Supporting information

Dandelion-like $CaCO_3$ microsphere: ionic liquid-assisted biomimetic synthesis and *in-situ* fabrication of poly(ε-caprolactone)/$CaCO_3$ composites with high performance

Hai-Chun Dang, Wu-Cheng Nie, Xiu-Li Wang*, Wen-Tao Wang, Fei Song and Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

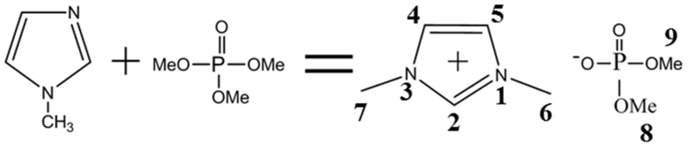
Experimental

Materials

1-Methylimidazole with a concentration of 99% was purchased from Kaile Chemical Co. Ltd. (Zhejiang, China) and distilled under reduced pressure before use. Trimethyl phosphate was supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). ε-Caprolactone (ε-CL) was a gift from Solvay Interox Ltd. It was dried by CaH_2 before use and distilled twice under reduced pressure. Stannous octoate ($Sn(Oct)_2$) was purchased from Sigma (USA) and used as received. RCC (AR), anhydrous $CaCl_2$ (AR), NaOH (AR), stearic acid (AR) and other materials were purchased from Kelong Chemical Industries Reagent Co. (Chengdu, China).

Synthesis procedure

1,3-dimethylimidazolium dimethyl phosphate ([MMIM][Me_2PO_4]) was synthesized according to the literature[1,2] (**Scheme S1**), and its chemical structure was determined by ^{1}H-NMR. [MMIM][Me_2PO_4]: δH (400 MHz, DMSO, Me_4Si) 9.66 (s, 1H, N–CH=N), 7.85 (m, 2H, N–CH_2CH=CH), 3.87 (s, 6H, H_3C–N–CH=N–CH_3), 3.28 (d, 6H, $P(OCH_3)_2$).



Scheme S1. Synthesis route of ionic liquid [MMIM][Me_2PO_4]

Aqueous solutions of calcium chloride, sodium hydroxide and ionic liquids were used as reserving solutions. In a typical synthesis of $CaCO_3$, 10 mL 1 M NaOH solution and deionized water were added into 1 M ionic liquids solution and mixed thoroughly. Then, 20 mL 1 M $CaCl_2$ solution was dropped into the above solution under slightly stirring. The glass vessel containing the resultant mixture was covered with parafilm punched with several needle holes and placed under the ambient environment. After the completion of incubation time, the parafilm was removed and the precipitate was centrifuged with distilled water at 5000 rpm for 10 min as well as rinsed several times by this method. The obtained products were dried by lyophilization. In order to recycle ionic liquids, all the centrifugation and decantation solutions were collected and rotary evaporated under vacuum. All the detailed reaction conditions for synthesis of $CaCO_3$ are listed in the Table S1.

Table S1 The obtained polymorph of $CaCO_3$ under different reaction conditions

Ionic liquids	C_{IL} (mmol L^{-1})	Time (day)	Morphology
-	-	5	rhombohedron
$[Me_2MIM][Me_2PO_4]$	10	5	cockscomb-like
$[Me_2MIM][Me_2PO_4]$	50	5	dandelion-like microsphere
$[Me_2MIM][Me_2PO_4]$	100	5	irregular sphere-like aggregation
$[Me_2MIM][Me_2PO_4]$	50	1	bundle-like

Preparation of PCL/$CaCO_3$ composites

Before preparation of PCL/$CaCO_3$ composites, $CaCO_3$ was organo-modified by stearic acid. The presence of stearic acid not only can improve the compatibility with PCL matrix, but also prevent the aggregation of $CaCO_3$ in the polymerization. In a typical procedure for preparation of organo-modified $CaCO_3$, 1.00 g synthesized $CaCO_3$ was put into 10 mL 0.01M stearic acid toluene solution and ultrasonicated at 60 °C for 3 h. The resulting suspension was centrifuged at 5000 rpm for 30 min. The solid was washed with ethanol for twice, and dried at room temperature.

The PCL/$CaCO_3$ composites were prepared by in-situ ring opening polymerization. The detailed synthesis procedures are as follows: A given amount of organo-modified calcium carbonate with different morphologies was introduced to a dried vial. The vial was subsequently vacuumed and purged with argon for three times. Then, a certain amount of ε-CL was injected into the vial and mixed with organo-modified $CaCO_3$ under ultrasonication for 1 h to obtain a uniformed mixture. Finally, a predetermined amount of catalyst, stannous octanoate, was added into the vial [molar ratio of monomer to catalyst (M/C) =2000] and polymerizations were conducted at 100 °C for 24 h. At the end of polymerization, the mixture was quenched by immediately immersing into ice water.

The morphology of $CaCO_3$ crystal was examined by scanning electron microscopy (SEM) (Philips XL-3, FEI, Oregon, USA) with an accelerating voltage of 15 kV. The samples were sputtered with a thin layer of gold before testing. The fracture morphologies of PCL/$CaCO_3$ composites were also observed by SEM. Prior to the test, the specimens were cryo-fractured and the broken surfaces were sputtered with gold. Transmission electron microscopy (TEM) photographs were obtained with a Philips CM200

Transmission Electron Microscope, which was operated at an accelerated voltage of 120 kV. The as-prepared calcium carbonate were analyzed by X-ray powder diffraction (XRD) (DX-1000 CSC, Fangyuan, Dandong, China) using Cu-Kα radiation at a scanning rate of 3.6 ° min^{-1} in the 2θ range of 20-70 ° to determine crystal phase constitution. The accelerating voltage and the applied current were 40 kV and 25 mA, respectively. Desired amounts of ILs and D_2O were placed into a 5 mm NMR tube, and the IL was allowed to be completely dissolved. After that, ^1H spectra of [MMIM][Me_2PO_4] in D_2O with different concentration were collected on a Bruker Avance-400 NMR spectrometer operating at 400 MHz. The intrinsic viscosity ([η]) of PCL/$CaCO_3$ composites was determined in DMF solution with an Ubbelohde viscometer at a concentration of 0.1 g dL^{-1} at 30 °C. Thermal transition behaviors of PCL/$CaCO_3$ composites were investigated by a TA Instrument DSC Q200 with 3~10 mg of samples. Each sample was first heated from room temperature to 80°C above the melting temperature. The samples were held for 5 min to ensure complete melting and eliminate the previous thermal history and then cooled to -85 °C at a cooling rate of 10 °C min^{-1}(the first cooling scan). The crystallization temperature (T_c), crystallization enthalpy (ΔH_{c1}) was determined from this cooling scan. Subsequently, the sample was reheated to 120 °C at a rate of 10 °C min^{-1} (the second heating scan), from which melting temperature (T_m), and melting enthalpy (ΔH_m) were determined. Dumbbell-shaped samples of PCL/$CaCO_3$ composites were prepared according to GB/T 1040.3-2006 by injection molding using HAAKE Mini-Jet injection molding apparatus at a pressure of 400 bar with molding temperature of 30 °C. The injection (barrel) temperature was varied from 50 °C to 90 °C according to the fluidity of the different samples. All samples were pre-conditioned in 50% relative humidity (RH) at 23 °C for 24 h before testing. The tests were performed on an electronic universal testing machine (CMT4104, SANS Co. Ltd., China) at a cross-head speed (a tensile rate/an extension rate) of 5 cm/min. Five replications were used in each treatment to give the average.

Result and discussion

Critical aggregation concentration (CAC) of IL probed by ^{1}H NMR

Based on the literatures[3,4], we know that NMR is a very sensitive technique for the study of the aggregation behaviour ionic liquid. The observed chemical shift (δ_{obsd}) for [MMIM][Me_2PO_4] in D_2O according to Scheme S1 are listed in Table S2. At lower IL concentrations, δ_{obsd} is almost constant and then changes rapidly and levels off at higher concentrations. This behaviour is a consequence of IL aggregation, the sudden increase of $\partial\delta_{obsd} / \partial C$ corresponds to the aggregate formation.[4] The δ_{obsd} (the prone of C-6, 7) as a function of reciprocal concentration for IL is shown in **Fig. S1**. The plots of δ_{obsd} versus of $1/C_{IL}$ give two straight lines, and their intersection is corresponded to the CAC.

Table S2 The observed chemical shift δ_{obsd} (ppm) of the aqueous solutions of [MMIM][Me_2PO_4] as a function of concentration for various protons

C (mM)	δ_{obsd}	δ_{obsd}	δ_{obsd}	δ_{obsd}	δ_{obsd}
	C-2	C-4,5	H_2O	C-6,7	C-8,9
54.05	8.5758	7.3504	4.7049	3.5443	3.8282
112.61	8.5753	7.348	4.7056	3.5376	3.8284
139.64	8.5751	7.3476	4.7056	3.5353	3.8241
186.94	8.5761	7.3486	4.7068	3.5324	3.8244
247.75	8.5754	7.3478	4.7059	3.5315	3.8236
337.84	8.5751	7.3468	4.7062	3.5226	3.8211
436.94	8.5732	7.3443	4.7071	3.5134	3.8170
515.77	8.5726	7.3432	4.7067	3.5093	3.8153
680.18	8.5736	7.3428	4.7062	3.4983	3.8122

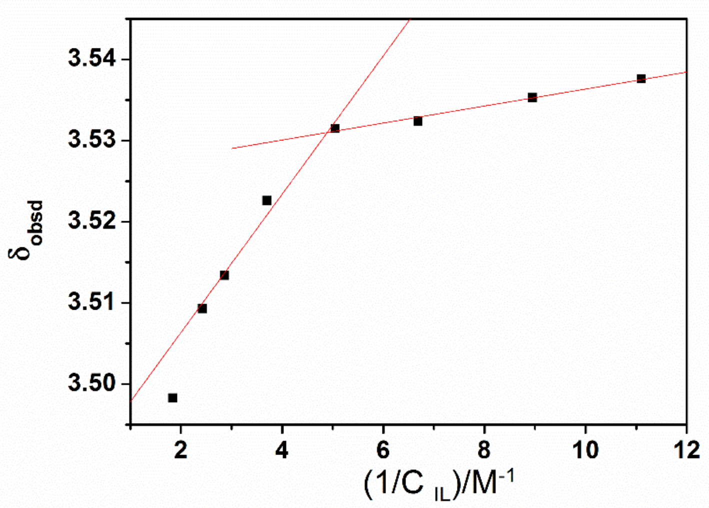


Fig. S1 Variation of δ_{obsd} for the protons of the methyl of imidazole ring (the prone of C-6, 7) against the reciprocal concentration of [MMIM][Me_2PO_4]

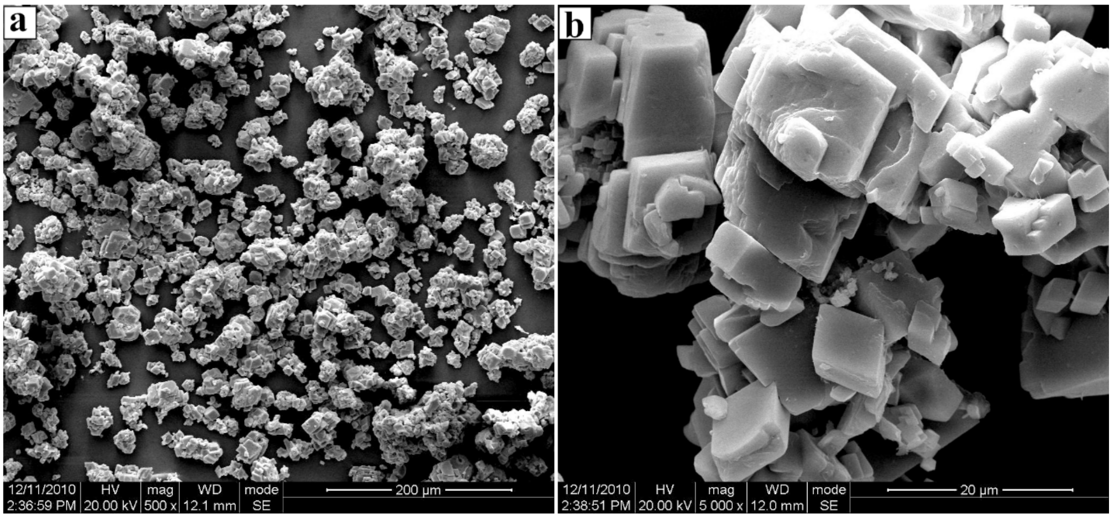


Fig. S2 SEM images of RCC under different magnification (a, b)

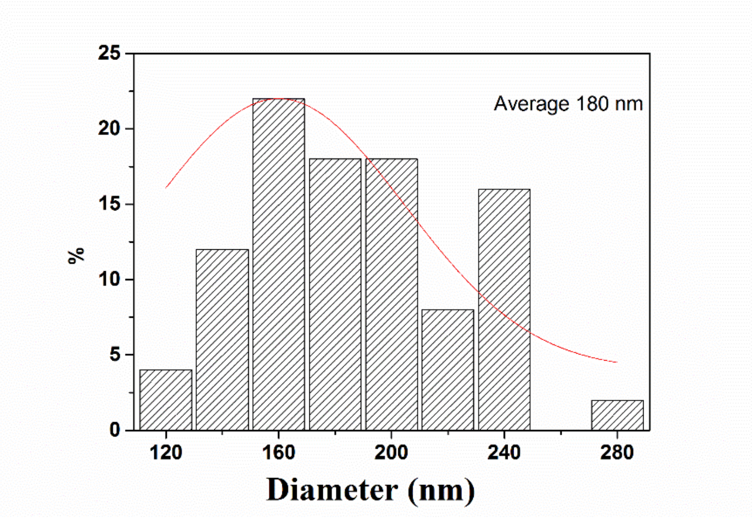


Fig. S3 The $CaCO_3$ particles in the cryo-fractured surface of PCL/3%DCC composites matrix with average diameter of 180 nm (n =50)

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