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Chacterization of Properties of PVDF/Poly(Dimethyl Silicone) Composities Separator With Blending Membrane Method

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Abstracts

The aims of this research to make poly(vinylidene fluoride) (PVDF) and poly(dimetilsiloksan) (PDMS) composites separator with blending membrane method. Synthesized of PVDF/PDMS composites separator used various ratio were 10/0, 9/1, 8/2, and 7/3. The purpose of increasing concentration of PDMS/PVDF to improve the performance of the composites separator which includes a dimensions of porosity, a pore density, and a electrical conductivity. Based on crystallographic analysis using XRD, the increasing concentration number of PDMS to make compositess was influence decreasing of crystallinity until 29.26% in a ratio 7/3. The analysing of FTIR have sound the wavenumber of each phase can distinguish, which this material includes in the criteria of the composites. The result using XRD and FTIR to material PVDF/PDMS composites in all of the ratio constituens have shown the identification of the structure α-phase of PVDF. The increase of concentration number PDMS influenced decreasing of pore dimension and increasing of pore density with the small of pore dimension 1.71 μm and pore density 4.07×10^{11} count/m^2 in the ratio 7/3. In a ratio 7/3, the value of the electrical conductivity was 3.45×10^{-4} S/cm and the resistance increased up to 80%. ©2017 JNSMR UIN Walisongo. All rights reserved

Keywords: PVDF/PDMS, separator, compositess, pore, resistance and conductivity

1. Introduction

Lithium ion batteries have played a very significant role as power sources in various portable electronic devices, hybrid and electric vehicles [1]. Lithium ion batteries appeal to many users because they offer a high specific energy, a high energy density, a long cyle lifetime, a low self-discharge rate, and a high operational voltage [2]. Separator is a kind of microporous membrane and it is an important part of lithium ion batteries. The main function of separator is to ensure the flow of ions and prevent from internal short circuiting [3]. An ideal separator should have a zero ionic resistance, however in practice a low ionic resistance can be achieved by a high porosity [2].

Generally, separator composed of a polymer membrane and form a microporous layer or porous layer. The pore size is very important to the functioning if the separator. The pore size must be smaller than the particle size of the electrode components. Ideally the pores should be uniformly distributed. This terms is ensure current distribution uniformly in separator to hold Li in anode. The separator must have the correct amount of porosity in order to hold a sufficient amount of liquid electrolyte in order to enable the movement of ions between the electodes. Typically, a Li-ion batteries separator will have a porosity of 40 %. Pore size is also very important to the functioning of the separator [4].

Both porous structure and electrolyte uptake influence ionic conductivity. The separator with higher porosity can contain more liquid electrolyte. This leads to higher electrolyte uptake and more carrier ions [4]. Another ways, to increase the electrolyte uptake in the polymer matrix are controled its components and its morphology.

The conventional separator materials used in lithium ion batteries are polyolefin, such as polyethylene (PE) and polypropylene (PP). Due to the low polarity, these materials show poor liquid electrolyte retention and have difficulty in absorbing electrolytes with high dielectric constants [5]. These disadvanteges lead to lower ionic conductivity and higher electrolyte leakage. Semicrystalline polyvinylidene flouride (PVDF) has received special attention from researchers as separator of lithium ion batteries due to its higher polarity and electrolyte uptake [6]. However, the limits of porous PVDF membrane for separator application lie in the higher crystallinity of PVDF. To decrease the crystallinity of PVDF used two methods. The first method is by incorporating asymmetric groups to the main chains of the polymer. The other method, which is more widely adopted, is by blending the polymer matrix with suitable polymers [4].

Blending method is a simple method to modify polymer matrix. Several polymers, such as polyethylene oxide (PEO), polyacrylonitrile (PAN), poly (dimethylsiloxane) (PDMS) and polymethyl methacrylate (PMMA), had been used to blend with PVDF matrix. In recent years, many progress focused on preparing separators via blending were made [3]. For example, the studies of Xi et al and Li e al. revealed that the addition of PEO into PVDF matrix improves the porosity and pore connectivity. This research used PDMS, the addition of PDMS can reduce crystallinity of PVDF and increase electrolyte uptake [7].

Polysiloxane have some characterization are lower surface voltage, good flexibility, lower transitition temperature, high temperature stability, high compresibility, and et al. Polysiloxane was found to be beneficial to the increase of both the ion mobility and ion density, which resulted in the improvement of the conductivity [8].

Based on morphology measurements, phase analysis, functional groups band, electrical conductivity, resistance and et al. will be research for PDMS effect in the membrane structure of PVDF with different PVDF/PDMS ratio in casting solution.

2. Experiments Procedure

The first step in this experiment were preparation of equipment and materials. The materials were polyvinylidene flouride (PVDF), polydimethyl siloxane (PDMS), glycerol, N-N dimethyl acetamide (DMAc) as a solvent of PVDF, and alcohol 96%. PVDF was the main material, which dissolve in DMAc and add glycerol until soluble and then add PDMS under stirring at 70 °C over 6 hours to yield a homogenous cast solution. In an air atmosphere with room temperature, the solution was cast into thick film on ITO glass by spin coating process. After evaporating for 10 s, the supported thick film immersed into water bath until 48 hours at temperature of 30^{0}C and the solidified porous blending membrane formed. This process have a purpose to remove glycerol, solvent, and additive. After being driedin

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vacuum at 40^0C over 24 h, the blending PVDF/PDMS membrane was obtained. To know the porosity of PVDF/PDMS was done identification with Archimedes principle.

The characterization of PVDF/PDMS composites separator werw done by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and conductivity with two probe principle.

3. Result and Discussion

Identification morphology with SEM

Scanning Electron Microscopy (SEM) have a purpose to know the surface morphology, thickness of film, and pore size of PVDF/PDMS composites separator. With glycerol as co-solvent in casting solution, the PVDF and PVDF/PDMS separators were prepared with similar morphology and symmetric porous strusture as shown in Figure 1. In the ratio 10/0, the geometry of pore were oval and circularity. When the concentration of PDMS were increase the geometry of pore tend to circular. Figure 1 show too the pore size was more small with the increasing of PDMS concentration in the PVDF/PDMS composites separator. The reduction of pore size because of PDMS concencentration was caused infiltration of liquid phase of PDMS into porous strusture of PVDF and centrifugal force makes pore surface layering of PVDF. The result was the pore size more small in the solidification process.

The pore size of ratio PVDF/PDMS have an average diameter 13,58µm, 7,18µm, 5,62µm, 1,71µm for the ratio 10/0, 9/1, 8/2, dan 7/3. The reduction of pore size caused the number of pore and pore density were increase. High pore density show that the number of pore were increase with a large spesific area which supported in the ion exchange process. If it is compare with separator without PDMS, Separator with the increasing of PDMS concentration have a pore density 10 times more than without PDMS. High pore density was $4{,}07x10^{11}$ count/m² in the ratio 7/3. It can be proven by qualitative and quantitative, qualitative likes in the figure 1, analysis SEM and quantitative in the Table 1.

The porosity of PVDF/PDMS composites separator ranged from 69,33% - 81,53%. The higher porosity was 81,53% in the ratio 8/2. The porosity was membrane volume absorbed by butanol divided total volume, It means butanol volume was absorbed by membrane was high in ther ratio 8/2 and porosity was not related with concentration PDMS.

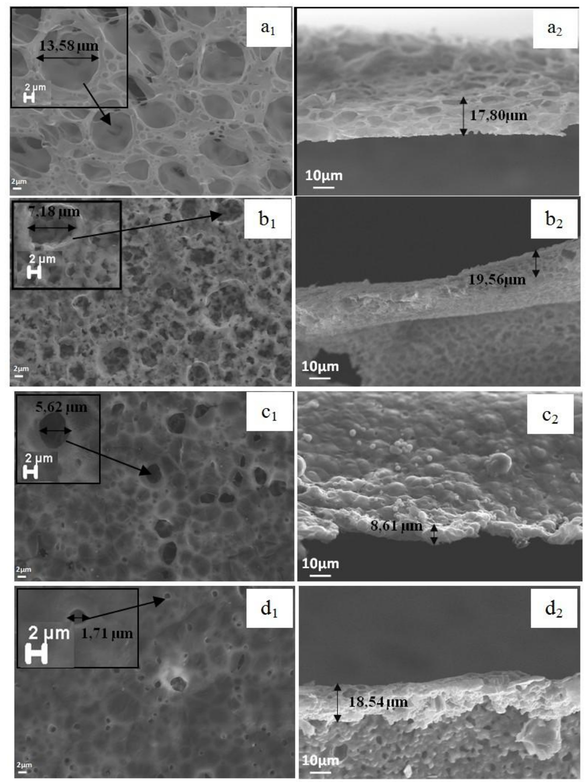

Figure 1. SEM micrographs of porous separator with different PVDF/PDMS ratio in casting solution / (a)10/0 (b) 9/1 (c) 8/2 (d) 7/3. 1 / surface and 2 / thickness

Table 1. Pore density of PVDF/PDMS composites separator

Blend Membrane composition PVDF/PDMS	Amount of pore	Membrane area (m²)	Pore density (m²)
10/0	$1{,}44x10^5$	$3{,}23x10^{-5}$	$4{,}47x10^9$
9/1	$3{,}13x10^5$	$6{,}16x10^{-5}$	$5{,}08x10^9$
8/2	$2{,}90x10^6$	$2{,}92x10^{-5}$	$9{,}90x10^{10}$
7/3	$5{,}82x10^6$	$1{,}43x10^{-5}$	$4{,}07x10^{11}$

Table 2. Porosity of composites PVDF/PDMS separator

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Blend Membrane composition PVDF/PDMS	Membrane density (gr/mL)	Dry Mass (gr)	Wet Mass (gr)	Porosity (%)
10/0	1,74	0,0010	0,0013	73,65
9/1	1,66	0,0020	0,0022	69,33
8/2	1,59	0,0004	0,0009	81,53
7/3	1,51	0,0004	0,0006	73,65

Identification of phase and cristallinity with X-Ray Diffraction (XRD)

Identification XRD has a function to know a phase of separator and crystallinity. Figure 2 shows the X-ray diffraction of PVDF/PDMS composites separator. Depending on the preparation conditions, PVDF chains mainly aggregate into three crystalline forms, e.g., α-type crystal with TGTG monoclinic, β-type crystal with planar zigzag conformation, and γ-type crystal with TTTGTTTG. Increasing of PDMS concentration not makes a angle changes (2θ), not makes a new peaks, and not changes a phase of PVDF. It can show in Figure 3, in the pattern of PVDF has a four peaks at angels $17{,}70^0$(100), $18{,}31^0$(020), $19{,}94^0$(110), dan $26{,}53^0$(021). Those angels have α-phase PVDF. X-ray diffraction patterns of PVDF/PDMS composites separators show a pattern of pure PVDF with the angels 18^0 dan 20^0 and there is not PDMS peaks in the XRD patterns of PVDF/PDMS. PDMS concentration caused intensity of PVDF/PDMS composites separators decrease. It caused liquid phase of PDMS increase. PVDF is semicrystallin polymer, 50% is crystallin and 50% is amorphous. Thus, increasing of PDMS concentration caused the depressed crystallization of PVDF/PDMS composites separator. The crystallization of pure PVDF is 63,84% and PVDF/PDMS composites separator is more smaller up to 29,26% with the ratio 7/3 in the Table 3.

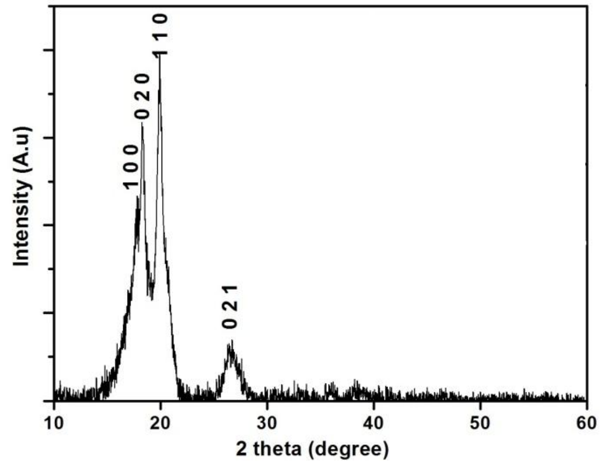

Figure 2. XRD curves of pure Polyvinilidene flouride (PVDF)

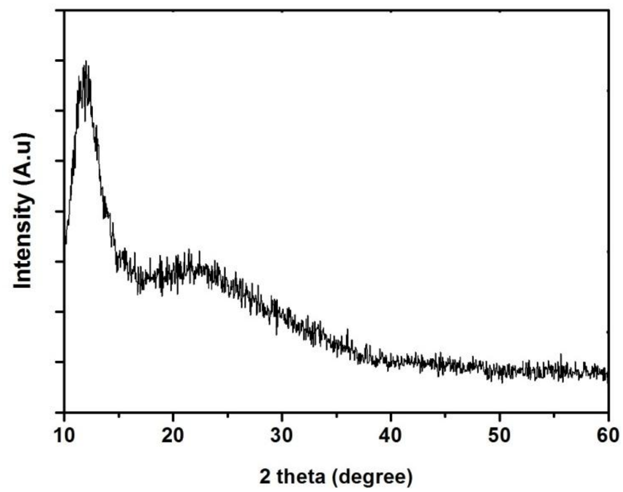

Figure 3. XRD curves of pure Polydimethil siloxane (PDMS)

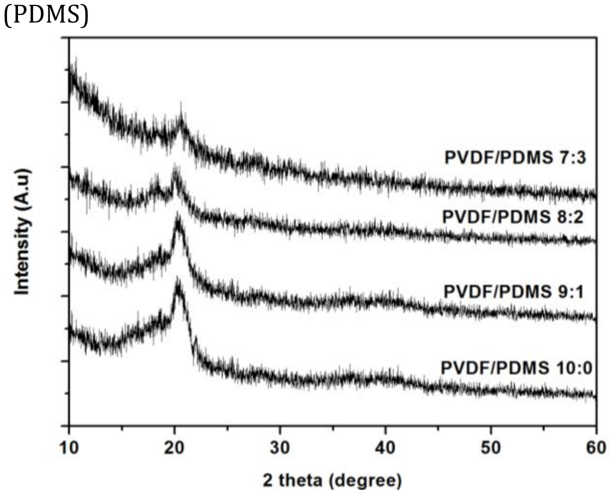

Figure 4. XRD curves of porous separators with different PVDF/PDMS ratio in casting solution / (a)10/0 (b) 9/1 (c) 8/2 (d) 7/3.

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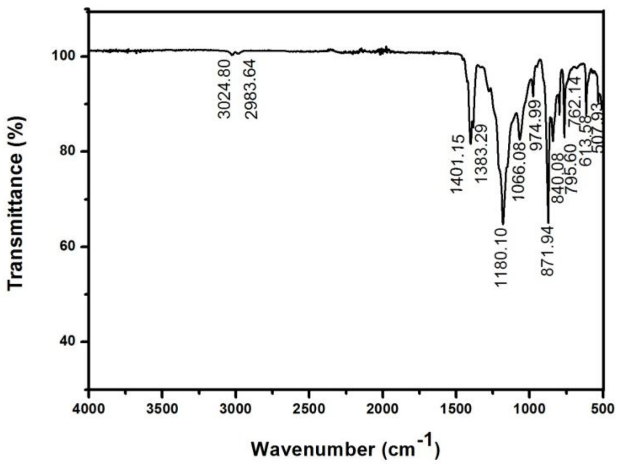

Figure 5. FTIR spectra of PVDF/PDMS composites separators

Table 3. Crystallinity of PVDF/PDMS composites separators

Blend Membrane composition PVDF/PDMS	Crystallinity
10/0	63,84 %
9/1	59,75 %
8/2	61,46 %
7/3	29,26 %

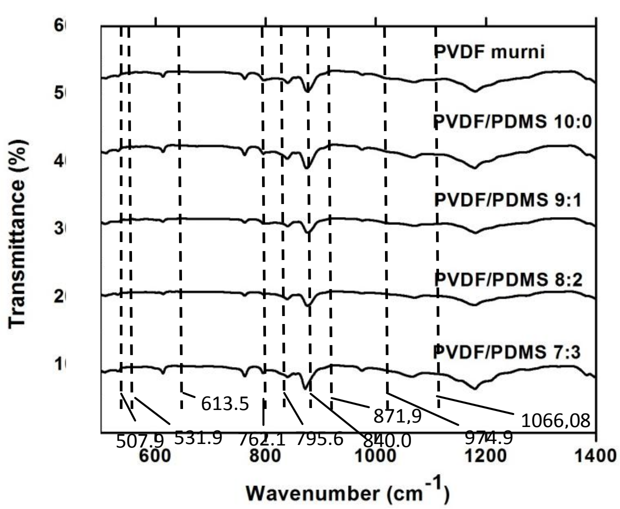

Figure 6. FTIR spectra of pure PVDF and PVDF/PDMS

Identintification of functional groups and phase with FTIR

Functional groups of a compound in organic and anorganic materials can be identified using spectroscopyc, Fourier Transform Infrared (FTIR). FTIR is used to identification types of functional groups and vibrational modes of PVDF/PDMS composites separators, likes figure 5 and 6. In the picture show transmittance peaks in the wavenumber 531.90, 613.58, 762.14, 795.60, and 974.99 cm^{-1} as a α-phase and wavenumber 507.93 dan 840.08 cm^{-1} as β-phase and γ-phase. Although, PVDF/PDMS composites separator tend to has a α-phase of PVDF because FTIR showed a lot of wavenumber are α-phase. The wavenumber of PDMS in the region 871.94 cm^{-1} which is Si – O bands with stretching vibration Si – OH, the 1066.08 cm^{-1} region is Si – O bands with stretching vibration, the 2983.64 cm^{-1} is C – H bands with stretching vibration. This condition is agree with FTIR spectrum data of PVDF/PDMS composites separator in the figure 5 that PVDF spectrum and PDMS have each peaks according to the peaks that have been mentioned.

Identification of electric conductivity and resistance

In the application of Lithium Ion Batteris, separator must have a lower electric conductivity and high resistance. Electric conductivity measurement of PVDF/PDMS composites separators with LCR meter two probe principle. Electric conductivity of PVDF/PDMS composites separators with different PVDF/PDMS ratio in the Table 5.

Electric conductivity decreased with the increased of PDMS and the lower conductivity in the ratio 7/3, 3,45 x 10^{-4} S/cm. Electric conductivity of separator for lithium ion batteries must be have a lower value. This is to prevent a short circuits. Short circuits occurs when voltage source has a low resistance, thus

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in this experiment the resistance must be increased in each ratio. Resistance of PVDF/PDMS composites separator can be seen in Table 6, the resistance without the addition of PDMS was very small reached 0,298, when the increasing of PDMS concentration up to ≈1 and increasing of resistance reached 80%.

Table 5. Electric conductivity of PVDF/PDMS composites separator

Blend Membrane composition PVDF/PDMS	Electric Conductivity (S/cm)
10/0	$3,20 \times 10^{-3}$
9/1	$5,67 \times 10^{-4}$
8/2	$3,97 \times 10^{-4}$
7/3	$3,45 \times 10^{-4}$

Table 6. Resistance of PVDF/PDMS composites separator

Blend Membrane composition PVDF/PDMS	Resistance (Ω)
10/0	0,293
9/1	1,08
8/2	1
7/3	0,957

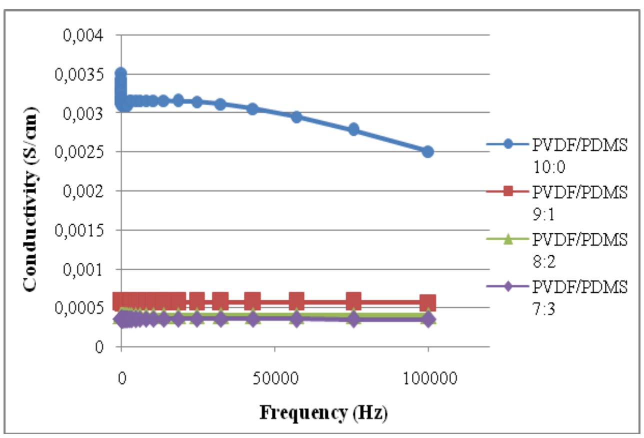

Figure 6. Electric conductivity of PVDF/PDMS composites separator.

4. Conclusion

PVDF/PDMS composites separators for lithium ion battery were prepared through a blending method. Blending method can make a composites separator in micro orde with the smaller pore size was 1,71 in the ratio 7/3. The increasing of PDMS concentration can reduce the pore size of separator that showed the high pore density in the ratio 7/3 was reached $4,07 \times 10^{11}$ count/m^2 with crystallinity up to 29,26% in the ratio 7/3 too. With the addition of PDMS, resistance of separator increased up to 80 % and electric conductivity of separator decreased up to $3,45 \times 10^{-4}$ S/cm in the ratio 7/3.

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