Tubule Nanocontainers for Corrosion Inhibitors

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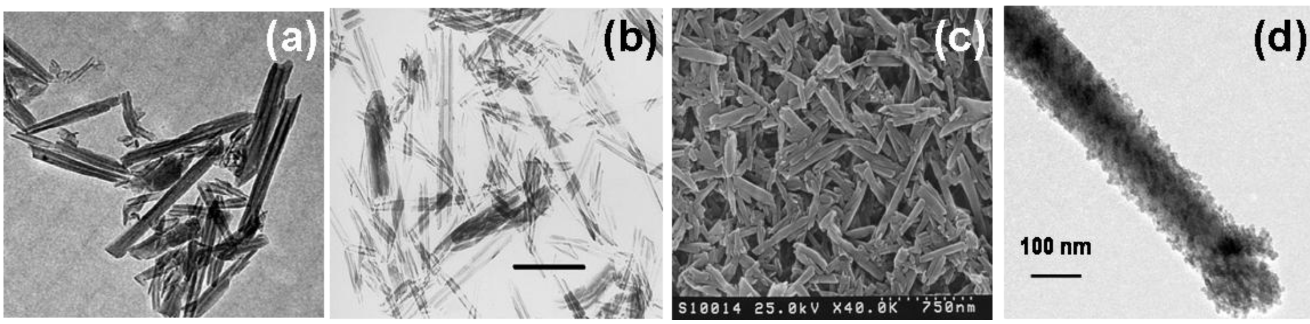
Project objectives: Long lasting protection of engineering devices from mechanical destruction, chemical (corrosion) and biological (fouling) degradation would have tremendous economic and social benefits. We will pursue this goal by developing the clay nanotube-polymer composites accomplished with slow release of anticorrosion, flame-retardant, and antifouling agents in response to external impacts. Our work is based on natural clay nanotubes available in thousand tons at low price. This new natural clay nanomaterial does not bring a danger for environment.

Natural halloysite clays are developed as functional reinforcing nanotubes for polymer composites. Loading these tubes' 15-nm diameter lumens with chemical agents (anticorrosion, flame-retardant and antimicrobial agents) allows for smart materials with protective self-healing properties due to a controlled sustained release of encapsulated chemicals during many months. Doping such loaded clay nanotubes into polymers provides triggered release of healing agents in the composite defects. An addition of 5 % halloysite synergistically increases polymer strength on 50-70 %, doubles the composite adhesivity and adds new functions due to release of needed chemicals.

Halloysite tubes have ca. 1000 nm length, 50 nm diameter and chemically different inner and outer walls (inner surface - aluminum oxide and outer - silica). Due to this, the selective etching of alumina from inside of the tube was realized, while preserving their external diameter (lumen diameter changed from 15 to 25 nm). This increased 3-4 times the tube lumen capacity for chemical agents (e.g., halloysite loading efficiency for the benzotriazole increased 4-times). Specific surface area of these acid treated tubes also increased from 40 to 280 m^2/g. Selective hydrophobization of inner or outer surfaces was also achieved allowing for loading of hydrophobic chemicals like flame-retardant bis (diphenyl phosphate).

Anticorrosive coatings for metals have been developed based on halloysite loaded with triazoles. The corrosion inhibitors' loaded tubes were admixed with acrylic or polyurethane paints providing sustained agents release and corrosion healing in the coating defects. Long lasting anticorrosive coatings for steel have been developed based on halloysite nanotubes loaded with three corrosion inhibitors: benzotriazole, mercaptobenzothiazole and mercaptobenzimidazole. The inhibitors' loaded tubes were admixed at 5-10 wt % to oil based alkyd paint providing sustained agents release and corrosion healing in the coating defects. Slow 20-50 hours release of the inhibitors in defect points caused remarkable improvement in anticorrosion efficiency of the coatings. Further time expansion (for months) of anticorrosion agents release has been achieved by formation of the tube-end stoppers using complexation of urea-formaldehyde or copper sulphate with benzotriazole. Corrosion protection efficiency was tested on iron A365 alloy plates in 0.5 M NaCl solution with micro-scanning of corrosion current development, by microscopy inspection and studying paint adhesion. The best protection was found using halloysite / mercaptobenzimidazole and benzotriazole inhibitors. Stopper formation with urea-formaldehyde copolymer provided additional increase in corrosion efficiency due to longer release of corrosion inhibitors.

Halloysite is well mixable with polar and medium polar polymers. Antibiotic loading into halloysite tubes enhances their antimicrobial efficiency due to extended function both in direct applications and in polymer composites. These ceramic nanotubes form a kind of a "skeleton" in the bulk polymers enhancing the composite strength and adhesivity. Besides, these "skeleton bones" may be loaded with bioactive compounds like real bones are loaded with marrow providing additional functionality. Halloysite is biocompatible "green" material and its simple processing combined with low cost make it a perspective for nano-architectural polymeric composites.



TEM images of halloysite nanotubes dispersed in water, scale-bar 1 mkm (a-b), SEM image of layer-by-layer nanocoating with halloysite multilayer (c), and halloysite nanotube coated with polyelectrolyte + 7 nm diameter silica

References

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