



## Self-assembly of covalently bonded nano-silicates with controllable modulus and thermal stability



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### ABSTRACT

Modified vermiculites (MVMTs) that self-assembled into fiber or nacre-like structures were fabricated by covalent bonding with hexamethylene adipamide (HA) during in situ polymerization. Unlike previous researches where self-assembled silicates have been fabricated via physical interactions, covalent bonding of vermiculites demonstrated in this research provided substantially higher mechanical properties and thermal resistance to the assembled materials. In addition, the shape and size of the self-assembled structures could be controlled by varying the amount of coupling agent and the modulus of the fiber-like assemblies could be controlled by heating. X-ray Photon Spectroscopy proved the covalent attachment of the HA onto vermiculites. At low concentrations (11%) of coupling agent, the MVMTs self-assembled into fiber like structure and into nacre-like structures at a coupling agent concentration of 17% thereby enabling us to control the shape and size of the self-assemblies. Atomic force microscope measurements showed that the elastic modulus of the self-assemblies were about 17–18 GPa, compared to the modulus of 0.3 and 1.5 GPa for the pure polymer and unmodified clay, respectively. The ability to covalently bond and control the self-assemblies and the resulting high performance properties of the self-assemblies could be useful to develop materials for various applications.

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### 1. Introduction

Self-assembly of nanosilicates found in nature has been mimicked as a means to obtain materials with exceptional properties [1,2]. Such self-assembled structures in the form of nanospheres, rings, fibers and filaments have wide applications in electronic, magnetic and photonic devices [1,3]. Methods including self-assembly at toluene–water interface, in polymer matrices, self-piling, electron beam bombardment are some of the approaches used to develop the self-assembled structures [4]. Type and dimensions of the silicates, interactions between the matrix and clay and method and conditions of self-assembly are the major factors that are used to control the self-assembly and properties of the products obtained [1]. The ability to control the self-assembly of the nanoclays into desired geometric shapes and sizes, although possible, has been challenging [5,6].

Silicate assemblies in various morphologies have been developed, such as rods [4], dendrite [7] and 3D network structure [8]. Lengthy rod-like structures (0.1–0.8 μm in width and 2–40 μm in length) could be produced by adjusting the ratio of organic and

inorganic constituents [4]. The rod-like assemblies could further be rearranged into fern-leaf dendrites using ultrasonic treatment [7]. Besides rods and dendrites, assemblies in 3D networks could also be developed via tethering thermoresponsive polymer chains onto silicates platelets covalently [8].

Usually, assemblies with an ordered arrangement of inorganic and organic components possess higher toughness than corresponding single component [9]. For example, nacre, the structure found in molluscan shells and bone is a hybrid organic–inorganic component with exceptional properties [10,11,3]. Nacre from the shell of molluscs was reported to have an elastic modulus of 70 GPa when dry and 60 GPa when wet [3]. Several attempts have been made to mimic the nacre-like structures and demonstrated that the mechanical properties of self-assembled layered composites can be greatly enhanced through proper selection of the assembly components or suitable chemical modification [12,13]. A layer-by-layer assembly of montmorillonite clay on polyelectrolytes was used to develop artificial nacre. The developed nacre had tensile strength of 109 MPa, similar to that of natural nacre (130 MPa) and modulus of 13 GPa, lower than that of natural nacre (64 GPa) [14]. In another approach, silica solutions and organic monomers were dip-coated to form micelles that were later self-assembled into nacre-like structure after polymerization [15].

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In situ polymerization has also been a common approach to produce self-assembled clay structures to reinforce polymer matrices [16,17]. Linear low-density polyethylene (LLDPE)-nanoSiO<sub>2</sub> composites were developed by in situ polymerization with zirconocene/MAO catalyst and it was found that particle size of SiO<sub>2</sub> played a significant role in determining the properties of the composites. In another report, in situ polymerization was used to produce polyfurfural alcohol nanocomposites without using any solvents or surfactants resulting in composites with high thermal resistance [18]. In this research, we proposed that in situ polymerization of inorganic and organic components could produce assemblies with unique mechanical properties.

Vermiculites in their natural state have shape and size similar to mica and exhibit to dehydration–rehydration and swelling behaviors. The unique morphology and structure of vermiculites has been used to reinforce rubbers, building materials, thermoplastic polymers and also as catalysts and environmental absorbents

[19]. In this research, we have modified vermiculites by adding –NH<sub>2</sub> groups and added the MVMTs into hexamethylene adipamide to form in situ polymerized PA66-MVMTs composites. Self-assembly of the VMTs in the PA matrix and effect of addition of coupling agents and thermal treatment on the self-assembly process and properties of the resulting assemblies have been investigated.

## 2. Experimental section

### 2.1. Materials

Vermiculites (VMTs) were purchased from Zhongyan Building Material Company, Hebei, PR China and the  $\gamma$ -aminopropyltriethoxysilane was purchased from Yaohua chemical Company, Shanghai, PR China. HA (Molecular weight of 262, purity of 99.5%) and formic acid were purchased from Huayang (Jiangsu), PR China and China Medicine Group, respectively.

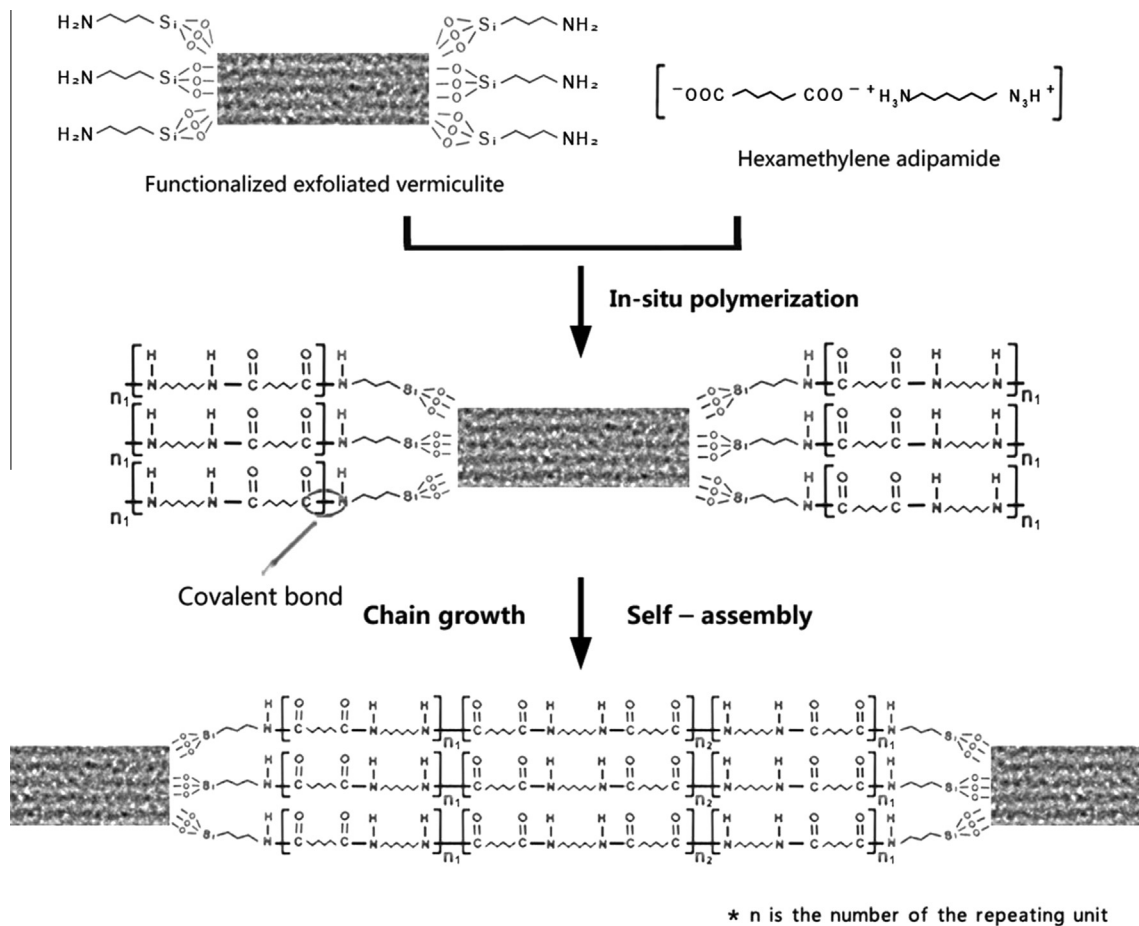


Fig. 1. The schematic of the self-assembly of MVMTs.

Table 1

Surface chemical composition of the samples determined by XPS.

Materials	Atomic concentrations (%)						
	C (284 ev)	N (398 ev)	Si (101 ev)	Mg (50 ev)	Al (74 ev)	Na (1068 ev)	O (531 ev)
VMTs	–	–	13.03	4.76	6.42	1.51	60.52
MVMTs (11%)	27.40	3.33	11.78	2.11	3.88	0.43	51.24
MVMTs (17%)	32.60	4.08	9.56	1.98	3.15	–	49.00
PA66-g-MVMTs (11%)	59.79	7.41	2.35	–	–	–	38.60
PA66-g-MVMTs (17%)	63.83	8.11	1.75	–	–	–	32.46

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