA) were used to encapsulate halloysite nanotubes. Initially negatively charged halloysite particles were suspended in solution containing 5 mg/mL solution of PEI for 15 minutes which was followed by removal of halloysite from solution by centrifugation and resuspension in 5 mg/mL polyacrylic acid (PAA) solution. Halloysite samples were washed with water before suspending them in consecutive polyelectrolyte solution. Assembly of the polyelectrolytes was monitored by surface (electrokinetic) potential (Zeta-potential).

RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images of halloysite samples are shown in Fig. 1, and the cylindrical nature of the halloysite nanotubes is clearly evident.

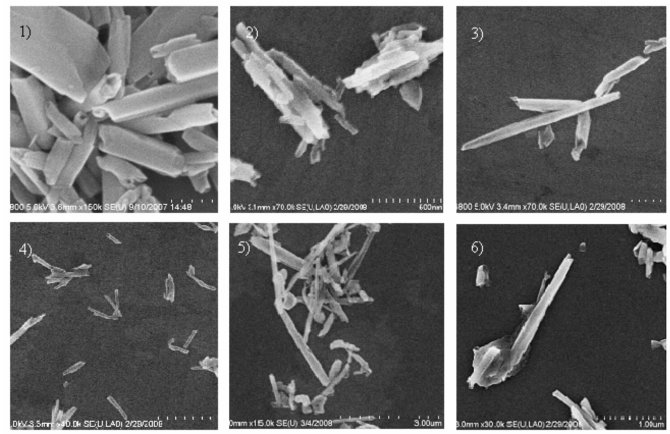

Figure 1. SEM images of halloysite samples. 1 – Sample 1, 2 – Sample 2, 3 – Sample 3, 4 – Sample 4, 5 – Sample 5, and 6 – Sample 6.

Sample 1 has complete rolled nanotubular structure, with big variations of tubule diameters and lengths. External diameters of the most of the tubes are of 50 nm. Tubes with diameters as big as 300 nm also exist. Sample 2 shows clear nanotubular morphology; external diameters of the tubes vary in the range of 50 – 150 nm. Sample 3 has clear nanotubular shape with ~ 40 nm external diameter; lengths of the tubes vary from 200 nm to 1500 nm. Sample 4 has uniform distribution of lengths and diameters of the tubes. Besides clear tubular shaped minerals, there are also incomplete rolled tubes. This sample contains the smallest tubes. Besides clear nanotubes, sample 5 has some platy particles and small peaces of broken tubes. Tubule external diameters range from 80 to 200 nm, while lengths of the tubes range from 800 nm to 2000 nm. Sample 6 contains larger tubules with diameters ranging from 200 to 500 nm and lengths up to 3 microns.

Table 1. Some Important Characteristics of Halloysite Samples

Sample	Particle Size (nm)	Zeta Potential (mV)	Elemental Composition (atomic %)
1	328 ± 7	-42.6 ± 2.1	18.5% Al, 19.1 % Si, 62.2% O, 0.3% Fe
2	382 ± 11	-48.5 ± 0.3	18.3% Al, 18.9% Si, 62.2% O, 0.6% Fe
3	445 ± 23	-21.4 ± 1.0	17.3% Al, 16.9% Si, 64.0% O, 1.6% Ca, 0.3% Fe
4	279 ± 3	-29.4 ± 0.4	18.7% Al, 18.7% Si, 62.1% O, 0.3% Na, 0.2% Fe
5	265 ± 9	-31.7 ± 1.5	17.9% Al, 19.6% Si, 61.5% O, 0.4% Na, 0.6% Fe
6	456 ± 11	-48.4 ± 2.8	13.0 % Al, 25.0% Si, 61.6% O, 0.4% Fe

In Figure 2 release profiles of benzotriazole from halloysite samples are shown. Benzotriazole dissolution rate in water is close to y axis (almost vertical). Complete dissolution of benzotriazole in water takes place within few minutes, while its entrapment with halloysite resulted in sustained release up to 50 hours.

Benzotriazole release rate can be described either by logarithmic or power functions. Release rates from halloysite with diameter 40-50 nm (samples 1-5) are close to each other, (95 % within 48 hours). Sample 6 of 200-500 nm diameter shows fastest benzotriazole release rate: 99% within 20 hours. Maximum loading efficiency was achieved for sample 3: 4.5% by weight, while minimum loading efficiency was obtained for sample 4: 1.5 %.

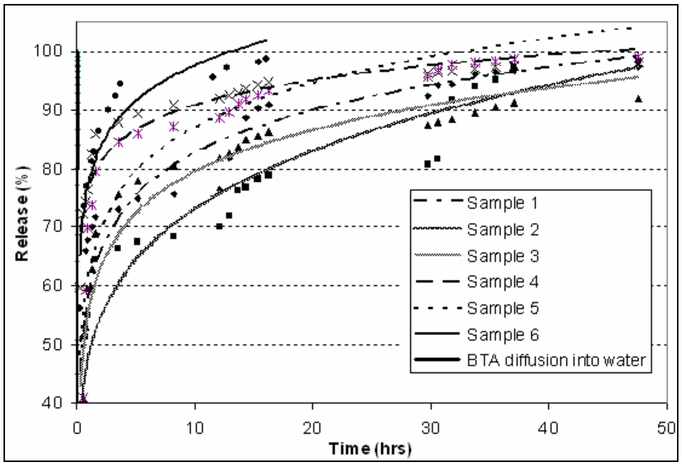

Figure 2. Benzotriazole release profiles from halloysite samples of different diameter.

Layer by layer shell assembly on halloysite nanotubes was conducted by using polyelectrolytes PEI and PAA. Assembly of polyelectrolytes was monitored by the change of the Zeta-potential during LbL process. Surface charges of the samples were alternated during the deposition of the polycations and polyanions as it is shown in Fig. 3. Aggregation behaviors of the halloysite samples were monitored by measuring the size of the halloysite particles in their colloids before and after LbL process, and results showed that halloysite particle sizes changed during LbL process insignificantly, which is the indication that the little or no aggregation took place during LbL process (Table 2).

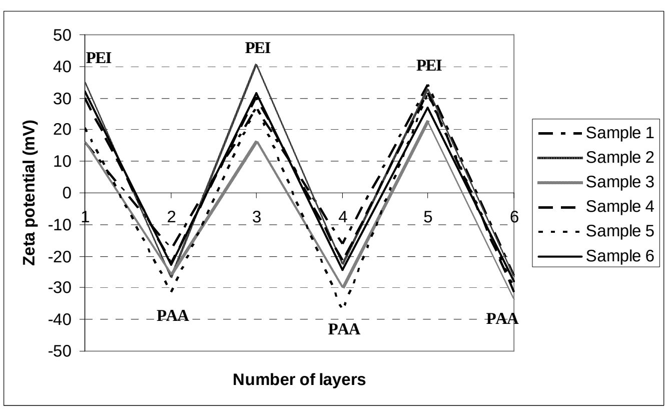

Figure 3. Alteration of Zeta potentials of the halloysite samples during LbL process.

CONCLUSIONS

Halloysite minerals having tubular geometry are excellent materials for encapsulation of corrosion inhibitors in the paint. Tubules from six different deposits were studied as potential capsules for corrosion inhibitors and in all of the cases significant reduction of benzotriazole release rate was obtained, which demonstrates that the mineral can be used for sustained release of corrosion inhibitors in the pain. Possibility of further encapsulation by using layer-by-layer assembly of polyelectrolytes was also demonstrated. Tubules show little or no aggregation behavior during the assembly process.

ACKNOWLEDGEMENTS

This work is supported by Louisiana Board of Regents – post-Katrina Research grant.

REFERENCES

1. Sease, C. *Studies in Conservation*, 1978, 23, 76.
2. Faltermeier, R. B. *Studies in Conservation*, 1998, 44, 128.
3. Shchukin, D. ; Zheludkevich, M.; Yasakau, K.; Lamaka, S.; Ferreira, M.; Möhwald, H. *Adv. Mater.*, 2006, 18, 1672.
4. Abdullah, A. M.; F. Al – Kharafi, M.; Ateya, B. G.*Scripta Materialia*, 2006, 54, 1673.
5. Shchukin, D.; Möhwald, H. *Adv. Func. Mater*, 2007, 17, 1451.
6. Shchukin, D.; Möhwald, H. *Small,* 2007, 3, 926.