

FABRICATION AND MODIFICATION OF CHITOSAN/PAHAE NATURAL ZEOLITE/REDUCED GRAPHENE OXIDE (CS/PNZ/rGO)–BASED POLYMER ELECTROLYTE MEMBRANES

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ABSTRACT

Integration of reduced graphene oxide (rGO) to membranes and its effect on the physicochemical properties with chitosan/natural zeolite from Pahae (PNZ) was investigated. Membranes were fabricated using a solution casting method and sulfuric acid crosslinking. The results showed that the CS/PNZ/rGO membrane (0.5% w/w) exhibited the highest tensile strength of 17.8 MPa. All rGO-modified membranes displayed a higher tensile strength than CS/PNZ-based membranes with only 10.8 MPa. The optimum elongation at break properties of CS/PNZ/rGO (1.5% w/w) was 2.9%. The membrane was stable under oxidative stress for 416 min while the CS/PNZ/rGO membrane (1.5% w/w) persisted until 686 min. The modified rGO membranes crosslinked with sulfuric acid were improved through tensile strength and stable against oxidation. As the modified membranes showed desirable properties from our study, it was then possible to be utilized as renewed polymer electrolyte membranes (PEM).

Keywords: Chitosan, Pahae Natural Zeolite, Polymer Electrolyte Membranes, Reduced Graphene Oxide, Sulfuric Acid.

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INTRODUCTION

Fuel cells are materials capable of exchanging ions to generate potential green energy due to their zero carbon dioxide emission in portable devices, with high efficiency and energy density.¹ In recent decades, the materials have been embedded with natural biopolymers including polysaccharides and chitosan to improve their safe utilization and cost-effectiveness.² Furthermore, polysaccharides, including chitosan, are biodegradable, hydrophilic, and abundant in nature.^{3,4} Chitosan chains have free amino functional groups with ionic conduction that are suitable for application as cationic polyelectrolytes although limited in terms of mobility of hydrogen ions that may reduce the electrical conductance.⁵ Zeolite is a rock material containing silica-alumina paired with oxygen with a tetrahedral structure. The adsorption ability of zeolite is facilitated through cation exchange.^{6,7} Impregnation of zeolite and its modification such as PVA into products of polymer electrolyte membrane (PEM) is meant to improve the membrane functionality, heat resistance, and as a filter material.^{8,9,10} In addition, chitosan-based PEMs have been developed with different matrices such as carbon nanotubes (CNT) and sulfonated graphene oxide to increase membrane conductivity,^{11,12,13} polyaniline/nano-silica (PAni/SiO₂), to increase oxidation stability,¹⁴ natural zeolites to improve physicochemical properties and conductivity,^{15,16} and sulfonated polystyrene (SPS) to increase proton conductivity.¹⁷ In a previous study, a natural zeolite from Pahae District, North Sumatra has been integrated into a chitosan-based PEM and successfully improved the oxidation stability and tensile strength of the material,¹⁶ followed by modification using a Reduced Graphene Oxide (rGO).^{18,19} In this study, rGO will be further modified and crosslinked with sulfuric acid to improve the physical properties of the membrane as supported by a previous study.²⁰

EXPERIMENTAL

Medium molecular weight chitosan (MMWC) is the main component. Fillers such as natural zeolite were collected from Pahae, Tarutung, North Tapanuli Regency, North Sumatra, Indonesia, and reduced

graphene oxide (rGO) from Sigma-Aldrich. Meanwhile, acetic acid, sulfuric acid, aqua dest, hydrogen peroxide, and iron (II) sulfate were available locally.

Sample Preparation

The rock or natural zeolite of Pahae was pulverized into powder using mortar and pestle. The zeolite powder was sieved using a 200 mesh sieve and dissolved into A 6.0% (v/v) sulfuric acid solution and homogenized at 350 rpm, 70°C for 240 min. The zeolite solution was neutralized using aqua dest following a chemical activation process at 100°C for 60 min. Then, 0.015 g of rGO was mixed into 15 mL of distilled water (0.1% w/v) and sonicated for 6 hr. In the process of fabricating PEM, 3 g of chitosan (CS) was added to 150 mL of 2% acetic acid solution and homogenized at 350 rpm until dissolved completely. The activated zeolite was mixed with 0.15 g (5% w/w CS) and stirred evenly for 24 hr to obtain CS/PNZ samples. For CS/PNZ/rGO membranes, 0.015 g of sonicated rGO (0.5% w/w) was mixed with CS/PNZ solution and stirred again evenly for 24 hr. The CS/PNZ/rGO solution was poured into a glass mold and dried in an oven at 65°C for 16 hr. This procedure was repeated for rGO variations of 0.030 g (1.0% w/w), 0.045 g (1.5% w/w) and 0.060 g (2.0% w/w). The next step is the process of PEM crosslinked with sulfuric acid. The membrane was immersed in a 0.5 M sulfuric acid solution for 90 min and washed with distilled water. The modified CS/PNZ/rGO-based PEMs were air-dried at room temperature.

Characterization of CS/PNZ/rGO-based PEMs

All PEMs were characterized for their chemical characteristics using Fourier Transform-Infra Red (FTIR) of Agilent Technologies-Cary 630 with detection at 650-4000 cm^{-1} (16 cm^{-1} resolution) at room temperature. The crystallographic structure of PEMs was analyzed using X-Ray Diffraction (XRD) Panalytical Empyrean Model. The position angle of the XRD pattern was set at 2 θ by 5° and the final position by 90°. The anode material used is Cu K α with a generator setting of 40 kV and 30 mA, with a measuring temperature of 25°C. Morphological images of the samples were obtained from the Zeiss Evo MA 10 Scanning Electron Microscopy (SEM) with a magnification of 500 times and Extra High voltage Tracking (EHT) of 10 kV. Thermal stability analysis using Thermo Gravimetric Analysis (TGA) with an increase in heating temperature from 30–450°C at 5°C/min using a reference Al nitrogen gas. Mechanical properties of PEMs were checked using RTF 1350 to determine the mechanical properties such as tensile strength and elongation at break recorded for 3 mm/minute at 25°C using a membrane sample dimension of 2 cm $\times$ 8 cm $\times$ 0.1 mm. Oxidation stability was tested by immersing a PEM sample (2 $\times$ 2 cm) in Fenton's reagent (3%, w/v hydrogen peroxide and 2 ppm of FeSO₄) pre-heated for 1 hour at 80°C. The oxidation stability was observed until the presence of a crack indicated a loss of mass by the PEMs.

RESULTS AND DISCUSSION

FTIR Spectra of PEMs

Figure-1 shows the FTIR spectrum of CS/PNZ/rGO PEMs crosslinked with sulfuric acid. The absorption peak occurred at 3198 cm^{-1} which indicated the hydroxide (-OH) functional group. Another peak was detected at 2922 cm^{-1} indicating the presence of the aliphatic group (CH₂ and -CH₃) and at 2102 cm^{-1} , which showed the presence of isocyanate functional group (-NCO) in the range 2100-2270 cm^{-1} . Augmentation of rGO concentration further eliminated the formation of the isocyanate functional group (-NCO). Additional absorption peaks were detected for the amino group (C=O stretching and -NH₂ bending). The amino group I (C=O stretching) was detected at 1640 cm^{-1} for the CS/PNZ membrane.²¹ The peak shifted to 1625 cm^{-1} due to the augmented rGO. The amino group II (-NH₂ bending) absorption peak occurred at a 1528 cm^{-1} in the sample (CS/PNZ/rGO). This shift also occurred due to rGO integration with the PEMs.²¹⁻²³ The C-O stretching functional group was detected at 1379 cm^{-1} . The final absorption peak at 1013 cm^{-1} confirmed the presence of the glycosidic functional group (C-O-C). The absorption peak with the epoxy band (C-O-C) stretching at 1220 cm^{-1} is a unique band of rGO-based material. However, this peak was not detected due to crosslinking with sulfuric acid.

Surface Morphology of PEMs

The morphology of PEMs was visualized using Scanning Electron Microscopy (SEM). The results of the membrane surface are shown in Fig.-2. Figure-2(a) is a CS/PNZ-based membrane

that has a smooth surface and there is no agglomeration on the sample surface. While the CS/PNZ/rGO shown in Fig.-2 (b-e) shows the distribution of white granules that form black cavities on the surface of the sample. This black cavity feature is identified as reduced graphene oxide (rGO).

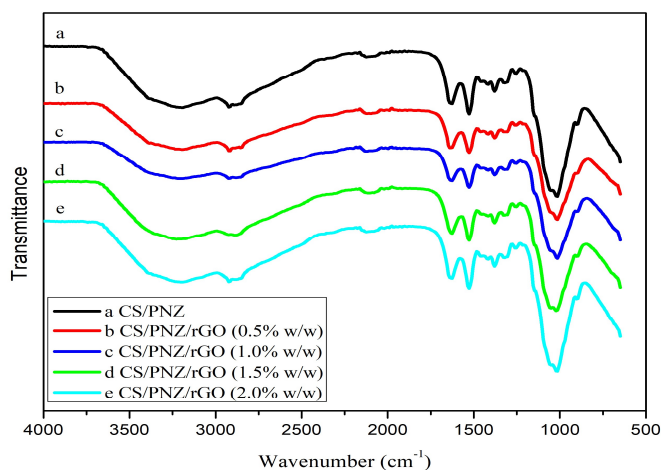


Fig.-1: FTIR Spectra of CS/PNZ/rGO-Based PEMs Crosslinked with Sulfuric Acid

The intensity measured by the detector is weak because the carbon atoms that make up rGO have a lower weight than zeolite. The light intensity is identical to that of a bright-field SEM image. The darker coloration in the SEM image is indicated by the more augmented rGO composition. The distribution of high-intensity (bright light) zeolite is evenly distributed. As a result, all samples can be considered homogenous. Based on the surface morphology, there was no aggregation or flaws, indicating that the sulfuric acid crosslinking procedure was successful in the fabrication of a homogeneous membrane.

X-Ray Diffraction (XRD) Patterns

The results of the X-Ray Diffraction (XRD) characterization of CS/PNZ-based PEMs with and w/o rGO are shown in Fig.-3. All samples showed amorphous and semicrystalline phases. Based on the Segal method,²⁴ the average degree of crystallinity of the membrane was 25%. Typical peaks of chitosan in the XRD spectrum are 11.84° , 16.46° , and 18.72° .¹⁵ However, the diffraction angle decreased with increasing rGO on the CS/NPZ membrane. The diffraction angle occurred at 11.82° ; 11.80° ; 11.78° and 11.70° for rGO variation 0.5% (w/w), 1.0% (w/w), 1.5% (w/w) and 2.0% (w/w) respectively. The zeolite peak was shown at 23.57° for the CS/PNZ membrane. The typical peak of this zeolite shifts to 23.65° ; 23.73° ; 23.84° and 23.89° for rGO variation, respectively. The inclusion of rGO induced a shift in the value of the usual zeolite angle, showing a connection between the CS/NPZ membrane and rGO. As for the rGO diffraction peaks, all CS/NPZ/rGO membranes exhibited diffraction intensity at 9.5° .²³ Overall, the intensity of the diffraction peaks decreased due to the presence of rGO in the membrane which disrupted the hydroxyl chain of chitosan. Furthermore, the interaction of hydrogen bonds between chitosan and zeolite/rGO disrupted the crystalline structure of chitosan.

Thermal Stability

Based on Fig.-4, the first decomposition temperature occurred in the room temperature range up to 100°C . This stage was also known as the loss of water molecule stage.^{8,16,15,25,26} The CS/PNZ/rGO membrane (2.0% w/w) lost about 18.7% of its weight. The result also indicated that the membrane had a water content of 18.7%. The membrane weight loss in this first stage was the highest of all stages. The CS/PNZ membrane only decreased in weight by 13.5%. Chitosan chain decomposition occurred in the second stage with a temperature range of $175\text{--}350^\circ\text{C}$. The CS/PNZ/rGO membrane (2.0% w/w) experienced the highest weight loss of 61.4% followed by all membranes with a similar chitosan composition with a weight loss of 42%. The results indicated that the presence of rGO exhibit no significant effect on the intermolecular hydrogen bonding of CS and rGO.

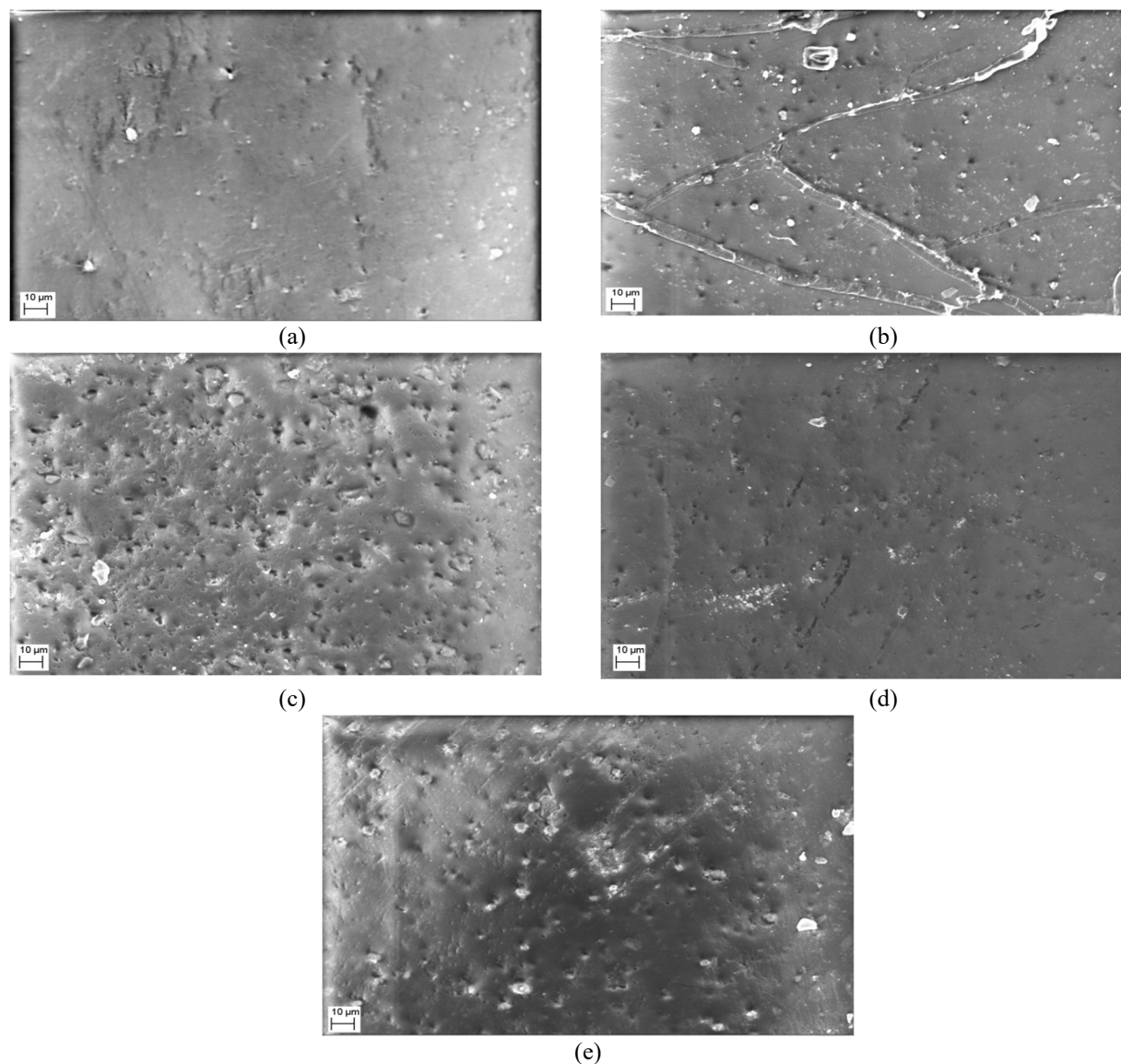


Fig.-2: SEM Image of (a) CS/PNZ, CS/PNZ/rGO (b) 0.5% w/w, (c) 1.0% w/w, (d) 1.5% w/w and (e) 2.0% w/w

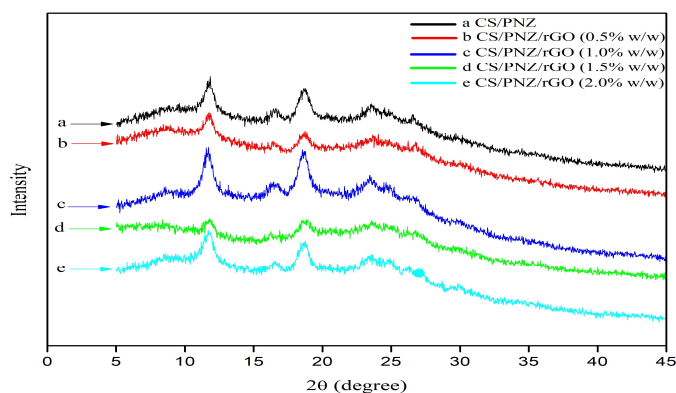


Fig.-3: XRD Patterns of CS/PNZ and CS/PNZ/rGO–Based PEMs Crosslinked with Sulfuric Acid

However, the intermolecular hydrogen bonds between CS and PNZ may increase the thermal stability of the membrane.^{16,27} The last stage (3rd) occurred at temperatures above 450°C. During this stage, the average mass loss of the membrane was 46%.

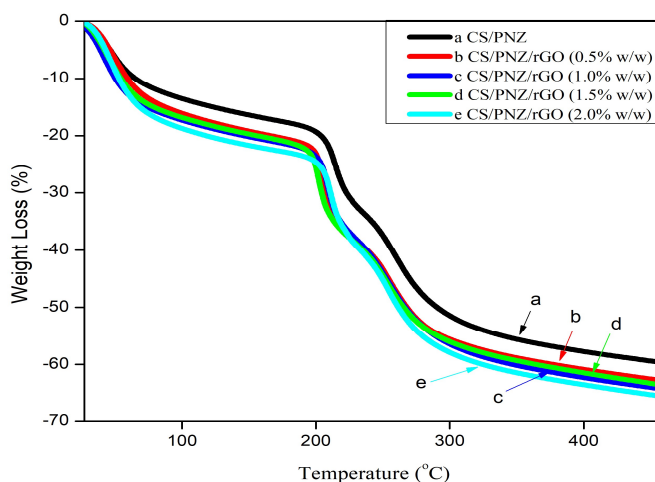


Fig.-4: Thermogravimetric Analysis (TGA) Curve for the Decomposition of CS/PNZ and CS/PNZ/rGO–Based PEMs Crosslinked with Sulfuric Acid

Mechanical Properties

The elongation at break and tensile strength of the PEMs is presented in Fig.-5. The CS/PNZ membrane crosslinked with sulfuric acid exhibited a tensile strength of 10.8 MPa and elongation at a break value of 1.5%, respectively. The tensile strength of the membrane crosslinked with sulfuric acid is greater than in the previous study, namely 1.3 MPa.¹⁶ The crosslinking using sulfuric acid also bonds with chitosan chains resulting in more compact chitosan with shorter chains. However, the elongation at break is getting smaller compared to the previous study, namely 18.2%.¹⁶ This is due to the formation of rigidity from the chitosan-sulfuric acid link. As a result, the membrane was more easily broken. All membranes augmented with rGO had higher tensile strength and elongation at break than CS/PNZ membranes. The physical properties were improved with good bonding between rGO and CS/PNZ implying the mechanical strength provided by the rGOs. The highest tensile strength was obtained in the CS/PNZ/rGO membrane (0.5% w/w) with 17.8 MPa. The properties increased about 1.6 times from the tensile strength of the membrane without rGO. Meanwhile, the largest elongation at break was 2.9% which occurred in the CS/PNZ/rGO membrane (1.5% w/w). The properties correspond to the amorphous semicrystalline membrane with the lowest degree of crystallinity compared to other membranes.

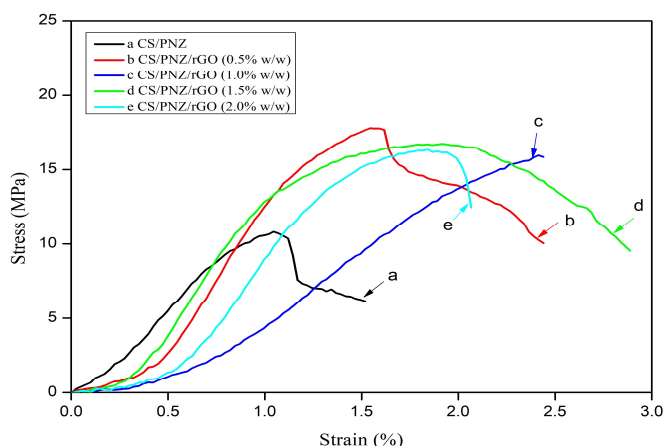


Fig.-5: Mechanical Properties of CS/PNZ and CS/PNZ/rGO–Based PEMs Crosslinked With Sulfuric Acid

Oxidative Stability

The results of the oxidation stability test on CS/PNZ and CS/PNZ/rGO-based membranes are presented in Table-1. The membrane stability under oxidative stress was calculated when the membrane was damaged into pieces after being immersed in Fenton's reagent.^{12,16} The oxidation stability of the CS/PNZ membrane was 416 minutes. The result was higher than the previous study which only had oxidation stability for 1690

103.2 min.¹⁶ The cross-linked membrane with sulfuric acid was responsible for this increase. This method of crosslinking can improve the membrane's resistance to Fenton's solution oxidation. At 686 minutes, the CS/PNZ/rGO membrane (1.5%, w/w) showed the best oxidation stability. The properties were improved regarding the oxidation stability of CS/PNZ by roughly 65% following the augmentation of rGOs. This improvement showed that the CS/PNZ-rGO binding was effective.

Table-1: Result of Oxidative Stability test of CS/PNZ and CS/PNZ/rGO–Based PEMs Crosslinked with Sulfuric Acid

No	Sample	Duration of Stability (min)
1	CS/PNZ	416
2	CS/PNZ/rGO 0.5% w/w	612
3	CS/PNZ/rGO 1.0% w/w	660
4	CS/PNZ/rGO 1.5% w/w	686
5	CS/PNZ/rGO 2.0% w/w	668

CONCLUSION

Polymer electrolyte membranes (PEM) have been successfully fabricated based on chitosan and natural zeolite from Pahae with the addition of rGOs and crosslinking with sulfuric acid. The crosslinking method was proven to improve the strength value of the CS/PNZ membrane to 10.8 MPa and the break resistance decreased to 1.5%. The sulfuric acid cross-linked membranes bonded with the chitosan chain resulted in a shorter and compact material. The addition of rGO material to CS/PNZ also improved the tensile strength and oxidation stability. In this study, the highest tensile strength occurred in the CS/PNZ/rGO membrane (0.5% w/w) of 17.8 MPa with a yield of 1.6 times compared to the CS/PNZ membrane of 10.8 MPa. The most stable membrane under oxidative stress was also obtained in the CS/PNZ/rGO membrane (1.5% w/w) for 686 min. The properties increased 65% better than membranes w/o rGOs or 416 min. Based on the results of the analysis, it can be concluded that the addition of rGO to the crosslinked CS/PNZ PEMs improved the mechanical properties and resulted in good material for fuel cells.

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