Study on Mechanical Behaviors and Electrolyte Uptake of PVDF/PES/TiO₂ Composite Fiber Separators

Kai Cheng¹, Xin Chen¹, Shuai Liu¹, Qingyuan Cao¹, Weiwei Yu¹, Weiwei Cui¹,²*  
¹School of Material Science and Engineering, Harbin University of Science and Technology, Harbin, China  
²Suzhou Taihu Electrc New Material Co., Ltd, Suzhou, China  
*Corresponding author e-mail: cuiww@hrbust.edu.cn

Abstract. In this paper, polyvinylidene fluoride (PVDF)/polyether sulfone (PES) spinning solution with different TiO₂ content was obtained by in-situ generation. The prepared spinning liquid was fabricated into PVDF/PES/TiO₂ composite membranes via electrospinning. The scanning electron microscopy (SEM), differential scanning calorimetry (DSC), mechanical properties, electrolyte uptake were conducted to test the performance of the obtained separators. The effect of TiO₂ contents on the properties of PVDF/PES separators was discussed. The experimental results show that the doping of nano-TiO₂ particles will enhance the performance of the separators. DSC test and electrolyte uptakes showed that the enthalpy of the polymer decreased and the electrolyte uptake increased with TiO₂ contents. When the separators contents 2 wt% TiO₂, the enthalpy changes reach the maximum (28.259 J/g), and the crystallinity is measured to 26.99%. With the TiO₂ addition increases, the tensile strength of the membrane also showed the tendency of increasing first and then decreasing. At 6 wt%TiO₂, the tensile strength of the membrane was better, reaching 5.606 N/mm², and the toughness was the best. It shows that the addition of TiO₂ helps to enhance its tensile strength as well as toughness When the TiO₂ content is 6 wt%, the overall performance of the membrane is the best.

1. Introduction  
Lithium-ion batteries are promising candidates for advanced secondary batteries due to their high energy density, long cycle lifetime, low self-discharge and no memory effect properties. [1-3]. Lithium-ion batteries can potentially satisfy the urgent needs of miniaturization, light weight of mobile communication and notebook computers, and they have been widely used in the dominant position in communication and other portable electronic products [4-7].Several countries have conducted special engineering schemes to popularize the application of batteries and gradually occupy a dominant position in the market [8].  
As a semi-crystalline polymer, PVDF has an amorphous molecular segment, which facilitates the absorption of the electrolyte. Compared with the commercial polyolefins separator, a PVDF electrospinning separator possesses increased conductivity, better electrolyte uptake, higher porosity as well as greater mechanical properties. As an amorphous polymer, PES has good high temperature and low temperature performance, high mechanical strength and modulus, extremely stable electrical and chemical properties, and easy to process [9-15].

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Nano-TiO$_2$ particles have many excellent properties, such as excellent weather resistance, excellent resistance to chemical corrosion, excellent chemical stability as well as possessing non-toxic, photosensitivity, high dispersion and other characteristics\cite{16}. The mutual attraction between the polar groups on the surface of inorganic particles and the polar groups of polymer chains potentially enhance the bonds among the fibers. The presence of the inorganic particles can expand the amorphous region and allow the lithium-ions to migrate more easily. Thus, doped nano-TiO$_2$ particles can improve the mechanical properties of the separator and ionic conductivity\cite{17}.

In this paper, the traditional PVDF polymer matrix was modified by blending the polymer PES from the viewpoint of enhancing both the thermal stability and mechanical properties of the lithium ion battery separator while maintaining and improving its electrochemical performance. PVDF/PES composite fiber membranes were prepared by electrospinning. TiO$_2$ is generated by in situ hydrolysis of tetra-n-butyltitanate, and the effects of TiO$_2$ content on the mechanical and electrochemical properties of the separators were studied.

2. Experimental parts

2.1. Experimental raw materials

PVDF (KYNAR 761, $M_w=3\times10^5$) and PES(LNP) were dried at 90°C for 5 h before utilization. N, N-dimethylformamide, tetrahydrofuran, ethanol, glacial acetic acid, tetra-n-butyltitanate(TBTI) are all analytical purity and untreated before use.

2.2 Experimental steps

The dried PVDF and PES with a mass fraction of 18% (according to the mass ratio of PVDF to PES is 8:2) were dissolved in the mixed solvent of DMF and THF with a mass ratio of 8:2. Four drops of glacial acetic acid were added during the stirring. Different amount of TBTI was added into the mixed solution, and the stirring was continued for 4 hours. PVDF/PES spinning solutions with different TiO$_2$ mass fractions were obtained. The above spinning solution was loaded into a spinning machine, spinning parameters were set as follow: the spinning speed was 0.8 ml/h, the distance between the needle and the plate receiver was 20 cm, voltage was 16 kV. Eventually, the PVDF/PES/TiO$_2$ separators vary with various TiO$_2$ contents were attained after drying at 80°C for 12 h.

SEM (FEISirion200, FEI) was utilized to observe the surface morphology of the composite separators. Differential scanning calorimetry (Pyris6, Perkin-Elmer) was utilized to measure the separators’ crystallinity. The mechanical property test was completed by electronic material tensile tester (AGS-J, Shimadzu Corporation).

3. Results and discussion

3.1 Morphology and diameter

The SEM images of composite separators vary with different TiO$_2$ contents were demonstrated in Fig.1. The image analysis software is used to analyze the average fiber diameters, and the results was summarized in Table 1. From Fig.1 and Table 1, the obvious interpenetrating microporous structure was observed. There was no obvious bead phenomenon. With the increase of TiO$_2$ content, the average fiber diameter increases firstly and then decreases, and the fiber diameter distribution is relatively uniform. In addition, the hydrolysis of TiO$_2$ will reduce the water content in the solution, increase the viscosity of the solution, and show the overall fiber coarsening. With the further increase of TiO$_2$ content, the dehydration condensation reaction of Ti(OH)$_4$ will occur. Therefore, the viscosity of the spinning solution will be reduced, and the fiber diameter will be reduced. The fiber diameter is the largest when the content of TiO$_2$ is 4 wt%, and the fiber diameter was the smallest when the content of TiO$_2$ was 12%.
Figure 1. PVDF/PES composite separators with various TiO₂ contents, (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%, (e) 8 wt%, (f) 10 wt% and (g) 12 wt%.

Table 1. Average fiber diameters of PVDF/PES/TiO₂ composite separators with various TiO₂ contents.

| TiO₂ contents (wt%) | AFD (um) |
|---------------------|----------|
| 0                   | 0.35     |
| 2                   | 0.38     |
| 4                   | 0.67     |
| 6                   | 0.55     |
| 8                   | 0.54     |
| 10                  | 0.53     |
| 12                  | 0.28     |

3.2 Crystallinity

DSC test on the resulting composite membrane were performed and the results are shown in Table 2 and Fig. 2.

From the results, we find that with the continuous increase of TiO₂ content, the enthalpy change is constantly decreasing, and the crystallinity of the composite membrane is also continuously decreasing. The enthalpy of the composite membrane with 2 wt% TiO₂ was 28.259 J/g, while the enthalpy of the composite membrane with 12 wt% TiO₂ was 21.425 J/g, and the corresponding crystallinity was 26.99% and 20.463% respectively. It might ascribe the decrease in the enthalpy to the increase of the TiO₂ contents, which destroys the regularity of the polymer, and makes the amorphous region of the polymer increase, and the crystallinity decreases.
Figure 2. DSC curves of PVDF/PES/TiO$_2$ composite separator.

Table 2. Enthalpy change of PVDF/PES composite separators with various TiO$_2$ contents.

| TiO$_2$ contents (wt%) | enthalpy change (J/g) | Crystallinity (%) |
|------------------------|------------------------|-------------------|
| 0                      | 28.160                 | 26.890            |
| 2                      | 28.259                 | 26.990            |
| 4                      | 27.844                 | 26.594            |
| 6                      | 26.638                 | 25.442            |
| 8                      | 26.606                 | 25.412            |
| 10                     | 26.096                 | 24.925            |
| 12                     | 21.425                 | 20.463            |

Figure 3. Stress-strain curves for PVDF/PES/TiO$_2$ composite separator with different TiO$_2$ contents.

Table 3. Tensile strength and fracture strain of membranes under different TiO$_2$ contents.

| TiO$_2$ contents (wt%) | Tensile Strength (N/mm$^2$) | Fracture Strain (%) |
|------------------------|----------------------------|---------------------|
| 2                      | 3.303                      | 25.374              |
| 4                      | 3.889                      | 21.419              |
| 6                      | 5.606                      | 25.567              |
| 8                      | 5.657                      | 21.795              |
| 10                     | 3.411                      | 11.787              |
| 12                     | 3.103                      | 11.569              |

Fig. 3 and Table 3 manifest the stress-strain diagrams and data of different TiO$_2$ doped PVDF/PES/TiO$_2$ composite fiber separator, respectively.
We can intuitively see through Fig. 3 and Table 3 that with the increase of TiO$_2$ content, the tensile strength shows a trend of increasing first and then decreasing. The tensile strength of the 8 wt% TiO$_2$ membrane is the largest, reaching 5.657 N/mm$^2$. The fracture strain of 6 wt% TiO$_2$ separator is much higher than other membranes, reaching 25.567%.

With the increase of TiO$_2$ content, the regularity structure of the polymer is destroyed, the crystallinity and the tensile strength is reduced. However, its tensile strength has been increasing until the TiO$_2$ contents is 8 wt%. The reason why the tensile strength increases at this time may be due to the mutual attraction between the polar groups on the TiO$_2$ surface and the fluorine atoms on the PVDF molecules. The mutual attraction plays the physical cross-linking role, which increases the tensile strength of the membrane. However, as the TiO$_2$ content continues to increase, the increased mechanical properties caused by the attraction between the polymer and TiO$_2$ groups was weaker than the decrease in mechanical properties caused by the crystallinity reduction, which leads to the low tensile strength of the membrane will be low. In summary, when the content of TiO$_2$ is less than 8 wt%, the TiO$_2$ content helps to enhance the tensile strength and toughness.

3.3 Electrolyte uptake

The composite fiber separators were cut into 25 × 25 mm$^2$ samples, and the dry separator was weighed first, then immersed in the electrolyte until the separator mass does not change. The sample mass was measured after wiping excessive liquid with filter papers, and finally calculate the electrolyte uptake. The is given as below:

$$\varepsilon = \frac{(M-m)}{m} \times 100\%$$

Where $\varepsilon$—electrolyte uptake (%);
$M$—mass of the composite membrane after immersing in the electrolyte (g);
$m$—dry membrane mass (g).

| TiO$_2$ contents (wt%) | Electrolyte uptake (%) |
|------------------------|------------------------|
| 0                      | 501.3                  |
| 2                      | 603.2                  |
| 4                      | 638.6                  |
| 6                      | 656.8                  |
| 8                      | 657.8                  |
| 10                     | 684.4                  |
| 12                     | 703.1                  |

Table 4 shows the electrolyte uptake of PVDF/PES/TiO$_2$ composite separator with different TiO$_2$ contents. After the dry separator mass is measured, the sample was placed in the prepared electrolyte for 40 min. Through weighing the mass of the sample and utilizing the formula (1), we obtained the Table 4. As shown in Table 4, the saturated electrolyte uptake of PVDF/PES composite separator without doping TiO$_2$ is the smallest, which is 501.3%. The electrolyte uptake of PVDF/PES composite membrane doped with TiO$_2$ is larger than that of the non-doped separator, and the absorption rate increases with TiO$_2$ content. The electrolyte uptake of PVDF/PES composite separator doped 2 wt% TiO$_2$ was 603.2%, while that of 12wt% TiO$_2$ was 703.1%. The reason for this trend is that with the increase of TiO$_2$ content, the amorphous area in the fiber is also increasing, the crystallinity decreases, and the electrolyte is mainly absorbed in the amorphous region, thus the increase of TiO$_2$ content will help to improve the electrolyte uptake of PVDF/PES/TiO$_2$ composite membranes.

4. Conclusion

PVDF/PES/TiO$_2$ composite fiber separator were obtained via electrospinning method, in which TiO$_2$ was introduced through in-situ generation method. With the increase of the TiO$_2$ content, the average fiber diameter of the separator s increased first and then decreased. The enthalpy of the
separator's decreased, indicating the addition of TiO$_2$ can effectively destroy the crystal structure and result in a decrease in the crystallinity of PVDF. The tensile strength of the composite membrane showed a tendency of increasing first and then decreasing. It shows that the addition of TiO$_2$ helps to enhance the tensile strength and toughness. The addition of TiO$_2$ is beneficial to increase the electrolyte uptake of the composite membranes. Above all, when the TiO$_2$ content is 6 wt%, the composite membrane with the best comprehensive performance can be obtained.

5. Acknowledgments

This study was encouraged by the National Natural Science Foundation of China (No. 51603057) and College Students' Innovative Entrepreneurial Training Plan Program (201810214010)

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