Preparation of highly exfoliated epoxy/clay nanocomposites by clay grafted with liquid crystalline epoxy

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1. A pre-weighed amount of organophilic clay, the certain quantity of concentrated sulfuric acid and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$ are added to distilling flask. Organic ammonium of organophilic clay is decomposed and NH_4HSO_4 can generate in the reaction when the mixed system are heated to boil, and then the excess concentrated sulfuric acid is neutralized using concentrated sodium hydroxide solution. Since then, 0.1 mol/L HCl is used to absorb NH_3 when the above system is treated by steam distillation. The residual HCl in the process is measured by 0.05 mol/L NaOH and phenolphthalein used as an indicator, therefore, the ion exchange capacity can be calculated according to NaOH consumption in the titration process.

$$\text{CEC} = \frac{C_1V_1 - C_2V_2}{M} \times 100$$
$$X = \frac{\text{CEC}}{\text{CEC}'} \times 100\%$$

CEC: Cation-exchange capacity (mmol/100g);

C1: Hydrochloric acid solution concentration (mol/L);

V1: Dosage of hydrochloric acid solution (ml);

C2: Sodium hydroxide solution concentration (mol/L);

V2: Dosage of sodium hydroxidesolution (ml);

m: The quality of organophilic clay;

CEC': Pristine clay cation-exchange capacity (mmol/100g);

X: Ion exchange ratio (%)

2. synthesis routes of 4-(Oxiran-2-ylmethoxy)-benzoic acid cholesterol ester (SOAC)

4-Hydroxybenzaldehyde (6.10 g, 50.0 mmol) was dissolved in 2 M NaOH (30 ml).

Epichlorohydrin (4.68 g, 50.0 mmol) was added dropwise to the solution stirred at

0 °C. Reaction mixture was stirred overnight at room temperature. The solution was extracted with dichloromethane (3×25 ml) and the combined organic phases washed with 1 M HCl (3×40 ml), water (40 ml), and brine (25 ml). The organic phase was dried with Na₂SO₄, and the solvent removed under reduced pressure. The crude product was purified with flash column chromatography on silica (MF: petrolether/ethyl acetate = 2:1). Yield 79%.

4-(Oxiran-2-ylmethoxy)benzaldehyde (5.80 g, 32.6 mmol) was pulverized in a 100-ml flask and 30% hydrogen peroxide (50 ml) was added. The reaction mixture was stirred vigorously for 30 min at room temperature. Dichloromethane (100 ml) was added and the phases were separated. The organic phase was washed with brine, dried over Na₂SO₄, and the solvent removed under reduced pressure. White solid. Yield 86%.

A mixture of 4-(Oxiran-2-ylmethoxy)benzaldehyde (0.01 mol) and cholesterol (0.01 mol) was dissolved in 200 ml dry N,N-dimethylformamide (DMF) in a round-bottomed flask. The DCC solution (0.01 mol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) in 50 ml of DMF was added dropwise to the above system under continuous stirring. The reaction system was stirred for 24 h at room temperature, and the by-product (N,N-dicyclohexylurea) was then filtered off. After removal of the solvent, the product was precipitated by the addition of water to the residue and the crude product was obtained by filtration and recrystallised from ethyl acetate: ethanol (2:1). Yield: 78%.

¹H-NMR (600 MHz, CDCl₃, δ): 7.97–7.95 (d, *J*=9 Hz, 2H, Ar–H), 6.92 (d, *J*=9 Hz, 2H, Ar–H), 4.30 (m, 1H), 3.99 (m, 1H), 3.36 (s, 1H), 3.26 (s, 1H), 3.11 (s, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 2.30–0.61 (m, 44H, cholesteryl–H).

3. Synthesis routes of 4-(4-Oxiranyl-methoxyl)-benzoic acid cholesterol ester (DOAC)

Potassium hydroxide (8.0 g, 0.14 mol) and potassium iodide (0.35 g, 0.002 mol) was added to a solution of p-hydroxybenzoic acid (8.3 g, 0.06 mol) in 200 mL of ethanol. After the reaction mixture was stirred at room temperature for 1 h, allyl bromide (9 g, 0.08 mol) was added dropwise to the mixture. The resulting mixture

was heated under reflux overnight. After this had cooled to room temperature, 1mol/L HCl solution was added to neutralize the reaction mixture. The white precipitate was filtered and recrystallized from ethanol twice to give white piece crystals in 88% yield and with melting point (T_m) at 165 °C.

8.9 g of 4-(2-allyloxy)benzoic acid, 15 mL of thionyl chloride were added to a round-bottomed flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 4 h, and then heated to 60 °C for 6 h, the excess thionyl chloride was distilled under reduced pressure to give the corresponding acid chloride. Yield: 97%.

7.84 g (0.04mol) of 4-(2-allyloxy)benzoicacyl chloride was added dropwise to a cold solution of 15.44 g (0.04 mol) of cholesterol in 40 ml of chloroform and 2 ml of pyridine. The reaction mixture was heated to reflux for 16 h. The mixture was cooled to room temperature, poured into 200 mL of methanol. The precipitated crude product was filtered and recrystallized from ethanol:toluene (2:1). The yield of AC is 84% with T_m at 116 °C.

5.46 g of AC was dissolved in 50 mL of dry CH_2Cl_2 was added dropwise to a solution of metachloroperbenzoic acid (MCPBA, 4.3 g, 0.025 mol) in 300 mL of dry CH_2Cl_2 under continuous stirring. The reaction mixture was stirred and refluxed for 48 h. After cooling and subsequent filtration, the solvent was evaporated to dryness in rotary evaporator. The crude product obtained was washed with ethanol and then filtered three times. The yield of OAC is 80% with T_m at 129 °C.

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , δ): 7.97–7.95 (d, $J=9$ Hz, 2H, Ar–H), 6.92 (d, $J=9$ Hz, 2H, Ar–H), 4.30 (m, 1H), 3.99 (m, 1H), 3.36 (s, 1H), 3.26 (s, 1H), 3.11 (s, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 2.30–0.61 (m, 44H, cholesteryl–H).

Figure S1 ^1H -NMR (CDCl_3/TMS , d, ppm) spectrum of SOAC.

Figure S2 ^1H -NMR (CDCl_3/TMS , d, ppm) spectrum of DOAC.

Figure S3 Polarized optical micrographs ($\times 200$) of DOAC at heating process. (a) 140 $^{\circ}\text{C}$, (b) 200 $^{\circ}\text{C}$.

Figure S4 Polarized optical micrographs ($\times 200$) of SOAC at 140 °C of heating process.

Figure S5 Dispersion state of (a) M-clay and (b) DOACM-clay in trichloromethane.