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Research paper

Clay-polystyrene nanocomposite from pickering emulsion polymerization stabilized by vinylsilane-functionalized montmorillonite platelets

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ABSTRACT

Controlling the chemical nature and functionality of a Pickering stabilizer in surfactant-free emulsion polymerization plays a salient role in the nucleation and growth of latex particles. Silane-functionalization of montmorillonite (Mt) platelets is expected to tune the partition behavior of the clay platelets toward a monomer phase and enhance their stabilizing ability in oil-in-water (o/w) system. Such fabrication should result in prompted heterogeneous coagulative nucleation of latex particles, and therefore, drive a fabrication of clayhydrophobic polymer latex nanocomposites.

In this paper, Pickering emulsion polymerizations of styrene and n-butyl acrylate, stabilized by Mt. platelets onto which various silane agents were chemically grafted, were formulated. Along with characterizations of silane-functionalization on Mt. platelets, a kinetic study on the clay-polymer latexes was performed via a dy-namic light scattering method and morphological observations. Polystyrene latex particles stabilized by the silane-functionalized Mt. platelets showed faster heterocoagulative nucleation even at the early stage of particle formation, owing to their attractive interaction with the monomer. The secondary participation of vinyl moieties on the Mt. platelets in radical reactions was followed, and it reinforced the adsorption behavior via covalent linkages. This is the first report that presented kinetic evidence of an attractive interaction between hydrophobic monomers and silane-functionalized Mt. platelets which led to the formation of a clay-latex clustered structure.

1. Introduction

The fabrication of organic-inorganic hybrid materials has recently attracted attention by virtue of their tailored features that have been facilitated through the incorporation of hard inorganic fillers in soft polymeric materials. In particular, polymer-silica and clay-polymer nanocomposite (CPN) has been extensively researched in the last few years. One promising way to overcome the weak interaction between the polymer matrix and inorganic fillers is introducing the inorganic fillers into emulsion polymerization in situ so that a sufficient degree of dispersion and intercalation within the CPN can be achieved owing to the swelling behavior of clay minerals (Sposito et al., 1999). Among the methods that have been exploited for fabricating CPN, surfactant-free emulsion polymerization employs clay platelets as so-called Pickering stabilizers. Thanks to their higher specific surface area and surface charge density, clay platelets effectively stabilize latex particles in surfactant-free emulsion polymerization (Bon and Colver, 2007).

Moreover, the anisotropic morphology of many layered clay minerals provides an additional stability at liquid interfaces (Machado et al., 2019). Thereby, various inorganic materials have been reported as Pickering stabilizers, including silica nanoparticles (Zhang et al., 2009; Li and Stöver, 2010; Ma et al., 2010; Ji et al., 2014; Monégier du Sorbier et al., 2016; Zhao et al., 2016; Li et al., 2018), kaolinite (Ferreira et al., 2017; Liang et al., 2018; Cai et al., 2019), Laponite (Teixeira et al., 2011; Guimarães et al., 2014; Delafresnaye et al., 2017; Morgen et al., 2018), halloysite (Cavallaro et al., 2019), and montmorillonite platelets (Yilmaz et al., 2010; Bonnefond et al., 2013). By using the Pickering emulsion technique, the clay-armored polymer latexes are simultaneously formulated since the solubilized inorganic materials are drawn to the oil-and-water interface, minimizing the interfacial surface tension. However, the CPN from hydrophobic monomers are very unlikely to gain on account of a highly polar nature of clay platelets with a lower wettability toward the oil(monomer)-phase, and it results in insufficient adsorption of the monomer onto clay

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Table 1

Characteristics of various	silane-functionalized Mts v	with different amounts	of initial input of silane agents.

Run	Abbreviation	Silane Agents	Initial Silane Input [mmol g _{clay} ⁻¹]	Silane Grafted Amount ^a [mmol g_{elay}^{-1}]	d _p ^b [μm] (PdI)	Zeta Potential ^c [mV]	$\log(K_{sw})^{d}$
1	C.Pristine	_	-	-	0.24 (0.35)	-41.8	-
2a	C.ETMS(1)	Ethyltrimethoxysilane (ETMS)	1	0.70	2.94 (0.51)	- 36.7	0.65
2b	C.ETMS(2)		2	1.60	64.27 (0.59)	- 36.6	1.07
2c	C.ETMS(5)		5	3.60	64.08 (0.59)	- 37.3	1.66
2d	C.ETMS(10)		10	7.97	59.20 (0.59)	- 37.5	1.75
3a	C.VTMS(1)	Vinyltrimethoxysilane (VTMS)	1	0.34	1.41 (1)	- 35.0	0.21
3b	C.VTMS(2)		2	0.59	1.64 (0.98)	- 36.6	0.73
3c	C.VTMS(5)		5	2.23	37.41 (0.80)	- 38.8	1.58
3d	C.VTMS(10)		10	3.17	75.88 (0.81)	- 39.1	1.86
4a	C.DMEVS(1)	Dimethylethoxyvinylsilane (DMEVS)	1	0.14	1.35 (1)	- 35.1	-0.88
4b	C.DMEVS(2)		2	0.16	1.34 (0.95)	- 34.6	-0.72
4c	C.DMEVS(2)		5	0.15	1.36 (0.91)	-34.4	-0.51
4d	C.DMEVS(10)		10	0.19	1.44 (0.97)	- 33.1	-0.45
5a	C.ATMS(1)	Allyltrimethoxysilane (ATMS)	1	0.83	2.01 (1)	- 35.2	0.10
5b	C.ATMS(2)		2	1.35	5.04 (1)	- 34.9	1.02
5c	C.ATMS(5)		5	2.40	54.04 (0.51)	- 35.3	1.42
5d	C.ATMS(10)		10	4.62	63.09 (0.60)	- 35.5	1.48

^a Determined by elemental analysis on the basis of the difference between the carbon contents of the pristine and silane-functionalized clay platelets (see Supplementary materials for details).

^b Particle size and polydispersity index of clay platelets dispersed in water, determined by DLS.

^c Determined by zeta potential measurement.

^d Styrene/water partition coefficient determined by gravimetric analysis on the relative concentration of the clay platelets dissolved within the two immiscible phases, styrene and water (see Supplementary materials for details).

surface (Björkegren et al., 2017). To enhance the chemical affinity and favorable interactions between them, chemical modifications of the clay platelets must take precedence. In this context, silane-functionalization, grafting organosilane molecules onto the clay platelets via covalent bonds, asserts its superior durability and reliability even in emulsion polymerization conditions by its chemical stability of siloxane bonds.

Silane-functionalization takes place at interlayer spaces and external surfaces of clay platelets, and frequently at the broken edges of the clay platelets (Asgari et al., 2017). The hydroxyl groups on clay platelets react with silane coupling agents containing hydrolyzable alkoxy groups that form siloxane bonds through hydrolysis and subsequent condensation reaction. The reaction is completed after the available sites for the adsorption and intercalation of the silane coupling agents on the clay platelets are depleted (He et al., 2013). Successful silane-functionalization immensely stretches the basal spacing between clay platelets; hence a consequent increment in the intercalation of bulky polymeric materials between the clay platelets can be achieved (He et al., 2005). To the best of our knowledge, only a small number of studies have employed silane-functionalized Laponite (Herrera et al., 2004; Bourgeat-Lami et al., 2005), kaolinite (Liang et al., 2018), and montmorillonite platelets (Lanchis et al., 2009) in surfactant-free emulsion polymerization. Also, studies on the behavior of silane-functionalized Mt. platelets in the o/w emulsion polymerization and their role in latex particle formation remained inconclusive. Herein, we report surfactant-free emulsion polymerizations stabilized by silane-functionalized Mt. platelets as Pickering stabilizers. Through a comparative evaluation of the stabilizing abilities of different types of Mt. platelets and the morphological observation of the latex particles at reaction time points, we demonstrate chemical interactions between the monomers and Mt. platelets and the consequent surface-assisted particle formation resulting in clustered clay-polymer latex particles.

2. Experimental section

2.1. Materials

Styrene (Sty; Samchun Chemical, > 99.5%), n-butyl acrylate (BA; Aldrich, > 99%) and potassium persulfate (KPS; Aldrich, > 99%) were purified by distillation under reduced pressure and recrystallization with ethanol. All the other chemicals were highly pure and used as received. The organosilane agents with polymerizable moieties, vinyl-trimethoxysilane (VTMS; > 98%), dimethylethoxyvinylsilane (DMEVS; > 98%), allyltrimethoxysilane (ATMS; > 97%) and the organosilane agent without polymerizable moieties, ethyltrimethoxysilane (ETMS; > 97%), were purchased from Tokyo Chemical Industry Co. Ltd. Cloisite*-Na⁺, having a dry mean particle size (d₅₀) of 25 μ m, was kindly supplied by BYK Additives & Instruments. Tetrasodium pyrophosphate (Na₄P₂O₇, Aldrich, > 95%) was used as the peptizing agent. Extra pure ethanol (EtOH, Merck Millipore, ACS, ISO, Reag.) was used as the co-solvent. Deionized pure water was used for all the experiments.

2.2. Preparation of silane-functionalized montmorillonite platelets

Prior to silane-functionalization of Mt. platelets, 10 g of Cloisite®-Na⁺ powder was added into deionized water, mechanically stirred and sonicated for an hour using a Vibra-Cell™ Ultrasonicator (Sonics, USA), equipped with a titanium alloy vibratory probe, with 80% of amplitude at 20 kHz, and 750 W. Thereafter, the fully dispersed solution was dispensed into conical tubes and centrifuged at 4000 rpm for 10 min to separate the impurities from the clay powder. The supernatant was collected and dried at 80 °C for at least two days. After the consecutive purifications, the fully dried pristine clay powder (C.Pristine, Table1) was employed for the silane-functionalization and emulsion polymerization processes. The silane functionalization was performed in a 10 L four-neck jacketed reactor, equipped with a condenser, thermometer, and funnel. 10 g of C.Pristine powder was added into 1 L of ethanol: water (7:3, v:v) solution with a pH of 5, which was adjusted by hydrochloric acid (HCl, Aldrich, 35-37%). After an hour of sonication to induce broken edges on the Mt. platelets, the solution was poured into the reactor. The reactor was purged with nitrogen for 30 min and then heated up to 60 °C. When the set temperature was reached, a given amount of various types of silane agents (Table 1), diluted in 10 mL of ethanol, was added dropwise into the reaction medium and allowed to react under 200 rpm of magnetic stirring for 12 h. The reaction medium was filtered with cellulose filter papers (Advantec, 5C grade), and intensively washed with ethanol to remove the free silane agents within

Table	2
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Characteristics of final latexes from emulsion polymerization with different monomer compositions and types of Mt. Pickering sta	abilizer
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Run	Monomer	Pickering stabilizer	Emulsion stability ^a	$X_{\rm M}^{\ \ b}$ [%]	$M_{\rm w} [10^3 {\rm g mol^{-1}}]$	$M_{\rm w}/M_{\rm n}^{\rm c}$	Initial/final pH	Initial/final Zeta Potential ^d [mV]
6	Sty	-	0	53.3	155.2	5.29	6.1 / 5.5	-14.8 / 0.28
7		C.Pristine	0	78.9	190.5	3.72	6.0 / 5.5	-25.4 / -55.4
8a		C.ETMS(1)	0	68.9	120.6	3.80	6.0 / 5.0	-56.1 / -70.1
8b		C.ETMS(2)	0	87.9	255.9	4.98	6.1 / 4.9	-46.1 / -63.6
8c		C.ETMS(5)	0	60.3	230.3	4.40	6.0 / 5.4	-48.2 / -64.3
8d		C.ETMS(10)	0	55.5	150.6	3.76	6.0 / 4.9	-36.4 / -50.4
9a		C.VTMS(1)	0	79.1	211.0	4.28	5.9 / 4.9	-47.8 / -43.3
9b		C.VTMS(2)	0	93.4	231.3	3.25	6.0 / 4.9	-64.9 / -55.0
9c		C.VTMS(5)	0	93.1	236.7	3.52	6.0 / 4.9	-42.6 / -60.2
9d		C.VTMS(10)	0	54.2	209.6	3.79	5.9 / 4.6	-56.0 / -54.8
10		C.DMEVS(10)	Ø	89.1	243.7	3.57	6.0 / 5.5	-52.8 / -56.2
11		C.ATMS(10)	\bigtriangleup	32.1	113.5	3.67	6.0 / 4.9	-39.3 / -58.7
12	Sty/BA	-	0	70.0	149.5	2.99	6.1 / 4.8	-52.1 / -54.7
13		C.Pristine	0	99.8	207.3	2.97	6.0 / 5.0	-56.3 / -60.4
14a		C.VTMS(1)	0	81.1	192.5	2.96	6.0 / 5.0	-44.4 / -52.6
14b		C.VTMS(2)	0	67.2	147.4	2.87	6.0 / 4.6	-44.0 / -51.0
14c		C.VTMS(5)	\triangle	46.5	153.2	2.85	5.9 / 5.1	-41.6 / -52.4
14d		C.VTMS(10)	\triangle	56.2	158.4	2.85	6.0 / 4.5	-50.8 / -55.5
15	BA	-		-	-	-	-	-
16		C.Pristine	\bigtriangleup	96.3	203.4	2.58	6.1 / 4.9	-35.7 / -46.9
17		C.ETMS		-	-	-	-	-
18		C.VTMS		-	-	-	-	-
19		C.DMEVS		-	-	-	-	-
20		C.ATMS		-	-	-	-	-

^a Evaluated for the final latexes stored in 50 mL vial for a month; \odot excellent; \bigcirc good; \triangle fair; \blacktriangle aggregated.

^b Overall monomer conversion was determined by gravimetric analysis on the final latexes.

^c Weight-averaged molar mass and polydispersity, determined by GPC.

^d Determined by zeta potential measurement.

the medium. The resulting wet clay remnants were dried in a vacuum oven under ambient conditions to prevent the possible radical reaction of the vinyl moieties chemically grafted on the Mt. platelets. The final fully dried clay products were grounded using a mortar and pestle and then characterized to identify the silane-functionalization reaction.

2.3. Pickering emulsion stabilized by various types of montmorillonite platelets

For the solution used in surfactant-free emulsion polymerization, 0.50 g of the respective Mt. platelets (Table 2) was dispersed in 180.0 g of deionized water. Na₄P₂O₇ (0.094 mol, 5 wt% with respect to clay) was also added for clay dispersion. For complete exfoliation of the clay platelets in the water phase, the solution was sonicated by the aforementioned instrument for an hour while being continuously cooled with an ice bath to prevent the evaporation of the solvent and the followed aggregation of the clay platelets. In a typical experiment (Run 6), Sty (20.0 g) was added to the clay-dispersed solution, followed by pH adjustment to 6. The resulting medium was introduced into a 250 mL five-neck jacketed glass vessel equipped with a condenser, dropping funnel, thermometer, nitrogen inlet tube, and three-bladed stainless-steel anchor. The reaction medium was bubbled with nitrogen for 30 min under stirring fixed at 400 rpm and then heated up to 70 $^\circ$ C using an external water bath. When the set temperature was reached, emulsion polymerization was initiated by the addition of 0.26 g of KPS, pre-dissolved in 10.0 g of water. At certain time points, aliquots were collected from the reaction medium through a septum and characterized for monomer conversion (X_M) and latex particle analysis. The final products were purified and characterized as described below.

2.4. Characterizations

2.4.1. Chemical properties of montmorillonite platelets

Fourier-transform infrared spectroscopy (FT-IR) was performed on a Nicolet 6700 (Thermo Scientific, USA). The clay powder samples for FT-IR measurement were fully dried at 60 $^{\circ}$ C, stored in a vacuum oven

for at least two days, and analyzed in the attenuated total reflectance (ATR) mode with a ZnSe/diamond crystal, 32 scans at a resolution of 8 cm⁻¹ in the spectral range of 4000–650 cm⁻¹. ²⁹Si cross-polarization/magic-angle-spinning (CP/MAS) solid-state nuclear magnetic resonance (NMR) spectra of the pristine and silane-functionalized Mt. platelets were measured using a 500 MHz Solid NMR system (Bruker Advance III HD, Germany), equipped with a 7 mm CP/MAS probe. The contact time, recycle delay, and spinning rate were 5 ms, 240 s, and 5 kHz, respectively. The chemical shift of ²⁹Si was referenced to 4,4dimethyl-4-silapentane-1-sulfonic acid (DSS). Elemental analysis (EA) was performed on a Flash 2000 Organic Elemental Analyzer (Thermo Scientific, USA) equipped with a thermal conductivity detector. The pre-dried clay powder samples were used for the measurement of the elemental composition, especially in terms of the content of carbon atoms in the pristine and silane-functionalized Mt. platelets. The logarithm of the Sty/water partition coefficient, $log(K_{sw})$, was determined by the ratio of the equilibrium concentrations of a solute dissolved in the two immiscible layers for quantitative analysis of the partition behavior of the various types of Mt. platelets between the Sty and water phases.

2.4.2. Kinetic and morphological analysis on CPN

The $X_{\rm M}$ during the emulsion polymerization was monitored using gravimetric analysis on the sols collected from the reaction medium at certain time points. Hydroquinone dissolved in methanol was added to the sols to prevent further reaction. The proportional masses of the clay, initiator, and the peptizing agent in the given amount of the sol were subtracted to calculate the solid content and the derived $X_{\rm M}$. Gel permeation chromatography (GPC) was used for the pre-dried emulsion products dissolved in tetrahydrofuran, at 35 °C under a flow rate of 1 mL min⁻¹, on a YL9100 GPC system (YL Instruments, Republic of Korea) with Styragel HR 5E columns. To calculate the weight-average molar mass ($M_{\rm w}$) and polydispersity ($M_{\rm w}/M_{\rm n}$), the equipment was calibrated with the universal polystyrene standard (Polymer Standards Service Inc., USA). ¹³C liquid NMR spectra of the final latexes from the emulsion polymerization, dissolved in deuterated chloroform, were

recorded on a 600 MHz high-resolution NMR spectrometer (Bruker, Germany). Field-emission scanning electron microscopy (FE-SEM) was performed on JSM-6700F (JEOL, Japan) microscope, operated at a working distance of 7 mm. The accelerating voltage and the beam of current was set at 15 kV and 1×10^{-10} A, respectively. For SEM sample preparation, the aliquots from the emulsion polymerization batch were highly diluted to a solid content of 0.1 wt%, and the resulting solutions were dropped onto the front side of typical double-sided carbon adhesive tape and air-dried under ambient conditions. Field-emission Transmission electron microscopy (FE-TEM) was performed on JEM-F200 (JEOL, Japan) microscope, operated at a working distance of 120 mm. The accelerating voltage and beam of current was set at 200 kV and 7.5×10^{-9} A, respectively. The TEM-EDX instrument was equipped with a JEOL Dual SDD system, which enabled elemental mapping with a different spectrum of X-ray energy for the respective TEM samples. For TEM sample preparation, the aliquots from the batch were diluted to a solid content of 1 wt% and a drop of the solution was deposited on a carbon/Formvar-coated copper grid and air-dried under ambient conditions. The direct observation of the latex particles dispersed in the water system was enabled by cryogenic transmission electron microscopy (cryo-TEM), performed on a Talos L120C (ThermoFisher Scientific, USA). The accelerating voltage and beam of current was 120 kV and 5×10^{-6} A, respectively. After a second of blotting, the highly diluted sol was mounted onto a cryo-holder and processed into a quench-frozen thin film using liquid ethane. The hydrodynamic diameter of both the polymer latex particle (D_p) and the Mt. platelets in the sol was measured via the dynamic light scattering (DLS) method, performed on a Zetasizer Nano ZS (Malvern Instruments, USA) equipped with 633 nm wavelength He-Ne laser. The sol was highly diluted to a solid content of 0.1 wt% and analyzed at a noninvasive backscattering angle of 173° at 25 °C. The Malvern Dispersion Technology Software used the Rayleigh approximation and Mie theory to convert the intensity of scattered light into the $D_{\rm p}$ and its degree of distribution, which is indicated by a polydispersity index (PdI), obtained by the cumulative analysis of the correlation function of light intensity (see the Supplementary materials for details). Zeta potential measurements were performed on the same instrument. The Smoluchowski approximation and phase analysis light scattering mode were used for determining the electrophoretic mobility and deriving the zeta potential value. The pH of all the samples for the DLS and zeta potential measurements were adjusted to 6 using HCl, before the tests. The pH measurements were performed using a pHTestr30 (Eutech Instruments, USA), calibrated with pH 4.01, 7.00, and 10.01 buffer solutions.

3. Results and discussion

3.1. Silane-functionalized montmorillonite platelets and their partition behavior at the O/W interface

A series of silane-functionalization reactions are presented in Table 1. Each run was named according to the type, and the initial input of the silane agent used. Prior to silane-functionalization, we applied intensive sonication to the clay platelets in an attempt to induce broken edges and crystal defects, which are widely known as the most reactive sites of silane molecule grafting (He et al., 2013). The hydroxyl groups located at external surfaces and broken edges can easily be subjected to the hydrolysis and subsequent condensation reaction with the alkoxy groups of the silane molecules in the vicinity of the active sites of the Mt. platelets (Scheme 1).

In the ethanol/water medium, sufficient diffusion and intercalation of silane molecules within the Mt. platelets were expected since the solution had lower surface energy compared to that of the Mt. platelets (Vazquez et al., 1995; Shanmugharaj et al., 2006). Additionally, in the polar-protic solvent with a slightly lower pH, the condensation reaction between the adjacent alkoxyl groups of silane molecules, producing polysiloxane bonds that lock the adjacent platelets, is restrained (Su et al., 2013). Hence, the swelling property of 2:1-type layered Mt. platelets can be maintained even after the silane functionalization. The ability of the intercalation of polymeric molecules into the Mt. platelets is, therefore, retained in the emulsion polymerization.

Herein, we report the characterization of silane-functionalization on the pristine Mt. platelets using four different types of silane agents. Qualitative characterizations of the silane-functionalization were conducted using FT-IR and ²⁹Si CP/MAS solid-state NMR. The IR spectra of the pristine and silane-functionalized Mt. platelets are reported (Fig. 1), and all the spectra showed a band at 1050 cm^{-1} , corresponding to the stretching motions of the Si-O and Si-O-Si bonds on the Mts (Romanzini et al., 2015). The bands of the aliphatic CH₂ and CH₃ groups (2850 and 2980 cm⁻¹, respectively) were observed in the IR spectra of the C.ETMS and C.ATMS platelets, and the band of the CH₂ group alone was observed in the IR spectra of the C.VTMS and C.DMEVS platelets, which indicated that silane-functionalization was achieved for all the clay samples used. Also, characteristic bands at 3060 and 3080 cm^{-1} were observed in the IR spectra of the C.VTMS and C.ATMS, respectively, corresponding to the stretching motions of the = C-H end group. However, no observable bands around this range were visible in the IR spectra of the C.DMEVS platelets. For all the bands assigned to these bands, the absorbance increased as a function of the initial input of silane agents. The ²⁹Si CP/MAS solid-state NMR spectra of the C.Pristine and C.VTMS(1) (Fig. S1) also gave supporting qualitative evidence of silane-functionalization. An additional weak signal at -57.3 ppm, corresponding to the units of $T^2[Si(OSi)_2(OR')R]$ (R: CH=CH₂, R': CH₃ or H), was recorded in the ²⁹Si CP/MAS NMR spectrum of the C.VTMS(1) platelets, and the common signals of Q³[Si (OSi)₃OM] (M: Al, Mg) and Q⁴[Si(OSi)₄], were basically observed for the pristine Mt. platelets (Shanmugharaj et al., 2006). A broad signal around -42 to 43 ppm, corresponding to the units of $T^{1}[Si(OSi)]$ (OH)₂R], indicated that most of the Mt, sheets were hydrolyzed within the ethanol/water solution, as stated in the earlier report (He et al., 2005). To further analyze the chemical nature of the Mt. platelets, a quantitative evaluation via EA was used to determine the amount of silane agents grafted onto the Mt. platelets (see the Supplementary materials for details). The amount of each type of silane agents grafted (Fig. S2) showed a good causal relationship with the initial input of the agent, except for the Mt. platelets functionalized with mono-functional DMEVS (Runs 4a-d) with a leaving group of ethoxy, which was previously reported to exhibit a lower hydrolysis rate than that of the methoxy leaving group (Kang et al., 1990). A greater extent of silanefunctionalization was enabled using multi-functional silane agents with methoxyl leaving groups, and the degree of silane agents grafted was intuitively quantified and controlled as a function of the initial input of the agents.

For a basic understanding of the effects of the silane-functionalization on the chemical nature of the Mt. platelets, we demonstrate the partition behavior of the Mt. platelets at the o/w interface. A wellknown physicochemical parameter, the 1-octanol/water partition coefficient, has been used to account for the lipophilicity or hydrophobicity of organic compounds (Short et al., 2010). As an analogy, the Sty/water partition coefficient was adopted to describe the partition behavior of the Mt. platelets as Pickering stabilizers in an oil-in-water emulsion system. The stabilizing ability of a Pickering particle to reduce the interfacial tension between the organic and continuous water phase has been referred to as the wetting property of the solid particle. Owing to this, the prediction of the adsorption behavior of the solid particle stabilizer relied on the evaluation of its contact angle between the o/w phases (Ji et al., 2014) and the consequent desorption energy (Xue et al., 2017). Especially for an inorganic solid particle with a high surface charge density, the surface tension of the solid-liquid interface is generally evaluated using the Fowke's model, assuming the total surface tension of the solid is divided into dispersive and polar component parts (Fowkes, 1964). Based on the contact angle measurement,



Scheme 1. Schematic representation of silane-functionalization for mono- or multi-functional silane agents on pristine Mt. platelets



Fig. 1. FT-IR spectra range of $2800-3200 \text{ cm}^{-1}$ of the pristine and silane-functionalized Mt. platelets with different types of silane agents; (a) ethyltrimethoxysilane, (b) vinyltrimethoxysilane, (c) dimethylethoxyvinylsilane, and (d) allyltrimethoxysilane with different initial input of 0, 1, 2, 5, and 10 mmol silane per gram clay.

the partition coefficient of a solid particle at the o/w interface could be derived by the difference in interfacial free energy for a single particle to detach from water into the oil phase (Binks, 2002),

$$\Delta \mathbf{E} = 4\pi r^2 \gamma_{ow} \cos\theta = -k_B T ln K \tag{1}$$

Where k_B is the Boltzmann constant and *K* the partition coefficient described above. On account of the practical limitation of the sessile drop method, however, the method is obliged to represent the contact angle and surface tension of a dried polymeric film or a pressed layer of inorganic powder as a solid phase (γ_s), which is entirely different situation to that of a solid Pickering stabilizer at the o/w interface.

For an intuitive grasp and simple visualization of the situation, we contrived a simple miniature similar to the Pickering emulsion system, consisting of a monomer, water, and clay platelets (see the Supplementary materials for details). Assuming the interfacial localization of clay platelets between the o/w interface and that the subsequent adsorption/desorption behavior was dominated by their physicochemical nature (Hong, 2016), the K_{sw} of the Mt. platelets was calculated via gravimetric analysis. The K_{sw} values of all the four types of silane-functionalized Mt. platelets (Runs 2–5) with different initial inputs of the agents were measured as a function of elapsed time until equilibrium and determined as stable values after 24 h (Fig. S3). The plot of the K_{sw} value against the amount of silane agent grafted (determined by EA) demonstrated a good correlation at a moderate degree of silane-functionalization (Fig. S4). Each slope of the corresponding plot for the different types of silane agents indicated the differentiated chemical nature of the surface of each Mt. species. In conjunction with the partition behavior of the Mt. platelets at the o/w interface, their

chemical interaction with the polymer latexes was studied later on in the discussion.

3.2. Oil-in-water pickering emulsion polymerization

Surfactant-free emulsion polymerizations of Sty and Sty/BA (60/40, w/w) were carried out using the KPS anionic initiator and in the presence or absence of the Mt. platelets as Pickering stabilizers. Since the surfactant-free emulsion polymerization system using KPS was well-established in the literature (Delafresnaye et al., 2017; Morgen et al., 2018), a comparative study on the sole effect of the Pickering stabilizers of different chemical natures could be accomplished in this research. The Mt. platelets were hydrophobically modified by the silane-functionalization such that the hydrophobic monomers readily interacted with the solid stabilizer on their surface. As the solubility of the silane-functionalized Mt. platelets in the water phase decreased understandably, intensive sonication and agitation were required prior to the emulsion polymerization. The addition of Na₄P₂O₇ helped the Mt. platelets well dispersed within the medium without any gel-forming behavior.

For the Pickering emulsion polymerization using Sty as the monomer, stable latexes were produced, and a relatively higher $X_{\rm M}$ was observed in the presence of the pristine and silane-functionalized Mt. platelets (Table 2). The formulations that used BA as the sole or comonomer, on the other hand, exhibited a somewhat unstable emulsion and coagulation at the earlier stage of the surfactant-free emulsion polymerization, both in the absence of the pristine and in the presence of silane-functionalized Mt. platelets. Similar results were obtained in previous studies (Bourgeat-Lami et al., 2010; Delafresnaye et al., 2017), which reported the flocculation of BA when stabilized by a relatively low content of both Mt. and Laponite clay stabilizers. The $X_{\rm M}$, $D_{\rm p}$, and PdI values for the emulsion polymerization (Fig. 2) were changed in accordance with the absence (Run 6) and the presence of Mt. platelets (Runs 7, 8a, and 9b). The $X_{\rm M}$ values at the same reaction time gradually increased for the polystyrene latexes stabilized without-clay and those stabilized by the C.ETMS(1), C.Pristine and C.VTMS(2) platelets in order. From a qualitative viewpoint, the overall rates of polymerization at the earlier reaction time, obtained from each slope of the regression lines, sharply increased upon the incorporation of the Mt. platelets into the system. The latexes synthesized in the presence of Mt. platelets ended up a D_p (~150 and 250 nm for C.Pristine and C.VTMS(2), respectively) that was significantly smaller than that of the latexes synthesized in the absence of Mt. platelets (~430 nm), except for the latex stabilized by C.ETMS(1) (~580 nm), which showed small-scale flocculation at a later reaction time. To investigate the kinetics of the latex particle formation, the particle number density $(N_p$, the number of particles per liter of latex dispersion) of all the emulsion polymerization media were calculated using the following equation and presented in Fig. 2d.

$$N_p = C_p / [(4\pi/3)(D_p/2)^3 \rho_p]$$
⁽²⁾

Where C_p , D_p , and ρ_p are the concentration (from X_M), size (from DLS measurement), and density of the latex particles, respectively.

In a typical Pickering emulsion polymerization, the stabilization of polymeric latexes is solely relied on electrostatic repulsion, owing to the high surface charge density of solid stabilizers (Peach, 1998). In the absence of Mt. platelets (Run 6), on the other hand, the polystyrene latexes are stabilized solely by initiator-induced charged groups. In the earlier stage of particle formation (~5 min), the polystyrene latexes are naturally small, and their surface charge density is not sufficient for self-stabilization. Therefore, the primary particles continuously precipitate with the water-soluble monomers and the oligomeric free radical species. The resulting meta-stable small particles coalesce into insoluble and stable particles, attaining a high enough surface charge density and a resulted colloidal stability. As the microcoagulation

proceeded, a linear increment in the D_p was observed for the reaction medium in the absence of Mt. platelets (Fig. 2b, Run 6), and its PdI value drastically decreased (Fig. 2c) because of the competitive growth process. The characteristic homogeneous coagulative nucleation lasted for 60 min, at which the N_p became constant (Fig. 3, Run 6); this has also been previously reported for the emulsion polymerization of Sty in a soap-free system (Goodall et al., 1977). At the later stage of emulsion polymerization (~ 4 h), however, from the result of the decline in N_p , flocculation occurred within the latex since the specific surface area of the polystyrene particles became low, and the surface charge density diminished as a result.

In the presence of the solid stabilizer, the small metastable particles can instantly acquire a sufficient surface charge density by adsorption onto the Mt. platelets. Cloisite®-Na⁺ has a high enough negative surface charge derived from the cation substitution and dissociation of surface silanol groups (SiO⁻) (Sposito et al., 1999). In the presence of Mt. platelets, smaller particles were obtained (Fig. 2b) and their $N_{\rm p}$ instantly burgeoned (Fig. 2d) at an earlier reaction time, in contrast to the slowdown decline of N_p in the absence of Mt. platelets (Run 6), which denoted the typical homogeneous nucleation process of surfactant-free emulsion polymerization. These results, which are in line with the smaller $D_{\rm p}$ in the presence of Mt. platelets, indicate a different particle formation kinetics at the earlier nucleation stage, i.e., so-called heterogeneous particle nucleation between a growing latex particle and solid clay stabilizer. Zeta potential measurements of the final latexes also gave values between -40 and -70 mV in the presence of Mt. platelets (Table 2), inferring a higher surface charge density of the latex particles and less extent of flocculation at the final growth stage.

Nevertheless, the adsorption of the small metastable particles consisting of hydrophobic polystyrene on hydrophilic Mt. platelets was restrained. Consequently, clay-armored latex particles were rarely obtained when using Sty as the sole monomer; on this account, the auxiliary functional monomers have been exploited to increase the chemical interaction between the monomers and hydrophilic clay platelets, and attach them (Delafresnaye et al., 2017). Moreover, when using Mt. alone as the stabilizer, on account of its high aspect ratio (100–1000 nm in the lateral dimension), the sequential adsorption of Mt. platelets onto a latex particle is hardly expected because of steric hindrance and hence a lower coverage. Only bare polystyrene latexes were observed in the cryo-TEM image (Fig. 3a).

To compare the difference between the polystyrene latexes stabilized by the pristine and vinylsilane-functionalized Mt. platelets, the changes in $X_{\rm M}$, $D_{\rm p}$ (Fig. 4), and particle size distribution (Fig. S6) are presented. Both reaction media showed comparable $X_{\rm M}$ at an earlier reaction time (~30 min) and that of Run 9b surpassed after an hour of reaction time whilst the latex D_p of Run 9b consistently recorded almost twice that of Run 7, presumably denoting a different kind of particle formation at the earlier stage (under 10 wt% of $X_{\rm M}$). The significant difference in polystyrene latex D_p at the earlier reaction time was mainly attributed to the extent of hetero-coagulation, which depended on the chemical affinity of the metastable particles to microcoagulate onto the C.Pristine and C.VTMS platelets. The results that the latex particles stabilized by the C.VTMS(2) (Run 9b) maintained broader size distribution and concomitant higher PdI value in contrast to those of the latex particles stabilized by the C.Pristine, also indicated the difference in particle formation kinetics among them.

The hydrophobically modified Mt. platelets have better compatibility with Sty monomer, and hence the interfacial tension between a single Mt. platelet and a monomer phase decreases enabling a favorable interaction between them. The aforementioned partition coefficients of the Mt. platelets at the o/w interface gave a rough estimation of their partition behavior within the emulsion polymerization medium. The silane-functionalized Mt. platelets favored the Sty phase and coalesced to decrease the interfacial area toward a continuous water phase. This attractive interaction between the silane-functionalized Mt. platelets and the Sty monomer already took place at the earlier reaction time



Fig. 2. Changes in (a) monomer conversion (X_M), (b) latex particle size (D_p), (c) polydispersity index (PdI), and (d) particle number density (N_p) over time for emulsion polymerization media stabilized by without clay (Run 6, black), and with the C.Pristine (Run 7, red), C.ETMS(1) (Run 8a, blue), and C.VTMS(2) (Run 9b, cyan). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Cryo-TEM images of the clay-polystyrene latex particles from the emulsion polymerization media stabilized by (a) C.Pristine platelets (Run 7) after 1 h and the C.VTMS(2) platelets (Run 9b) after (b) 15 min and (c) 1 h upon the initiation. Scale bar = 200 nm.

(~15 min), producing clay-polystyrene latex adhered structures (Fig. 3b and c). The latex particles appeared as gray spheres and the C.VTMS(2) platelets as dark thin filaments, oriented perpendicular to the cryo-TEM grid. Because of the high aspect ratio and a consequent steric hindrance on the Mt. platelets, the morphology was different from that of the typical Laponite-armored latex particles, and it seemed that the polystyrene latex particles were placed on the basal plane of the Mt. platelet. The Mt. platelets served as a template onto which the small metastable particles adhered and micro-coagulated at the earlier nucleation stage. The respective data of D_p collected from DLS and cryo-TEM showed a significant difference for the polystyrene latex specimen stabilized by the C.VTMS(2), which indicated an adhered or aggregated

clay-latex structure, unlike that for the separate polystyrene latex particles stabilized by the C.Pristine.

To elucidate the heterocoagulation at the earlier nucleation stage, the SEM images of the latex particles stabilized by the C.Pristine (Fig. 5a-c) and C.VTMS(2) (Fig. 5d-f) at different reaction times, are demonstrated. The polystyrene latex particles showed no characteristic clay-incorporated structure in the presence of the C.Pristine on account of the lack of an attractive interaction between the hydrophilic Mt. platelets and Sty monomer. In the presence of the C.VTMS(2), on the other hand, a clustered structure was formed at the earlier reaction time, and it gradually grew centered on the hydrophobically modified Mt. platelets. Since the hydrophobic Mt. platelets were hardly dispersed



Fig. 4. Changes in monomer conversion (X_M) (closed square) and latex particle size (D_p) (open square) over time for the emulsion polymerization media stabilized by (a) the C.Pristine (Run 7) and (b) C.VTMS(2) platelets (Run 9b).

in continuous water phase despite the several mechanical treatments, the size distribution of the Mt. platelets after the emulsion Applied Clay Science 182 (2019) 105288



Fig. 6. (a) FE-TEM image of the final latex particles stabilized by the C.VTMS (2) platelets (Run 9b), and TEM-EDX mapping of (b) carbon, (c) oxygen, and (d) silicon elements. Scale bar = 100 nm.

polymerization process was barely controllable and hence the effect of aggregation between the Mt. platelets on the formation of the latex particles ought not to be ignored. Nevertheless, clustered structures on the clay-latex particles, irrespective of the size, were frequently observed throughout the dispersion collected from the reaction medium stabilized by the silane-functionalized Mt. platelets. Similar aggregation behavior of colloidal silica particles functionalized by methyl end-capped trimethoxy poly(ethylene glycol) silane was observed owing to the adsorption of polyethylene oxide on the silica surface, and flocculation occurred (Björkegren et al., 2015). Unlike the silica, the clustered clay-latex particles remained stable under storage for several months with no visible agglomeration. The TEM-EDX images (Fig. 6) illustrate the elemental mapping for carbon and silicon atoms on the clustered



Fig. 5. FE-SEM images of polystyrene latex particles from the emulsion polymerization stabilized by the C.Pristine platelets (Run 7) at different reaction times of synthesis; (a) 5 min, (b) 15 min, and (c) 30 min and by the C.VTMS(2) (Run 9b) at different reaction times of synthesis; (d) 5 min, (e) 15 min, and (f) 30 min upon the initiation. Scale bar = 200 nm.



Fig. 7. ¹³C NMR spectra of the final polystyrene latex media stabilized by (top) the C.VTMS(2), (middle) C.ETMS(2), and (bottom) C.Pristine platelets within a range of 39.0–48.0 ppm.

clay-latex particles, obtained from the final emulsion polymerization media. The *co*-existence of carbon and silicon elements centered around the clustered structure support the microcoagulation and irreversible adsorption of polystyrene latex on the silane-functionalized Mt. platelets.

Even if the adsorption of latex particles onto the silane-functionalized Mt. platelets was morphologically observed, the qualitative characterization of the chemical composition of the clay-latex particles was required and was carried out using ¹³C NMR spectroscopy. The ¹³C NMR spectra of the pre-cleaned final latex products swollen in CDCl₃ solvent were investigated within the chemical shifts of 39 to 48 ppm (Fig. 7). The common signals of 40.3 ppm for methylene carbon and 43.7 ppm for methine carbon, both located in the polystyrene backbone chain (Zhou et al., 2017), were obtained. However, for the latex incorporating silane-functionalized Mt. platelets, the assigned common signals turned into multiplets, and many additional weak signals were obtained, especially for the latex particles in the presence of the C.VTMS(2) platelets. We assumed that the vinvl moieties on the silanefunctionalized Mt. platelets were attributable to the possible participation of radical initiation and correspond to the secondary polymerization with the radicals on the polystyrene backbone main chain. To this end, the C.ETMS was selected as a vinyl-free control group for a direct comparison to the C.VTMS. The possibilities for the monomer molecules to reach each silane agent (VTMS and ETMS) grafted on the Mt. platelets were comparable since they had similar lengths of grafted (dangling) moieties (148.2 and 150.2 g mol⁻¹ of molar mass for VTMS and ETMS, respectively). Their Sty/water partition coefficients were also about the same (0.65 and 0.73 of $log(K_{sw})$, respectively). The X_M of the latex stabilized by the C.ETMS(1) (Fig. 2a, Run 8a) was considerably lower than that of the latex stabilized by the C.VTMS(2) (Run 9b). The radical reactions of vinyl moieties on the C.VTMS(2) platelets presumably formed covalent bonds between the polystyrene chains and Mt. platelets. The formation of this chemical linkage expedited the physicochemical adsorption of the small metastable particles on the Mt. platelets, and the prompted formation of the clustered structure of latex particles was achieved at the earlier stage of particle formation. The different kinetics of the latex particles stabilized by the Mt. platelets functionalized with vinylsilane and vinyl-free silane underpinned the assumption. To comprehend the impact of the quantities of vinyl moieties grafted on the Mt. platelets on the polymerization rate, several reaction media stabilized by the C.VTMS platelets with different degrees of grafted silane molecules (Runs 9a-d) were synthesized. The polymerization rates increased as a function of the degree of grafted silane molecules up to a certain point and then fell sharply in the presence of C.VTMS(10) (Run 9d), which exhibited the highest degree of silane-functionalization. Considering that the $X_{\rm M}$ in Run 9d was relatively low even at the earlier reaction time, the highest Sty/water coefficient and the resultant lowest solubility toward the continuous water phase acted as the prime factor that influenced the particle formation within the Pickering emulsion system. Similarly, based on the results of lower X_M and molar mass (Table 2), excessively hydrophobic Mt. platelets (Runs 8d, 9d, 11, and 14d) with higher Sty/water coefficients ($\log(K_{sw}) > 1.5$) coagulated with each other, deterring a chance encounter with polymeric materials and deteriorating the formation of stable emulsion.

Aside from Run 9d, the polymerization rates gradually increased as a function of the degree of silane-functionalization on the Mt. platelets. Considering the $N_{\rm p}$ of latex particles (Fig. 8d), however, the latex



Fig. 8. Changes in (a) monomer conversion (X_M), (b) latex particle size (D_p), (c) polydispersity index (PdI), and (d) particle number density (N_p) over time for emulsion polymerization media stabilized by the C.VTMS(1) (Run 9a, black), C.VTMS(2) (Run 9b, red), C.VTMS(5) (Run 9c, red), and C.VTMS(10) (Run 9d, cyan) platelets. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

medium stabilized by the C.VTMS(5) (Run 9c) with a lower N_p yielded a rather higher conversion rate after it reached the plateau of the N_p and stable emulsions were formed. From that point onwards, the conventional kinetic equation of emulsion polymerization was applied, that is,

$$R_{\rm p} = k_{\rm p} [\mathrm{M}]_{\rm p} (n_{\rm r} N_{\rm p} / N_{\rm A}) \tag{3}$$

Where k_p is the propagation rate constant, [M]_p is the monomer concentration in the latex particles, n_r is the average number of radicals per latex particle, N_p is the N_p of polymer particles and N_A the Avogadro constant.

In the presence of the C.VTMS(5) platelets, the two factors reversed the normal string relations between the $N_{\rm p}$ and polymerization rate. Firstly, the increment in partition behavior of the Mt. platelets toward the monomer phase promoted the microcoagulation of insoluble oligomeric radicals on the Mt. platelets, and hence a faster stabilization was achieved. Secondly, the additional participation of vinyl moieties on the silane-functionalized Mt. platelets in radical polymerization amplified the average number of radicals within the latex particles and the concomitant probability of mixed radical reaction events to induce additional linkages on the polymer chains, as shown in the ¹³C NMR spectroscopy. However, the role played by the participation of vinyl moieties on the Mt. platelets in the earliest stage of particle formation remains questionable. The free chain mobility and film-forming ability of polystyrene are relatively low, considering its higher glass transition temperature compared to the temperature of reaction media. Moreover, the chain mobility of dangling silane agents on the Mt. template is structurally limited. As a matter of convenience, the formation of covalent bonds by the vinyl moieties on the Mt. platelets has to be initiated only after the adsorption of the monomer molecules onto the Mt.

platelet, and the followed formation of stable latexes was preceded. In such circumstances, the distance between a latex particle and a Mt. platelet fits under the proximity where the chemical interaction between different functionalities easily occurs. The higher enhancement in $X_{\rm M}$ (Fig. 8a) of the latex in the presence of the C.VTMS(5) (Run 9c) compared to that with the C.VTMS(2) (Run 9b) after the stable emulsions were formed (Fig. 8, ~60 min), underpinned our assumption that it requires time to have an impact, but detailed studies are needed in this regard.

3.3. Surface-assisted nucleation and growth mechanism

We postulated the mechanism of latex particle formation for hydrophobic monomers in the presence of Mt. platelets in terms of a heterogeneous coagulative nucleation model (Scheme 2). At the initial stage of particle formation, the monomers stabilized by SO_4^- end groups from the homolytic decomposition of the initiator become water-soluble and propagate into insoluble oligomeric radical species as they reached a critical chain length. Upon the continuous inlet of hydrophobic monomers and precipitation against them, the resulting primary particles simultaneously microcoagulate with other small particles to attain sufficient surface charge density required for the stabilization of a latex particle. This microcoagulation into small metastable particles slowly proceeds in the absence of any stabilizers since the particle nucleation is only reliant on the capturing event of radical species into the nuclei or on encounters between the homogeneous particles that are sparsely dispersed in the continuous water phase. In the presence of a Pickering stabilizer, on the other hand, the formation of the metastable and stable latex particles is accelerated by the solid



Scheme 2. Presumed particle nucleation and growth mechanism for Pickering emulsion polymerization of polystyrene latexes; stabilized by (top) pristine and (bottom) vinylsilane-functionalized Mt. platelets.

stabilizer with higher surface charge density. Since the energy barrier of a solid particle to detach from the o/w interface is very high, the Mt. platelets are irreversibly adsorbed on the interface and are susceptible to chemical interaction with oligomeric species and latex particles faced on the surface of the monomer phase. Hence, the distance between a dielectric latex sphere and a Mt. platelet should be kept sufficiently short-ranged so that the mutual polarization and a consequent attractive interaction can occur between them (Lindgren et al., 2016). Thus, the primary and metastable particles rapidly attain a sufficient surface charge density by incorporating the Mt. platelets onto their exterior, forming the clay-armored latex, based on an effective heterogeneous coagulative nucleation process.

When using hydrophobic monomers solely in Pickering emulsion polymerization, however, bare latex particles are mainly produced due to the lack of an attractive interaction, which results from the difference in the chemical natures of monomers and hydrophilic Mt. platelets. The silane-functionalization on the Mt. platelets changes their chemical nature and the resulted partition behavior within the o/w emulsion so that the incorporation of the polymeric materials onto the Mt. platelets is favored at the earlier stage of particle formation. The kinetic data (faster $X_{\rm M}$, larger $D_{\rm p}$, and higher PdI) indicate the different aspects of the particle formation in the presence of the silane-functionalized Mt. platelets (Fig. 4). Along with the less extent of homogeneous coagulation and faster stabilization at the earlier stage of particle formation, the additional effect of the vinylsilane agents grafted on the Mt. platelets become distinguished after the stable emulsions are formed at the later stage of particle formation. The secondary participation of the vinyl moieties on the silane-functionalized Mt. platelets in the radical reactions occurs when the latex particles and the Mt. platelets are placed within proximity. The polymerization rate of the latex stabilized by the Mt. platelets with a higher content of the vinylsilane agent is relatively higher while its N_p was kept lower (Fig. 8); this corresponds to the effect of mixed radical reactions of the vinyl moieties within the latex particles.

4. Conclusions

On the basis of the previously reported clay-stabilized emulsion systems (Lanchiş et al., 2009; Bonnefond et al., 2013; Guimarães et al., 2014; Delafresnaye et al., 2017), this work demonstrated that the extent of participation behavior and resulted stabilizing ability of Mt. platelets

could be controlled by the degree of silane-functionalization. The silane-functionalized Mt. platelets showed enhanced affinity toward the hydrophobic monomer phase, which turned out to be an essential characteristic of a Pickering stabilizer in terms of their chemical interaction and the consequent formation of CPN. The kinetic results, including the $X_{\rm M}$, $D_{\rm p}$, and concomitant $N_{\rm p}$, indicated a faster polymerization at the earlier stage of particle formation, and hence the heterogeneous coagulative nucleation occurred in the presence of Mt. platelets. Based on the cryo-TEM observation, however, bare latexes of polystyrene were mainly obtained since the hydrophilic pristine Mt. platelets failed to achieve an attractive interaction with the Sty monomer. On the other hand, the use of silane-functionalized Mt. platelets, C.VTMS(2) and C.ETMS(1), with moderate Sty/water partition coefficients (0.73 and 0.65 of $log(K_{sw})$, respectively) led to the prompted microcoagulation of monomers on the Mt. platelets and enhanced the incorporation of Mt. platelets within the polymer latex via a heterocoagulative nucleation. The results so far demonstrated a competitive fabricating method of the CPN that does not require any additional substances, which has been indispensable for assisting adsorption of Pickering stabilizers onto hydrophobic monomers (Delafresnaye et al., 2017).

The kinetic results of the latexes stabilized by the vinylsilane-functionalized Mt. platelets exhibited enhanced polymerization rates with a higher amount of vinyl moieties grafted on the Mt. platelets, which was accelerated by the secondary radical reactions within latex particle loci, similar to what was presumed from vinylsilane-modified clay-latex systems (Bourgeat-Lami et al., 2005; Lanchis et al., 2009). Covalent linkages between the polymer latex particles and the Mt. platelets reinforced the formation of a clustered clay-polystyrene latex structure, which was confirmed via the FE-SEM observation during the reaction period. Vinylsilane-functionalization of Mt. platelets leads to irreversible adsorption of polymeric materials onto the surface of Mt. platelets and consequently enhanced the formation of clustered clay-polystyrene latexes with high emulsion stability. This strategy can be extended to other hydrophobic monomers, fabricating various combinations of CPN, thereby tailoring important characteristics of latex products, such as thermal expansion, heat resistance, thixotropic behavior, and miscibility to matrix polymer, which makes the CPN as a functional additive for high-temperature engineering plastics.

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Declaration of Competing Interest

The authors confirm that there are no conflicts to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2019.105288.

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