SUPPORTING INFORMATION

Photo-induced SI-ATRP for the synthesis of photoclickable intercalated clay nanofillers

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Experimental part

1. Materials

Soda montmorillonite clay (MMT-Na: CEC = 92 mequiv./100g, d_{001}= 11.7 A°, surface area 750 m^2/g) sample was kindly donated by Southern Clay Products. 3-Aminopropyl trimethoxysilane (APTMS), α-bromoisobutyryl bromide (BIBB), propargyl methacrylate (PGM), copper (I) bromide (CuBr), copper (II) bromide ($CuBr_2$), pentamethyldiethylenetriamine (PMDETA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), triethylamine (TEA), 4-dimethylaminopyridine (DMAP), Irgacure 819, ethylenediaminetetraacetic acid (EDTA), mercaptosuccinic acid (MSA), bromomethyl benzene (C_6H_5-Br) were purchased from Sigma-Aldrich and used as received. The solvents, namely hydrochloric acid (HCl), anhydrous toluene, anhydrous N,N-dimethyl formamide (DMF), ethanol (EtOH), sodium hydroxide (NaOH), dichloromethane (DCM) and acetone, were purchased from Alfa-Aesar and used without further purification. Ultrapure water was purified using a Milli-Q plus purification system.

2. Synthesis methods

2.1. Activation of clay, step (*i*) in Figure 1 (MMT-OH)

2 g of MMT-Na were introduced in 200 mL of 0.1 M HCl during 24 h under stirring at room temperature. Then, this activated powder was collected by centrifugation and thoroughly washed with ultrapure water until total removal of chlorine ions (as tested by $AgNO_3$). The resulting clay was finally dried in a vacuum oven at 60 °C for 24 h this sample is denominated as MMT-OH.

2.2. Silanisation of clay, step (*ii*) in Figure 1 (MMT-NH_2)

1 g of MMT-OH was first dispersed for 1 h in 25 mL of anhydrous toluene using magnetic stirring, and then sonicated for 5 min in order to obtain well-dispersed solution. To this suspension, 1 mL of 3-aminopropyl trimethoxysilane (APTMS) was added and the silanisation reaction was carried out under stirring for 16h at reflux under N_2 inert atmosphere. The functionalized clay was then centrifuged and washed several times with toluene, dichloromethane and ethanol and then dried in a vacuum oven at 60 °C for 24 h, the resulting sample is denominated MMT-NH_2.

2.3. Grafting of ATRP initiator on clay, step (*iii*) in Figure 1 (MMT-Br)

1 g of the MMT-NH_2 was dispersed into 25 mL of anhydrous N,N-dimethyl formamide. After 10 min of stirring at room temperature, 6 mL of anhydrous triethylamine (TEA) and 100 mg of DMAP were added to the dispersion. The mixture was degassed by bubbling with nitrogen and left to stir for 30 min and then cooled down to 0°C in an ice bath. To this dispersion, were added dropwise 6 mL of bromoisobutyryl bromide (BIBB) solubilized in 10 mL of anhydrous DMF. Ssubsequently, the reaction was allowed to proceed under stirring for 24h at ambient temperature, while maintaining the suspension under nitrogen atmosphere. The obtained clay was collected by centrifugation and successively washed with DMF, ethanol, and acetone and then dried in a vacuum oven at 60 °C for 24 h. This procedure yields bromine-terminated clay denominated as MMT-Br.

2.4. Synthesis of poly (propargyl methacrylate)/clay nanofiller *via* photoinitiated SI-ATRP, step (*iv*) in Figure 1 (MMT-PPGM)

Polymerization of propargyl methacrylate from the bromine-clay surface was carried out using UV irradiation at 365 nm in a spectrolinker XL-1500 UV under stirring. Typically, 100 mg of MMT-Br were introduced in a deoxygenated three-necked flask containing 25 mL of anhydrous DMF, where was added a mixture of 52 mg of CuBr, 8 mg of $CuBr_2$, 84 mL of PMDETA, and

48 mg of DMPA was added under stirring, while maintaining a nitrogen stream. On the other hand, 5mL of MPG and 2 mL of anhydrous DMF were bubbled with nitrogen for 10 min, and then were injected via a degassed syringe into the clay suspension. The mixture was then irradiated at 365 nm under stirring for 2 h to initiate the polymerization from the clay surface. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with DMF and EtOH followed by a Soxhlet extraction in chloroform. Finally, the clay was dispersed in a 10 mL solution of 0.1 M of EDTA in 0.1 M NaOH overnight in order to remove the copper ATRP-catalyst and then followed by washing with water and drying in a vaccum oven at 60°C for 24 h.

2.5. Functionalization of clickable clay nanofillers *via* photo-initiated thiol-yne click reaction, MMT-COOH.

20 mg of MMT-PPGM were dispersed in 2 mL of methanol for 10 min under stirring, and then 300 mg of mercaptosuccinic acid were added. The mixture was degassed under nitrogen flow for 10 min. On the other hand, 30 mg of DMPA photo-initiator were solubilised in 1 ml of methanol and bubbled with nitrogen for 5 min, and then introduced in the clay suspension via a degassed syringe. The mixture was then irradiated at 365 nm under stirring for 3 h. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with methanol and EtOH followed by drying in a vacuum oven at 60°C for 24 h.

2.6. Azidation of bromomethyl benzene (C_6H_5-N_3)

1g of bromomethyl benzene and NaN_3 were solubilized in 13 mL of DMSO. After 2h of stirring at room temperature, the mixture was diluted with 50 mL of water and then the organic product was extracted using ether for three times followed by washing with water and saturated NaCl solution and finally dried over $MgSO_4$. The mixture was then filtered and the solvent was evaporated. The obtained product was analyzed by IR ($\nu = 2090$ cm^{-1}; $-N_3$) and by ^1H NMR ($\delta = 4.33$ (s, 2 H); $C\underline{H_2}-N_3$)

2.7. Functionalization of clickable clay nanofillers via photo-initiated CuAAC click reaction, MMT-Phe.

20 mg of MMT-PPGM were dispersed in a 4 mL of DMF for 10 min, and then 100 mg of azido methyl benzene, 167 mg of $CuBr_2$, and 470 µL of PMDETA were added. The mixture was degassed under nitrogen flow for 10 min. On the other hand, 385 mg of Irgacure 819 as photo-initiator were solubilised in 1 ml of DMF and bubbled through nitrogen for 5 min, and then introduced in the clay suspension via a degassed syringe. The mixture was then irradiated at 365 nm under stirring for 3 h. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with DMF and EtOH followed by drying in a vacuum oven at 60°C for 24h.

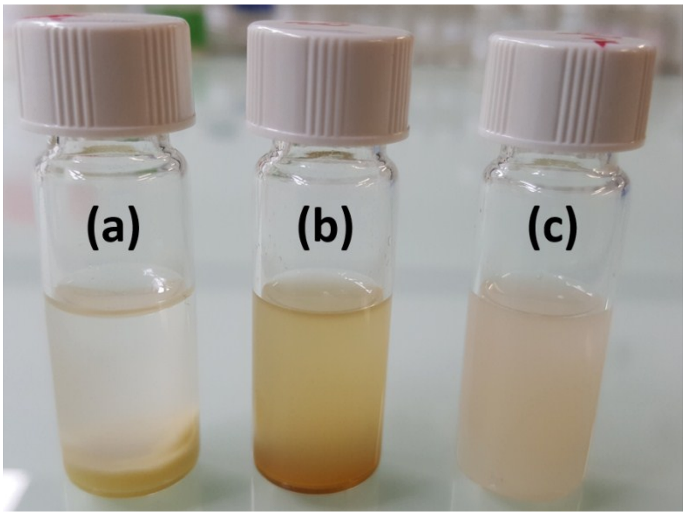

Fig. SI1. Comparison of dispersion state of 2 mL DMF suspensions of 10 mg of (a) MMT-Na, (b) MMT-PPGM after SI-ATRP time of 1 h (c) MMT-PPGM after SI-ATRP time of 2 h. The digital photos are taken after 1h stirring followed by 24h standing period.

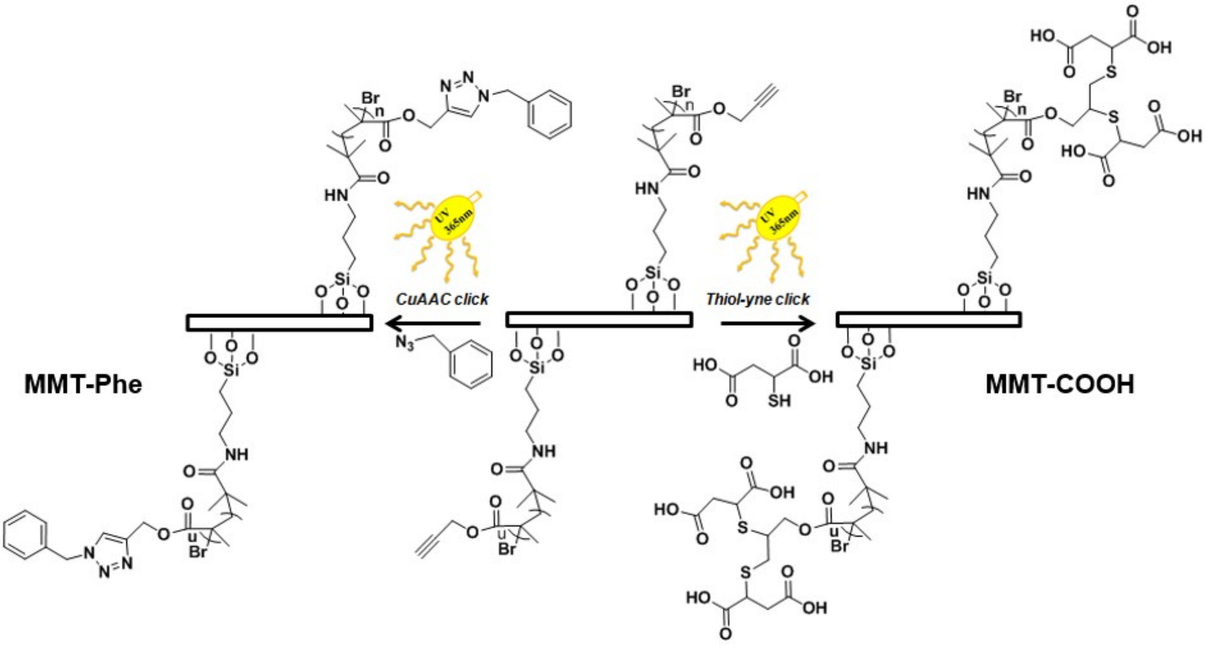

Fig SI2. Schematic illustration for the surface functionalization of MMT-PPGM with mercaptosuccinic acid and azidomethyl benzene via photodriven thiol-yne and 1,3 dipolar cycloadditon click strategies, respectively.

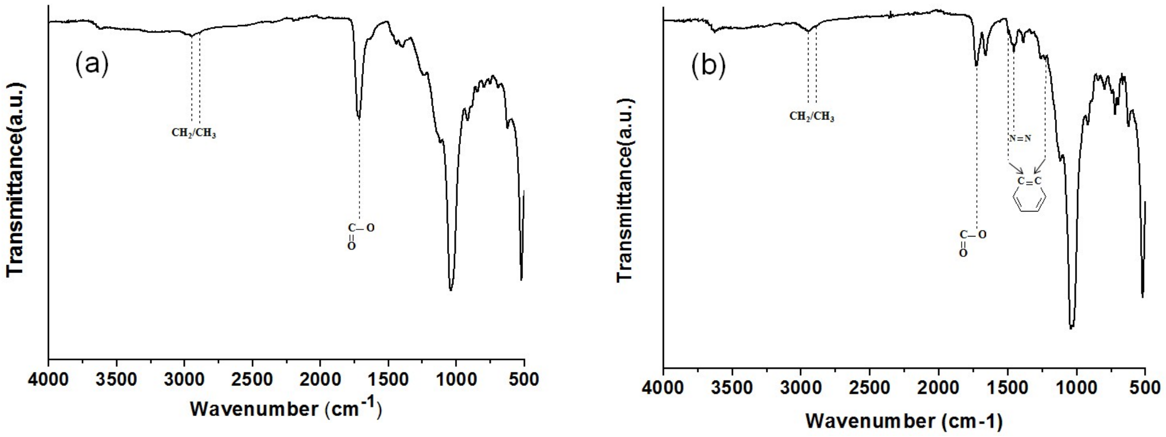

Fig. SI3. FTIR spectra of (a) acid- (MMT-COOH) and (b) benzene-functionalized (MMT-Phe) clay nanofillers *via* thiol-yne and Huisgen cycloaddition surface Click grafting reactions, respectively.