

# The Effect of Silica Addition on the Microstructure and Properties of Polyethylene Separators Prepared by Thermally Induced Phase Separation

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**ABSTRACT:** Novel composite polyethylene (PE) separators were prepared via thermally induced phase separation using SiO<sub>2</sub> as the inorganic dopant and dioctyl phthalate as solvent. Through the control of silica content, the microstructure, thermal and crystalline properties, electrolyte uptake, thermal stability, and mechanical properties of the as-prepared separators were investigated. The results showed that the doped silica particles favored the formation of the large pore size. The crystalline degree of PE was enhanced when doping silica in the ternary system below 3 wt %. The liquid electrolyte uptake was increased from 30.2% to 63.2% with doping silica content at 5 wt % in the mixed system, which benefits from the large pore size structure and the hydrophilicity of silica. The thermal decomposition temperature of the composite PE separators is 40°C higher than the pure PE separator due to the steric stabilization and the more stable space structure induced by the doped silica. The tensile strength was increased from 12 MPa to 13.3 MPa when doping 1 wt % silica, but decreased with further silica addition. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40724.

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## INTRODUCTION

Separator is an important component of lithium-ion batteries (LIBs), which keeps the positive and negative electrodes apart and plays a key role in ensuring batteries' safety. Among various separators, polyethylene (PE) separator is the most important one due to its electrochemical stability, high mechanical strength, and non-toxicity.<sup>1</sup> The development of higher power-density and higher energy-density LIBs has brought the security problems and put forward challenges to the safety use of separators. The use of high-power LIBs would emit large current and generate a large amount of heat, which might fuse the separator and make the battery in danger.<sup>2</sup> Besides, the PE separator is hydrophobic and it has a lower surface energy, resulting in a poor compatibility with liquid electrolyte and a poor electrolyte uptake.<sup>3</sup> To overcome these disadvantages, researchers have done a lot of work. With the aim of improving the thermal stability of separators, some organic or inorganic materials were coated on the surface of separators to modify its thermal resistance.<sup>2,4-9</sup> In order to enhance the wettability of liquid electrolyte on separator surface and increase the electrolyte uptake, some surface technologies, such as, surface grafting, radiating

the separators, coating the gel polymer electrolyte etc, were also used to modify the surface properties of PE.<sup>10,11</sup> The thermal stability and the electrolyte uptake could be improved by these processes. However, the thickness of the separators would be increased, and the coated microporous membranes might also block the pores, which goes against the flow of Li-ion through the separators and deteriorates the separators' performance. Meanwhile, all of these approaches mentioned above mainly focused on reinforcing and modifying the existing separators, it added more procedures, needed more chemical reagents, and wasted more resources. It is of great significance to improve the separators' performance with less procedures and materials.

Melt stretching method and thermally induced phase separation (TIPS) process are the main methods to prepare PE separators. TIPS process plays an important role in preparing porous membrane, especially in macromolecular polymer porous membrane. Compared with melt stretching method, the porosity and the pore size distribution of separator can be easy to control through TIPS process. Moreover, the performance of separator can be improved from aspects of raw material by adding additional components to the mixed system directly before melt

**Table I.** Compositions of the Samples

Sample name	HDPE/SiO <sub>2</sub> /DOP (wt/wt/wt)
S0	40/0/60
S1	40/1/59
S2	40/3/57
S3	40/5/55

mixing.<sup>12</sup> Recently, only a few researchers have introduced the blend methods to modify PE separator based on the TIPS process. For example, Shi et al. blended amphiphilic poly(ethylene-*block*-ethylene glycol) copolymer with high density polyethylene (HDPE) to prepare separators with good hydrophilicity and improved electrochemical properties.<sup>3</sup>

Inorganic materials such as SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> are very stable in the temperature below 300°C. Many studies reported the toughening and strengthening mechanism of inorganic fillers to develop novel organic-inorganic composite materials, which have higher mechanical and thermal properties compared with pure organic materials.<sup>13,14</sup> However, few researchers have attempted to prepare organic-inorganic composite PE separators via TIPS process.

In this article, we proposed a new method to prepare composite PE separators via TIPS process. Nano-silica was chosen as the inorganic filler, the special effects of silica on the crystallization and melting behaviors of HDPE separator, separator microstructure, thermal stability, and mechanical properties were discussed.

## EXPERIMENTAL

### Materials

HDPE (MH502, melt mass flow rate = 5 g/10 min) was provided by China Petrochemical Corporation. Silicate dioxide supplied by Aladdin Corp. has an average grade size of 7–40 nm. Dioctyl phthalate (DOP, average molecular weight: 390.55 g/mol) and ethanol, supplied by Sinopharm Chemical Reagent Co., was used as diluent and extractant. The electrolyte solution being made up of LiPF<sub>6</sub> and solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (LiPF<sub>6</sub> concentration, 1 mol L<sup>-1</sup>, EC/DMC = 1/1 wt/wt) was purchased from Guo Tai Hua Rong Company (China). The ionic conductivity of the liquid electrolyte is reported as 11.5 × 10<sup>-3</sup> S cm<sup>-1</sup>. All of them were used without further purification.

### Preparation of HDPE/SiO<sub>2</sub>/DOP Blend Samples and HDPE/SiO<sub>2</sub> Blend Separators

The mixture of HDPE/SiO<sub>2</sub>/DOP system was prepared by melt blending in the mixing chamber of the torque rheometer (Haake Polylab OS). With a fixed mixing ratio (Table I), the mixture was heated and stirred into a uniform system at 180°C. The solution was removed from chamber and stored in a freezing condition.

To prepare HDPE/SiO<sub>2</sub> blend membranes, a chopped certain amount of HDPE/SiO<sub>2</sub>/DOP blend sample was placed between a pair of stainless steel plate. A teflon film with a square opening in the center was inserted between the steel plates to adjust

the thickness of membranes to about 100 μm. The stainless steel plate was heated up to 220°C for 2 min and pressed. Quench the stainless steel plates with liquid film in a water bath (25°C) for 10 min, a solid film was obtained. The diluent was extracted by immersing the membrane in ethanol for 24 h. Dry the extracted membrane in oven at 60°C for 8 h, we get the porous HDPE/SiO<sub>2</sub> separator. The code of the porous separator is shown in Table I.

### Characterization

The cross-section of separator was observed by a field-emitting scanning electron microscope (FEI, Magellan 400, USA).

The thermal and crystalline properties of separators were investigated using a Netzsch differential scanning calorimeter (Netzsch DSC 200F3, Germany). For DSC measurements, the porous separators were heated to 180°C and maintained for 3 min to eliminate the thermal history. Then the samples were cooled to 80°C and heated to 180°C once again. The cooling and heating rate is 10 °C/min. The degree of crystallinity ( $X_c$ ) of the separators can be calculated by the following equation:<sup>15</sup>

$$X_c = \frac{\Delta H_m}{(1-\Phi)\Delta H_m^0} \times 100\% \quad (1)$$

where  $\Delta H_m^0 = 273$  J/g is the fusion enthalpy for a total HDPE crystalline phase and  $\Delta H_m$  is the fusion enthalpy calculated from the area of the endothermic peak.  $\Phi$  is the mass fraction of silica in the porous separator and it was measured by thermogravimetric analysis (TGA) as shown in the TGA characterization.

The crystal structure of the separator was studied by X-ray diffractometer (D/MAX-RBX, Japan) with CuK $\alpha$  radiation. The scanning angle is 5°–40°, and the scanning rate is 4°/min.

The electrolyte uptake of separator was measured by immersing it in liquid electrolyte solution for a 24 h and calculated by following equation:

$$\Delta W = \frac{W_t - W_i}{W_t} \times 100\% \quad (2)$$

where  $W_t$  is the weight of separator after absorbing electrolyte for 24 h, and  $W_i$  is the initial weight without absorbing electrolyte.

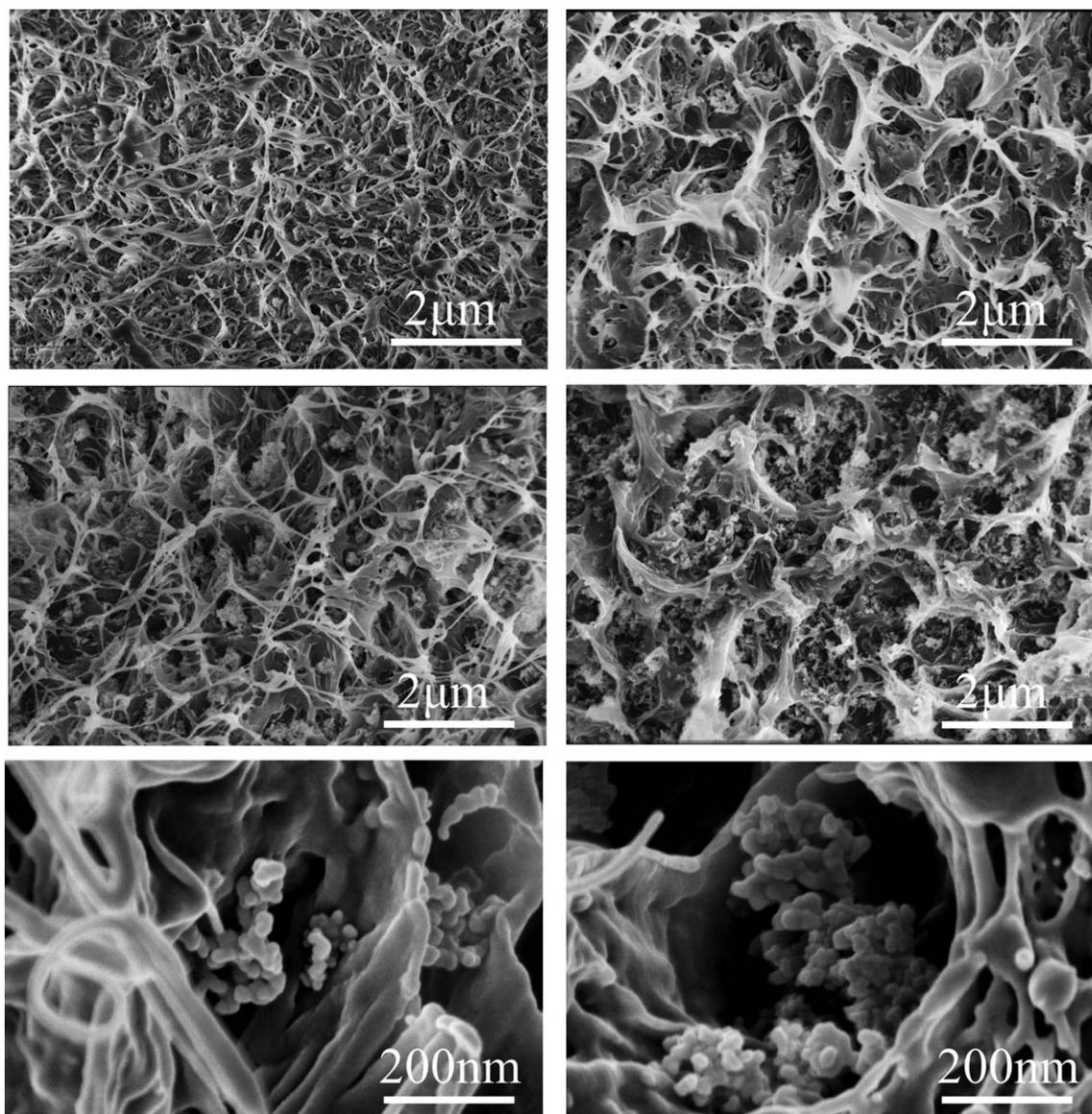
The thermal stability of composite separators was measured by TGA (Netzsch STA 449C, Germany) under Argon atmosphere from room temperature to 1000°C at a heating rate of 10 °C/min. The silica content ( $\Phi$ ) remaining in the matrix of separators was measured simultaneously.

The tensile strength of the separator was measured using a tensile tester (Instron 5867, USA) with a constant elongation rate of 10 mm min<sup>-1</sup>. The size of the separator used for this measurement was 10 mm × 50 mm. The tensile strength of each sample was tested for five times.

## RESULTS AND DISCUSSION

### The Microstructure of Separators

Figure 1 shows the scanning electron microscope images of the separator doped with different contents of SiO<sub>2</sub>. It can be



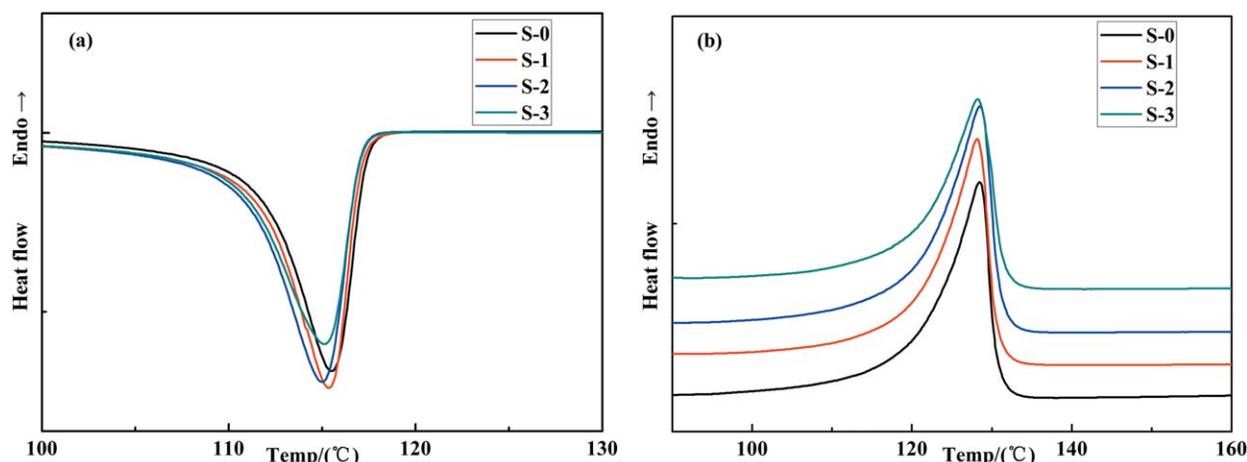
**Figure 1.** SEM micrographs of the cross-section for the separators of (a) S0; (b) S1; (c) S2; (d) S3; (e) enlarged S1; (f) enlarged S3.

seen that for the separator without SiO<sub>2</sub> (S0) doping, the PE branches interweave and constitute porous space network structure. With the increasing content of silica, the pore size becomes bigger and the slender branches of the PE grow thicker. Figure 1(e) shows the scanning electron microscope (SEM) of sample S1 at high magnification. When 1 wt % SiO<sub>2</sub> was doped in the system, the silica can be well dispersed in the matrix. However in Figure 1(f), the silica showed a slightly agglomeration. It is clear that the pore size in S3 sample is bigger than in S1 sample.

In the PE-DOP system, there is a weak polymer–diluent interaction between them. Put the raw materials in the high temperature and stirred for an adequate time, the homogeneous polymer solution was formed. The mixture becomes unstable and undergoes liquid–liquid phase separation when the homogeneous solution was cooled. Then the system separates into a

PE-rich phase and a DOP-rich phase. The PE-rich phase becomes the matrix of the PE separator, while the DOP-rich phase composed of nearly pure diluent uniformly dispersed in the continuous phase, and it will be removed from the matrix to form the cells in the PE separator.<sup>16,17</sup> The microstructure of the as-prepared separator is shown in Figure 1(a).

When inorganic particles were added in the system, it affected the phase separation process. Due to the high surface energy and activity, the silica particles would partially become the core of DOP-rich phase droplets in phase separation process, and silica would absorb DOP molecules, which favors the growth of DOP-rich phase droplets. Besides, the volume effect of inorganic particles further increased the size of the droplets. Larger droplets lead to the formation of large pores in the separator. With the increase of silica content, the large pores formed easily as shown in Figure 1(e,f).



**Figure 2.** DSC curves of composite separators: (a) First cooling curves and (b) Second heating curves. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermal and Crystalline Properties of the Blend Samples and Separators

Figure 2(a,b) shows the crystallization and melting curves of the separators, respectively. We can see from the crystallization curves that the doped silica particles had little effect on the crystallization temperature. But the heat of the exothermic peaks distinctly differed from each other. The crystallization and melting properties of PE can be characterized by the melting curve accurately. As shown in Figure 2(b), the melting temperature of the composite separators is almost the same, but the area of the melting peaks is different. During the extracting progress, the doped silica was partially extracted from the solid films. The silica content remained in the PE separators and the crystallinity of composite PE separators is shown in Table II. We can see that as the remained silica increased from 0 to 3.74 wt %, the crystallinity increased from 44.91% to 50.04%. While the silica content increased further, the crystallinity decreased subsequently.

The doped silica affected the course of crystallization obviously.<sup>18</sup> The nano-silica doped in the matrix plays a role in heterogeneous nucleation and accelerates the crystal growth. The nucleation density was increased and the crystallization rate was speeded up, which favors the crystallization. However the doped silica may increase the viscosity of the matrix,<sup>19,20</sup> which reduced the mobility of the system and made the movement of PE molecular chain hard. When the content of silica exceeded 3 wt % in the ternary system, the negative effects played a leading role and the crystalline degree of PE was decreased subsequently.

To investigate the effect of the silica addition on the crystalline structures of PE separators, X-ray diffraction (XRD) measurements were performed. As shown in Figure 3, the peak patterns of four samples showed the same trends: there existed two obvious diffraction peaks at  $2\theta = 21.5^\circ$  and  $24^\circ$ , and one unobvious peak at  $2\theta = 36^\circ$ , which corresponds to the reflections of (110), (200), and (020) lattice planes of the orthorhombic crystalline form of PE, respectively. With the increase of silica addition, the intensity of diffraction peaks became weaker and the peaks at  $2\theta = 36^\circ$  almost disappeared.

In the process of crystallization, the PE chains reorganized and developed into a stable space structure, while the existence of silica retarded the movement of the molecular chain by forming crosslinking centers and increasing the viscosity of system. As a result, the crystallinity of polymer was reduced, as shown in Table II. Besides, the existence of silica blocked the folding of PE chains, thus decreasing the grain size.

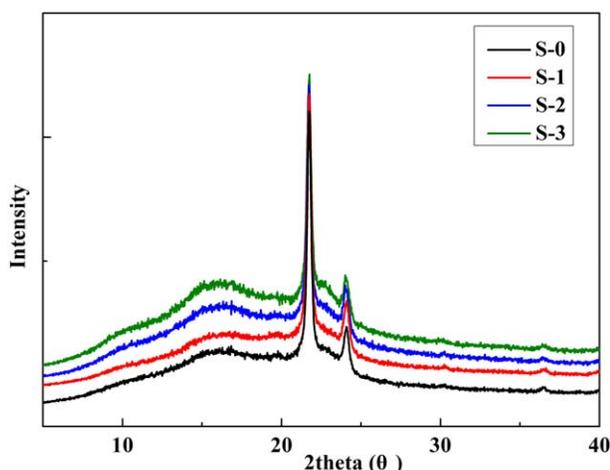
PE is semi-crystalline polymer. In the area around  $2\theta = 16^\circ$ , there is an amorphous peak. With the increase of doped silica content, the amorphous peak becomes larger. This may be partially affected by the existence of silica on the surface and inner of separators. The silica used in this experiment was non-crystalline materials, and it has the amorphous peak with a large angles. The XRD would reflect the silica crystal forms besides the PE. With the increase of silica addition, the amorphous peak regions became bigger.

### Electrolyte Uptake of Separators

Figure 4 shows the liquid electrolyte uptake with different contents of silica in separators. It can be seen that the electrolyte uptake of the separators increased with the increasing contents of silica. There are three main facts that affect the electrolyte uptake: pore size distribution, swelled amorphous domains, and the hydrophilic surface of separator. From the analysis of the SEM, it is more likely to get big pore structure when doping silica in separators and favors the increase of electrolyte uptake. Besides, the doped inorganic particles are conducive to the formation of inter-connected pore structures, which is beneficial to the permeability of separator. The surface of nano-silica particles is rich in hydroxyl group, which made it hydrophilic to the electrolyte.<sup>2</sup> The absorption capacity of PE to the electrolyte

**Table II.** The Crystallinity of Composite PE Separators

Sample name	S0	S1	S2	S3
SiO <sub>2</sub> content ( $\Phi$ , wt %)	0	1.48	3.74	4.03
$X_c$ (%)	44.91	46.21	50.04	43.6



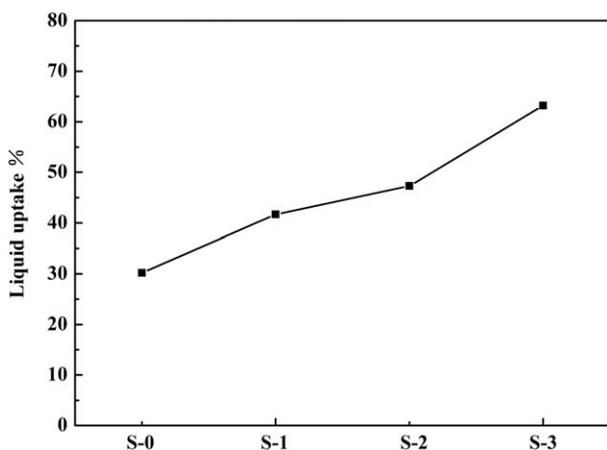
**Figure 3.** XRD curves of separators with different content of silica. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

can be improved by the nano-silica particles distributed in the internal and the surface of separator.

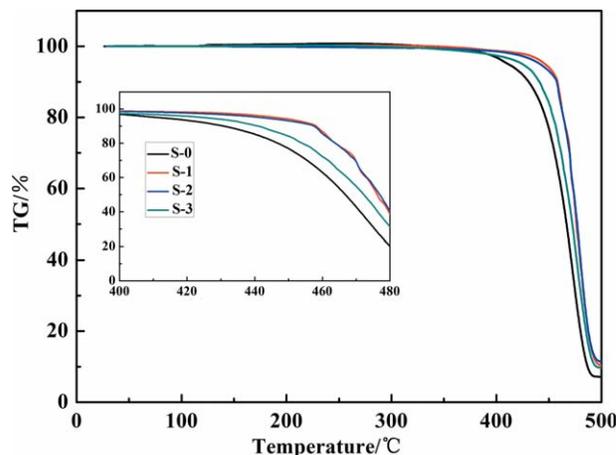
#### Thermal Stability of Separators

As shown in Figure 5, the thermal decomposition temperature of the pure PE separator S0 is around at 410°C, while the thermal decomposition temperature of the composite separator S1 and S2 reached to 445°C. The decomposition temperature of composite separators was retarded with the doped silica and the temperature at which the maximum thermal decomposition rate was also postponed. When the silica content reached to 5 wt % of the original ternary system, the decomposition temperature was slightly decreased, but it is still higher than the pure PE separator. The TGA results showed that the composite separators have better thermal stability.

This enhanced thermal stability was mainly due to two reasons: firstly, the nano-silica particles have a higher specific surface area and specific surface energy, and its surface is rich in hydroxyl groups. When silica was doped in the PE matrix, it tightly absorbs to the PE molecular chains, thus increasing the whole bond energy. Through the interaction between the silica



**Figure 4.** Electrolyte uptake of separators with different contents of silica.

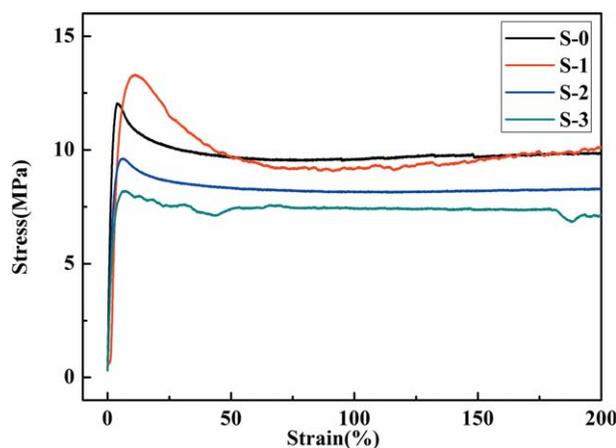


**Figure 5.** Thermo-gravimetric curves of composite separators. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

particles and the PE molecular chains, the system is more likely to form a stable space structure. Secondly, the silica particles can play a steric stabilization role in the matrix. Silica particles occupied a certain space and hindered the movement of molecular chains when separator was subjected to high temperature. The obstructed channels go against the decomposition of PE molecular chains, and retarded its decomposition temperature.

#### The Mechanical Strength

Figure 6 shows the stress versus strain curves of the composite separators. The tensile strength of the pure PE separator was 12 MPa, while it increased to 13.3 MPa when doping 1 wt % silica in the system. With the further increasing content of doped silica, the sample shows a weaker strength. The SiO<sub>2</sub> was well dispersed in the matrix and exhibited fine interfacial adhesion with the PE molecular chains when the doped SiO<sub>2</sub> was low. The SiO<sub>2</sub> particles and HDPE chains are connected through the “bridge-connection” and form a three-dimensional crosslinking network.<sup>15</sup> It can distribute the stress evenly and restrain the rupture of the materials when the separators are subjected to



**Figure 6.** The strain–stress curves of the composite separator. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

exterior stress. But when the doped content of silica is higher, the particles would agglomerate into big bulks, which weakened its interaction to the PE molecular chains and reduce the stress dispersion effects. Even, the silica aggregates existed in the matrix occupied a certain volume and formed the defect center to the matrix, which caused the strength of the composite separators decline. Besides, the SEM analysis has shown that the mean pore size of separator was increased with the doped silica and the larger pores have a poor effect on the mechanical properties.

## CONCLUSIONS

A series of HDPE/SiO<sub>2</sub> composite separators were fabricated via TIPS by blending HDPE with silica particles. The cross-section SEM of the separators showed that the doped silica favored the formation of large pore size distribution of the separator. On account of the large pores of the separator and the hydrophilic of the silica, the liquid electrolyte uptake was increased. The doped silica played a role as nucleating agent and increased the crystalline degree of PE when the content of silica in ternary mixture was below 3 wt %. The thermal stability of composite separator was better than pure PE separator, and the thermal decomposition temperature of composite separator has raised to about 40°C. The tensile strength of separator was first increased and then decreased afterwards. We conclude that TIPS process is an effective way to prepare composite separators and it would be promising to get high performance separators.

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