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# SYNTHESIS OF PROTON CONDUCTIVE MEMBRANE BASED ON ACID-BASE COMPLEX PAIR: BACTERIAL CELLULOSE AND BENZOTRIAZOLE

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## ABSTRACT

Synthesis of proton conductive membranes based on acid-base complex pair: bacterial cellulose (BC) and benzotriazole (Btri) has done. Microbial cellulose is derived from bacterial cellulose market, known as nata de coco. Nata de coco was pulverized and washed with solution of NaClO 2% then heated for 30 minutes to boil. Proton conductive membranes have made by mixing the bacterial cellulose powder and distilled water, stirred for 24 hours with a magnetic stirrer, after it was added benzotriazole with the mass ratio between bacterial cellulose and benzotriazole; 1: 0.20, 1: 0.25 and 1: 0.30, and stirred for 24 hours with a magnetic stirrer continued at the casting stage, drying at a temperature of 50˚C for 36 hours. Characteristics of the material obtained was studied by using FTIR analysis for functional groups, XRD analysis to study diffractogram pattern of the resulting material, and SEM analysis to show the morphology of the material, as well as proton conductivity. The results show that conductivity of membranes based on acid-base complex pair bacterial cellulose and benzotriazole in the ratio 1: 0.25 g/g has proton conductivity 1.7 x $10^{-5}$ S/cm.

**Keywords:** Bacterial cellulose, Benzotriazole, Acid-base, Proton conductivity.

## INTRODUCTION

The need for energy is very high at the present time not indisputable, many attempts have been made to find alternative energy sources. The main source of energy is fossil fuels, which are non-renewable. Exploration of fossil fuels continuously causes the fossil-fuel reserves to diminish. The fossil fuel crisis has begun to be felt in society. According to S.M. Javaid Zaidi and Takeshi Matsuura[1], fossil-fuel production will peak in 2020 and thereafter decrease. In addition, continuous use of fossil fuels can cause serious environmental problems, such as global warming, climate change, melting of ice caps, acid rain, pollution, ozone layer depletion, forest and agricultural land damage[2]. Therefore, we need alternative energy sources that are environmentally friendly and renewable. One such environmentally and renewable energy source is the fuel cell[3].

Electronic conducting polymers have been a new class of materials in the recent years and have received extensive attention in academic and industrial research activities because of Reviews their great potential applications in electrical, optical, biological, and other sectors. Cellulose pulp, cellulose derivatives, cotton cellulose, microcrystalline cellulose, and bacterial cellulose (BC) membrane have been used for preparation of conducting nanocomposites. Bacterial cellulose is a special kind of cellulose that is produced through fermentation of bacteria in static or agitated culture. Having similar molecular structure as natural cellulose, BC provides specific network ultrafine structure and particular properties, such as sufficient porosity, large purity and crystallinity, good mechanical properties, great water holding capability, excellent biodegradability, and biocompatibility[4-9].

Syntheses of multifunctional composites which combine the physical properties of two or more constituents in synergistic manner are of significant interest as they facilitate controlling/tuning properties between the two limits. Several different material combinations metal/ceramic, metal/ polymer, ceramic/polymer have been developed and are being used for various applications. The two materials of interest to the current investigation are: bacterial cellulose and benzotriazole. BC has a unique fibrous network structure which provides high strength and as a result has received considerable industrial attention. The biocompatibility of BC together with its low density and high strength has made it equally important for biological applications. The fibrous network structure, apart from providing high mechanical strength, offers micro/nanoporous spaces[10-14]. Proton conductive membranes based on acid-base complex pair have been previously reported to the polymer backbone: polysulfone and polystyrene[15-16].

In this paper reported bacterial cellulose have derived from bacterial cellulose market, known as nata de coco as a backbone. Proton conductive membranes based on acid-base complex pair blends were prepared using bacterial cellulose and benzotriazole at several mass ratios. The membranes were characterization through the analysis of functional groups using FTIR, XRD analysis to studies diffractogram pattern of the resulting material, and SEM analysis to studies the morphology of the material, as well as proton conductivity.

## EXPERIMENITAL

### Materials

Commercial bacterial celullose (BC) was purchased from home industry, 1H-benzotriazole (Btri) from Alfa Aesar, and sodium hypochlorite from Merck.

### Procedures

Nata de Coco was obtained from the market Bengkulu, first washed using distilled water in order to clean than other materials during fermentation. After washed with distilled water, Nata de Coco pulverized in order to obtain BC in the form of slurry. BC then in bleaching using NaClO 2% solution and heated for 30 minutes. After that, BC washed with distilled water until pH neutral. To be obtained BC dry without water, BC heated in an oven at a temperature of 100ºC and dried then crushed to obtain powders with similar particle size.

Proton conductive membranes based on acid-base complex pair have been made by mixing powder BC with distilled water and stirred for 24 hours with a magnetic stirrer to obtain a mixture evenly, then added benzotriazole with the mass ratio between BC and benzotriazole is 1: 0.2, 1: 0.25 and 1: 0.3 and then stirred for 24 hours with a magnetic stirrer, continued at the casting stage, and subsequent solvent evaporation of water at a temperature of 50ºC.

### Characterization

The FT-IR spectra of cellulose, benzotriazole and proton conductive membranes were characterized using a FTIR spectrometer (Shimadzu IR PRESTIGE-21). The samples were taken at wave numbers in the range of 400 to 4500 cm$^{-1}$.The X-ray powder diffraction (XRD) analysis was performed using an X-ray diffractometer (Rigaku D-MAX 2200, Japan) with Cu Ka ($\lambda$ = 1.5406 A) radiation over the range 2θ between 0° and 80°.

The morphology of the membranes was observed by SEM-type JEOL 7001 FESEM (Tokyo, Japan). The samples were previously coated with gold in a sputtering device.

Conductivity of membrane was measured at room temperature using IM 3590 Chemical Impedancy Analyzer HIOKI.

## RESULTS AND DISCUSSION

The interaction functional groups between BC with benzotriazole have been analyzed using FTIR.Figure-1 shows the spectrum of benzotriazole.

Figure-2 show spectra of BC, BC-Btri-0.30, BC-Btri-0.25, and BC-Btri-0.20. In wave number 2900.94 cm$^{-1}$ shows the stretching vibration of C-H alkanes. Next on the wave number 3416.15 cm$^{-1}$ with a peak width indicates stretching vibration of O-H. Then the wave number 1111.00 cm$^{-1}$ shows the peak C-O cyclohexane contained in the cellulose structure and the wave number 956.69 cm$^{-1}$ was associated with a peak of C-H aromatic chain. When compared between the spectrum of pure BC and the spectrum BC-

Btri-0.2 in Figure-2, it is obvious that the differences intensity of this is evident in the wave number 1157.29 to 1303.68 cm$^{-1}$ are peak of C-N.

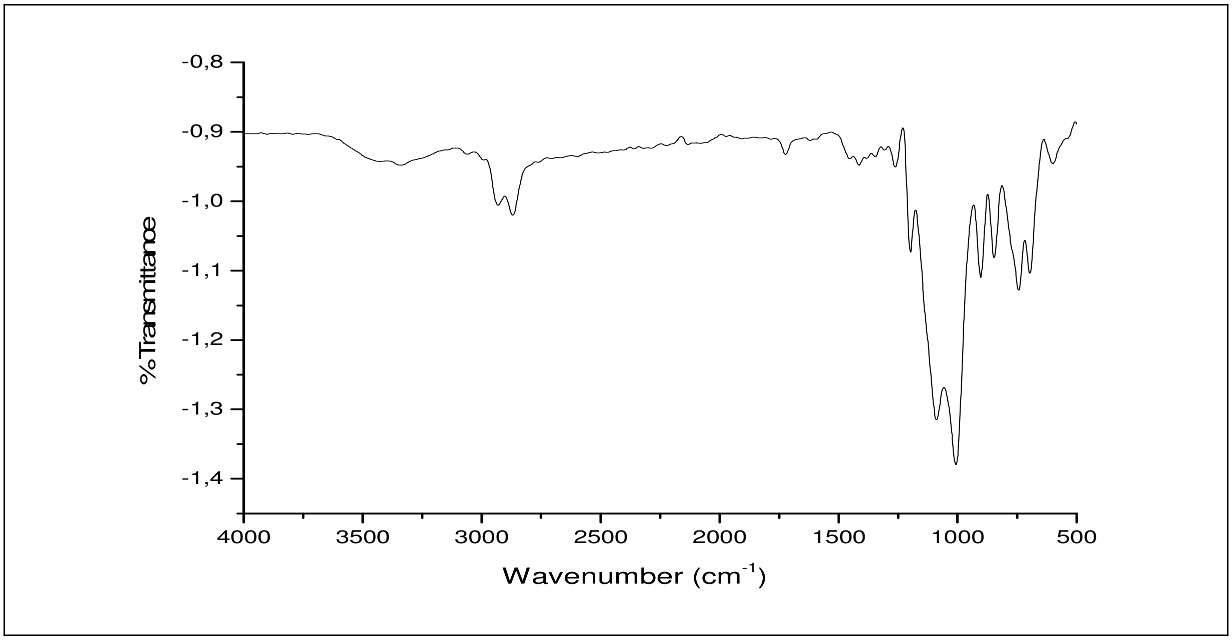

Fig.-1: Spectrum of benzotriazole

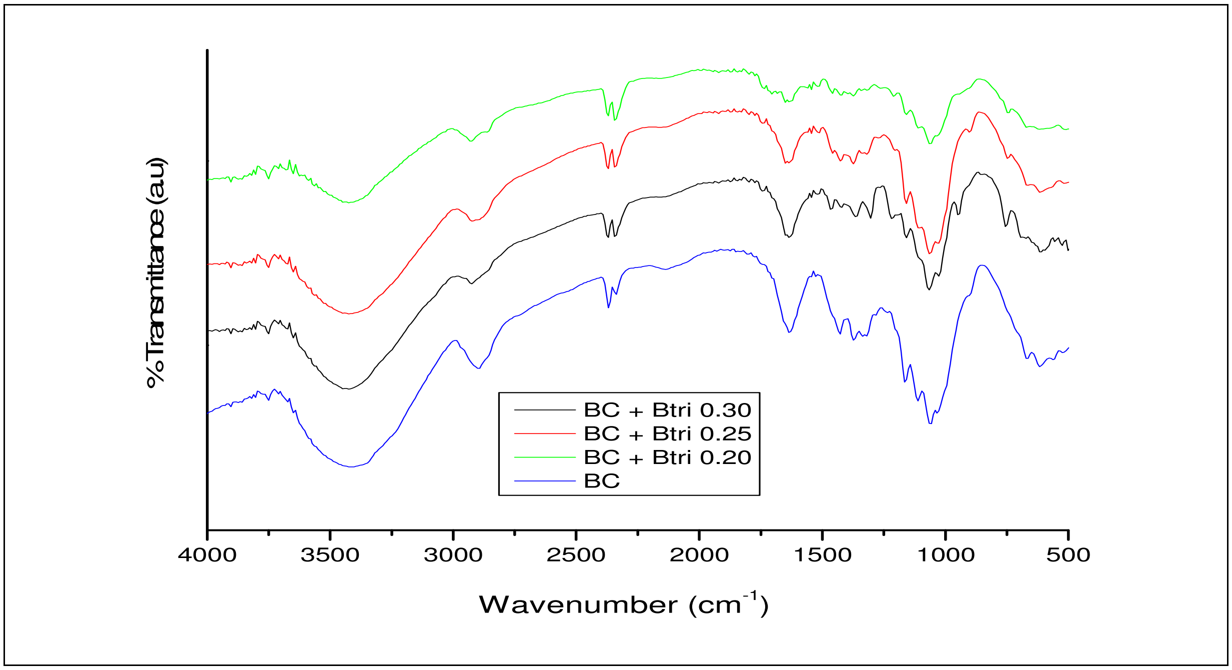

Fig.-2: Spectra of BC, BC-Btri-0.30, BC-Btri-0.25, BC-Btri-0.20.

Next on the wave number 3425.58 cm$^{-1}$ is the stretching vibration of OH and then the wave number 2924.09 cm$^{-1}$ is a CH stretching vibration of alkanes, the wave number 671.23 to 756.10 cm$^{-1}$ indicates the presence of vibration buckling aromatic CH, then the wave number 1064.71 to 1157.29 cm$^{-1}$ is the peak of C-O. Based on the results of FTIR analysis of membrane-BC-Btri 0:25 in Figure contained NH peak at wave number 3425.58 $cm^{-1}$ then there is also the peak of C-H wide while at wave number from 1373.32 to 2152.56 $cm^{-1}$ is the culmination of C = C. In wavenumber 1319.31 $cm^{-1}$ is a peak that shows the interaction between BC with benzotriazole, at wave number 1064.71 $cm^{-1}$ is the peak of a C-O and the wave number 617.22 to 906.69 $cm^{-1}$ is the peak of a C-H aromatic. Similar to spectrum of membrane BC-Btri-0.30, the wave number 3410.15 $cm^{-1}$ which is the peak of NH, from 2854.65 to 2924.09 $cm^{-1}$ and is the peak of alkane CH, at wave number 1319.31 to 1543.05 cm $^{-1}$ is the peak of a bond N and the wave number 1064.71 to 1157.29 $cm^{-1}$ is the peak of CO.

The band between 3000 and 2000 $cm^{-1}$ can be attributed to the possibility of the formation and interaction between BC and Btri, the which were supported in the 1800-900 $cm^{-1}$ region and peak near 1100 $cm^{-1}$ and 979 $cm^{-1}$. Interactions such as hydrogen bonding that occurs between BC-Btri also occur in sulfonated polystyrene and benzotriazole have been reported previously[15] and also sulfonated polysulfone and benzotriazole[16]. Meanwhile, other studies have reported that in the study of FT-IR, has shown the formation of hydrogen bonds in the polymer to cause the formation of new material character[17]. Acid-base pair BC and Btri complex are shown in Figure-3.

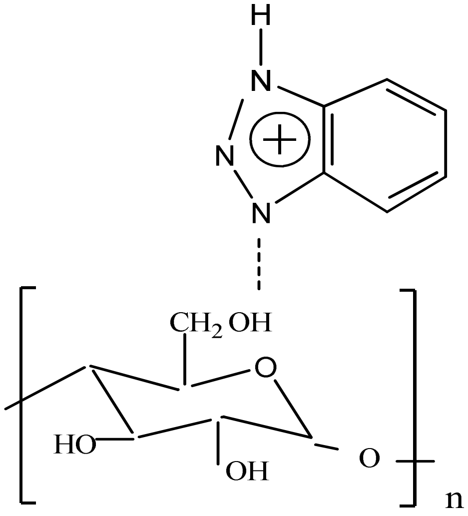

Fig.-3: Acid-base complex pair BC and Btri.

The diffractogram pattern of the material proton conductive membranes based on acid-base complex pair bacterial cellulose (BC) and benzotriazole also have characterized using X-ray diffraction (XRD) to determine. Figure- 4 is diffractogram of BC and BC-Btri-0.30, BC-Btri-0.25, BC-Btri-0.20. Diffractogram arise from the specific peak at 2θ with an angle between 20°-30°. The diffraction pattern having a high intensity is 1600 with a sharp peak shows that BC has crystalline phases. An amorphous phase can be show from the angle 2θ between 10° -20˚ which has a broad peak with the highest intensity of 800. Based on diffractogram, the membrane BC are semi-crystalline phase because it has a crystalline phase and an amorphous phase.

The diffractogram pattern BC-Btri-0.20, there is a maximum intensity at 2θ with an angle between 20°-25° is 1000. The intensity at an angle 2θ between 10°-20° which has a peak width of the intensity of 600. This suggests the addition of benzotriazole has influenced BC crystallinity. In composite diffractogram BC-Btri-0.25 decrease the intensity at an angle 2θ between 20°-25° is 700. And there are specific peaks at an angle 2θ between 10° -2 ° which has an intensity of 600. This indicates that the addition of benzotriazole more have been able to influence the crystallinity BC. Diffractogram of membrane BC-Btri-0.30, more benzotriazole were added, the greater the effect on the crystallinity of the material. From Figure 4. showed that their specific peaks at an angle 2θ between 10°-20° to the intensity of 1600 and an increase in intensity at 2θ with an angle between 20°-25° ie into 1000. Benzotriazole greatly affects crystallinity BC, and is able to raise the intensity of the phase crystallinity of BC. The three variations of comparison, the ratio of 1: 0:30 amorphous phase that has the most.

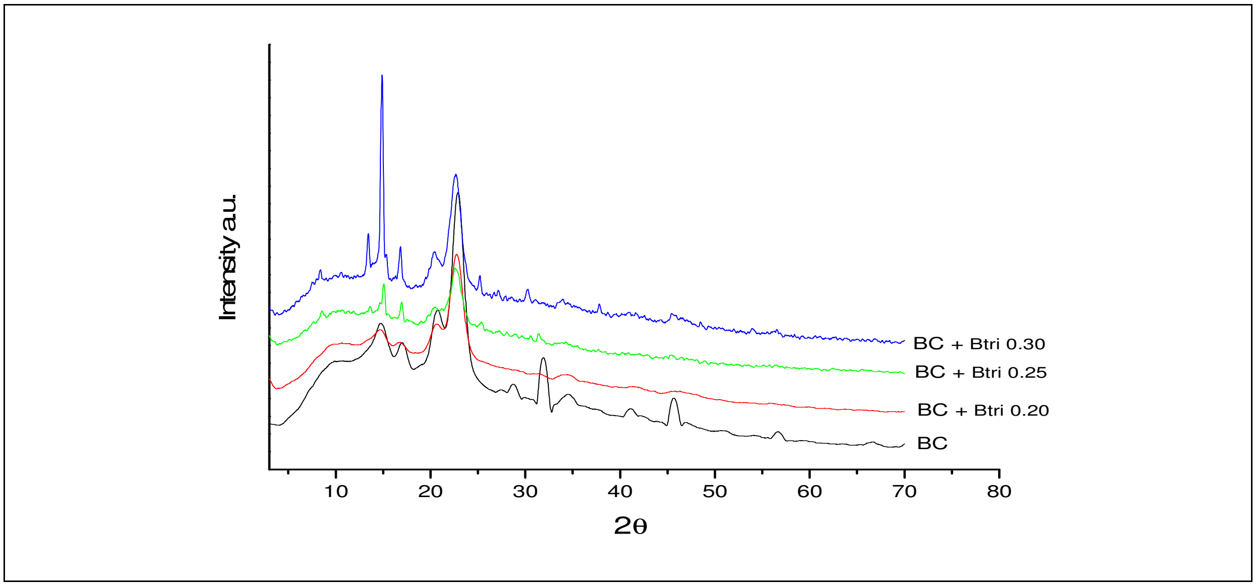

Fig.-4: Diffractograms of membranes BC, BC-Btri-0.30, BC-Btri-0.25, BC-Btri-0.20.

An amorphous phase greatly affect the transport of protons for conductive membranes. Membranes are more amorphous regions will provide greater proton transport[18]. From the previous study reports that using a polymer with amorphous structure and dopant added phosphoric acid and X-ray diffraction characterization, discovered the phenomenon of formation of hydrogen bonds along the main chain in the form of inter-chain and intra-chain. The formation of hydrogen bonds allows us to produce more regular structure and give the characters new crystal polymers[19].

Morphology study, the results of SEM membrane BC-Btri-0.30 shows porosity that are many but small pore width of the membrane with the membrane ratio BC-Btri-0.20. So that in later in the synthesis needs to be improved, although the membrane BC-Btri-0.30 better. Because the proton conductive membrane desired membrane is a membrane tight and not porous to prevent fuel crossover, but the pore shown (Figure-5) from SEM analysis only superficially so it could not be ascertained whether the pore is evident from the results of SEM analysis will be up on the inside of the membrane.

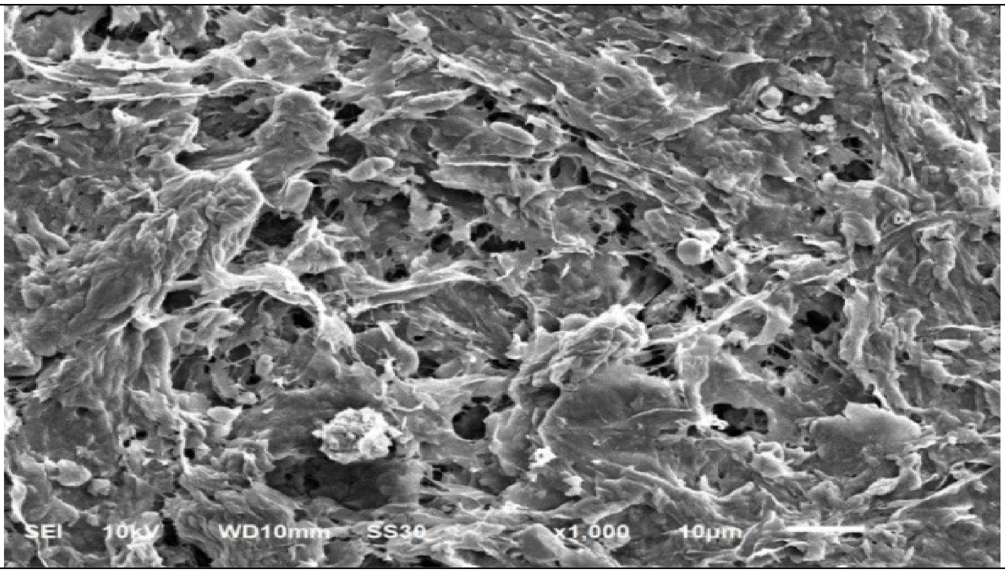

Fig.-5: Morphology of BC-Btri-0.30.

Proton conductivity of the membrane can be defined as the ability of the membrane to conduct protons from the anode to the cathode [20]. From the measurement of proton conductivity, the membrane nata de coco was composited with benzotriazole with a mass ratio of 1: 0.2 has proton conductivity 1.27 x $10^{-5}$ S/cm, the membrane with a ratio of 1: 0.25 has a proton conductivity values sebasar 1.7 x $10^{-5}$ S/cm which showed that the addition of benzotriazole are more able to improve proton conductivity of the membrane. As for the ratio of 1: 0.3 proton conductivity value of 1.22 x $10^{-5}$ S/cm. Based on the proton conductivity of three membranes with different comparison, the membrane with a ratio of 1: 0.25 has a proton conductivity values were highest when compared with a ratio of 1: 0.2 and 1: 0.3. In addition benzotriazole with a ratio of 1:0.3 proton conductivity values declined suspected this could happen because the distribution is uneven benzotriazole membranes that are affected by the long process of mixing the same with the ratio of 1:0.2 and 1: 0.25 while its benzotriazol amount more. The resulting proton conductivity compared with results of previous studies[15], polyelectrolyte membranes based on acid-base complex pair sulfonated polystyrene (PSS) and benzotriazole was found 1.53 x $10^{-6}$ S/cm at room temperature is still greater one order for membranes BC-Btri i.e. 1.7 x $10^{-5}$ S/cm.

## CONCLUSION

We have synthesized and characterization of proton conductive membranes based on acid-base complex pair: bacterial cellulose and benzotriazole. The FTIR spectra of the membranes exhibited the presence of interaction between bacterial cellulose and benzotriazole, the band between 3000 and 2000 $cm^{-1}$ can be attributed to formation and interaction between BC and Btri, the which were supported in the 1800-900 $cm^{-1}$ region and peak near 1100 $cm^{-1}$ and 979 $cm^{-1}$. From the diffractogram obtained information that there is maximum intensity at 2θ with an angle between 20°-25°, more Btri added more areas resulting crystalline phases. The maximum proton conductivity obtained on proton conductive membranes based on acid-base complex pair bacterial cellulose and benzotriazole with a ratio of 1:0.25 has proton conductivity 1.7 x $10^{-5}$ S/cm at room temperature.

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## REFERENCES

1. S.M.J. Zaidi, T. Matsuura, *Polymer Membranes for Fuel Cells*, Springer, New York, (2009).
2. L.O. Vasquez, *Fuel Cell Research Trends*, Nova Science Publishers, Inc., New York, (2007).
3. S.T. Gonggo, L.R. Cynthia, B.Bunbun, A.I Made, *ITB J. Sci.*, **44 A**, 285 (2012).
4. H. Lin, C. Du, Z.Lin, *Research of Materials Science*, **3**, 1 (2014).
5. X. Qian, J. Shen, G. Yu, and X. An, *BioResources.*, **5**, 899 (2010).
6. W. Yin, J. Li, Y. Li, Y. Wu, T. Gu, C. Liu, *Polymer international*, **42**, 80 (1997).
7. N. Onar, A.C. Aksit, M.F. Ebeoglugil, I. Birilik, E. Celik, *Journal of Applied Polymer Science*, **114,** 10 (2009).
8. M.L. Auad, T. Richardson, W.J. Orts, E.S. Medeiros, L.H.C. Mattoso, M.A. Mosiewicki, N.E. Marcovich, M.I. Aranguren, *Polymer International*. **60**, 50 (2011).
9. D. Muiiller, J.S. Mandelli, J.A. Marins, B.G. Soares, *Cellulose*, **19**, 54 (2012).
10. S. Vitta, M. Drillon, A. Derory, *Journal of Applied Physics*, **108**, 053905 -7 (2010).
11. H. Yamamoto and F. Horii, *Macromolecules*, **26**, 1313 (1993).
12. H. Yamamoto, F. Horii, and A. Hirai, *Cellulose*, **3**, 229 (1996).
13. K. Watanabe, M. Tabuchi, Y. Morinaga, and F. Yoshinaga, *Cellulose*, **5**, 187 (1998).
14. W. Czaja, D. Romanivicz, and R. M. Brown, Jr., *Cellulose*, **11**, 403 (2004).
15. I. Gustian, Ghufira, W. K. Fajar, Prosiding Seminar Semirata BKS-PTN Barat, Bogor-Indonesia, p 510, (2014).

16. I.Gustian,S.U Celik, A. Bozkurt, A. Zainuddin,W. Suratno, R.E. Siregar, *J Math. Fund. Sci*., V **46**, 50 (2014).
17. R.Bouchet, E. Siebert, *Solid State Ionics* **89**, 118 (1999).
18. S.Handayani, L.D. Eniya, W.P. Widodo, W.S. Roekmijati, *Journal Sains Materi Indonesia,* **8**, 192 (2007).
19. P. Staiti, and M. Minutoli, *Journal of Power Sources,* **94**, 9 (2001).
20. P. Piboonsatsanasakul, J. Wootthikanokkhan, S. Thanawan, *Journal of Applied Science*, **107**, 1325 (2008).

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