Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One Step Synthesis of MOF-Polymer Composites

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Experimental

Materials

Methyl methacrylate (MMA, 99%), vinyl acetate (VA, 99%), poly(ethyleneglycol)dimethacrylate (PEGDMA), stearyl methacrylate (STM), 1,6-hexanediol dimethacrylate (1,6-HDDA), copper(II) nitrate hemi(pentahydrate) (purum ≥98%), benzene-1,3,5-tricarboxylic acid (Trimesic acid, 95%) were purchased from Sigma-Aldrich and used as received. 2,2'-Azobis(isobutyronitrile) (AIBN, 97%, Fisher Scientific UK) was recrystallized from methanol and dried prior to use. 2,2'-Azobis[N-(2-carboxyethyl)-2-methylpropionamidine] hydrate (VA-057) was purchased from Wako and used without purification. Surfactant Arlacel P135 was kindly provided by Croda. All solvents, including deionized water, dimethylformamide (DMF, VWR Chemica), Ethanol (EtOH, VWR Chemical) were used as received.

Synthesis of HKUST-1

HKUST-1 was synthesised following procedure described in details elsewhere.[17] In brief, copper nitrate hemipentahydrate (10 g) and 1,3,5 benzenetricarboxylic acid (5 g) were mixed with DMF (85 ml), EtOH (85 ml) and deionized water (85 ml) in a round bottom flask and placed into oil bath at 85°C for 21 h under constant shaking. Formed crystals were filtered using a Buchner funnel and immersed in DCM, which was changed 3-4 times before crystals were collected and dried at 150°C in a vacuum oven for 28 h.

Synthesis of polymer and polymer-MOF composites via precipitation polymerization

An initiator, AIBN (1 mol% per C=C total), was dissolved in the monomer at room temperature, followed by the addition of the stock solution (DMF: EtOH: water in ratio 1:1:1

vol%) or MOF precursor ($Cu(NO_3)_2 * 2,5\ H_2O$, Trimesic acid, DMF, EtOH, water). After solution was formed a cross-linker was added and the polymerization mixture was placed in a 15 ml PTFE jar (d = 2.5 cm) closed with the subaseal. The reaction mixture was purged with nitrogen for at least 15 min before placing it into an oven for 21 hours at 85 °C. The diameter of the resulting samples varied between 2.0 and 2.5 cm and thickness between 1.1 and 2.8 mm.

Using an emulsion templating approach for synthesis of polymer and polymer-MOF composites

High internal phase emulsions (HIPE) were prepared in a glass reaction vessel equipped with a glass paddle rod connected to an overhead stirrer. The external phase (20 vol%) of the emulsion was prepared by dissolving initiator (VA-57, 1 mol.% with respect to the total C=C) and surfactant (Arlacel P135) in a mixture of monomer and crosslinker (monomer to cross linker 1:1 molar ratio). The amount of surfactant was calculated with respect to the total weight of monomer and crosslinker. The dispersed phase (80 vol%) contained stock solution (DMF: EtOH: water in ratio 1:1:1 vol%) for synthesis of conventional polyHIPEs or MOF precursor ($Cu(NO_3)_2 * 2,5\ H_2O$, Trimesic acid, DMF, EtOH, water) for synthesis of polymer-MOF composites. All solutions were purged with Argon for 30 min before the dispersed phase was added dropwise into the external phase at a constant agitation (at 430 rpm). After all of the dispersed phase had been added, the stirring rate was increased to 2000 rpm for 10 min to obtain homogeneous emulsion. Formed HIPEs were transferred immediately after preparation in an argon purged PP centrifuge tube with screw cap and placed into the oven at 85 °C for 21 hours. The resulting polyHIPEs were submerged into EtOH to remove all unreacted monomers, surfactants and internal phase and subsequently dried in the vacuum oven for 28 h at 85 °C.

Characterization of polymers and polymer-MOF composites

X-ray diffraction (XRD) measurements were conducted at room temperature using an X'Pert PRO (PANanalytical) X-ray diffractometer and a Cu Kα radiation (α1 = 1.54057 Å, α2 = 1.54433 Å, weighted average = 1.54178 Å). The samples were ground before the analysis due to the small amount of MOF in the sample. The data was collected between 3 to 40° angular range in 2θ in continuous scan mode.

Scanning electron microscope (SEM; LEO 1525, Karl Zeiss) was used to establish the microstructure of the surfaces and cross-sections of samples after extraction of porogen/internal phase and drying. For cross-section imaging a membrane sample was broken in liquid nitrogen and pasted vertically onto SEM stubs covered with carbon tape. For surface imaging a membrane sample was cut and pasted horizontally onto SEM stubs covered with carbon tape. The samples were then coated with a chromium-layer in a Q150T turbo - pumped sputter coater (Quorum Technologies Ltd.). SEM images of the surface and cross section of membrane samples were recorded using accelerating voltage of 5 kV and under dry conditions at room temperature.

Specific surface area of the extracted and dried polymers and polymer-MOF composites was estimated by physical adsorption of N_2 sorption at -196 °C using a porosity analyser (Micromeritics, 3Flex). Prior to the analysis, samples were dried overnight at 120 °C under low vacuum and then further degassed overnight at 120 °C (around 0.2 mbar). Finally, the samples were in-situ degassed on the sorption analyzer at 120 °C for 4 h (around 0.0030 mbar). The surface areas were calculated using the Brunauer-Emmett-Teller method.

Thermal gravimetric analysis (TGA) of the as-synthesized polymers and polymer-MOF composites was carried out on a TG 209 ***F1** Libra* Thermogravimetric Analyzer (NETZSCH instruments) in a temperature range from 25 to 900 ^{o}C in air (100 mL min^{-1}). Experiments were performed using 10-17 mg of sample.

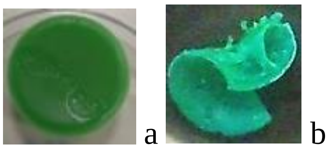

Figure SI 1. Images of samples synthesised using 1:1 mol.eq MMA:PEGDMA and different (M+XL)/S; a – 75:25 vol%; b- 50:50 vol%.

Table SI1. Char yield for polymer-HKUST-1 composites

Sample	Image	M:XL [mol.eq.]	Remaining mass at 600 °C [wt.%]
PP_MMA_1		1:1	1.97
PP_MMA_2		3:1	1.89
PP_VA_1		1:1	5.60
PP_VA_2		3:1	1.90

Polymerization temperature 85°C; initiator – 1mol.% AIBN to the total C=C bonds; XL = PEGDMA; S = MOF precursor; (M+XL)/S = 75:25

Table SI 2. Composition and properties of MOF/polyHIPE composites and polyHIPE

Sample	Internal phase	Arlacel P135 [wt.%]	BET specific surface area [m^2/g]	Remaining mass at 600 °C [wt.%]
PolyHIPE	Stock solution	15	0	0.18
MOF/ polyHIPE_15	MOF precursor	15	16.4	9.3
MOF/ polyHIPE_20	MOF precursor	20	8.4	10.8

Polymerisation temperature 16h at 50^{o}C then 8h at 85 ^{o}C; initiator – 1 mol.% VA-057 to the total C=C bonds; M:XL 1:1 mol.eq; internal phase volume – 80 vol.%; M - SMA; XL - 1,6 HDMA.