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ORGANO-MODIFICATION OF MONTMORILLONITE

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Abstract—Modification of the surfaces of montmorillonite (Mnt) by organic molecules is an effective method for improving their affinity toward non-aqueous substances, and has resulted in extensive industrial applications as rheological control agents, drilling fluids, and other functional materials used in applications ranging from environmental remediation to coatings. The present study reviewed recent progress in organo-modification of Mnt, and provides state-of-the-art insights into proposed modification mechanisms and the peculiar functionalities of the resulting organo-montmorillonite (OMnt). Several routes have been employed to modify Mnt, including ion exchange with organic ions, surface adsorption, and grafting of organics. Commonly used organic modifiers include cationic, anionic, zwitterionic, non-ionic, and polymeric species. Organo-modification is driven by multiple interactions: van der Waals forces, cation exchange, electrostatic interaction, hydrogen bonds, and ion–dipole interaction. OMnt, in general, exhibits synergistic and/or antagonistic effects when used in oil-based drilling fluids, environmental remediation, or layered silicate/polymer nanocomposites. The detailed mechanisms of non-ionic and zwitterionic modification of Mnt remain unclear. This literature survey suggests that future work should emphasize deeper understanding of interactions between the Mnt and the organic modifiers, and meanwhile expand the applications of OMnt into catalysis, drug carriers, and the biomedical field.

Keywords—Hydrophobicity · Ion exchange · Montmorillonite · Organic grafting · Organic modification · Surface adsorption

INTRODUCTION

Montmorillonite (Mnt) is a 2:1 layered aluminosilicate mineral (Brigatti et al. 2006). Each layer of Mnt consists of two tetrahedral silica sheets bonded to both sides of an octahedral alumina sheet (Fig. 1a,b). Some of the Al^{3+} in the octahedral sheet can be substituted by divalent metal cations (Mg^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}) and some of the Si^{4+} in the tetrahedral sheet can be substituted by trivalent metal cations (predominantly Al^{3+}). The isomorphous substitutions result in a net negative surface charge and, to maintain neutrality, the interlayer spaces of Mnt adsorb exchangeable hydrated metal cations.

The generally high hydrophilicity of natural Mnt limits its application in some organophilic polymerics (Jovic-Jovicic et al. 2010; Xi et al. 2010). Organic modification is an effective method to solve this problem, most importantly in meeting the practical requirements of rheological control agents of, for example, drilling fluids (Silva et al. 2014; Zhou et al. 2016a), organic adhesives (Ye et al. 2005; Brantseva et al. 2016), organic supplementary cementitious material (Taylor-Lange et al. 2014; Ye et al. 2014), and organo-montmorillonite (OMnt)/polymer nanocomposites (Qin et al. 2011; Al-Mulla et al. 2017; Bee et al. 2018; Zhu et al. 2019). OMnt is obtained through cation exchange, surface adsorption, or grafting (Fig. 1c–e). Until 10 years ago organic cations were the most commonly used modifiers for the preparation of OMnt. During the past 10 years, anions (Zhang et al. 2010), zwitterions (Lazorenko et al. 2018), and other molecules (Borrego-Sánchez et al. 2018) have been used increasingly as modifiers. OMnt is generally prepared in solution (Hu et al. 2017; Martinez-Costa and Leyva-Ramos, 2017; Zhuang et al. 2017a), but semi-solid-state (Zhou et al. 2016c) or solid-state reactions (Zhou et al. 2016a, 2016c) are also common. Recently, by not being limited to heating, ultrasound (Zhang et al. 2010) and microwave (Cao et al. 2010) have also been shown to assist in the processing of OMnt.

Organo-modification of Mnt by introduced modifiers often increases the interlayer space (Gu et al. 2014; Ezquerro et al. 2015). Correspondingly, improving the adsorption capacity to organics (Zhou et al. 2012) enhances compatibility in the polymer matrix (Theng 2012; Scarfato et al. 2016) and improves the swellability in the organic solvent (Yu et al. 2017b; Zhou et al. 2019). OMnt has been used widely as an additive in rheological control agents of paints, inks, adhesives, greases, varnishes (He et al. 2010), adsorptive materials (Bajda and Klapyta, 2013; Yang et al. 2014), drilling fluids (Zhou et al. 2016a), and organic supplementary cementitious material in hydrating cement binders (Papatzani and Paine 2017). OMnt can also be used as an adsorptive material for viruses (Liang et al. 2014), organic contaminants (Wang et al. 2014; Hassani et al. 2015), heavy metals (El Adraa et al. 2017; Yu et al. 2017a), and dyes (Kohno et al. 2011; Zhou et al. 2012). Organic modification of Mnt can also strengthen the interfacial interaction between Mnt and polymers, significantly improving the mechanical strength and thermal stability and properties of the Mnt/polymer nanocomposites (Bujdak, 2015; Gardi and Mishael 2018; Zhu et al. 2019). In the last 10 years, with the development of advanced technology, OMnt application has been transformed to high-tech fields such as gene engineering (Yu et al. 2013; Hou et al. 2014), bone-tissue engineering (Mauro et al. 2017), and biosensors (Seleci et al. 2012; Unal et al. 2018; Yilmaz et al. 2020).

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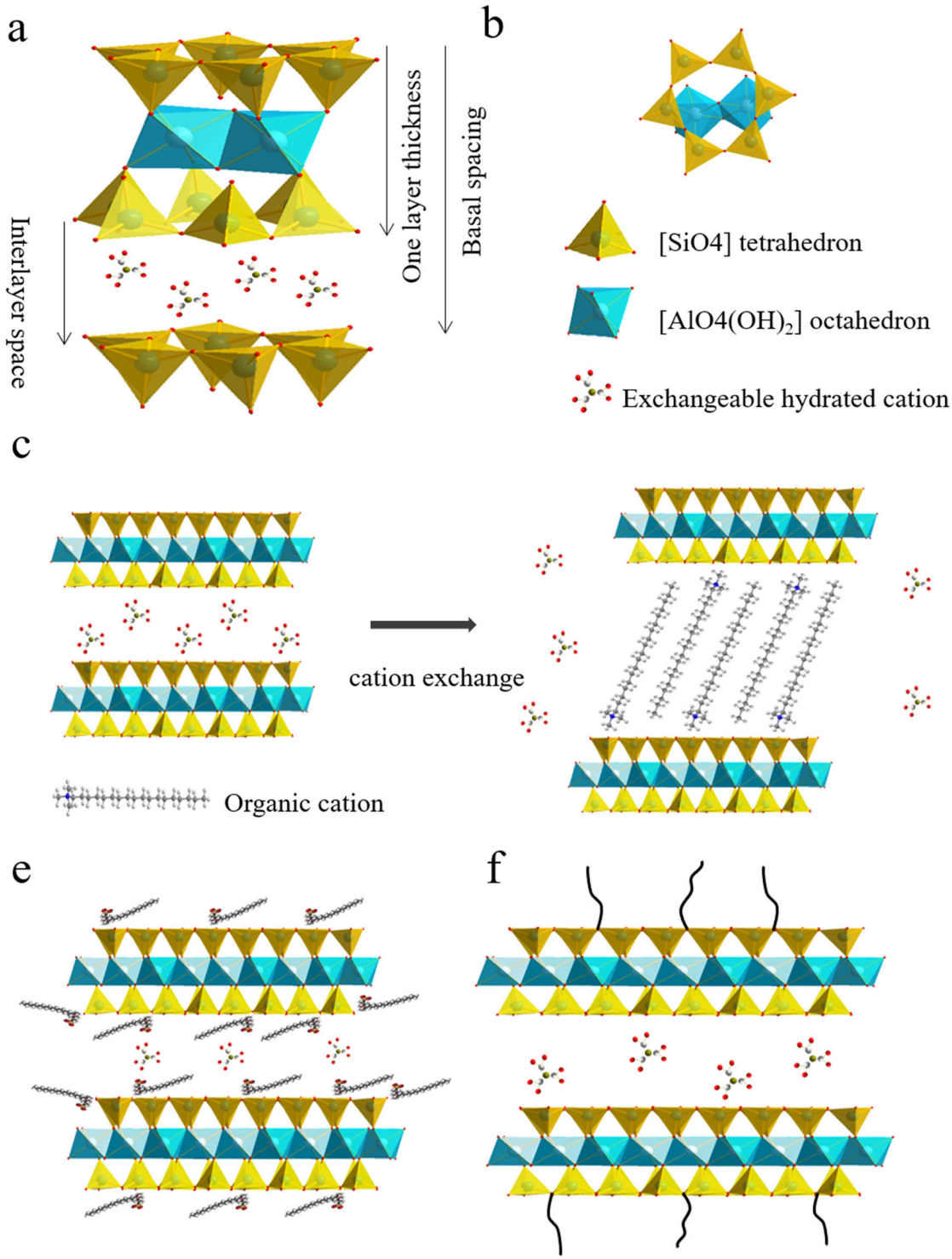


Fig. 1. Crystal structure of Mnt and schematic illustration of organo-modification of Mnt. **a** main view; **b** dioctahedron; **c** organic cation exchange; **d** surface adsorption; and **e** organo-grafting

The past 10 years have increasingly witnessed new preparation technologies and new modification mechanisms for OMnt. This review summarizes the technological progress in organo-modified Mnt and highlights scientific insights into the modification mechanisms of Mnt. An exhaustive understanding of mechanisms of modification is important for the industrial design of OMnt-based nanomaterials. Finally, remaining problems and future work are noted.

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ORGANIC CATION-MODIFIED MONTMORILLONITE

Cation-modified Mnt ($OMnt_c$) can be obtained using organic cations to modify Mnt through cation exchange (Fig. 2). The electrostatic interactions between organic cations and the negative charge of a Mnt surface (Lagaly et al. 2013), inherent hydrophobicity of alkyl chains, and hydrogen bonds are the main driving forces for surface modification (Bate and Burns 2010; Michot et al. 2013; Yu et al. 2014).

$OMnt_c$ can be prepared from suspension, a semi-solid-state, or a solid-state reaction (Zhou et al. 2016c; Lazorenko et al. 2018). The preparation of $OMnt_c$ from suspension, particularly aqueous suspension, is the preferred method at present (Wang et al. 2017b; Ahmed et al. 2018). In aqueous dispersion, the introduction of organic cations to the interlayer of Mnt occurs quickly even at room temperature with the assistance of stirring or sonification. Typically, however, surface coverage is more complete at slightly elevated temperatures (50–80°C) (Zhang et al. 2016; Lazorenko et al. 2018), and microwave heating has been useful for cationic modification of Mnt (Peng et al. 2019). For example, Peng et al. (2019) created $OMnt_c$ by reacting the mixing suspension of dioctadecyltetrahydroxyethyldibromopropanediammonium and Mnt in a microwave synthesis system. Microwave heating can also be combined with ultrasonic dispersion to prepare $OMnt_c$. The combined action of microwave and ultrasound treatment was used by Luo et al. (2019) to modify Mnt with butane-1, 4-bis(dodecyldimethylammonium bromide) (gBDDA). The gBDDA-modified Mnt was better able to sequester phenol and chromate dyes.

$OMnt_c$ created by solid-state or semi-solid-state reactions, such as ball milling, has advantages in water conservation and environmental protection by minimizing the amount of water used and wastes created (Zhou et al. 2016c; Wei et al. 2018). $OMnt_c$ is created through the solid-state reaction by adding Mnt and a cationic modifier into the ball mill and milling (Yan et al. 2016a; Wei et al. 2018). An alternative method is through semi-solid-state reaction by adding Mnt, cationic modifier, and a little water into the ball mill (Yan et al. 2016b). The performances of $OMnt_c$ prepared by these two methods, plus the aqueous dispersion method, were compared by Zhou et al. (2016c). The properties tested included thermal stability, hydrophobicity, dispersibility, and thixotropy of the suspensions. At lower concentrations of hexadecyltrimethylammonium bromide (HDTMAB, also known as cetyltrimethylammonium bromide, CTAB), $OMnt_c$ prepared in the semi-solid-state reaction was found to have similar properties to that prepared from aqueous dispersion. At high concentrations, the $OMnt_c$ prepared from suspension had better property characteristics. Of the three preparation methods, $OMnt_c$ prepared in the solid-state reaction had inferior properties in all HDTMAB/CTAB loadings tests. Modifiers in a liquid phase can cover the surface of Mnt evenly, thus leading to improved performance. For the preparation of $OMnt_c$ by semi-solid-state or solid-state reaction, modifiers would be expected to be unevenly distributed on the surface of $OMnt_c$.

Cationic modification affects many properties of Mnt, including the basal spacing (Wu et al. 2014a; Martinez-Costa and Leyva-Ramos 2017), surface hydrophobicity (Gu et al. 2014; Yang et al. 2016), catalytic properties (Wallis et al. 2010; Wang et al. 2010; Qin et al. 2014), and the rheological behavior of suspensions (Tunç et al. 2012; Yu et al. 2017b). The extent of modification of the properties of $OMnt_c$ depends on alkyl chain length (Lagaly et al. 2013; Wu et al. 2014a; Zawrah et al. 2014; Acisli et al. 2017), chain number (He et al. 2010; Wang et al. 2017b), and modifier loading (Zhou et al. 2015; Martinez-Costa and Leyva-Ramos 2017; Zhang et al. 2017) (Table 1).

After modification of Mnt by a long alkyl-chain organic cation, the basal spacing of $OMnt_c$ increased with increases in chain length, chain number, and loading of the cationic modifier (He et al. 2010; Sun et al. 2013; Flores et al. 2017; Wang et al. 2017b; Zhuang et al. 2017a). For instance, the $OMnt_c$ intercalated with hexadecyl trimethylammonium bromide and octyl trimethylammonium chloride were in a paraffin bilayer arrangement with basal spacing of 3.9 and 4.1 nm at 4.0 CEC (He et al. 2010). When the added modifier was 4.0 CEC, the basal spacings of $OMnt_c$ modified by a cationic modifier with a different alkyl chain number (octadecyl-trimethylammonium bromide and dioctadecyl-dimethylammonium bromide) were 4.1 nm

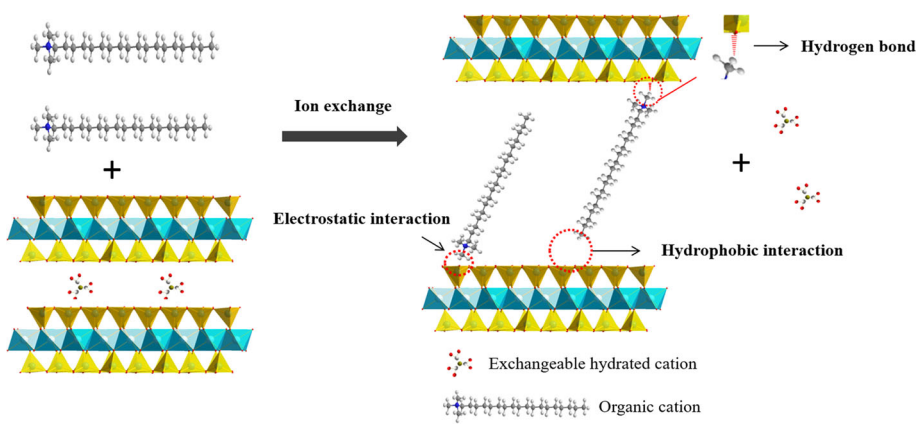


Fig. 2. Schematic illustrations of the cation modification mechanism of Mnt

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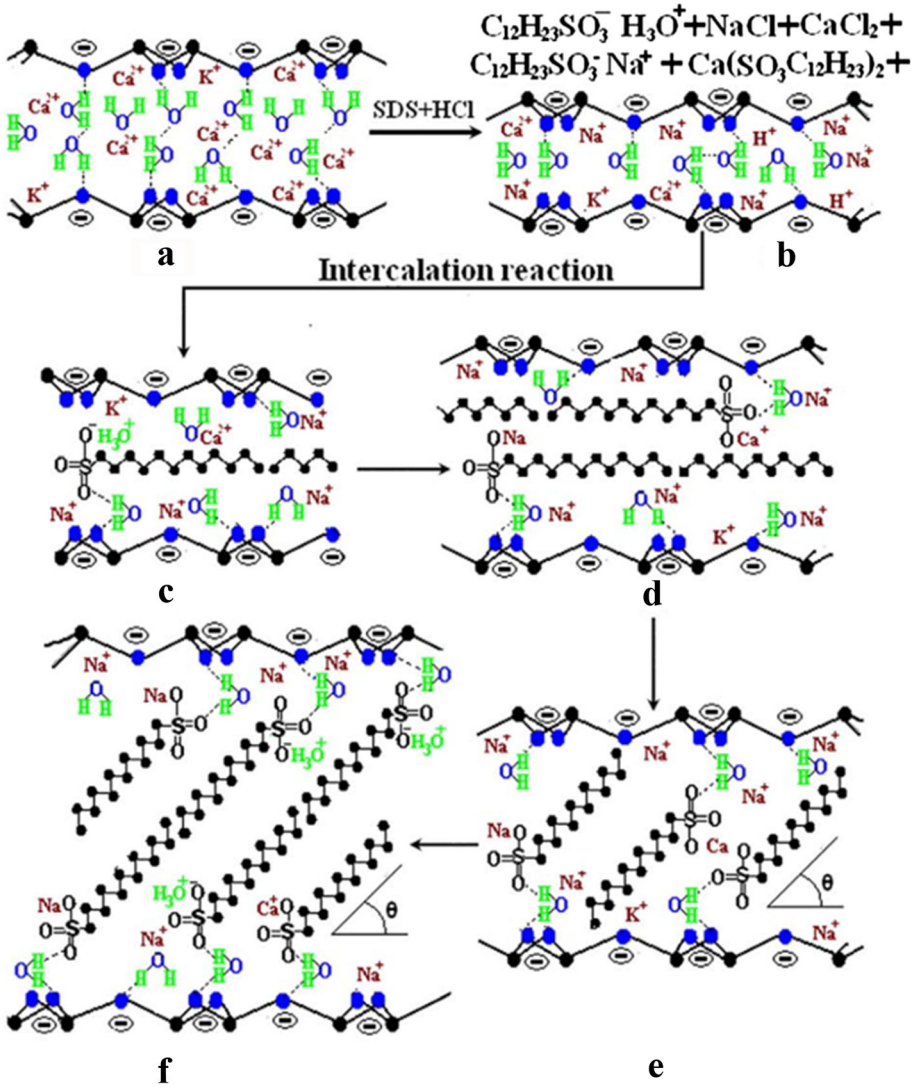


Fig. 3. Intercalation of DS^- in **a** Ca^{2+}-Mnt, **b** Na^+-Mnt, **c** Mnt-DS^- (monomolecular of flat-lying), **d** Mnt-DS^- (bimolecular of flat-lying), **e** Mnt-DS^- (monolayer of tilted chains), and **f** Mnt-DS^- (pseudo tri-layer of tilted chains) (reproduced from Zhang et al. (2010), copyright 2010, with permission from Elsevier). DS^-: dodecylsulfate

and 5.5 nm, respectively. For a small loading of organo-cationic modifier, the alkyl chains occur in a parallel arrangement on the Mnt layer (Sun et al. 2013; Naranjo et al. 2017). For a large loading of organo-cationic modifier, the alkyl chains were arranged in a disordered bilayer or paraffin-type arrangement (Bagherifam et al. 2014; Bujdak, 2015; Flores et al. 2017). A well-known phenomenon is that OMntc hydrophobicity increases with increasing organo-cation chain number (Sun et al. 2013; Flores et al. 2017; Zhuang et al. 2017a) as well as with loadings of organo-cationic modifiers (He et al. 2010; Wang et al. 2015; Zhou et al. 2015; Yang et al. 2017). The hydrophobicity can be demonstrated directly by contact-angle tests. $OMnt_c$ modified by single long alkyl chain cationic modifiers, such as octadecyltrimethylammonium chloride (OTAC) and N,N-dimethyl-N-octadecyl chloride, shared similar hydrophobicity. $OMnt_c$ modified by dimethyldioctadecylammonium chloride (DDAC) had greater hydrophobicity than $OMnt_c$ modified by OTAC, because of the hydrophobic interaction resulting from the long alkyl chain within the Mnt layer (Zhuang et al. 2017a).

$OMnt_c$ displayed superior catalytic properties (Wallis et al. 2010; Wang et al. 2010; Qin et al. 2014). Fe^{3+}-Mnt modified by hexadecyltrimethylammonium ($HDTMA^+$) enhanced catalytic activity for oxidative coupling reactions, which can enhance the development of substrate-specific clay catalysts (Wallis et al. 2010). Similar materials have been made from Fe^{3+}-Mnt modified by choline cations, which was shown to enhance catalytic activity for certain oxidative coupling reactions and a conjugate addition reaction (Wallis et al. 2011). The study by Wallis and colleagues indicated that maximum catalytic activity could be achieved by varying the ratios of Fe^{3+}/$choline^+$ in specific reaction types for specific substrates.

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Table 1. Typical, recent methods and results of organo-cation modification of Mnt

Mnt	CEC (mmol/100 g)	Modifier	Modifier concentration	d_{001} (nm)	Total pore volume (cm^3/g)	BET surface area (m^2/g)	Average pore diameter (nm)	Water contact angle Θ (°)	References
Mnt	106.4	CTAB	1.0 CEC	1.93				49	(Zhou *et al.* 2016c)
			1.5 CEC	1.96				52	
			1.0 CEC	1.94				47.5	
			1.5 CEC	1.98				46	
			1.0 CEC	1.98				43.5	
			1.5 CEC	1.97				43.5	
	120	LTAC	1.0 CEC	1.81				67	(Zhuang *et al.* 2017a)
		ODTMAC	1.0 CEC	2.04				68	
		N,N-dimethyl-Noctadecyl chloride	1.0 CEC	3.64				68	
		DC18	1.0 CEC	4.06				86	
Ca^{2+}-Mnt	65	(11-Ferrocenylun-decyltrimethyl ammonium bromide	0.2 CEC	1.56					(Hu *et al.* 2017)
			0.4 CEC	1.64					
			0.6 CEC	1.78					
			0.8 CEC	1.9					
			1.0 CEC	2.11					
	138.6	$HDTMA^+$	70 mmol/L	2.01	0.014	4.2	15.6		(Martinez-Costa and Leyva-Ramos, 2017)
		$DDTMA^+$		1.74	0.013	3	120		
		$BTMA^+$		1.51	0.022	8.6	9.9		
Na^+- Mnt	88	HEMBP	1.0 CEC	1.3627	0.03272	17.37	7.532		(Gu *et al.* 2014)
	97.1	TTAC*	1.0	2.1					(Wang *et al.* 2017b)
		CTAC	1.0	2.23					
		STAC	1.0	2.31	0.04	3.3	24.5		
		$HDTMA^+$	0.5	1.427	0.051	7.84	8.78		(Yang et al., 2017)
			1.0	2.028	0.0154	1.98	15.81		
			2.0	2.038	0.0012	0.328	19.23		
		TMA^+	0.5	1.384	0.073	52.98	5.531		
			1.0	1.378	0.11	101.68	4.32		
			2.0	1.380	0.13	120.26	4.36		
	76	HDTBPh	0.6	1.9		30.42	14.69	65	(Hojiyev *et al.* 2017b)
			0.8	2.24		29.45	15.23	73	
			1.0	2.31		32.89	15.39	79	
			1.25	2.34		28.9	13.8	82	
			1.5	2.32		24.11	14.43	93	

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Table 1. (continued)

Mnt	CEC (mmol/100 g)	Modifier	Modifier concentration	d_{001} (nm)	Total pore volume (cm^3/g)	BET surface area (m^2/g)	Average pore diameter (nm)	Water contact angle Θ (°)	References
	85	Hydroxyethyl-alkyl imidazoline	1.0	4.4		2.4		83	(Lazorenko *et al.* 2018)
		OMDAB	1.0 CEC	2.04	0.079385	16.6972	17.6186		
		DTDD	0.5 CEC	1.96	0.067917	13.6788	17.4353		
			1.0 CEC	4.09	0.041604	6.8778	22.0996		
			1.5 CEC	4.09	0.018469	2.6192	26.2874		
	112.0	ODTMAC	0.50	2.96					(Zhou *et al.* 2019)
			0.75	2.97					
			1.00	2.88					
			1.50	2.99					

*APTES: 3-triethoxysilylpropylamine; BTMA: benzyltrimethylammonium bromide; CTAB: cetyltrimethylammonium bromide; HDTMAB: hexadecyltrimethylammonium bromide; CTAC: hexadecyltrimethylammonium chloride; HDTMAC: hexadecyltrimethylammonium chloride; DC18: dimethyldioctadecylammonium chloride; LTAB: lauryltrimethylammonium bromide; DDTMAB: dodecyltrimethylammonium chloride; LTAC: lauryltrimethylammonium chloride; DDTMAC: dodecyltrimethylammonium chloride; DTDD: dioctadecyltetrahydroxyethyldibromopropanediammonium; HDTBPh: hexadecyltributylphosponium bromide; HDTMA: hexadecyltrimethylammonium (cation); HEMBP: hexamethylenebispyridiniumdibromide; STAC: octadecyltrimethylammonium chloride; ODTMAC: octadecyltrimethylammonium chloride; OMDAB: octadecylmethyldihydroxyethylammonium bromide; TMA: tetramethylammonium; TTAC: trimethyltetradecylammonium chloride.

$OMnt_c$ can provide improved rheological properties, such as viscosity and gel strength, due to the interfacial interactions between $OMnt_c$ and organic solvent and interparticle interaction (Yu et al. 2014; Zhuang et al. 2017a, 2019a). The van der Waals forces between the alkyl chains of $OMnt_c$ are weakened by certain organic solvents, leading to more organic solvent intercalating into the interlayer space of $OMnt_c$ and enhancing interlayer swelling of $OMnt_c$ (Zhuang et al. 2017a, 2019a). The rheological properties (such as viscosity and thixotropy) of $OMnt_c$ in organic solvents were found by Zhuang et al. (2017a, 2019b) to be influenced by the ability of $OMnt_c$ to swell and/or exfoliate. Cationic modifiers with larger molecular size generally led to easier exfoliation of $OMnt_c$ in organic solvents (Zhuang et al. 2017a, 2019b). Exfoliation of $OMnt_c$ results in more layers contributing to a strong gel structure, resulting in the improved viscosity and thixotropy of $OMnt_c$. Excessive exfoliation leading to dispersion and loss of gel structure can affect viscosity negatively, however, due to the decrease in connection among $OMnt_c$ units.

$OMnt_c$ can be used as a biosensor because the ion-exchange process in Mnt can incorporate charged molecules and facilitate the transfer between the electrode and biomolecules (Shumyantseva et al. 2007; Seleci et al. 2012; Demir et al. 2013; Yilmaz et al. 2020). 4-aminothiophenol intercalated montmorillonite (4ATP-Mt) can be used as an immobilization layer for the pyranose oxidase (PyOx) enzyme on a glassy carbon electrode (Yilmaz et al. 2020). Glucose in artificial body fluids and drinks can be analyzed by the compounded 4ATP-Mt/PyOx. Similar materials have been made from Mnt modified with dimethylamine (Seleci et al. 2012). Trimethylamine (TM)-intercalated Mnt can be used as the immobilization matrix for microbial biosensors (Demir et al. 2013). *Gluconobacter oxydans* cells were immobilized on the TM/Mnt matrix, and the consumption of oxygen was monitored at electrodes by using glucose as a substrate to monitor the respiratory activity of the cells.

ORGANIC ANION-MODIFIED MONTMORILLONITE

Interest in modifying Mnt with organic anionic modifiers is a result of the excellent thermal stability of anionic modifiers compared to traditional cationic modifiers. Some researchers assert that anions cannot intercalate effectively into the interlayer space of Mnt due to the electrostatic repulsion between negatively charged Mnt layers and negatively charged heads of the anionic modifier (Zheng et al. 2013; Wu et al. 2014b; Fu et al. 2016). Others, however, have presented alternative viewpoints, based on experimental results. Anions can enter the interlayer spaces of Mnt through interaction with hydroxyl groups at the Mnt layer edges (Yu et al. 2018) or ion–dipole attraction to the exchangeable cations located within the interlayer (Sarier et al. 2010; Zhang et al. 2010).

The mechanism for the intercalation of anionic modifiers into Mnt, however, is still unsettled. Mnt modified by an anionic modifier ($OMnt_a$) is best prepared in an acidic medium (Zhang et al. 2010; Cao et al. 2015; Yu et al. 2018). Acidic conditions promote H^+ exchange as well as acid attack at charge sites in the layer structure, which leads to partial dissolution (Wallis et al. 2007; Liu et al. 2013; Yi et al. 2017). The attack of acidic Mnt may help the anions to penetrate between the layers.

Ca^{2+}-Mnt was modified by sodium dodecylsulfate (SDS) and octadecylcarboxylate (also known as sodium stearate, SSTA) in acidic medium by sonication (Zhang et al. 2010). The anionic modifiers expanded the basal spacing to 3.87 nm (Mnt-DS^-) and 4.80 nm (Mnt-STA^-) from 1.53 nm, thus proving that intercalation of anions into Mnt interlayer space was possible. A possible intercalation mechanism for anionic modification under acidic conditions is depicted in Fig. 3. The anions and the hydronium ions or the exchangeable cations in the interlayer of Mnt probably form ion pairs that allow the anions to enter the interlayer of Mnt. Ca^{2+}-Mnt was modified by Yu et al. (2018) using sodium laurylsulfonate/dodecylsofonate (SLS) in acidic medium (pH = 1) with vigorous stirring. The interlayer distance of the $OMnt_a$ increased to 1.52 nm from 1.21 nm. The chain of organic molecules may prefer a horizontal orientation relative to the Mnt surface. The anion may also have intercalated into the Mnt interlayer spaces by replacement of, or interaction with, hydroxyl groups at the Mnt layer edges. In acidic media, many hydroxyl groups can be present at the edges of Mnt due to electrostatic interactions with hydronium ions. The anion could, therefore, intercalate into the Mnt by replacing or interacting with hydroxyl groups in acidic media. 50 wt.% naphthalene sulfonic acid (NSA) was intercalated into Mnt using microwave irradiation (Riaz et al. 2011). Mnt modified with linear alkylbenzene sulfonic acid (LABSA) or sodium lauryl ether sulfate (SLES) had better hydrophilicity. The hydrophilicity of 5 wt.% LABSA/Mnt was less than that of 5 wt.% SLES/Mnt (Akbhyulut et al. 2012). The d_{001} values of $OMnt_a$ with 5 wt.% LABSA and 10 wt.% SLES were 1.501 nm and 1.496 nm, respectively (Akbulut et al. 2013).

$OMnt_a$ could be used for synthesis of OMnt/polymer nanocomposites (Sarier et al. 2010; Yu et al. 2018) as a scaffold for composites (Cao et al. 2015) or to assist in the avoidance of virus infection (Liang et al. 2014). $OMnt_a$ for the synthesis of OMnt/polymer nanocomposites possessed better dispersibility, greater antiwear property, and greater stability to thermal decomposition (Sarier et al. 2010; Yu et al. 2018). The onset degradation temperature of Mnt-3 wt.% SLS was increased by 30.1°C compared to pure Polystyrene (PS) (Yu et al. 2018). The coefficient of friction of the Mnt-3 wt.% SLS/PS particles as an additive to polyalphaolefin was 0.09, which means Mnt-3 wt.% SLS/PS nanocomposites are effective friction reduction and antiwear substances. $OMnt_a$, formed by modification by sodium salts of octadecanoic acid, would enhance thermal stability and dispersivity in the production of polyurethane (PU) nanocomposite foam (Sarier et al. 2010). The temperature of onset of thermal decomposition of 2 wt.% OMnt-SOD/PU moved to 238°C from 200°C for pure PU. $OMnt_a$ made by modification by sodium stearate (SST) enhanced the thermal stability and flame retardancy of polyurethane (Yi et al. 2017). The addition of Mnt-SST to PU reduced the peak heat-release rate of PU by 38%; this means that Mnt-SST can be used in

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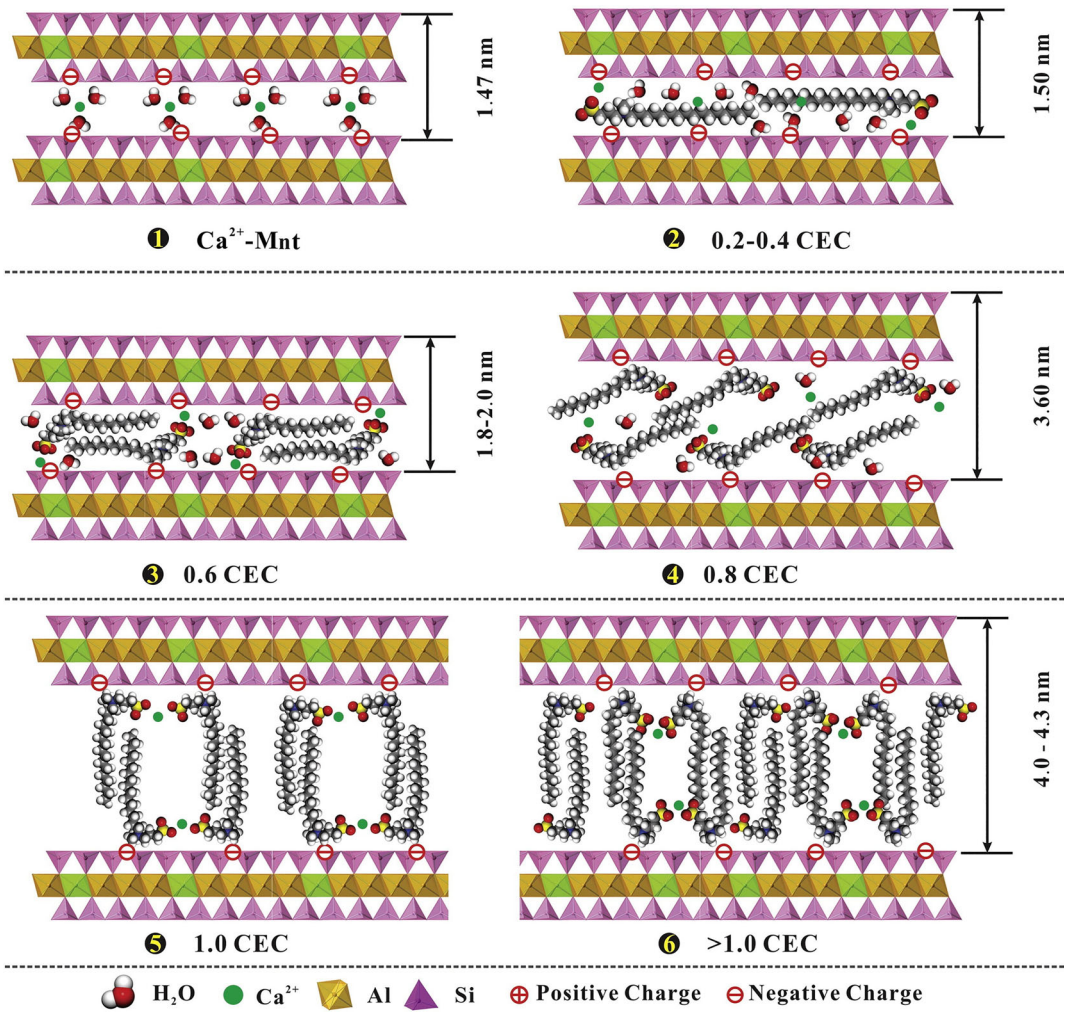


Fig. 4. Schematic diagram of the intercalation processes and mechanism of the zwitterionic modified Mnt (reproduced from Zhu et al. (2017), copyright 2017, with permission from Elsevier)

fire-proof material. $OMnt_a$ modified by sodium dodecyl sulfate interfered with viral binding and blocked infection by Japanese encephalitis, dengue virus, and influenza A virus through electrostatic interaction; this may provide a new way of developing novel antiviral nanomaterials (Liang et al. 2014). $OMnt_a$ can also improve the mechanical behavior, biodegradation, and biomineralization properties of chitosan-collagen/OMnt scaffold (Cao et al. 2015).

ORGANIC ZWITTERION-MODIFIED MONTMORILLONITE

Harnessing organo-cationic modifiers in biomedical applications is often hampered by the generally greater toxicity of cationic organic species, and the lack of biocompatibility evidence in biological fields (Wicklein et al. 2010). Modification of Mnt by zwitterions ($OMnt_z$) enhances the biocompatibility of OMnt and expands their applications into biological fields (Wicklein et al. 2010; Wang et al. 2018). Zwitterion modifiers contain both an organo-cationic hydrophobic group and an anionic hydrophilic group simultaneously. $OMnt_z$ can be obtained by cation exchange (Qi et al. 2008; Zhu et al. 2011), ion-dipole interaction (Zhu et al. 2017; Wang et al. 2019), or hydrogen bonding between end hydroxyl groups of the zwitterion and the siloxane surface of montmorillonite.

Different views exist on the reaction mechanism for modifiying Mnt with zwitterionic species. Some researchers hold that zwitterions can probably enter the interlayer of Mnt by exchanging with the inorganic cations in the interlayer space, or adsorbing on the surface due to their generally alkylammonium-based cationic group (Qi et al. 2008; Zhu et al. 2011). Zwitterions may also simply be adsorbed onto the Mnt surface due to electrostatic attraction between the positively charged group of zwitterions and the negative surface of Mnt, and not intercalate into the interlayer of Mnt (Ghafar et al. 2020). According to Zhu et al. (2017) and Wang et al. (2019), zwitterions are more likely

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to undergo bridging between Ca^{2+}-Mnt and zwitterion through ion–dipole interactions than through an exchange reaction. The ion–dipole interactions are generated between the hydrophilic head group and the negatively charged Mnt surface as well as the metal cations and the negatively charged component of the zwitterions (Fig. 4①). With small concentrations of 3-(N, N-dimethypalmitylammonio)propane sulfonate (SB16), $–SO_3$ groups of zwitterionic modifiers are closer to the interlayer surface of Mnt (Zhu et al. 2017). Due to negative $–SO_3$ groups not balancing all the Ca^{2+}, some Ca^{2+} ions are still bound to the negatively charged interlayer surface. With the zwitterionic modifier concentration increased, the terminating $–SO_3$ groups may be in the interlayer space. With the high zwitterionic modifier concentration, Ca^{2+} ions are removed from the interlayer surface due to two $–SO_3$ groups balancing one Ca^{2+} ion.

Zwitterionic modification also changes the physical characteristics of Mnt, such as the basal spacing (Zhu et al. 2011, 2014, 2017), hydrophobicity (Ma et al. 2016; Silva et al. 2017; Lazorenko et al. 2018), adsorption capacity (Eyama et al. 2012; Gu et al. 2015; Liu et al. 2016), and thermal stability (Zhu et al. 2011; Ma et al. 2015).

Zwitterions can be introduced into the interlayer space of Mnt (Soares et al. 2016; Wang et al. 2019). $OMnt_z$ was formed by modifying Mnt with dodecyldimethylbetaine (BS-12) or lauramidopropylbetaine (LAB-35) in an ultrasonic bath for 0.5 h and then transferred to a water bath at room temperature for 24 h (Wang et al. 2019). The arrangement of BS-12 in the interlayer of $OMnt_z$ was as a lateral monolayer and flat-lying bilayer; while the arrangements of LAB-35 in the interlayer of $OMnt_z$ was in a tilted way, perpendicular to the basal plane of the Mnt. Ciprofloxacin can be intercalated in the interlayer space of fluorohectorite, a synthetic smectite, at acidic pH (dos Santos et al. 2018).

The maximum basal spacing of $OMnt_z$ increased with increasing alkyl chain length of the zwitterionic modifier. $OMnt_z$ made by 0.8 CEC SB16 modifier had a maximum basal spacing of 4.37 nm. $OMnt_z$ made by 3.0 CEC 3-(N,N-dimethyldodecylammonio)propane sulfonate (SB12) and 2.5 CEC 3-(N, N-dimethylmyristylammonio)propane sulfonate (SB14) modifiers had maximum basal spacings of 4.13 nm and 4.23 nm (Fig. 5). $OMnt_z$ can achieve a larger interlayer spacing than $OMnt_c$ at the same modifier concentration. The maximum basal spacing of $OMnt_z$ (4.13 nm) was almost twice the maximum basal spacing of $OMnt_c$ made by dodecyl trimethylammonium bromide modifier (Zhu et al. 2011). The basal spacing of histidine-modified Mnt increased to 1.38 nm for an amino acid substituent with a ring structure from 1.14 nm for Na^+-Mnt (Songurtekin et al. 2013).

Zwitterionic modification also transforms the surface properties of Mnt from hydrophilic to hydrophobic (Ma et al. 2016; Lazorenko et al. 2018). Modification of Na^+-Mnt by hydroxyethylalkyl imidazoline (HEAI) and oleylmidopropylbetaine (OAPB) resulted in hydrophobization of the mineral surface. HEAI displaced more hydrated cations from Na^+-Mnt than OAPB, thereby promoting greater hydrophobicity of the Mnt surface. The wetting contact angles of $OMnt_z$ formed by HEAI modification increased from 37° to 83°, while the wetting contact angles of $OMnt_z$ formed by OAPB modification

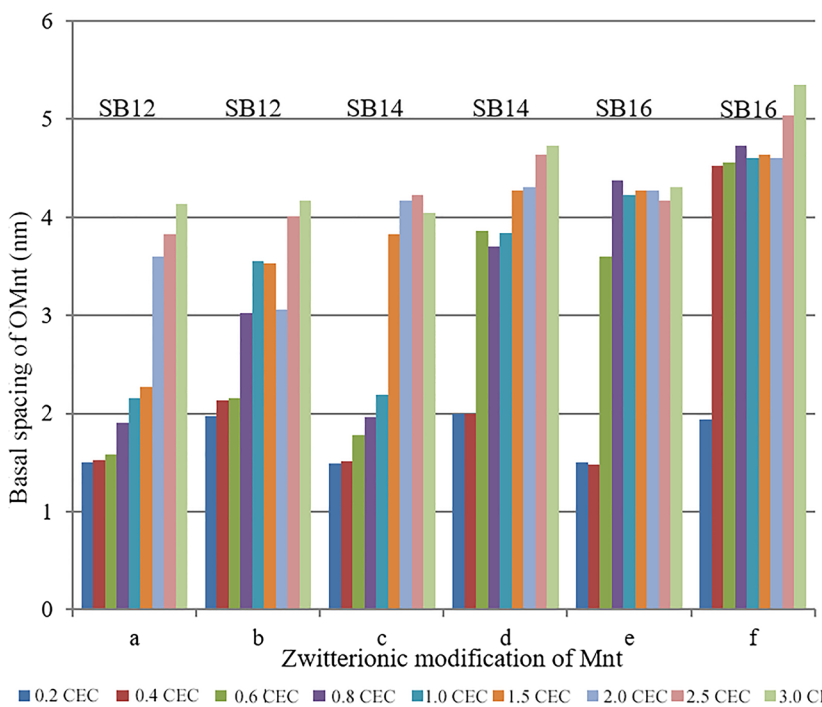


Fig. 5. The basal spacing of zwitterion-modified Mnt. **a**, **c**: (Zhu et al. 2011); **b**, **d**: (Zhu et al. 2017); **e**, **f**: (Zhu et al. 2014). SB12: 3-(N,N-dimethyldodecylammonio)propane sulfonate; SB14: 3-(N, N-dimethylmyristylammonio)propane sulfonate; SB16:3-(N,N-dimethylpalmitylammonio)propane sulfonate

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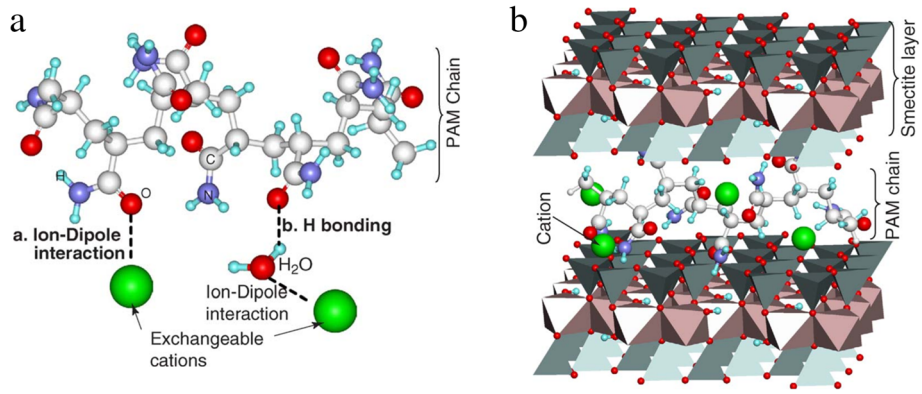


Fig. 6. a A conceptual model of major bonding between a polyacrylamide (PAM) chain and exchangeable cations in the interlayer of smectite; **b** A conceptual model of a non-ionic PAM-smectite complex with d_{001} spacing of ~1.5 nm. Water molecules are not shown (reproduced from Deng et al. (2006), copyright 2006, with permission from Elsevier). PAM: polyacrylamide

increased to only 47° from 37° (Lazorenko et al. 2018). $OMnt_z$ formed by hexadecyldimethyl(3-sulphonatopropyl)ammonium modification, however, had lower hydrophobicity than $OMnt_c$ formed by hexadecyltrimethylammonium bromide modification (Ma et al. 2016). The mechanisms by which zwitterionic phospholipids phosphatidylglycerol (PG) and phosphatidylethanolamine (PE) altered the hydrophobicity of montmorillonite were investigated by Kessenich et al. (2020). The PE can sorb onto the negatively charged montmorillonite surface, whereas negatively charged PG lipids cannot. On comparing PE and PG Mnt/lipid films, three characteristics were found to change Mnt/lipid film wettability: they must bind to the mineral surface, be solid at room temperature, and have a relatively continuous distribution throughout the film.

The alkyl chain length and the loading of zwitterionic modifier both influence the adsorptivity of the resulting $OMnt_z$ (Zhu et al. 2014; Gu et al. 2015; Wang et al. 2019). SB12-, SB14-, and SB16- Mnt were used by Zhu et al. (2014). When these modifier loadings were >1.8 CEC, the adsorbing ability of SB14-Mnt for nitrophenol and nitrobenzene was better than SB12-Mnt, but poorer than SB16-OMnt. The adsorption depends mainly on the distribution of the hydrophobic interaction between the zwitterionic alkyl chains. Further increase in the loading of zwitterionic modifier caused the adsorption of $OMnt_z$ formed by SB12 modification to increase with modifier levels. The adsorption of $OMnt_z$ formed by SB14 and SB16 modification, however, increased with modifier loading levels to a maximum then decreased. When the interlayer space of $OMnt_z$ was occupied by zwitterions, the adsorption capacity decreased because the steric effect of large zwitterions precluded further adsorption.

$OMnt_z$ could be used for the synthesis of OMnt/epoxy polymer nanocomposites (Soares et al. 2016), mycotoxin adsorbents (Wang et al. 2019), and contaminant adsorbents (Liu et al. 2016; Ma et al. 2016; Wang et al. 2019). The viscosity of the $OMnt_z$/epoxy polymer nanocomposites was increased significantly due to the dispersion of the $OMnt_z$ modified by zwitterionic imidazolium-based ionic liquid into the epoxy matrix (Soares et al. 2016). Moreover, the $OMnt_z$/epoxy polymer nanocomposites also presented very good transparency. $OMnt_z$ formed by BS-12 or LAB-35 modification used as adsorbents for mycotoxins were shown to simultaneously detoxify multiple polar and non/weak polar mycotoxins (Wang et al. 2019). This provides new insights into development of versatile mycotoxin adsorbents. $OMnt_z$, formed by modification of 3-(N,N-dimethylhexadecylammonio)propane sulfonate, had significant capacity to adsorb to anionic dye (methyl orange) and cationic herbicides (paraquat and amitrole) (Gu et al. 2015). It also indicated that $OMnt_z$ has potential in treating wastewater-containing anionic and cationic contaminants. $OMnt_z$ has simultaneously adsorptive properties for heavy metals and organic pollutants (Gu et al. 2015; Liu et al. 2016; Ma et al. 2016). The hydrophobic group of zwitterionic modifiers is beneficial in the adsorption of organic pollutants. The hydrophilic group of zwitterionic modifiers is beneficial in the adsorption of heavy metals. Mnt modified by amino acid, such as glycine and histidine, can immobilize the glucose oxidase on a glassy carbon electrode, applied to a biosensor to analyze catechol (Demir et al. 2014; Songurtekin et al. 2013). The synthesis of hydroxylapatite (HAP) in Mnt-modified 5-aminovaleric acid was presented by Ambre (2011). The nucleation mechanism of HAP may be due to chelation of the dissociated carboxylate groups with the calcium ions. The prepared material can be compounded with the chitosan to form chitosan/polygalacturonic acid (ChiPgA) composite films for culturing human osteoblast cells. Human osteoblasts were able to adhere to these films, form clusters on them, and exhibit good biocompatibility with them.

ORGANIC MOLECULE-MODIFIED MONTMORILLONITE

Mnt modified by organic, non-ionic species ($OMnt_n$) retain their original cation exchange capacity (CEC), resulting in $OMnt_n$ which can adsorb cationic compounds by cation exchange and polar molecules by ion–dipole and H-bonding interactions (Guégan et al. 2015). Organo-non-ionic modifiers adsorb onto surfaces and in the interlayer space of Mnt by hydrogen bonds, ion–dipole interaction, and electrostatic

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interactions (Guégan et al. 2019; Borrego-Sánchez et al. 2018; Wang et al. 2018; Hojiyev et al. 2017a).

Some non-ionic modifiers (e.g. nonpolar solvents) can be introduced easily into the interlayer space of Mnt due to their large dielectric values (Silva et al. 2014; Gates et al. 2016; Hojiyev et al. 2017a). The aqueous solution of OP-10 to Mnt suspension was introduced slowly using a peristaltic pump (Wang et al. 2018). The mixtures were treated for 0.5 h in an ultrasonic bath at 60°C, and then stirred for 24 h at room temperature. Non-ionic species were introduced successfully into the Mnt interlayer space. Hydrogen bonds can be formed between the polyoxyethylene ether chain of OP-10 and siloxane surfaces of Mnt. Non-ionic modifier octylphenolpolyoxyethylene ether (OP-10) can be intercalated into the interlayer of Mnt through hydrogen bonding. $OMnt_n$ modified by reacting Mnt with glycerol carbonate (GC) was prepared by Gates et al. (2016). First, oriented films of Na^+-Mnt were deposited under suction onto ceramic tiles from Mnt suspensions, followed by addition of GC solution to the wet Na^+-Mnt film and air-drying under ambient conditions for 3 h. GC interacted with the interlayer cations of Mnt through the carbonyl group, interacted with the interlayer surfaces of Mnt through its hydroxyl group. A loading of 100 wt.% GC (oven-dried Mnt basis) provided a highly ordered GC-Na^+-Mnt complex, but larger loadings resulted in layer stacking disorder. Loadings of <100 wt.% resulted in two distinct *d* values. A wide variety of OMnt complexes are possible with GC and its derivatives (Fehervari et al. 2016a, b) including polymeric-GC Mnt complexes (Shaheen et al. 2016). Na^+-Mnt was modified with octylphenylpolyoxyethylene ether (OPP) via wet ball-milling (Yan et al. 2020b) . During the wet ball-milling process, the Na^+-Mnt formed lattice defects easily under the forces of extrusion, collision, and friction, which favored the intercalation modification of OPP. The interlayer spacing of OMnt-OPP increased to 1.76 nm from 1.24 nm of Na^+-Mnt. Mnt was modified with tri-ethyleneglycolmono-n-decyl ether ($C_{10}E_3$) by Balme et al. (2013). The interlayer spacing of OMnt-$C_{10}E_3$ increased to 3.6 nm from 1.2 nm of Na^+-Mnt.

The probable bonding mechanisms between non-ion polyacrylamides (PAM) and Mnt were investigated by Deng et al. (2006). Their research found the ion–dipole interaction between the amide groups of the PAM and the exchangeable cations. Hydrogen bonding existed between the amide groups and water molecules in the hydration shells of exchangeable cations (Fig. 6). Similar observations by Gates et al. (2016), when intercalating Na^+-Mnt with glycerol carbonate (GC), indicated that strong ion–dipole interactions between the solvating GC and the interlayer cation were stable up to high salt concentrations but, at lower salt concentrations, H-bonding with interlayer water and the interlayer surface were important mechanisms. At very high salt concentrations, the $OMnt_n$-GC maintained a more swollen state and better hydraulic barrier performance (Fehervari et al. 2016a, 2016b). The adsorption of Ethomeen T/15 in the interlayer space of Mnt was modeled at the molecular level by Borrego-Sánchez et al. (2018) by computation. Hydrogen bonds formed between the H atoms of the modifier and the tetrahedral basal O atoms of the Mnt interlayer. These hydrogen bonds and the electrostatic interactions between cations and the phyllosilicate surface are the main driving forces of the adsorption.

Not all non-ionic modifiers can enter the interlayer space of Mnt. The basal spacing of $OMnt_n$, caused by OP-10 modification, increased to 4.26 nm from 1.45 nm (Zhuang et al. 2017b). The basal spacings of $OMnt_n$ made using Span-80 and Span-20 modifiers, however, were similar to Mnt (Table 2). This may mean that Span-80 and Span-20 fail to intercalate Mnt. The interlayer spacings of Mnt made by polypropylene glycol (PPG) 1200 and PPG 2000 modifiers remain unchanged within the range 0.25–2.00 CEC and remained below 2 nm (Ouellet-Plamondon et al. 2014). This is probably because some non-ionic modifiers inhibited intercalation. $OMnt_z$ shows a dual hydrophilic/hydrophobic character (Guegan et al. 2015). The contact angles of $OMnt_n$ formed by Span-80, Span-20, and OP-10 were 52, 50, and 33°, respectively (Zhuang et al. 2017b). However, the surface of $OMnt_n$ made using polyvinylpyrrolidone as a modifier became more hydrophilic (Hojiyev et al. 2017a).

$OMnt_n$ can be used in drug carriers (Yan et al. 2020b), as adsorbents of cationic compounds (Wang et al. 2017a), in the oil industry (Cardoso et al. 2012; Ouellet-Plamondon et al. 2014; Silva et al. 2014), and in geosynthetic clay liners (GCLs) (Fehervari et al. 2016a, 2016b; Shaheen et al. 2016). Plysorbate 20-modified Mnt nanocomposite material was applied as a drug carrier for the inhibition of intestinal efflux transporters. OMnt-OPP can enhance adsorption capacity for ibuprofen and exhibit well controlled release properties (Yan et al. 2020b). $OMnt_n$ formed by OP-10-modified OMnt had a significant adsorptivity for the cationic organic dye methylene blue (MB) due to the remaining cation exchangeability (Wang et al. 2017b). The polyoxyethylene ether chains of OP-10 can form hydrogen bonding with MB molecules, further improving the adsorptivity of MB. $OMnt_n$ is a potential adsorbent for simultaneous detoxification of polar and non-polar mycotoxins. $OMnt_n$ formed by ultramine 50 (TA50) had 100% swelling in diesel oil and kerosene (Silva et al. 2014). This means that $OMnt_n$ made in this way is suitable for use in organic-based drilling fluids. In addition, $OMnt_n$ is used as a swelling inhibitor in the oil industry (Cardoso et al. 2012; Silva et al. 2014). $OMnt_n$ formed by PPG modification acts as an intercalation inhibitor, limiting further expansion of the basal spacing (Ouellet-Plamondon et al. 2014). $OMnt_n$ has been considered for use in geosynthetic clay liners (GCLs) of hypersaline leachates (Fehervari et al. 2016a, 2016b; Shaheen et al. 2016). $OMnt_n$ formed by GC minimizes adverse effects associated with the loss of water from the interlayer space of Mnt as well as Ca^{2+}-for-Na^+ exchange in the hypersaline leachates (Fehervari et al. 2016a, 2016b). $OMnt_n$ formed by modification of OMnt by cyclic carbonate polyether, Poly(4-((oxiran-2-ylmethoxy)methyl)21, 3-dioxolan-2-one) (POMD), strengthened the hydraulic barrier capabilities of sodium bentonite to 3 M sodium chloride solution (Shaheen et al. 2016).

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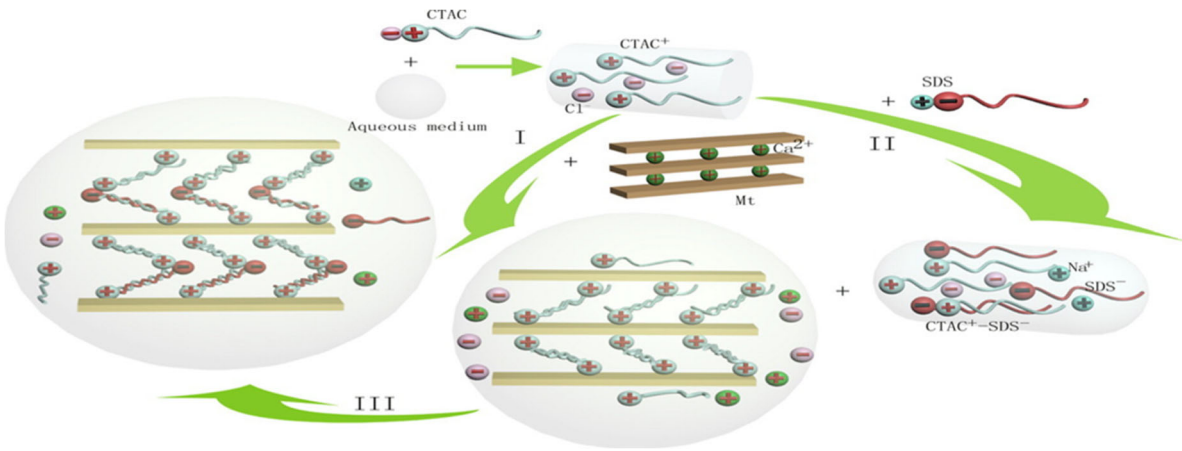


Fig. 7. Schematic illustration of the formation of CTA^+ and DS^- co-intercalated OMnt by the two-step method (reproduced from Fu et al. (2016), copyright (2016), with permission from Elsevier). CTA^+: cetyltrimethylammonium; DS^-: dodecyl sulfonate

Table 2. Recent, typical methods and results of Mnt modified by nonionic organic molecules

Mnt	CEC (mmol/100 g)	Modifier	Modifier concentration	d_{001} (nm)	Water contact angle θ (degrees)	References
Mnt	64.13	OP-10	0.25 CEC	1.53		(Wang *et al.* 2017a)
			0.5 CEC	1.56		
			0.75 CEC	1.69		
			1.0 CEC	1.84		
			1.5 CEC	1.86		
	120	Span-80	1.0 CEC	1.43	52	(Zhuang *et al.* 2017b)
		Span-20	1.0 CEC	1.45	50	
		OP-10	1.0 CEC	4.26	33	
	68.29	OP-10	0.5 CEC	1..56		(Wang *et al.* 2018)
			1.0 CEC	1.84		
			2.0 CEC	1.88		
Na^+-Mnt	80	Ethomeen T/15	0.1g/L	1.44		(Borrego-Sánchez *et al.* 2018)
			0.6g/L	1.72		
			1.0g/L	1.82		
			3.0g/L	1.96		
			5.0g/L	1.97		
			10.0g/L	2.11		
	112	EA	0.5 CEC	1.49	31.7	(Zhou *et al.* 2019)
			0.75 CEC	1.46	73.9	
			1.0 CEC	1.45	99.2	
			1.25 CEC	1.47	101.2	
			1.5 CEC	2.03	101.5	
		OA	0.5 CEC	1.43	28.9	
			0.75 CEC	1.4	35.8	
			1.0 CEC	1.33	37.6	
			1.25 CEC	1.45	42.2	
			1.5 CEC	1.93	59.5	

*EA: erucamide; OA: oleamide; OP-10: octylphenolpolyoxyethylene ether.

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TWO MODIFIERS IN CO-MODIFIED MONTMORILLONITE

Mnt can be co-modified by two (or more) organic modifiers. The mixtures of various types of modifiers exhibit different properties compared with the corresponding single modifiers, and can cause synergistic effects in both the liquid and solid systems (Sehgal et al. 2009; Zhang et al. 2012b). The types of modifiers used for Mnt co-modification are usually combinations of cations and anions (Zhang et al. 2012b, 2013), of cations and non-ionic species (Fan et al. 2015; Yin et al. 2015), and of anions and non-ions species (Zhang et al. 2012a).

Cation and anion co-modified OMnt can be prepared by one-step (Fu et al. 2016) or two-step methods (Chen et al. 2011; Zhang et al. 2013; Wu et al. 2014b; Fu et al. 2016). A one-step method can be used to mix an aqueous solution of cationic and anionic modifiers in Mnt dispersions. A two-step method involves adding aqueous solutions of one modifier to aqueous dispersion of Mnt first and reacting for some time, then adding aqueous solution of another modifier. The addition sequence of CTAC and SDS had an impact on the intercalation reaction, as did the choice of method. The simultaneous intercalation of CTA^+ and DS^- resulted in a sample with the largest basal spacing using the one-step method. The intercalation in which CTAC was added first resulted in a sample with larger basal spacing than that where SDS was added first. A co-modified mechanism resulting from the two-step method was proposed by Fu et al. (2016) (Fig. 7). Firstly, cations entered the interlayer of Mnt by ion exchange and formed an organic environment which then allowed CTA^+-DS^- ion-pairs to form within the Mnt layer. DS is presumed to enter the interlayer as neutralized molecules (e.g. DS^--Na^+) due to the concentration difference. The addition of CTAB to SDS was considered by Zheng et al. (2013) to decrease the negative charge density and charge repulsion of the anion. Thus, CTAB-SDS could interact with Mnt and intercalate into the interlayer space of Mnt.

Cation and non-ionic co-modified Mnt was prepared by the one-step method (Zhang et al. 2012a; Fan et al. 2015; Yin et al. 2015; Zhou et al. 2019). CTAB and OP-10 were added to the Mnt dispersion (Yin et al. 2015) and then sonicated at 40–60°C for 1 h. The CTA^+-OP-10-Mnt had a larger basal spacing than either CTA^+-Mnt and OP-10-Mnt. The change in the order of addition of CTAB and OP-10 had an insignificant effect on the basal spacing of CTAB-OP-10-Mnt. The hydrophobicity decreased with increases in OP-10 at a fixed concentration of CTAB. The hydrophobicity of CTA^+-OP-10-Mnt was greater than OP-10-Mnt and less than CTA^+-Mnt. The contact angles of CTA^+-OP-10-Mnt, OP-10-Mnt, and CTA^+-Mnt were 61.5, 30.5, and 65.5, respectively. Zhang et al. (2012b) presented a schematic diagram for the adsorption of cation-non-ionic mixed modifiers onto Mnt (Fig. 8a). At lower concentrations, both modifiers were adsorbed on the Mnt surface through electrostatic interaction and hydrogen bonding. Because the electrostatic attraction for the adsorption of cationic molecules is usually stronger than hydrogen bonding, a cationic modifier could be adsorbed more than a non-ionic modifier. At intermediate concentrations, the pre-adsorbed cationic molecules acted as anchors and more non-ionic species adsorbed through a hydrophobic chain–chain reaction and formed the mixed aggregates at the solid/liquid interface. At higher concentrations, the amount of non-ionic organic species adsorbed decreased with increases in concentration of cationic organic ions. Octadecyltrimethylammonium ($ODTMA^+$) cations and the non-ionic erucamide (EA) were co-introduced by Zhou et al. (2019) into OMnt. A two-stage intercalation was proposed: cation exchange of $ODTMA^+$ to form a paraffin-type monolayer in the interlayer space of Mnt, followed by hydrophobic entropy-driven adsorption of non-ion EA by

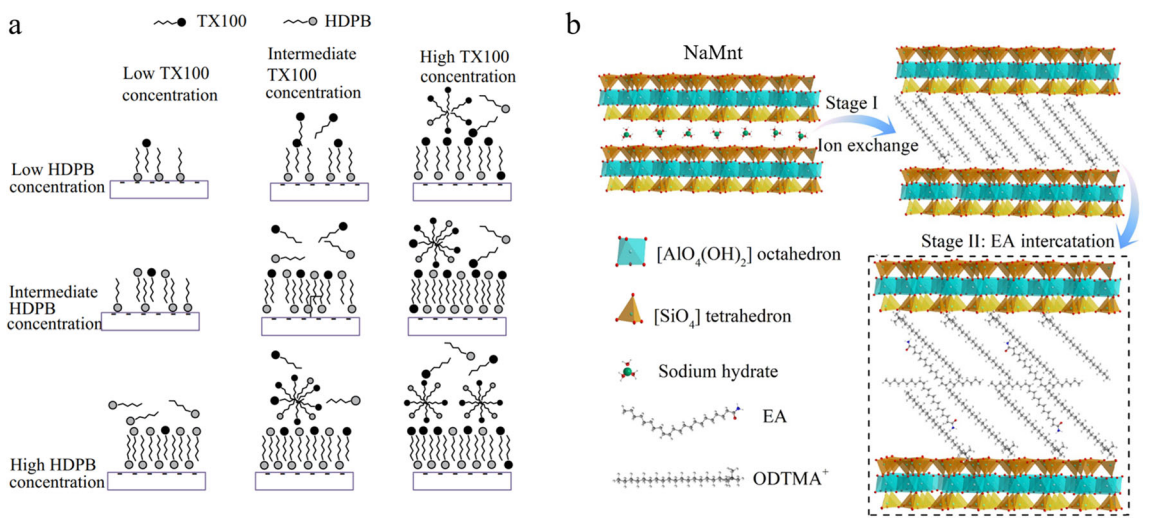


Fig. 8. Schematic illustration of the formation of **a** HDPB and TX100 co-intercalated Mnt (reproduced from Zhang et al. (2012b), copyright 2012, with permission from Elsevier); **b** $ODTMA^+$ and EA co-intercalated Mnt (reproduced from Zhou et al. (2019), copyright 2019, with permission from Elsevier). EA: erucamide; $HDPB^+$: hexadecylpyridinium; $ODTMA^+$: octadecyltrimethylammonium; TX100: Triton X-100

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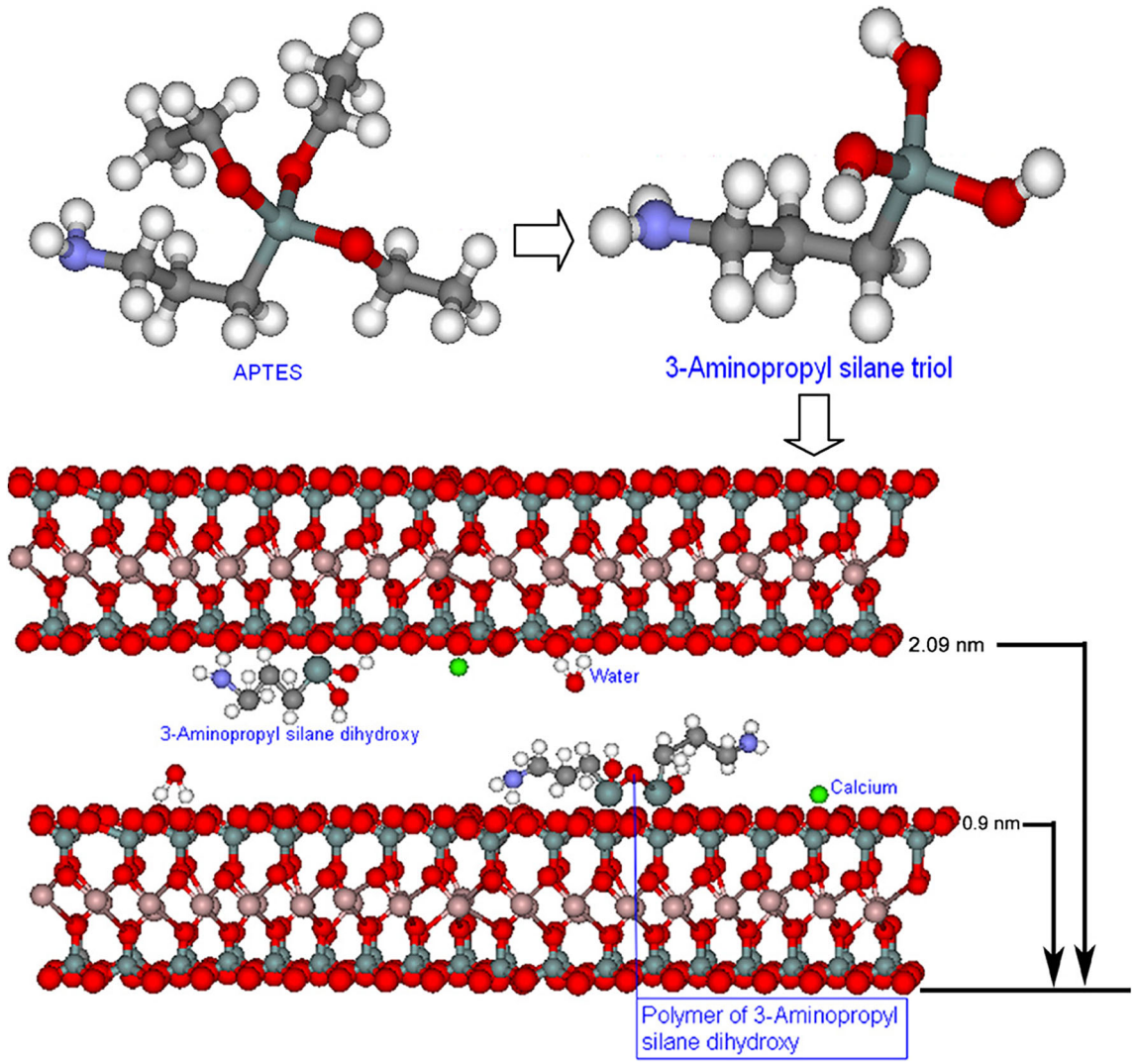


Fig. 9. Simulation of the grafting process of APTES to Ca^{2+}-Mnt (reproduced from Wu et al. (2012), copyright 2010, with permission from Elsevier)

intertwining organic chains into the interlayer spaces of the OMnt (Fig. 8b).

Anionic and non-ionic co-modified Mnt was produced following a one-step method. Non-ionic OP-10 and anionic sodium stearate (SSTA) were modified using a ball mill (Zhuang et al. 2015). The basal spacing of Mnt modified by an anionic-non-ionic modifier increased with increasing dosage of anionic modifier, in the case of fixed non-ionic dosage. The basal spacing of anion-nonionic-Mnt decreased as dosage of anionic modifier increased when the dosage of anion modifier is more than 1.0 CEC. The hydrophobicity of 0.9 CEC STA^--0.7 CEC OP-10-Mnt was better than that of 0.7 CEC OP-10 –Mnt and Ca^{2+}-Mnt (Table 3). Anionic modifiers were absorbed by OP-10 as the alkyl tails entwined with each other and formed molecular braids. The non-ionic modifier enters into the interlayer space of Mnt through the hydrogen bond with Mnt and thus expands the basal space of Mnt (Zhang et al. 2012a; Zhuang et al. 2015). The anionic-non-ionic modified Mnt can be used for the remediation of soils and groundwater contaminated by hydrophobic organic compounds (Chen et al. 2011; Zhang et al. 2012a). The mixture of anionic and cationic modifiers can form mixed micelles, which can synergistically solubilize organic compounds. This can improve the adsorption of organic compounds (Sehgal et al. 2009; Chen et al. 2011). The 1.0 CEC $CTMA^+$-0.1 CEC STA^--Mnt had greater adsorption of methyl orange than did 1.0 CEC $CTMA^+$-Mnt and 0.1 CEC STA^--Mnt (Chen et al. 2011). The cationic-non-ionic modified Mnt can be used as a fluid-control additive in oil-drilling engineering due to its excellent dispersibility in white oil (Fan et al. 2015). The anionic-non-ionic modified Mnt also expanded the application range of OMnt in the areas of paint and ink because of better dispersion in highly polar solutions (Yin et al. 2015). Cation-non-ion-modified Mnt has been investigated as a carrier for loading and controlled-release of hydrophobic drugs (Yan et al. 2020a). CTA^+-NPE-Mnt and alginate were constructed

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Table 3. Typical, recent methods and results of coupled modifier-modified Mnt

Mnt	CEC (mmol/100 g)	Modifier	Modifier concentration	d_{001} (nm)	Water contact angle θ (°)	Swell index (%)	Reference
Mnt	78	SDS and CTAC	1.5 CEC CTAB-0.9 CEC SDS	4.46	34	18(in xylene) 35(in butanol + xylene)	(Zhou *et al.* 2016a)
			1.0 CEC CTAC-0.5 CEC SDS	4.71	37	16(in xylene) 32(in butanol + xylene)	
			0.6 CEC CTAC-0.5 CEC SDS	1.53	41	12(in xylene) 25(in butanol + xylene)	
Ca^{2+}-Mnt	90	SDS and OP-10	1.0 CEC SDS-0.7 CEC OP-10 1.5 CEC SDS-0.7 CEC OP-10	5.15 3.7	57		(Zhuang *et al.* 2015)
			0.9 CEC SSTA-0.7 CEC OP-10	5.15	69.5		
			1.5 CEC SSTA-0.7 CEC OP-10	4.3			
	106	SDS and CTAC	1.3 CEC CTAC-0.7 CEC SDS 1.3 CEC CTAC-1.0 CEC SDS	3.98 4.26			(Fu *et al.* 2016)
			1.3 CEC CTAC-1.3 CEC SDS	5.13			
Na^{+}-Mnt		CTAB and SDS `	1.0 CEC CTAB–1.5 CEC SDS 1.2 CEC CTAB–1.5 CEC SDS `	6.30 6.21	23 29		(Sun *et al.* 2016)
			1.8 CEC CTAB–1.5 CEC SDS	5.30	44		
	80	DTAB and SDBS	1.0 CEC DTAB –0.2 CEC SDBS 1.0 CECDTAB –0.4 CEC SDBS	1.8 5.57	51 42.5		(Zhou *et al.* 2016b)
			1.0 CEC DTAB –0.6 CEC SDBS	5.96	39		
			1.0 CEC DTAB –0.2 CEC SDBS	5.73	40		
			1.5 CEC DTAB –0.2CEC SDBS	4.91	53.5		
			1.5 CEC DTAB –0.4 CEC SDBS	5.32	46.5		
			1.5 CEC DTAB –0.6 CEC SDBS	5.32	44.5		
			1.5 CEC DTAB –0.2 CEC SDBS	5.96	42		
			2.0 CEC DTAB –0.2 CEC SDBS	3.71	50.5		
			2.0 CEC DTAB –0.4 CEC SDBS	3.80	53.5		
			2.0 CEC DTAB –0.6 CEC SDBS	3.84	42		
			2.0 CEC DTAB –0.2 CEC SDBS	4.46	41.5		
			2.5 CEC DTAB –0.2 CEC SDBS	3.77	47		
			2.5 CEC DTAB –0.4 CEC SDBS	3.91	51.5		
			2.5 CEC DTAB –0.6 CEC SDBS	3.91	46		
			2.5 CEC DTAB –0.2 CEC SDBS	3.89	45		
		FTMA and Tween 80	0.6CEC FTMA-0CMC Tween 80	1.78			(Hu *et al.* 2017)

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Table 3. (continued)

Mnt	CEC (mmol/100 g)	Modifier	Modifier concentration	d_{001} (nm)	Water contact angle θ (°)	Swell index (%)	Reference
			0.6CEC FTMA-10CMC Tween 80	1.76			
			0.6CEC FTMA-20CMC Tween 80	1.84			
			0.6CEC FTMA-50CMC Tween 80	2.02			
	112	ODTMAC and EA	1.0 ODTMA*-0.5 EA	2.05	61.7	100 (in xylene)	(Zhou *et al.* 2019)
			1.0 ODTMA-0.75 EA	4.07	83.3	100 (in xylene)	
			1.0 ODTMA-1.0 EA	4.18	85.2	100 (in xylene)	
			1.0 ODTMA-1.25 EA	3.99	85.9	100 (in xylene)	
			1.0 ODTMA-1.5 EA	3.98	93.6	100 (in xylene)	
			1.0 ODTMA-1.75 EA	4.22	97.9	100 (in xylene)	
		ODTMAC and OA	1.0 ODTMA-0.5 OA	4.2	56	34 (in xylene)	
			1.0 ODTMA-0.75 OA	4.24	59.8	39 (in xylene)	
			1.0 ODTMA-1.0 OA	4.22	61.1	42 (in xylene)	
			1.0 ODTMA-1.25 OA	4.07	67	50 (in xylene)	
			1.0 ODTMA-1.5 OA	4.24	67.5	56 (in xylene)	
			1.0 ODTMA-1.75 OA	4.19	69.6	60 (in xylene)	

*CTAB: cetyltrimethylammonium bromide; HDTMAB: hexadecyltrimethylammonium bromide; CTAC: hexadecyltrimethylammonium chloride; HDTMAC: hexadecyltrimethylammonium chloride; DTAB: dodecyltrimethylammonium bromide; EA: erucamide; FTMA: (11-Ferrocenylundecyl)trimethylammonium bromide; OA: oleamide; STAC: octadecyltrimethylammonium chloride; ODTMAC: octadecyltrimethylammonium chloride; SDBS: sodium dodecylbenzene sulfonate; SDS: sodium dodecyl sulfonate.

to provide OMnt/Alg composite hydrogel beads. These composite hydrogel beads improved the stability of the drug carrier and its sustained release effect. The OMnt/Alg composite hydrogel beads displayed superior sustained-release properties for Na-Mnt/Alg, mainly ascribed to the good affinity of OMnt for hydrophobic drugs which retarded the drug diffusion.

ORGANIC GRAFTING-MODIFIED MONTMORILLONITE

OMnt is frequently used for the preparation of clay/polymer nanocomposites (CPN). Mnt modified by organosilane grafting ($OMnt_g$) enhanced the interfacial compatibility with a polymer. In addition, the modifiers in OMnt may leach into the surrounding solution when the OMnt are used in solution. This decreases the performance of OMnt and potentially limits its application in remediation of water pollution (Bertuoli et al. 2014). Modification of Mnt by grafting is an effective method to solve this problem. $OMnt_g$ is obtained by organosilane grafts bonding covalently to the surfaces as well as the interlayer space and the edges of Mnt (Bee et al. 2018).

Mnt is modified commonly by grafting through the emulsion polymerization method. Mnt was dispersed (Thue et al. 2018) in a solution of ethanol and ammonia at pH 10–11.5. Then, 3-triethoxysilylpropylamine (APTES) was added and stirred under reflux for 24 h until a brown product was formed. The addition of ammonia solution to the reaction led to the rapid hydrolysis and polymerization of APTES onto the surface and broken edges of Mnt and into its interlayer space. The triethoxysilane of APTES hydrolyzed first in the solvent, and then –OH connected to Ca^{2+}-Mnt (Fig. 9) (Wu et al. 2012).

The basal spacing of the $OMnt_g$ is related to the location of grafted organosilane (Silva et al. 2011), the number of functional groups present in the organosilane (Shen et al. 2007; Bruce et al. 2014), and chain length of the organosilane (Piscitelli et al. 2010; Varadwaj et al. 2016). Grafting into the interlayer space of Mnt increased the basal spacing (Silva et al. 2011). Grafting on the broken edges and external surface shows less change in basal spacing. The number of functional groups also determined the basal spacing of silylated Mnt (Shen et al. 2007; Bruce et al. 2014; Sepehri et al. 2014). Trifunctional APTES-grafted Mnt showed a larger basal spacing compared to the monofunctional trimethylchlorosilane-grafted Mnt (Shen et al. 2007). However, Sepehri et al. (2014) observed that the basal spacings of monofunctional dimethylchlorovinylsilane-grafted Mnt are larger than those of trifunctional trichlorovinylsilane-grafted Mnt. Trifunctional silanes may interact with each other and form siloxane bridges which prevent the penetration of other silane molecules into the interlayer space. Similarly, trifunctional silane was shown by Bruce et al. (2014) to have a tendency to exhibit a pillaring effect between adjacent Mnt layers which fixed and restrained the interlayer height. This pillaring effect fixes the interlayer height so it does not change upon intercalation of other species. The basal spacing of $OMnt_g$ also varies with the chain length of the organic silane moieties (Piscitelli et al. 2010; Varadwaj et al. 2016). Increasing the chain length of the silane resulted in a decrease in the basal spacing of the host material (Piscitelli et al. 2010). The basal spacing of Mnt grafted by 3-aminopropyltriethoxysilane with a short chain was greater than Mnt grafted by 3-[2-(2-aminoethylamino)ethylamino]-propyltrimethoxysilane with a long chain. The long chains of silane interacted with each other to form siloxane bridges due to intermolecular hydrogen bonding and hydrophobic interactions. The siloxane bridge fixes the interlayer height of the Mnt-grafted by 3-aminopropyltriethoxysilane.

$OMnt_g$ could be used for synthesis of OMnt/polymer nanocomposites (Theng 2012; Daitx et al. 2015; Scarfato et al. 2016) and contaminant adsorbents (Silva et al. 2011; Parolo et al. 2014; Thue et al. 2018). Organosilanes serve as a bridge to enhance the interfacial interaction between the silylated-OMnt, thus enabling better dispersibility of the $OMnt_g$ in the polymer matrix (Theng 2012). For example, 3-(glycidyloxypropyl)trimethoxysilane is able to bond chemically with certain polymers such as epoxy matrices using their epoxy functional group (Scarfato et al. 2016). This can greatly enhance the mechanical property of OMnt/polymer nanocomposites (Bruce et al. 2014). In addition, $OMnt_g$ modified by APTES adsorbed significant amounts of acid red 1 and acid green 25, 97.94% and 95.94%, respectively (Thue et al. 2018). Those authors proposed that this $OMnt_g$ adsorbent presented good applicability for the treatment of synthetic wastewaters; they also proposed that this $OMnt_g$, with significant hydrophilic properties, can open a new window for applications in the coating, self-cleaning, or humidity control industries.

SUMMARY AND REMARKS

Great progress has been made in the preparation, property assessment, characterization, and application of OMnt over the past 10 years. Organic cations were the most frequently used materials for the modification of Mnt up to 15 years ago. For the past 10 years, organic anion, zwitterion, and non-ionic molecules have been used for modification of the surface properties of Mnt. The combination of two modifiers can exhibit synergistic effects providing new opportunities for OMnt. Organosilane can also modify Mnt by grafting.

Organic cations can be intercalated easily into Mnt interlayer spaces by a cation exchange reaction. Anionic species have been intercalated successfully into the interlayer space of Mnt through ion–dipole interaction in acidic medium. Zwitterions and non-ionic species can intercalate into the interlayer space of Mnt by ion–dipole, hydrogen bond, and van der Waals force interactions. The co-intercalation of Mnt by two modifiers is relatively complicated. The alkyl tails of anionic and non-ionic molecules become entangled with the cation alkyl tails and form ion-pairs. Thus, anionic and non-ionic species can co-intercalate with cations into the interlayer space of Mnt. Non-ionic and anionic modifiers can co-intercalate efficiently into the interlayer space of Mnt if non-ionic modifiers entwine with anionic modifiers and form molecular braids. $OMnt_g$ is obtained by covalently binding organosilane to the surface and edge of Mnt. The modification mechanisms of OMnt continue to be debatable, especially non-ionic and

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zwitterion modification. The detailed interaction between organics and Mnt at the molecular or atomic level remain unclear or even unknown.

OMnt has been commercialized in applications such as drilling fluids, paints, and environmental adsorptive materials for more than 10 years. During the past decade, exfoliation of OMnt with nano-assembly has been used to create more functional materials. This clean, time-saving, non-toxic, and environmentally friendly way of producing such materials needs to be explored further. In addition to adsorbents, rheology controllers, and multifunctional materials, recent interests are in the uses of OMnt for catalysis, drug carrying, and biomaterials, and these areas remain open to exploration by means of organic modification of Mnt.

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Compliance with Ethical Statements

Conflict of Interest

The authors declare that they have no conflict of interest.

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