Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information

Solvent-Free Dual In-Situ Interfacial Engineering of Polyester Composites for Enhanced Capacitive Energy Storage

Li He, [1] Qian-Qian Liang, [2] Jia-Le Li, [1] Lin Pan, [1] Jun Liu, [1] Yin-Tao Li, [1] Nan Sun, *[1] Jinkai Yuan, *[3] Quan-Ping Zhang *[1, 2]

[1] *School of Materials and Chemistry, Southwest University of Science and Technology, Mianyang 621010, China*

[2] *Sichuan EM Technology Co., Ltd., Mianyang 621030, China*

[3] *Sorbonne Université, CNRS, Chimie de la Matière Condensée de Paris, LCMCP, F-75005 Paris, France*

Corresponding authors: Quan-Ping Zhang; Jinkai Yuan; Nan Sun
E-mails: zhangqp@swust.edu.cn; jinkai.yuan@sorbonne-universite.fr; nansun@swust.edu.cn

1 Experimental Section

1.1 Chemicals

Organic calcium borate ester (CaBE, as shown in **Figure S1**), ethylene glycol (EG), terephthalic acid (PTA) were supplied by Sichuan EM Technology Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS), anhydrous ethanol (Et-OH), phenol (Ph-OH), 1,1,2,2-tetrachloroethane, chloroform ($CHCl_3$), bromophenol blue (BPB), potassium hydroxide (KOH), and antimony trioxide (Sb_2O_3) were purchased from Chengdu Kelong Chemical Co., Ltd. All the chemicals were directly applied without purification.

1.2 Dual in-situ synthesis of polyester hybrid composite

First, 0.01wt% SDBS and 0.1wt% CaBE were dissolved in about 32wt% EG with intense stirring for 4 hours at 100C. After that, the transparent liquid, about 68wt% PTA and the catalyst 0.1 wt% Sb_2O_3 were added into a 70L steel reactor for a dual in-situ synthesis of polyester composite. It suffers from esterification (240 °C, 0.4 MPa) and polycondensation (280 °C, vacuum < 50 Pa) reactions in succession for the resulting polyester composite (CaBO-S/PET). CaBO/PETcomposite was fabricated with the same route.

1.3 Film preparation

First, compression molding was applied for preliminary films with a thickness of about 200 μm for neat PET and the hybrid composites. Second, the prefabricated films were further processed under biaxial stretching to obtain dielectric films with a thickness of about 10 μm.

1.4 Composite etching

The composite was repeatedly etched at 110 °C using a mixture of phenol and tetrafluoroethane (1:4). Eventually, a solid sample mainly composed of inorganic components was obtained.

1.5 Characterization and testing

A red laser pointer was used to shine on the sample bottle filled with various concentrations of CaBE in EG solution. An X-ray diffraction analyzer (Bruker Advance D8, Germany) was employed to analyze the structures of the polyester composite and its inorganic component. Superconducting nuclear magnetic resonance spectrometer (Avance 600, Germany), steady state was applied to determine the polyester composite and its inorganic component. Differential scanning calorimetry (Q2000, TA, America) was employed to analyze the thermal performance of the polyester hybrid composite. Morphological observation was performed on a field emission scanning electron microscope (SEM, JSM-7610F, JEOL, Japan), transmission electron microscopy (TEM, Libra 200, Carl Zeiss, Germany) and 3D optical microscope (3D OM, VHX-6000, Keyence, Japan). FT-IR (IS50, Thermo, America) and Raman spectrometer (inVia, Renishaw, England) were applied to determine the structure of the inorganic component (The laser wavelength of Raman spectroscopy is 514.5 nm.). Steady-state/transient fluorescence spectrometer (The excitation wavelength of fluorescence spectroscopy is 270 nm.) (FS5, Edinburgh company, UK). Injection molding was used to prepare the injection parts of the hybrid composite and neat PET according to ASTM D3039 for stress-strain testing. In addition, the hybrid composite and neat PET were subjected to biaxial stretching and then tailored into the film samples according to ASTM D882 for stress-strain testing. No less than ten injection and film samples of each neat PET and the hybrid composite were prepared and five samples were selected for testing at room temperature. The final performance data were obtained by taking their average value and an error analysis was also conducted. According to GB/T 1043.2-2018, unnotched specimens were selected for Charpy impact strength testing at room temperature using an impact energy (*E*) of 25 J and an impact velocity (V_0) of 3.8 m/s. The impact strength (a_{cU}) was calculated from the measured impact energy (*W*) using the following formula:

$$a_{cU} = \frac{w}{hb} \times 10^3 \tag{1}$$

where *w* is the calibrated energy absorbed (J) at specimen fracture, *h* is the specimen thickness (mm), and *b* is the specimen width (mm).

Dielectric properties were measured using an impedance analyzer (4294A, Agilent, USA). The leakage current and hysteresis loop were measured using a TF Analyzer 3000 ferroelectric polarization tester (aixACCT Systems GmbH, Germany) at room temperature with a frequency of 100 Hz. Diectric breakdown strength was evaluated with a withstanding voltage tester (DDJ-50KV, Beijing Guance Jingdian Equipment Ltd, China) with an increasing voltage of 200 V s^{-1}. The failure probability of neat PET and the hybrid composite is investigated according to the Weibull distribution function.

$$P(E) = 1 - \mathrm{e}^{-(E/E_{\mathrm{b}})^{\beta}} \tag{2}$$

where *P(E)* is the cumulative failure probability, *E* is the measured breakdown strength, E_b is the Weibull breakdown strength with 63.2% probability to breakdown, and β is the shape parameter or the slope of the derived logarithm equation as

$$\ln[-\ln(1 - P(E))] = \beta \ln E - \beta \ln E_{\mathrm{b}} \tag{3}$$

1.6 Carboxyl content testing

Prior to the experiment, three key components must be prepared in advance: the mixed solution, the standard titration solution, and the indicator. The indicator is specified as a 0.1% (mass fraction) bromophenol blue-ethanol solution, which requires pre-preparation before testing. The standard titration solution is a potassium hydroxide-ethanol solution with a concentration of c（KOH）=0.05 mol/L

To prepare the mixed solution: First, phenol is placed in an oven at 95°C to melt via heating. The molten phenol is then mixed with chloroform in a volume ratio of 2:3 (phenol: chloroform) until homogeneous. Accurately weigh 2 g of the sliced sample (precision: ±0.1 mg) and transfer it to a 250 mL conical flask. Add 50 mL of the pre-prepared phenol/chloroform mixed solution to the flask. The flask is then placed in an oven set to 105-125°C for heating to dissolve the sample. After complete dissolution, the mixture is allowed to cool to room temperature before titration. Once cooled, several drops of the bromophenol blue indicator are added to the solution using a dropper, followed by thorough shaking. Titration is performed with the potassium hydroxide-ethanol standard solution using a burette with a precision of 0.01 mL. The endpoint is reached when the solution color transitions sequentially from yellow to green, and finally to blue; the volume of the titration solution used at this blue endpoint is recorded.

The carboxyl end group content is calculated using the formula provided below:

$$X_2 = \frac{(V - V_0)c \times 10^3}{m} \#(4)$$

Where X_2 is the carboxyl terminal group content (mol/ton). V is the volume of titrant consumed by the slice sample (mL). V_0 is the volume of titrant consumed by the blank sample (mL). c is the concentration of the titrant (mol/L). m is the mass of the slice sample (g).

1.7 Intrinsic Viscosity (IV) Measurement

The Ubbelohde viscometer was used to determine the viscosity of the hybrid composite. The intrinsic viscosity ([η]) is calculated as follows:

$$m = \frac{0.125}{1 - (\omega_i + \omega_0)} \pm 0.005 \#(5)$$

$$\eta_r = \frac{t_1}{t_0} \#(6)$$

$$c = m\left[1 - (\omega_i + \omega_0)\right] \times \frac{100}{25}\#(7)$$

$$[\eta] = \frac{0.25(\eta_r - 1 + 3\ln \eta_r)}{c}\#(8)$$

Where *m* represents the mass of the sample, expressed in grams (g). ω_i and ω_j represent the mass fraction of inorganic filler and the mass fraction of other additives within the sliced sample, respectively. If either fraction exceeds 0.5%, m must be adjusted accordingly. η_r denotes the relative viscosity. t_1 and t_0 represent the efflux time of the polymer solution and the efflux time of the pure solvent, respectively, both expressed in seconds (s). *c* is the concentration of the polymer solution, expressed in grams per 100 milliliters (g/100 mL). *[η]* is the intrinsic viscosity, expressed in deciliters per gram (dL/g).

1.8 Adsorption behavior with numerical simulation

Based on the Materials Studio software platform, a comprehensive and systematic investigation was carried out regarding the adsorption behavior of polyethylene terephthalate (PET) on the (001) crystal plane of CaBO. The detailed simulation procedure is described as follows: To begin with, a molecular model of PET was constructed. Methyl capping was adopted to realistically mimic the finite length of the polymer chain. Once the construction was completed, the Forcite module was applied to conduct geometric optimization of the molecular structure. This optimization aimed to acquire an adsorbent structure with a stable configuration and the lowest possible energy, which was then designated as the initial model for the subsequent adsorption simulations. Next, the crystal structure of CaBO was retrieved from the crystal database, and its (001) crystal plane was carefully selected for surface modeling. In order to avoid the mutual interference between the upper and lower crystal layers under periodic boundary conditions, a vacuum layer with a thickness of 10 Å was introduced along the surface normal direction (z-axis). This step was crucial for constructing the substrate structure necessary for the adsorption simulation. During the adsorption simulation phase, the Adsorption Locator tool was utilized to explore the adsorption configurations of PET on the CaBO (001) surface. In this process, the Universal Force Field (UFF) was employed for energy assessment. The calculation accuracy was set at the medium level, the maximum adsorption distance was set to 5 Å, and the molecules were restricted to interact solely with the upper-layer atoms of the substrate. Through an extensive multi-configuration search, a stable adsorption configuration with the lowest total energy was ultimately obtained. Same procedures were applied to the simulation of control sample of CaBO/PET composites.

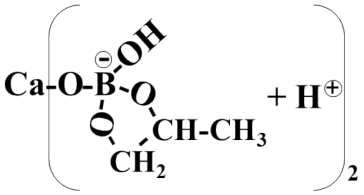

Figure S1 Molecular structure of CaBE.

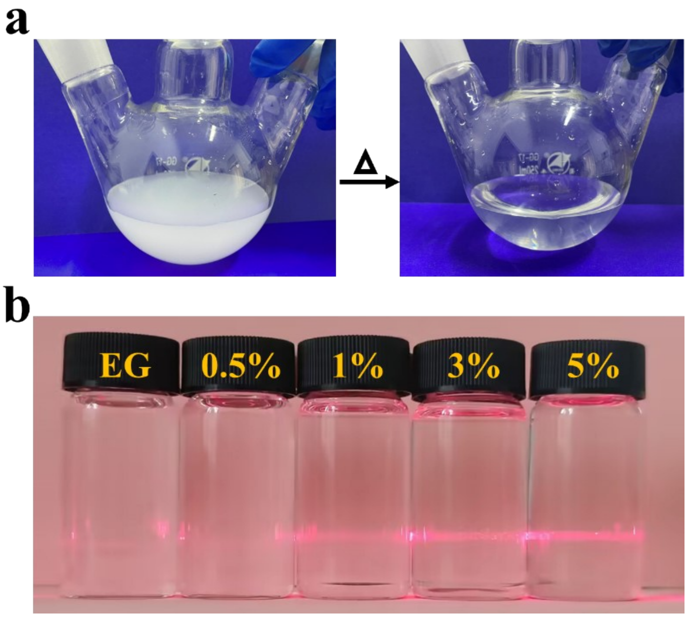

Figure S2 EG/CaBE colloidal solution. (a) Before and after dissolution of CaBE in EG solution. (b) Tyndall scattering of the colloidal solution with various mass concentrations of CaBE.

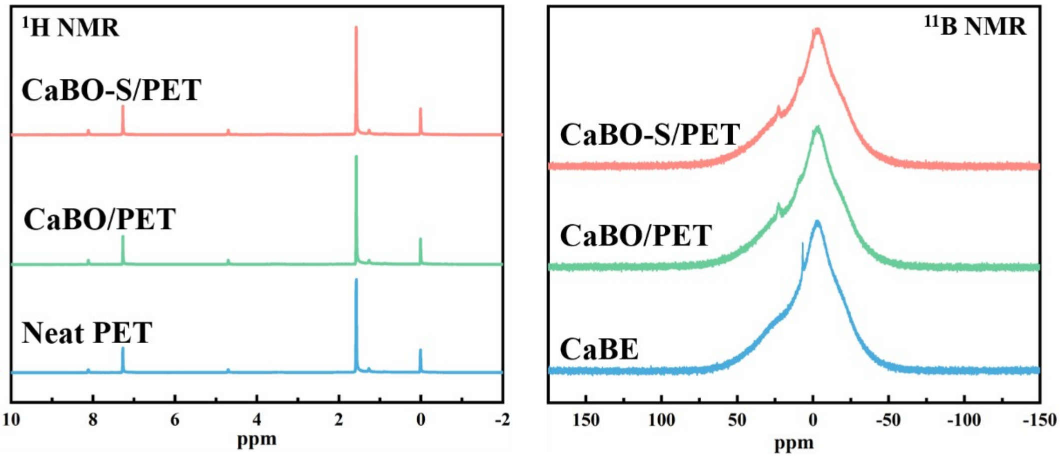

Figure S3 NMR results of neat PET and the hybrid composites.

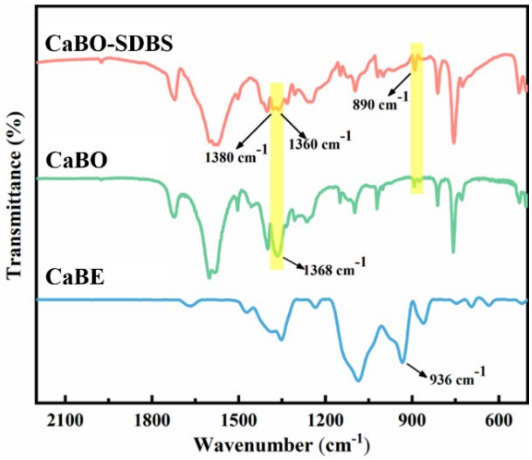

Figure S4 FT-IR spectra of CaBE, CaBO and CaBO-S.

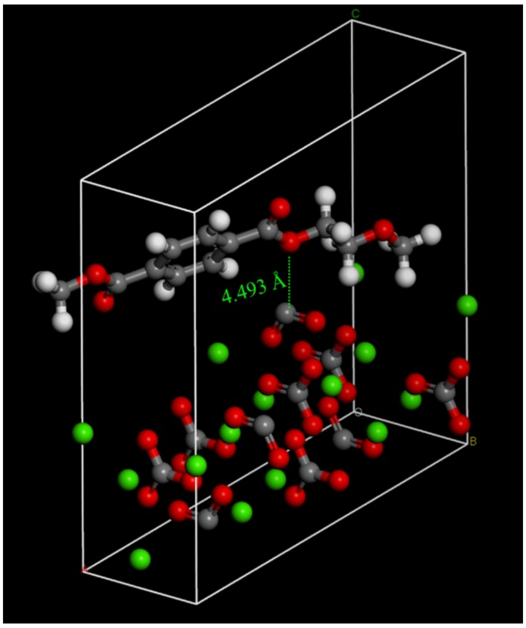

Figure S5 Numerical simulation of atomic adsorption behaviors in PET/$CaCO_3$ hybrid composite with Materials Studio.

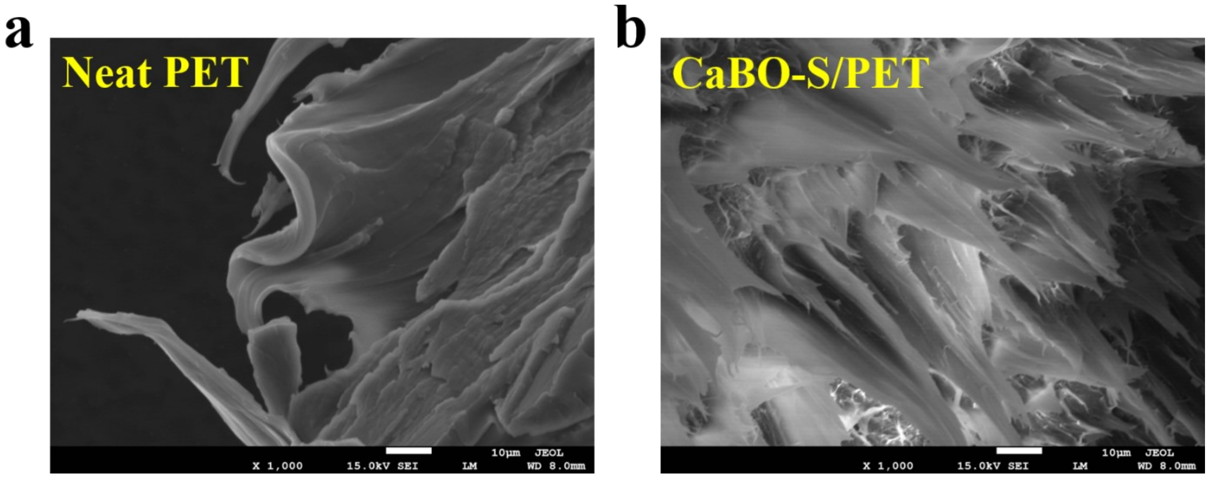

Figure S6 Tensile fracture of neat PET and CaBO-S/PET nanocomposite.

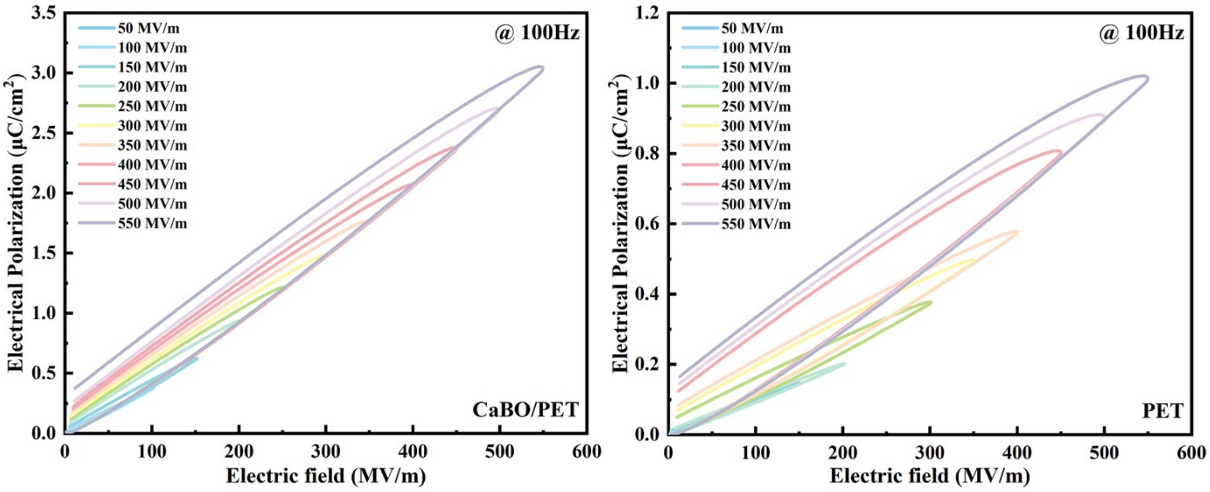

Figure S7 P-E loop of neat PET and CaBO/PET hybrid film at various electrical fields.

Table S1 Parameters comparison of neat PET and the hybrid composites.

Samples	**Intrinsic viscosity/(dL/g)**	**End carboxyl /(mol/t)**
PET	0.65±0.02	11.32±2.12
CaBO/PET	0.63±0.02	10.95±2.33
CaBO-S/PET	0.63±0.02	12.15±2.57

Table S2 DSC data of neat PET, CaBO/PET and CaBO-S/PET composites.

Sample	T_g(°C)	T_{cc}(°C)	T_m(°C)	T_c(°C)	X_c(%)
PET	68.1	130.4	244.2	203.5	62.2%
CaBO/PET	69.2	128.5	254.3	216.4	78.5%
CaBO-S/PET	71.8	126.9	256.3	217.4	84.5%

Table S3 Comparison of mechanical properties of neat PET and films

Sample	Tensile strength (MPa)		Elongation at break (%)		Young modulus (MPa)	
	MD	TD	MD	TD	MD	TD
PET	185.5±25.1	219.1±30.3	80.1±11.2	75.5±12.4	3441.8±392.3	3877.7±510.5
CaBO/PET	202.1±23.7	239.9±27.1	85.6±12.1	80.9±13.6	3789.2±455.5	4386.5±477.4
CaBO-S/PET	216.9±25.1	277.2±32.8	91.7±13.9	93.6±14.3	4063.3±537.9	4922.2±563.9

Notes: MD (Machine Direction) and TD (Transverse Direction).