

Novel Organic-Inorganic Hybrid Coating

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ABSTRACT

Self healing is a desirable property of a coating substrate to help arrest the development of micro-cracks and the propagation of corrosive species to the interfacial layer and eventually to the substrate. Amongst many approaches to self healing that have emerged recently, the use of hollow tube with controlled release of active ingredient offers a novel strategy to deliver sustainably the anticorrosive agents at the crack plane. With a view to achieve such self healing characteristics, nanotubes based on aluminosilicate have been employed as nanocontainers for active ingredients in a new generation of protective coating. Coatings have been prepared from organometallates and nanotube compositions. The nanotube based hybrid coating is found to be uniform, dense and essentially defect free. Characterisation of the hybrid coating was performed using thermal, spectroscopy, microscopic experiments to understand the nature of interfacial interaction of the inhibitor with the nanotube to achieve excellent performance of this type of coating.

Keywords: Nanotube, inhibitor, sol-gel coating

1 INTRODUCTION

Recently, self healing coatings have gained significant importance due to their ability to tolerate any damage and make necessary repair to restore the normal function of the substrate. The majority of metallic materials particularly active metals such as carbon steel on exposure to environmental conditions during their applications deteriorate and fail prematurely. Recently, interest has increased in the development of the 'smart self-healing' material, which has ability to protect metal from corrosive species attack and also repair cracks in the coating such as multicomponent systems¹, self-healing hydrogels², inhibitor loaded in to nano container with layer – by – layer (LbL) nano-organised multilayers.³ However, heterocyclic inhibitor loaded into nanocontainer especially Halloysite has demonstrated potential in the self-healing anti-corrosion coating formulation, which was first demonstrated by Price et. al.⁴ Halloysite is a naturally occurring clay with two-layered aluminosilicate, hollow tubular structure. Halloysite has similar structure and

composition of kaolinite except for its higher water content. Halloysite is inexpensive, abundant, and sensitive to specific pH, mechanical damage and ability to entrap active agents such as drug molecules⁵ biocides⁶, anti-corrosive inhibitor within the inner lumen followed by their retention and release³. The outer surface of the halloysite nanotube possesses properties similar to that of SiO₂ while the inner lumen shows properties similar to that of Al₂O₃. The zeta potential of halloysite is a combination of mostly negative (at pH 6-7) surface potential of SiO₂, with a contribution from the positive Al₂O₃ inner surface. The positive (<pH 8.5) charge of the inner lumen can allow loading of halloysite nanotubes with negatively charged species, which are at the same time repelled from the negatively charged outer surfaces.

Due to their enormous potential, in this study we have encapsulated 1,2,4-Triazole molecule into the Halloysite nanotube for controlled release of this anti-corrosive inhibitor. Besides this, the main aim is to understand the nature of interaction of the corrosion inhibitor in the nano container e.g. "active container" for new polymer coating e.g. "passive matrix". Deposition of dense active layers in Halloysite was done followed by thermal and spectroscopic characterizations. Salt spray test, scratch test and microscopic investigation were also performed to understand the interfacial adhesion properties compared to the conventional silane based systems.

2 EXPERIMENTAL

2.1 Material and Methods

Halloysite (Dragonite HP) was obtained from Applied Minerals, USA. 1,2,4-triazole (98%) and other inhibitors were obtained from Aldrich Chemicals, Australia and used without further purification. ethanol and other solvents were obtained from Merck, Australia and used without purification. Thermogravimetric analysis (TGA) was performed using TA Instruments (model 2950), at a heating rate of 10 °C/ min from 30°C to 800°C under a controlled gas flow rate of 50 ml/min. Differential Scanning Calorimetry (DSC) was performed using a TA Instrument (Discovery) with a heating and cooling rate of 10°C/min under nitrogen atmosphere.

2.2 Purification of Halloysite clay

A suspension of halloysite in water (10 wt%, 10 g in 100 ml) was prepared using milli-q water and the dispersion of the halloysite clay was improved by heat treatment at 60°C with stirring using magnetic stir bar for 12 h. The solution was then cooled to room temperature and 100 ml milli-q water was added and the clay solution was sonicated for 10 min. Then upper layer was separated out and again (4 x 100 ml) milli-q water was added in lower layer and sonicated the suspension for 10 min. Finally, lower aggregated solid was discarded (1.5 g). Obtained suspension of halloysite clay was separated using centrifuge, washed with milli-q water (100 ml), again separated by centrifugation. Finally the resulting halloysite clay was treated with ethanol (100 ml) and separated by centrifugation. The obtained halloysite clay was dried at room temperature for 3 h and then slowly sieved (315 µm) to eliminate the aggregation for uniform drying. Finally the halloysite clay was dried in an oven at 100°C for 12 h. The purified clay was whitish in colour with 80% yield.

2.3 1,2,4-Triazole loading in Halloysite Clay

Purified Halloysite clay nanotube was loaded with triazole by vacuum treatment adapting the procedure described by Abdullayev et.al.⁷ 0.7 g 1,2,4 – triazole was taken into 250 mL beaker and dissolved in 100 mL ethanol (1 mg/mL). In ethanol solution 1 g Halloysite clay nanotube was added and stirred with magnetic stir bar for 10 min for well dispersion of clay nanotube in ethanol solution. Then beaker was transferred into the vacuum jar and evacuated using vacuum pump. During encapsulation, ethanol solution was first observed to become slightly fizzy, which indicates interrupted air from Halloysite lumen being evacuated. Suspension was kept under vacuum for 5 h and then Halloysite nanotube was separated from solution by centrifugation. Triazole loaded Halloysite nanotube was dried at 80°C for 5 h. This protocol of loading of triazole into Halloysite nanotube was repeated four more times with above mentioned procedure in order to increase the maximum loading efficiency. Finally triazole loaded Halloysite nanotube was repeatedly washed with ethanol, several times in order to remove physically adsorbed triazole and then separated by centrifugation. Finally, triazole loaded Halloysite nanotube was dried in the oven at 80 °C for 6 h.

2.4 Sol-Gel Coating with triazole loaded Clay

The sol-gel coating was prepared from a sol by slow dropwise addition of 42.8 ml (0.19mol) 3-glycidoxypropyltrimethoxysilane (GPTMS) and 8.9 ml (0.06mol) tetraethoxysilane (TEOS) to 64.8 ml solution of

acetic acid in doubly distilled deionized (DDI) water. The solution was continuously stirred for 1h during addition. The TEOS: GPTMS molar ratio used was (1:3 mol ratio) respectively. Hydrolysis and condensation of silanes were conducted at high water/silane ratio of 15. On addition of all of the silanes and completion of hydrolysis, the solution was aged in closed container for 3 days under continued stirring at ambient temperature. The solution was then analysed for particle growth using NanoZetasizer Dynamic Light Scattering (DLS) apparatus. A wide range of particle size (nm to micron) can be obtained with the growth of surface features in the range of nm. In most cases the particles can be made following simple sol-gel procedures. Control over the wettability of the surface can be achieved by altering the surface chemical composition along with the topological nature of the surface. Thin hybrid coating on low carbon steel metal sample was prepared as follows: metal samples (2x2cm) was ultrasonically solvent cleaned to remove surface oils, followed by immersion in an alkaline cleaner at 80°C for 5 minutes. The purpose of the alkaline treatment was to produce a fresh oxide layer for chemical bonding to the hydroxyl groups of the SNAP solution. The prepared substrate was then dip-coated. SNAP coatings based on nano-sized silane macromolecules and also another batch containing inhibitor loaded clay nanotube that were pre-formed in solution, were subsequently crosslinked upon coating application. Diethylene triamine (DETA) was added to crosslink and to chemically connect the nanoparticles, thereby forming the organic coating. The coated sample was placed in an oven at 80°C for 24hr for curing. The evaporation of solvent followed by matrix cross-linking resulted in an optically transparent film.

3 RESULTS & DISCUSSIONS

Quality and quantity of inhibitor encapsulation in halloysite nanotubes is sensitive to purity and physical form (non-aggregation) of nanotubes. In this work, we have rationally purified the halloysite nanotubes with multiple treatments such as heat treatment, sonication, multiple washing with milli-Q water, and ethanol to improve the quality of nanotubes, and to avoid aggregation and impurities. The obtained pure halloysite nanotubes are whitish in colour. The washed and dry nanotubes were then used for loading of triazole. It was observed that during first three loading cycles, the loading (wt%) of triazole into halloysites nanotube increased gradually and the saturation loading level was achieved after fifth loading cycle. Loading (wt%) of triazole into halloysite nanotube was examined by TGA. The maximum triazole quantity loaded into the halloysite nanotube was estimated to be 1.6 wt % from TGA weight change thermogram (Fig1).

DSC study was used to investigate the nature of loading

Hence its release from the coating can be controlled from

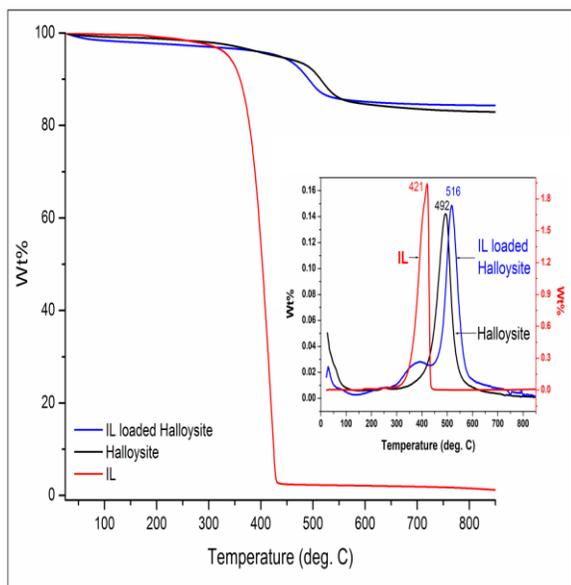


Figure 1: TGA thermogram of Halloysite, pure IL and IL loaded halloysite. The derivative curve is also shown in the plot.

and to determine the release profile of the triazole, as well as its decomposition profile. Stoichiometric amounts of the reactants were measured and dissolved in a minimum volume of solvent. A few drops of the concentrated reaction solution was transferred into a hermetic pan for DSC study. The majority of the solvent was evaporated under a stream of nitrogen; leaving the reactants. This evaporation method was repeated until a reaction mass of approximately 3-4 mg was attained. The heat flow signal of the reaction is shown in Figure 2. It can be seen from the plot that a few distinct thermal events occurred from 30°C to 350°C in different samples. Pure halloysite shows the presence of some bound water, which is released between 120-200°C. While pure Triazole shows a melting transition at 121°C and a decomposition temperature of 317°C, the triazole loaded halloysite shows three transitions at 179, 185°C (melting of strongly adsorbed triazole in the inner and outer lumens of the nanotube) and at 297°C due to decomposition of immobilised triazole, which is earlier than the pure triazole.

The second set of experiment was done in DSC using SNAP coating with inhibitor loaded halloysite. Fig 3 shows the DSC thermogram of sol-gel SNAP coating with triazole loaded clay. The first endothermic peak is due to the glass transition of three dimensional network followed by release of the strongly adsorbed inhibitor at 175 °C and 181°C from the inner and outer lumens of the halloysite. This result indicates the fact that the triazole remains strongly immobilised to the nanotube even within the SNAP coating.

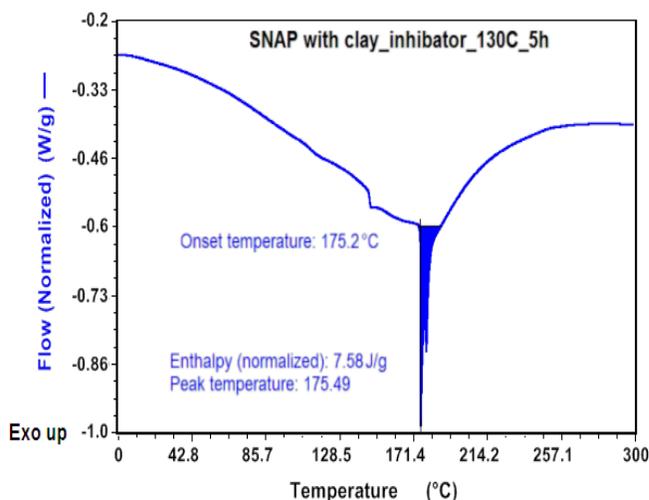


Fig 3. DSC thermogram of sol-gel SNAP coating with inhibitor loaded halloysite

the tubule nanoreactor on demand through crosslinking^{8,9} as the mobility of the matrix increases as it crosses the glass transition temperature of the matrix hence openings of the halloysite nanotubules and release of loaded triazole from inner and outer lumen to the bulk solution.

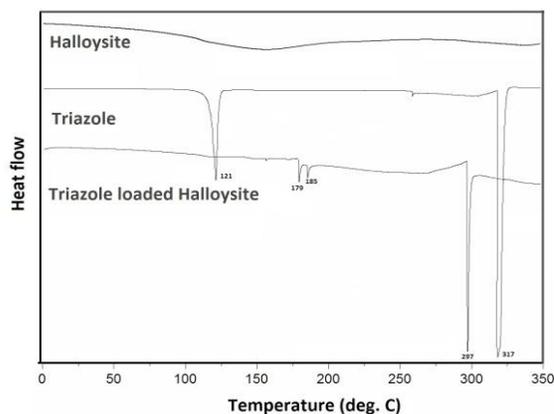


Fig.2. DSC thermograms of Halloysite, 1,2,4-triazole and triazole loaded Halloysite

4 CONCLUSIONS

We have successfully synthesized a new class of hybrid that is suitable for coating applications. Upon curing the hybrid forms a 3D network with nanostructure morphology. Importantly the clay nanotube components retain the inhibitor, which can give the coating self healing characteristics as compared to conventional clay based coating. As the release of immobilised triazole occurs well after the T_g , therefore, this could be used carefully to trigger the self healing characteristics. The work demonstrated that the release of inhibitor can be controlled by tuning the crosslinking of the matrix and hence the glass transition temperature (T_g). This was further demonstrated when upon repeated exposure to high and low temperatures the hybrid retained its chemical and structural integrity. The application of the hybrid as a coating resulted in the formation of a homogeneous one-phase lamellar coating with excellent surface coverage. Currently, work is underway to investigate the wettability of the coating and its performance under thermal cycling, which can induce cracking due to differential coefficients of thermal expansion and contraction. The integrity of the coated samples will be examined by microscopic techniques and will be presented in detail.

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