Supporting Information

Fabrication of water-resistant nacre-like polymer/clay nanocomposites via *in situ* polymerization

Kyungmo Sung,[†] Shintaro Nakagawa,[†] and Naoko Yoshie*[,†]

[†]*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan.*

AUTHOR INFORMATION

Corresponding author

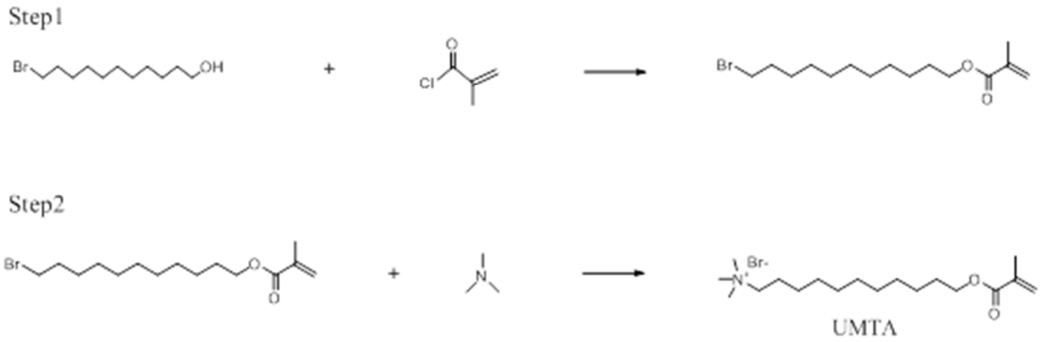
* E-mail: yoshie@iis.u-tokyo.ac.jp

Contents

1. Materials.

As solvents, we used dichloromethane (DCM, dehydrated), tetrahydrofuran (THF, dehydrated), hexane, methanol, diethyl ether, dimethyl sulfoxide (DMSO), *N*,*N*-Dimethylacetamide (DMA, dehydrated), chloroform, acetone, all of which were purchased from Wako Pure Chemical Industries, Ltd. Methacryloyl chloride, 1,12-dodecanediol, pyridine (dehydrated), sodium hydrogen carbonate, sodium sulfate and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were also obtained from Wako Pure Chemical Industries, Ltd. 11-bromoundecan-1-ol, trimethylamine (ca. 3mol/L in ethanol), 6-bromohexanoyl chloride, lithium bromide (LiBr), hydroquinone were obtained from Tokyo Chemical Industry Co., Ltd. All materials were used as received without further purification. The clay used in this study was sodium montmorillonite clay (Kunipia F, Kunimine Ind. Co., Japan) with a cation exchange capacity (CEC) of 115 mequiv/100 g. The aspect ratio was 300-500 as described by the supplier. Deionized water was obtained by Elix ® Essential 3 (Merck Millipore, USA) and used throughout the experiments.

2. Synthesis of 11-(methacryloyloxy)undecyltrimethylammonium bromide (UMTA).



Scheme S1. Synthesis of UMTA

As described elsewhere, UMTA was synthesized in two steps.[1, 2] The synthetic scheme and ^{1}H NMR spectra were provided in Scheme S1 and Figure S1, respectively. Briefly, 11-bromoundecyl methacrylate was obtained by the reaction of 11-bromoundecan-1-ol with an excess amount of methacryloyl chloride in dehydrated DCM. Then, UMTA was synthesized by the reaction of 11-bromoundecyl methacrylate with an excess amount of trimethylamine in ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 6.10 (s, 1H), 5.55 (s, 1H), 4.16-4.11 (t, 4H), 3.61-3.54 (t, 2H), 3.49-3.42 (s, 9H), 1.94 (s, 3H), 1.79-1.62 (m, 4H), 1.39-1.23 (br, 14H).

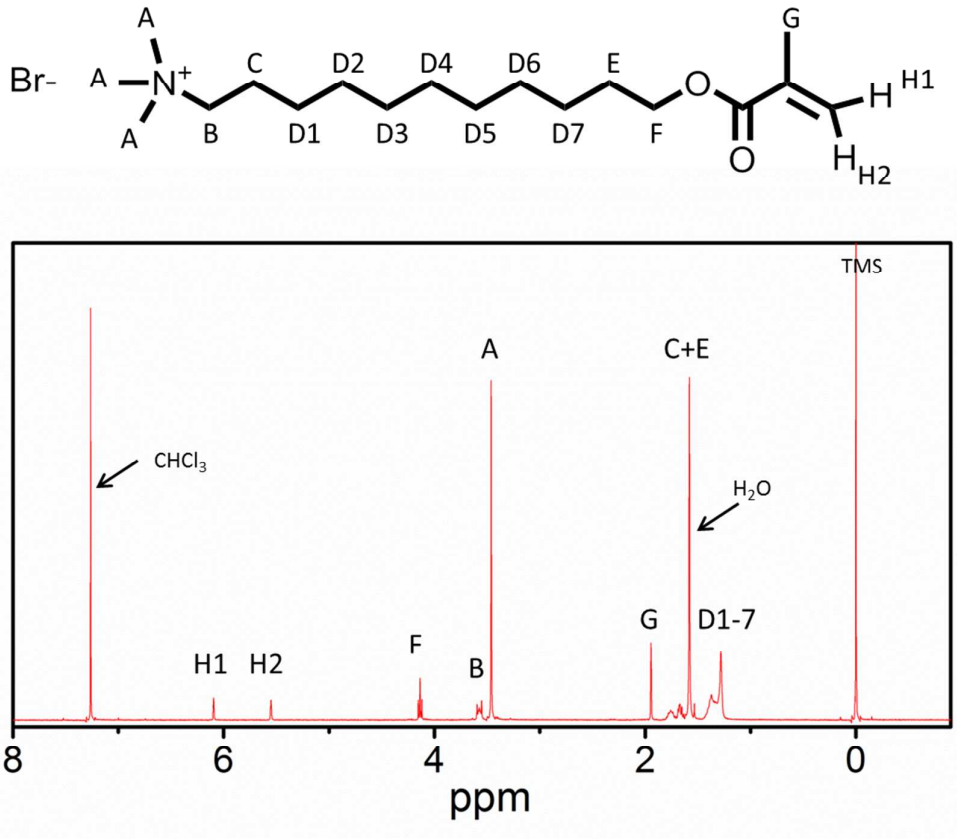
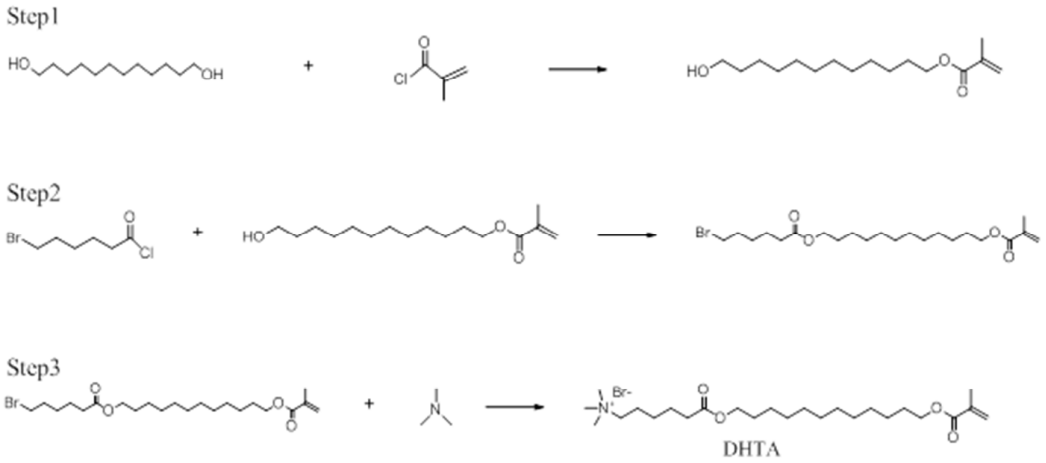


Figure S1. ^{1}H NMR spectra of UMTA.

3. Synthesis of 12-(methacryloyloxy)dodecyl 6-(hexanoyloxy)trimethylammonium bromide (DHTA).



Scheme S2. Synthesis of DHTA

3-1. 12-hydroxydodecyl methacrylate. The procedure was slightly modified from the previous method.[3] A mixture of 1,12-dodecanediol (21 g, 0.104 mol, 1 eq.), 300 mL anhydrous tetrahydrofuran, and dry pyridine (6.7 mL, 0.832 mol, 0.8 eq.) was stirred at 30-40 ℃ to obtain a clear solution. Methacryloyl chloride (8.1 mL, 0.832 mol, 0.8 eq.) was then added dropwise over 10 min. The reaction mixture was stirred for two days at room temperature. The white precipitate of pyridinium hydrochloride was filtered off and the solvent was reduced by rotary evaporation at 40℃. Unreacted 1,12-dodecanediol was precipitated by adding 300 mL hexane. The precipitate was filtered off and then the solvent was reduced by rotary evaporation. This process is repeated twice for thorough removal of unreacted 1,12-dodecanediol. The residue was purified by a silica column (eluent: Dichloromethane/MeOH, 95/5, v/v). 12-hydroxydodecyl methacrylate had an R_f of 0.4 checked by silica TLC. Clear colorless oil was obtained. The yield was 6.3 g (22%). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 6.11-6.08 (m, 1H), 5.56-5.53 (m, 1H), 4.13 (t, J = 6.7 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 1.94 (s, 3H), 1.72-1.50 (m, 4H), 1.42-1.19 (m, 16H).

3-2. 12-(methacryloyloxy)dodecyl 6-bromohexanoate. 12-hydroxydodecyl methacrylate (6.256 g, 0.0231 mol, 1 eq.) was dissolved in anhydrous dichloromethane (46 mL) in the presence of sodium hydrogen carbonate (3.89 g, 0.0462 mol, 2 eq.) and hydroquinone (0.005 g) in a two-necked round bottom flask (one neck fitted with a $CaCl_2$ tube). The contents were stirred for 10 min in ice-bath. 6-Bromohexanoyl chloride (7.4 g, 0.0347 mol, 1.5 eq.) was introduced dropwise for over 10 min. The reaction mixture was stirred in the ice-bath for 3h then was left at room temperature for further three days. The insoluble salt, sodium hydrogen carbonate, was filtered off and the organic layer was washed with 100 mL of 10 wt% sodium carbonate aqueous solution and 100 mL of water for two times respectively to remove unreacted acid chloride. The solution was dried over anhydrous sodium sulfate and filtered. The solvent was reduced by rotary evaporation under reduced pressure at 40 °C for 15min. The residue was purified by short column of activated alumina to remove unreacted alcohol with the eluent of dichloromethane. TLC (dichloromethane) was used to check the absence of starting materials. Finally, the solvent was removed by rotary evaporation under reduced pressure and further dried in high vacuum oven at 40 °C overnight. The weight of oily product obtained was 6.0 g (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 6.11-6.08 (m, 1H), 5.56-5.53 (m, 1H), 4.14 (t, J = 6.5 Hz, 2H), 4.06 (t, J = 6.8 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 2.32 (t, J = 7.4 Hz, 2H), 1.94 (s, 3H), 1.92-1.83 (m, 2H), 1.72-1.57 (m, 6H), 1.56-1.43 (m, 2H), 1.42-1.19 (m, 16H).

3-3. 12-(methacryloyloxy)dodecyl 6-(hexanoyloxy)trimethylammonium bromide (DHTA). 12-methacryloyloxydodecyl 6-bromohexanoate (5 g, 0.011 mol, 1 eq.), an excess of trimethylamine in ethanol (18.6 mL, 3 mol/L) and hydroquinone (0.005 g) were stirred in a round-bottomed flask fitted with a condenser at 30 °C for two days. The solution was cooled down to room temperature and added into 500 mL diethyl ether with stirring. White

precipitate of the product was observed. The product was filtered under nitrogen and washed with diethyl ether several times. Finally, it was dried under vacuum at 40 °C for 5 h to get white solid. It was stored in a desiccator. The weight of obtained product was 4.6 g (yield 83%). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 6.11-6.08 (m, 1H), 5.56-5.53 (m, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.63 (t, 2H), 3.47 (s, 9H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.94 (s, 3H), 1.85-1.76 (m, 2H), 1.74-1.56 (m, 6H), 1.50-1.41 (m, 2H), 1.40-1.22 (m, 16H). ATR-FTIR: [ν/cm^{-1}; 2949 (=C–H), 2850, 2916 (–C–H), 1735 (C=O), 1637 (>C=C<), 1297 (>C–N<), 978, 1039 (>C–C<), 679, 719, 1471 (–CH2–), 1409 (–CH3), 1187 (C–O)].

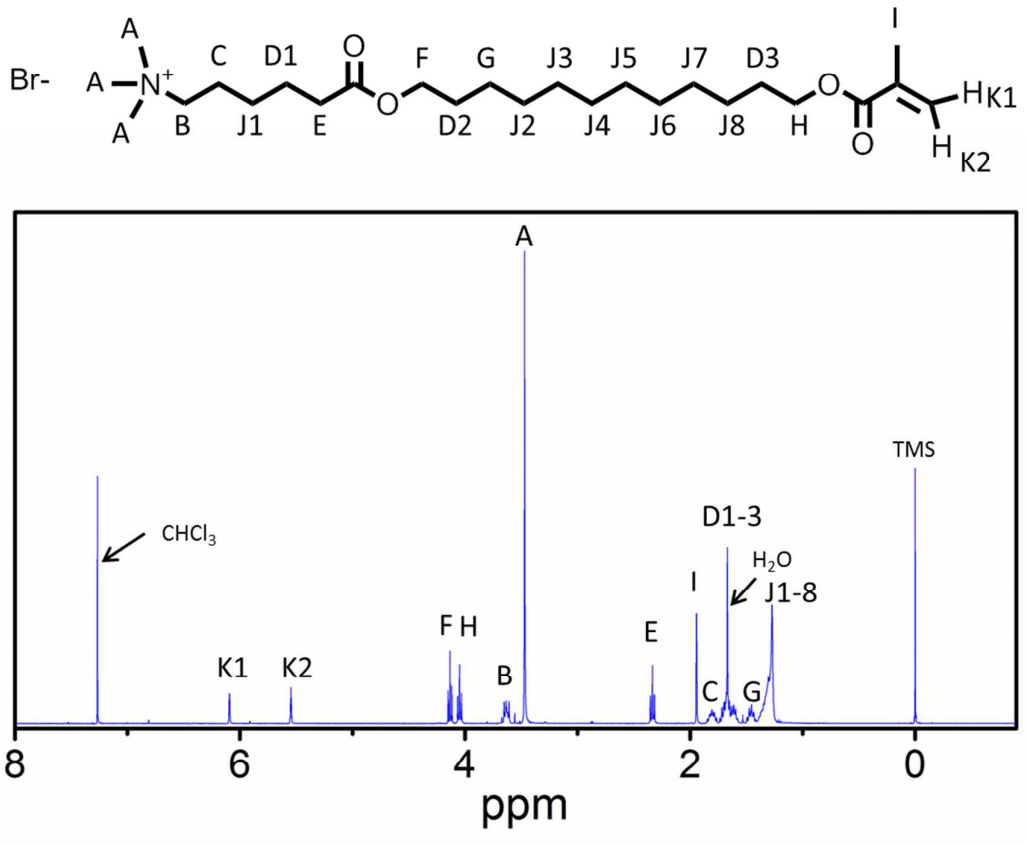


Figure S2. ^{1}H NMR spectra of DHTA.

4. ATR-FTIR spectroscopy of modified MMT.

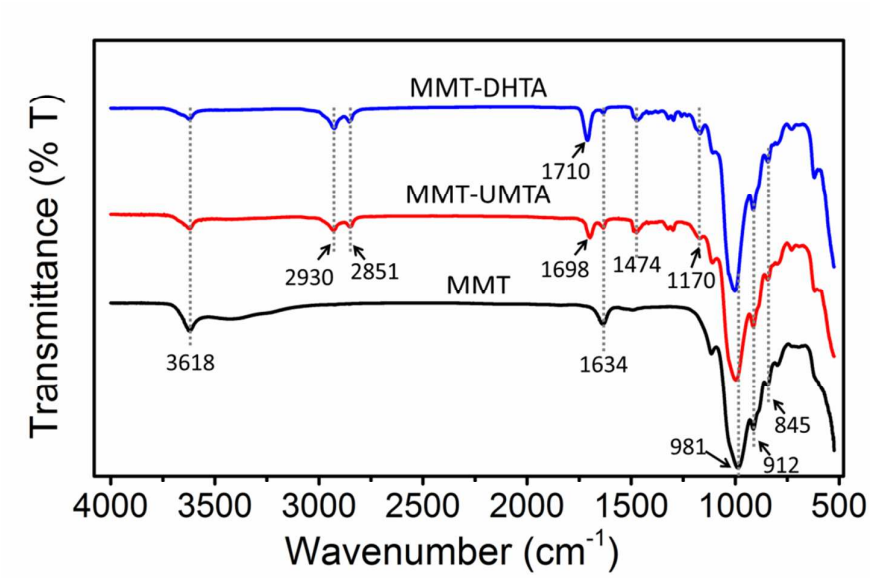


Figure S3. ATR-FTIR spectra of MMT, MMT-UMTA, and MMT-DHTA.

Table S1. Peak assignments of ATR-FTIR spectra for MMT, MMT-UMTA, and MMT-DHTA

Chemical group	Wavenumber (cm^{-1})		
	MMT	MMT-UMTA	MMT-DHTA
Stretching and deformation of Al–OH	3618, 912	3618, 913	3625, 913
Si-O stretching	981	997	1000
Deformation of Al-Mg-OH	845	843	842
Deformation vibration of interlayer water	1634	1633	1634
C=O stretching		1698	1710
C-H stretching		2851, 2930	2854, 2926
C-H bending		1474	1475
C-O stretching		1170	1169

5. Fabrication of nacre-like structure via *in-situ* polymerization.

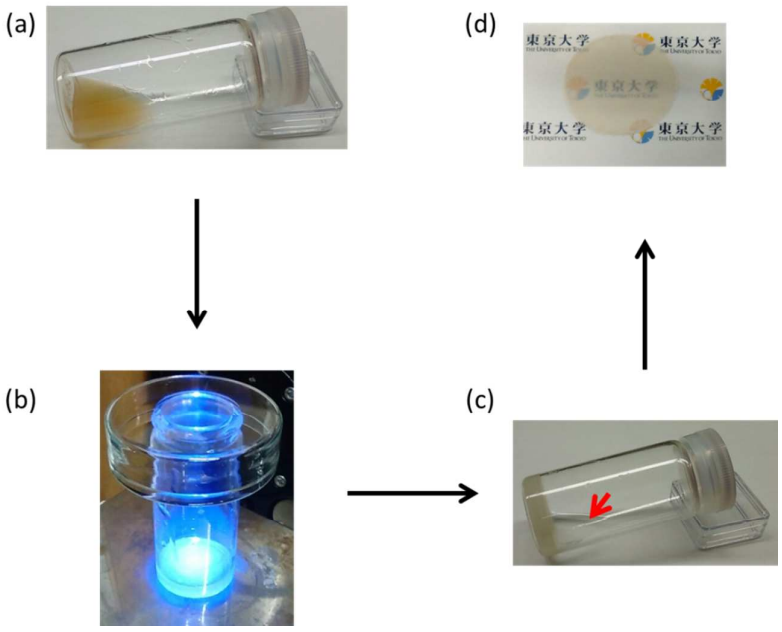


Figure S4. Photographs showing (a) 5 wt% dispersion of MMT-DHTA in DMA, (b) the dispersion during UV irradiation from the top for *in-situ* polymerization, (c) the gel-like deposit and transparent supernatant (red arrow) after UV irradiation, (d) composite film after removing DMA from gel-like deposit.

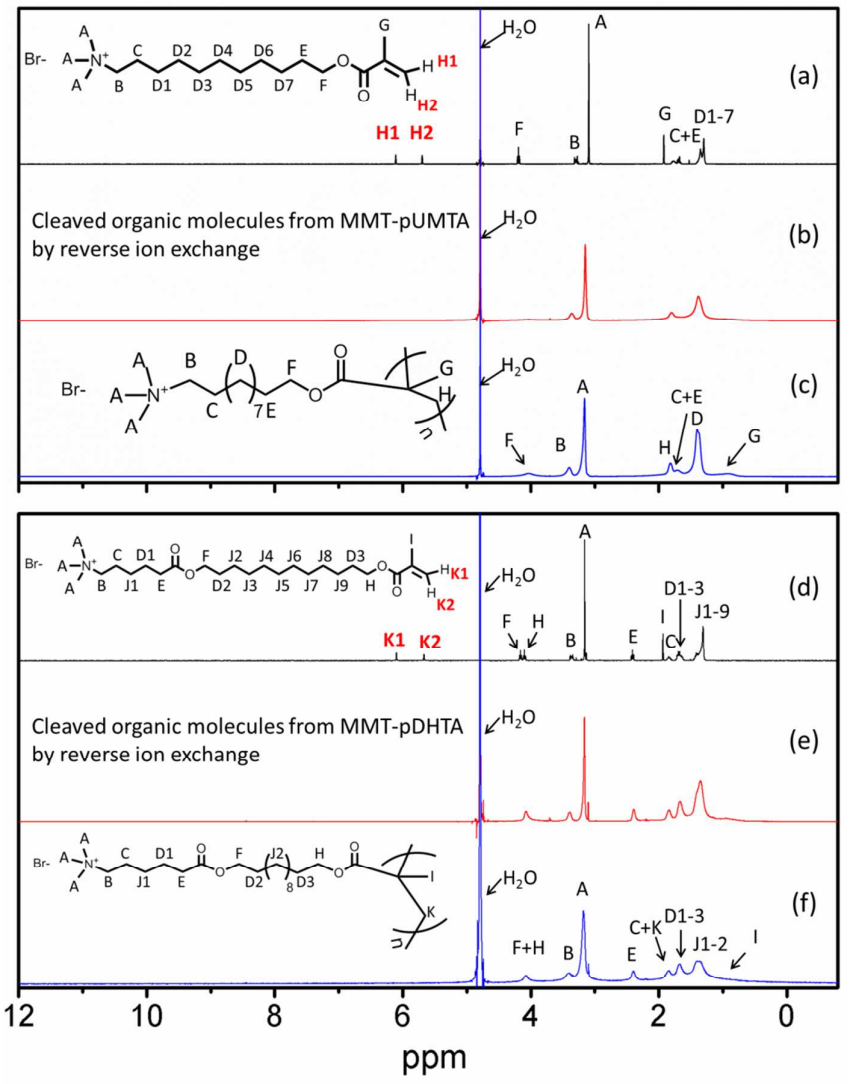


Figure S5. ^{1}H NMR spectra of (a) UMTA and (d) DHTA, soluble components obtained by reverse ion exchange of (b) MMT-pUMTA and (e) MMT-pDHTA, and (c) hpUMTA and (f) hpDHTA. In (a) and (d), UMTA and DHTA have the peaks characteristic to vinyl groups (H1, H2, K1, and K2), while in (b) and (e), these peaks are absent and the remaining peaks are broadened. Also, the spectra in (b) and (e) are, respectively, similar to the spectra of hpUMTA and hpDHTA in (c) and (f), indicating the successful *in situ* polymerization of MMT-UMTA and MMT-DHTA.

6. Trace of *d*-spacings in surface modified clays and those derivatives.

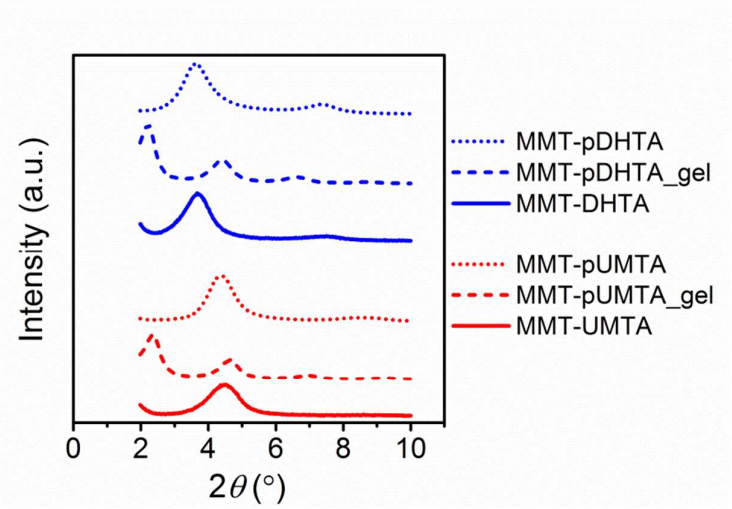


Figure S6. 1D-XRD profiles of the surface modified clays (MMT-UMTA and MMT-DHTA), gel-like deposits (MMT-pUMTA_gel and MMT-pDHTA_gel), and final composites (MMT-pUMTA and MMT-pDHTA).

Table S2. The diffraction peak positions of the (001) plane and corresponding *d*-spacing for the surface modified clays, gel-like deposits, and final composites.

State	Sample	2θ at the (001) peak (°)	*d*-spacing (nm)
Powder	MMT-UMTA	4.45	1.98
	MMT-DHTA	3.67	2.40
Gel-like deposit	MMT-pUMTA_gel	2.38	3.71
	MMT-pDHTA_gel	2.21	4.00
Composite film	MMT-pUMTA	4.38	2.03
	MMT-pDHTA	3.61	2.44

7. Mechanical property and solvent absorbency of MMT-pDHTA in various solvents.

Table S3. Mechanical property of MMT-pDHTA in the dry state and after immersion in water for different times

Immersion time (h)	Young's modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
0[a]	5.5 ± 0.3	96.9 ± 2.9	3.5 ± 0.6
0.5	5.3 ± 0.1	93.3 ± 4.8	3.4 ± 0.1
1	4.7 ± 0.2	85.5 ± 0.4	3.5 ± 0.2
2	3.9 ± 0.2	64.0 ± 6.8	3.1 ± 0.5
3	3.6 ± 0.4	41.3 ± 3.3	2.1 ± 0.2
6	3.0 ± 0.2	33.5 ± 2.4	2.0 ± 0.1
24	2.9 ± 0.3	29.6 ± 1.7	1.4 ± 0.1
96	2.9 ± 0.2	29.8 ± 3.9	1.6 ± 0.3

[a] Stored in a desiccator (< 20 % of RH at room temperature) for over 3 days.

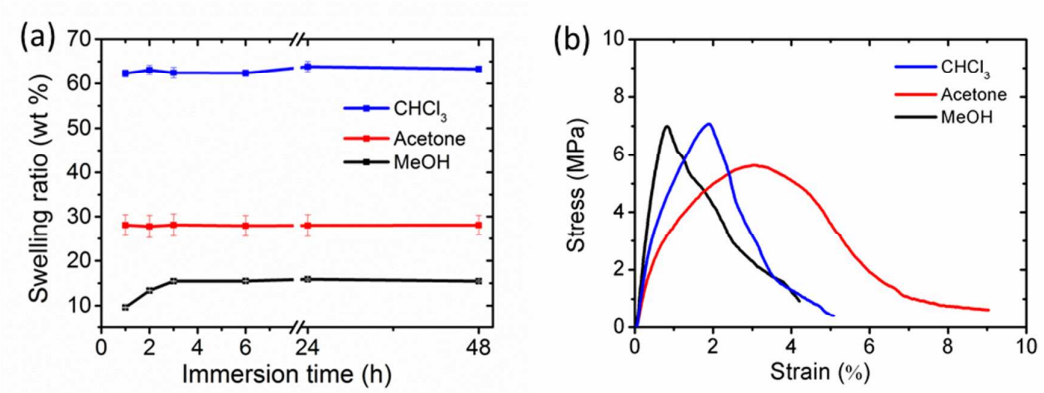


Figure S7. (a) Swelling ratio of MMT-pDHTA after immersion in methanol, acetone, and chloroform. The error bars represent the standard deviation. (b) Stress-strain curves of MMT-pDHTA measured after immersion in the organic solvents for 24 h.

REFERENCES

(1) Samakande, A.; Hartmann, P. C.; Sanderson, R. D., Synthesis and characterization of new cationic quaternary ammonium polymerizable surfactants. *J. Colloid Interface Sci.* **2006,** *296* (1), 316-323.

(2) Joynes, D.; Sherrington, D. C., Novel polymerizable mono-and divalent quaternary ammonium cationic surfactants: I. Synthesis, structural characterization and homopolymerization. *Polymer* **1996,** *37* (8), 1453-1462.

(3) Zhao, X.; Chen, W.; Liu, Z.; Guo, J.; Zhou, Z.; Crommen, J.; Moaddel, R.; Jiang, Z., A novel mixed phospholipid functionalized monolithic column for early screening of drug induced phospholipidosis risk. *J. Chromatogr. A* **2014,** *1367*, 99-108.