

Electronic Supplementary Information (ESI)

Curable Polymeric Binder/Ceramic Composite-coated Superior Heat-resistant Polyethylene Separator for Lithium Ion Batteries

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Table S1 Summary of various approaches carried out to improve the heat stability of PE separator.

Coating Method	Polymer only			Polymer/Ceramic Composite				
Material	Co-polyimide	Poly-dopamine	PLSS /Al ₂ O ₃	PVdF /Si ₃ N ₄	PVdF /Al ₂ O ₃	PVdF /Fillers	PVdF+Cyano-ethylpullulan/Active carbon or LTO	X-linkable acrylate binder/Al ₂ O ₃
Ratio by wt. (Resin : Filler)	-	-	2 : 1	1 : 10	1 : 1	1 : 9	1 : 9	4 : 1
Heat shrinkage (From ^{a)} → To ^{b)}) [%]	83.3 → 10.0	33 → 16	13.8 → 4.5	91.0 → 69.8	94 → 59	>80 → <10	>80 → <5	Stable (Hotbox test)
Test condition	140 °C/ 0.5 h	140 °C/ 1 h	105 °C/ 1 h	150 °C/ 0.5 h	140 °C/ 0.5 h	150 °C/ 1 h	150 °C/ 1 h	160 °C/ 2 h
Ref.	[32]	[28]	[36]	[39]	[37]	[33]	[34]	[35]

a) Heat shrinkage of bare PE separator.

b) Heat shrinkage of surface modified PE separator.

Table S2 Solubility of cPET material in various solvents and phase separation behavior after film formation from solution. Some representative properties of the solvents such as solubility parameter, surface tension, and boiling point are also presented^{a)}.

Solvent list	cPET Solubility	Phase separation	Solubility parameter δ [(cal/cm ³) ^{1/2}]	Surface tension γ [mN/m]	B.P. (°C)
n-Butyl acetate	O	O	8.6	25.1	126
Toluene	O	O	8.9	28.5	110.6
Xylene	O	O	8.9	28.6	136
Ethyl acetate	X	-	9.1	24	77
Tetrahydrofuran (THF)	O	O	9.1	28	66
Benzene	O	O	9.2	28.9	80
Methyl ethyl ketone (MEK)	O	O	9.3	24.6	80
Chlorobenzene (CB)	O	X	9.5	33	132
Dichloroethane	O	X	9.8	32.2	83.5
Cyclohexanone (CH)	O	X	9.9	34.5	156
Acetone	△	-	10	23.3	56
Dioxane	O	X	10	32.9 ^{b)}	101
Pyridine	O	O	10.7	36.6	115
Dimethyl acetamide (DMAc)	O	O	11	34	166
Cyclohexanol	X	-	11.4	32	161
Dimethyl formamide (DMF)	O	O	12.4	35	153
Ethanol	X	-	13.4	22.3	78

^{a)} Most of the data for the solvents are from "Ian M. Smallwood, *Handbook of Organic Solvent Properties*, Butterworth-Heinemann, UK 1996."

^{b)} From "Cal L. Yaws, *Thermophysical Properties of Chemicals and Hydrocarbons*, William Andrew, USA 2008, Ch. 21."

Uncured cPET molecules tend to generate phase separation on the surface of bare PE when coated from solutions of most solvents and the numbers of solvent that does not show phase separation is very limited. Here, only the solvents which satisfy certain ranges of both surface tension (32 ~ 35 mN/m) and solubility parameter (9.5 ~ 10 (cal/cm³)^{1/2}) produce uniformly coated surface without phase separation.

Table S3 Molecular characteristics of six different copolyesters (cPET) employed in this study.

	M_n ^{a)} [g/mol]	T_g ^{b)} [°C]	Hydroxyl Value [KOH mg/g]	\overline{M}_c ^{c)}
cPET1	28,000	17	3	18,700
cPET2	18,000	65	4	14,000
cPET3	16,000	47	6	9,300
cPET4 ^{d)}	18,000	71	8	7,000
cPET5	12,000	58	12	4,700
cPET6	7,000	30	19	3,000

a) M_n is the number average molecular weight.

b) T_g is the glass transition temperature.

c) \overline{M}_c is the average molecular weight between crosslinks calculated by following equation.

($\overline{M}_c = 56100/\text{hydroxyl value}$, where 56100 is the formular weight of KOH in mg/mol and hydroxyl value is [-OH] concentration determined by the titration with KOH)

d) cPET4 is the materials mostly used in the main texts.

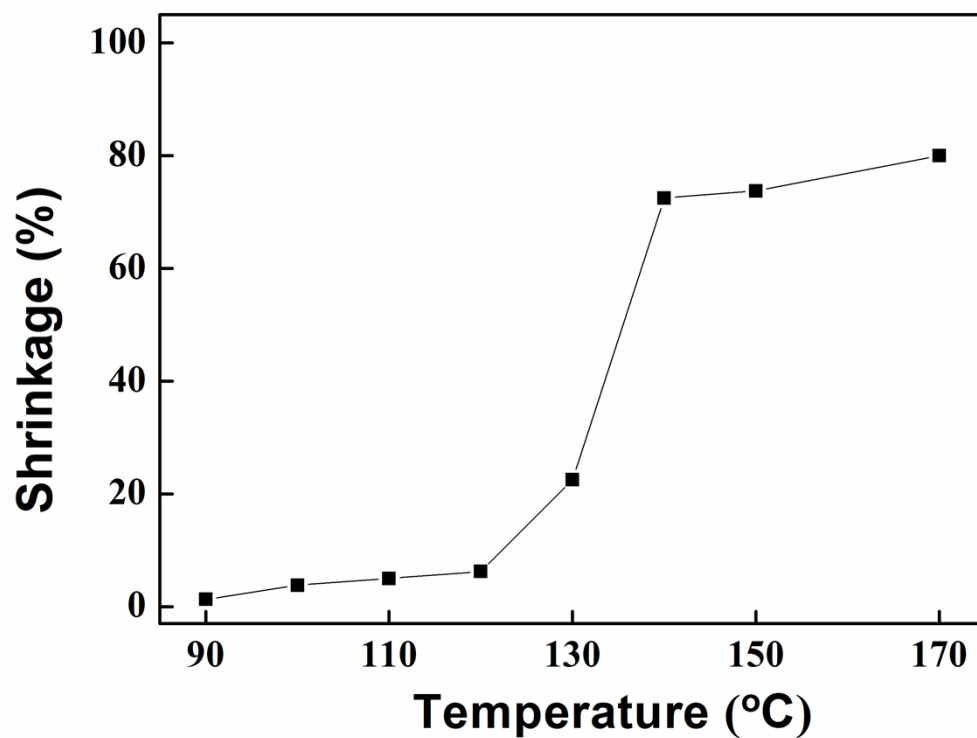


Fig. S1 Heat shrinkage of bare PE separator as a function of exposure temperature. The shrinkage values are measured in machine direction (MD).

Bare PE separator starts to shrink rapidly above 120 °C and the shrinkage levels off at about 140 °C, which corresponds to the melting temperature (T_m) of PE.

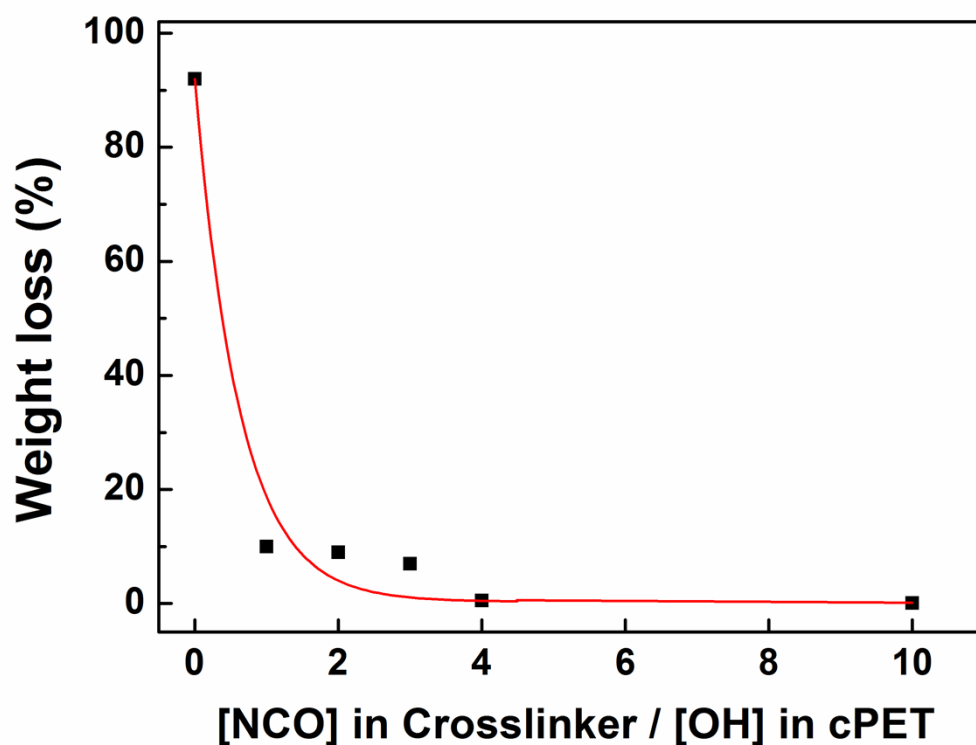


Fig. S2 Weight loss of cured cPET binder after dipping in THF for 1 day as a function of various concentration of crosslinker.

The cPET is slightly dissolved out when the amount of crosslinker is low. However, the dissolution does not occur when the amount of crosslinker exceeds 4 equivalents to hydroxy concentration. This figure shows the weight loss of crosslinked cPET after dipping in THF for 1 day. THF was chosen to secure the solvent resistance of cured cPET. The reason why THF is used instead of electrolyte is because the solubility of uncured cPET toward THF is much higher than that toward electrolyte.

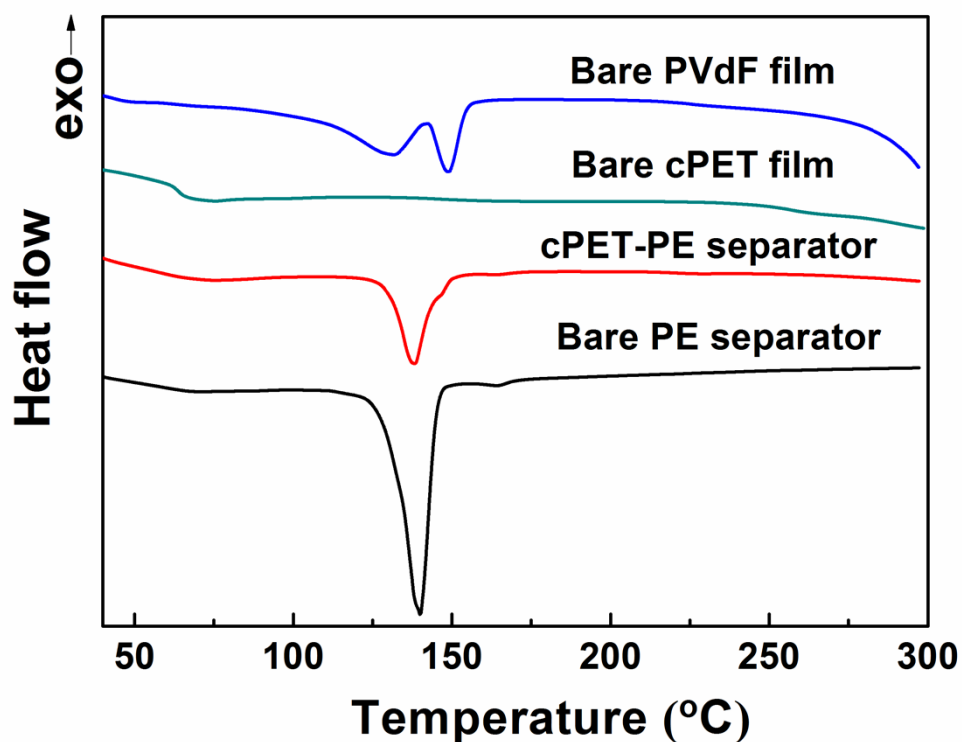


Fig. S3 DSC thermograms of bare cPET and PVdF films, and the cPET-PE separator employed in this study.

Bare PVdF film and bare PE separator show distinct endothermic melting peaks at 148.9 and 140.1 °C, respectively, resulted from the melting of crystalline regions of corresponding polymer. On the other hand, no melting peak is observed for bare cPET film. Instead, an endothermic transition which is believed to be related to the glass transition of cPET is observed at 63.8 °C. From these results, bare cPET can be considered to be a completely amorphous polymer.

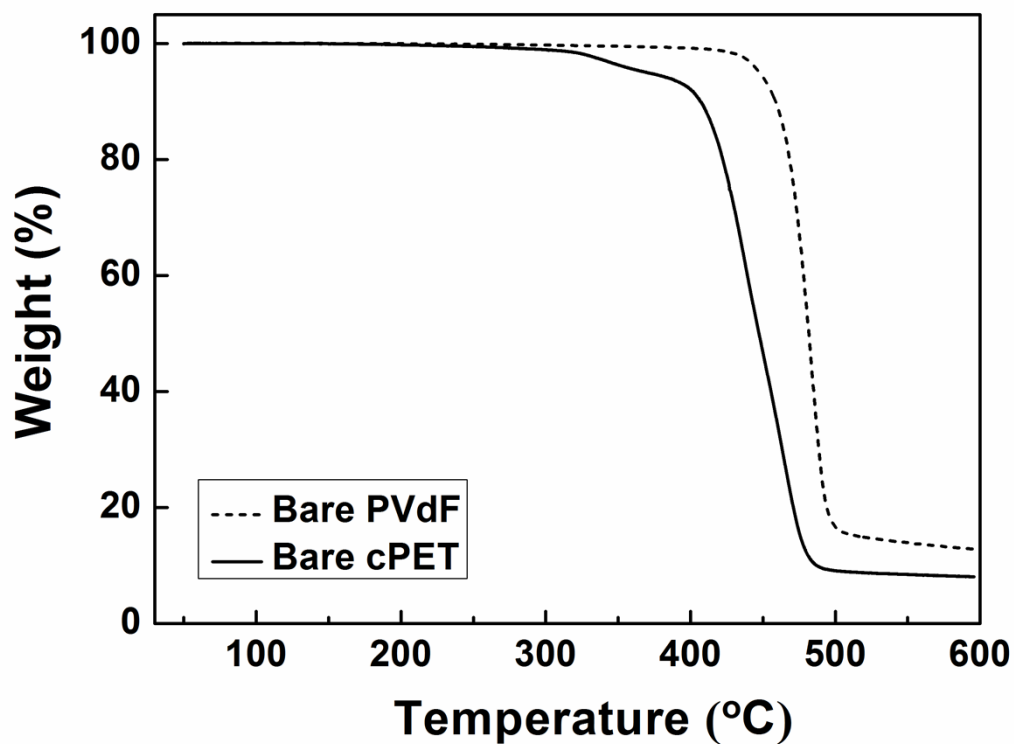


Fig. S4 TGA thermograms of bare PVdF and cPET films.

PVdF and cPET started to decompose at 430 and 390 °C, respectively. The initial decomposition temperature of the PVdF was slightly higher than that of the cPET. However, when considering the operating temperature of actual LIB, 390 °C is a quite sufficient temperature to certify the heat stability.

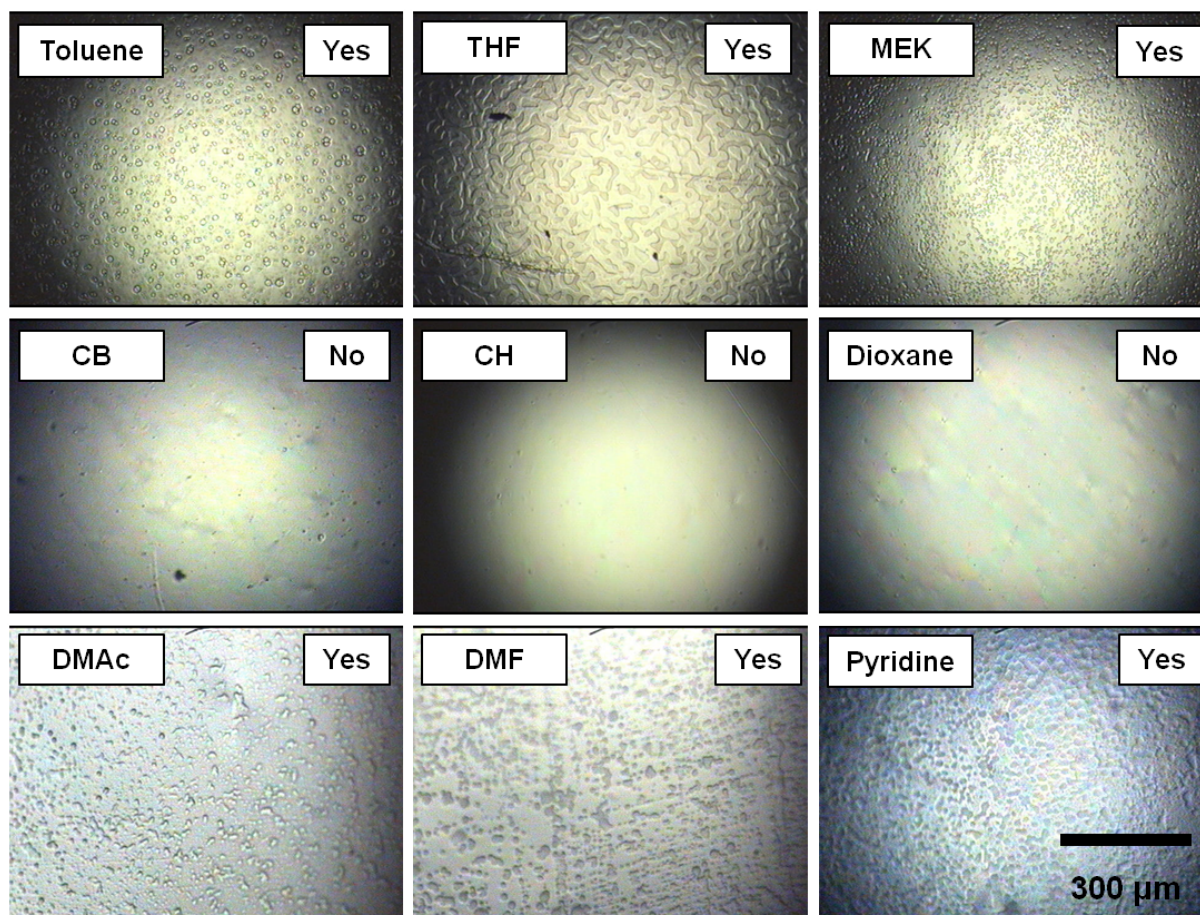


Fig. S5 Optical microscope images of cPET (without Al_2O_3) obtained from solutions dissolved in various solvents followed by solvent evaporation. (Yes : phase separation observed; No : no phase separation observed)

Phase separation phenomena can be easily observed by optical microscope. For the sake of clear observation, solutions are coated onto the transparent PET film instead of bare PE separator which is intrinsically opaque. From these results, cyclohexanone (CH) was chosen as a promising co-solvent to reduce undesirable phase separation.

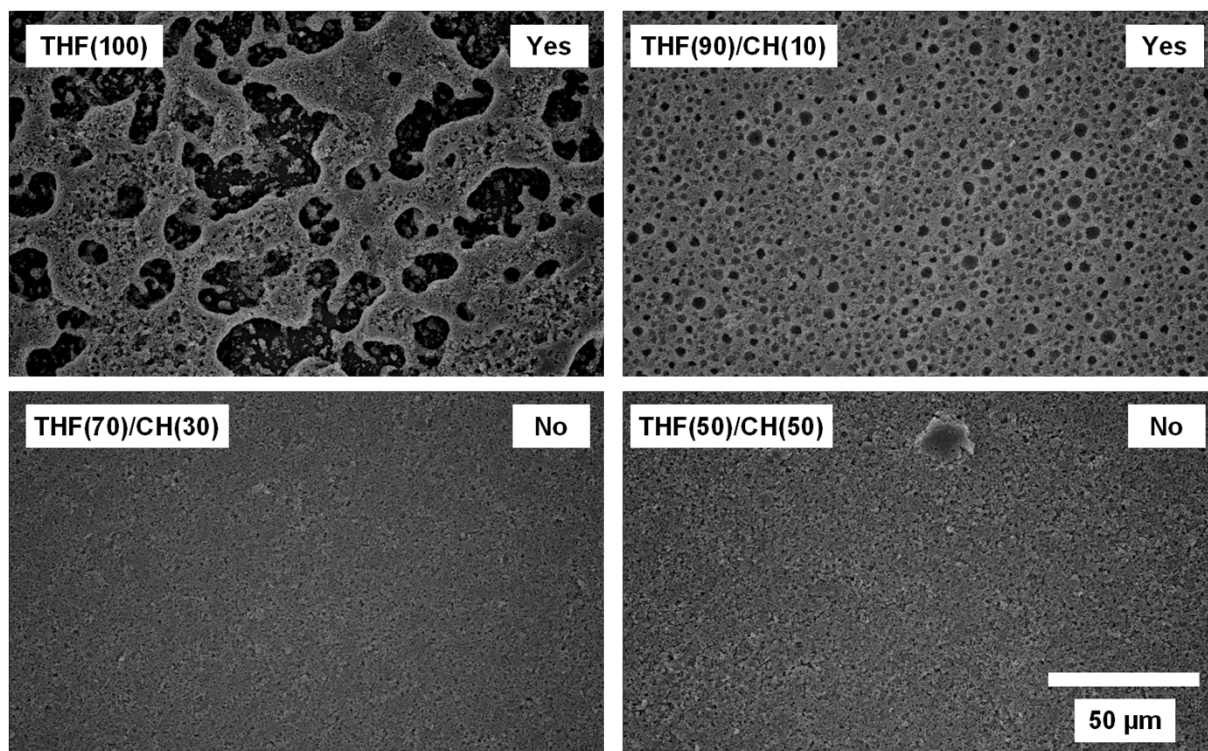


Fig. S6 SEM images of the surfaces of various cPET-PE separators differing in the ratio (by weight) between tetrahydrofuran (THF) and cyclohexanone (CH).

From SEM images, phase separation is more clearly observed and the use of co-solvent is found to be very effective on producing uniformly coated surface. When cyclohexanone (CH) increases more than 10 wt%, phase separation diminishes significantly.

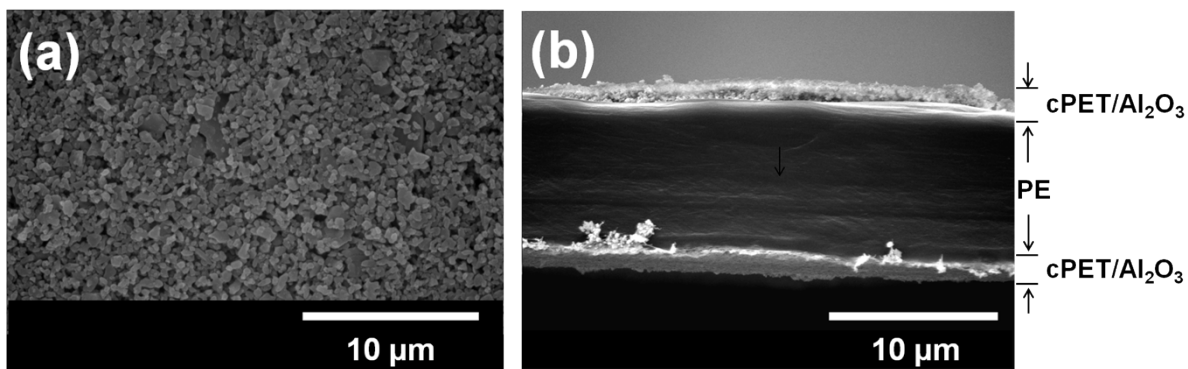


Fig. S7 SEM images of (a) the surface and (b) the cross-sectional view for cPET-PE separator.

In the surface view shown in (a), Al₂O₃ particles are uniformly dispersed throughout the separator and pores are also clearly observed. In the cross sectional view shown in (b), the cPET/Al₂O₃ composites are coated very thinly onto both sides of the PE separator. The thicknesses of PE separator and single cPET/Al₂O₃ composite layer are 9 and 3 μm, respectively, and the total thickness of the cPET-PE separator is 15 μm.

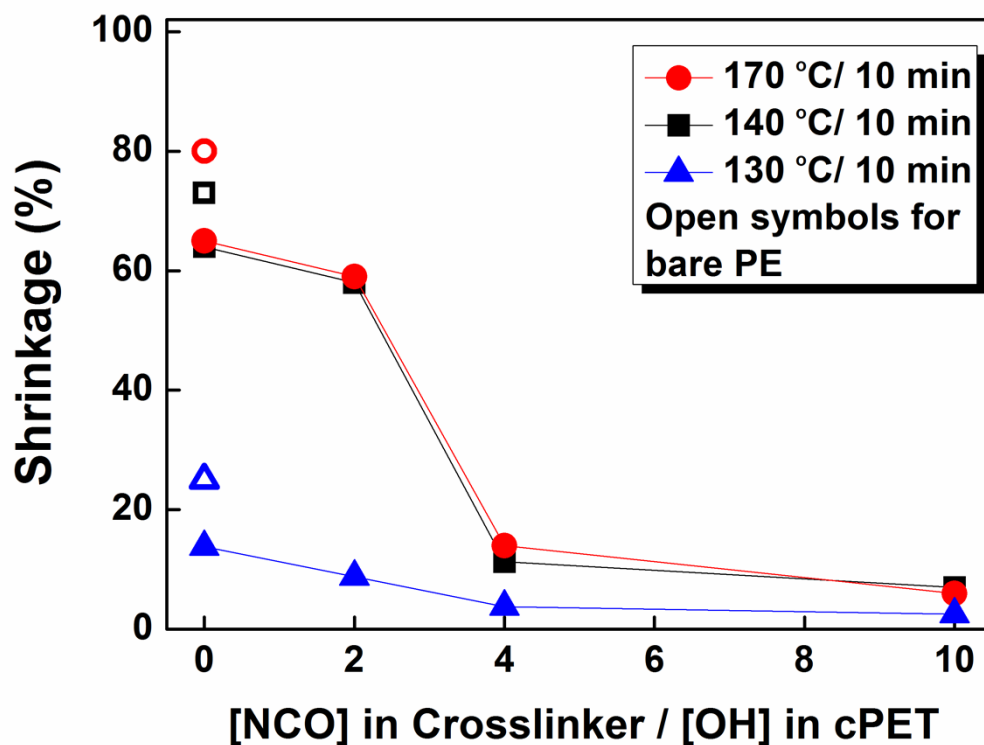


Fig. S8 Heat shrinkage of cPET-PE separator as a function of equivalent ratio between [NCO] reactant in crosslinker and [OH] group in copolyester under different heat exposure conditions.

Amount of crosslinker is one of the critical factors determining thermal dimensional stability of crosslinked cPET-PE. When the equivalent ratio of crosslinker is above 2, heat shrinkage of cPET-PE decreases significantly, indicating that crosslinking density between cPET and crosslinker is a dominant factor governing the heat stability and the thermally stable binder is not obtained when the crosslinker is not applied at an optimum amount.

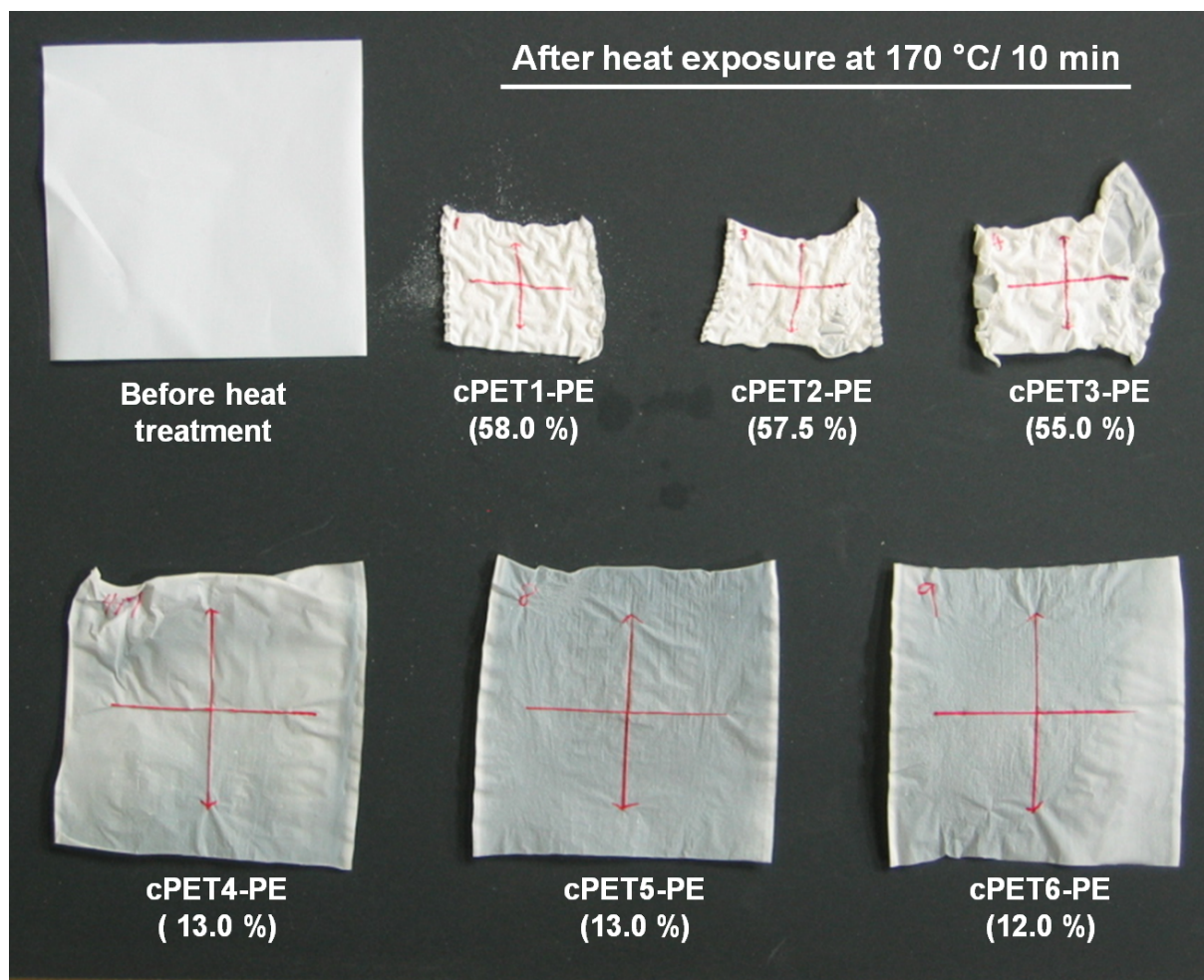


Fig. S9 Digital camera images of various cPET-PE separators differing in molecular characteristics of copolyesters (cPET). The molecular characteristics of six different cPET materials shown in above are given in Table S3. The numbers in parenthesis are shrinkage values measured in machine direction after heat exposure at 170 °C/ 10 min.

cPET1-PE, cPET2-PE, and cPET3-PE shrank more than 50 % while cPET4-PE, cPET5-PE, and cPET6-PE showed very good thermal dimensional stability. When comparing the properties of copolyesters, crosslinking density is believed to be much more impactful factor than M_n and T_g for the improved heat stability.

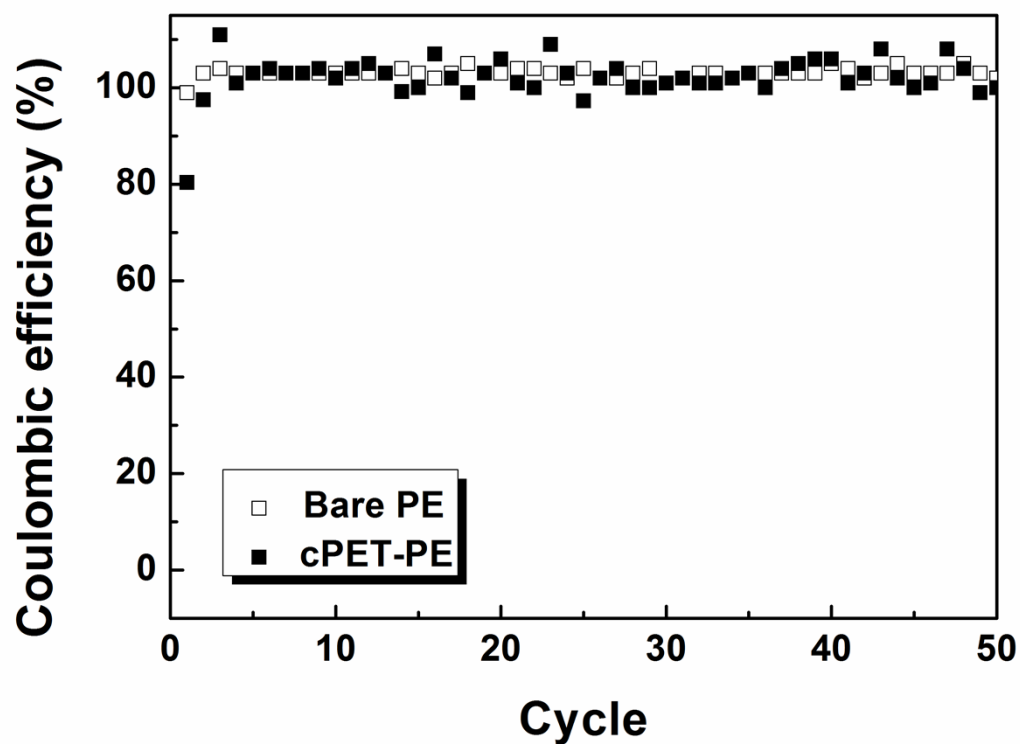


Fig. S10 A comparison of coulombic efficiency for batteries containing bare PE separator and the cPET-PE separator of this study during cycle tests.

When comparing coulombic efficiency, the cell containing cPET-PE separator showed a little bit lower stable cycle property than the cell containing bare PE separator. This might be one of the reasons causing the reduction of discharge capacity.

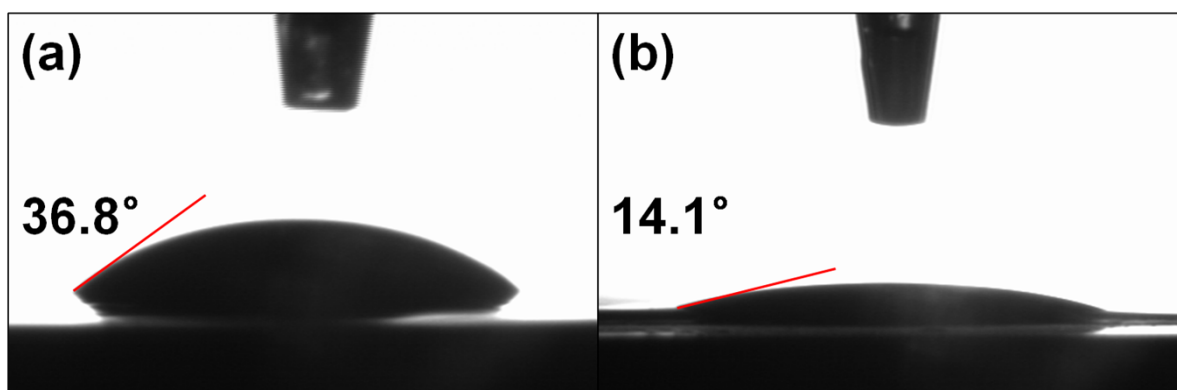


Fig. S11 Contact angle images of bare PE (a) and cPET-PE (b) separators. The images are taken just after dropping the electrolyte onto the separator surface.

When measuring the contact angle with the electrolyte liquid, wettability of bare PE separator was poorer than that of cPET-PE. PE consists of hydrocarbons without any hetero atoms so that the surface of bare PE separator is more hydrophobic. The molecular structure of cPET and the pores generated from coating of Al_2O_3 particles enhance the wettability toward electrolyte liquid.

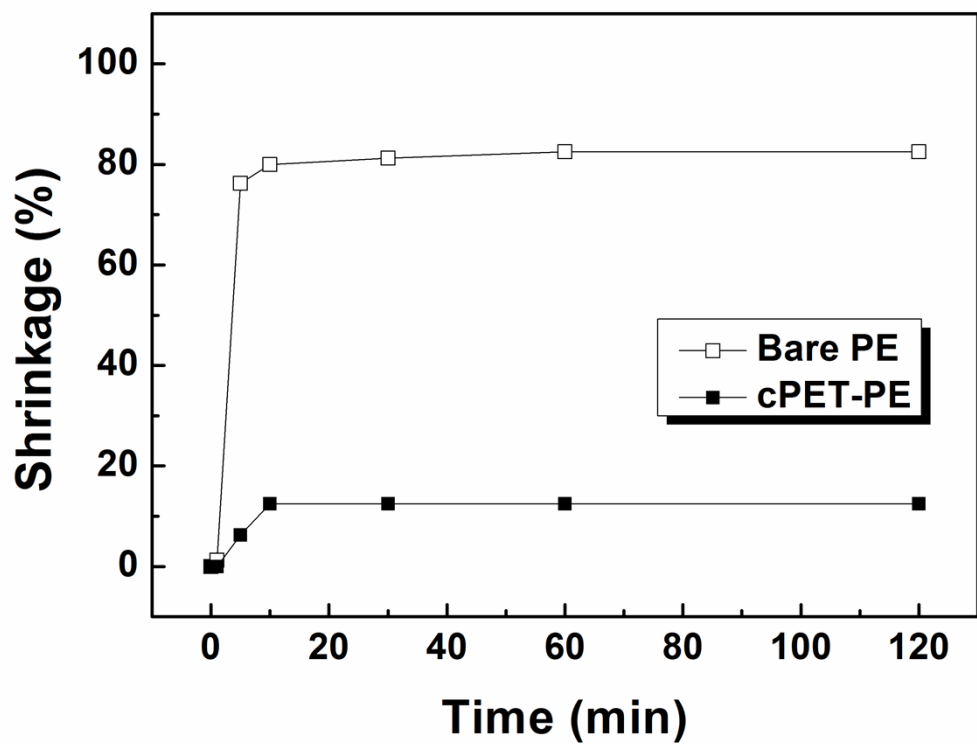


Fig. S12 The shrinkage of separators as a function of exposing time at 170 °C

The shrinkage of both PE and composite coated separators begins very fast upon heating and converges to maximum value within 10 min.