J. Myanmar Acad. Arts Sci. 2021 **Vol. XIX. No.1B**

PREPARATION AND CHARACTERIZATION OF CHITOSAN-POLYVINYL ALCOHOL-GRAPHENE OXIDE COMPOSITE MEMBRANE AND THEIR MECHANICAL PROPERTIES

Aung Paing[1], Khin Than Yee[2], Mya Theingi[3]

Abstract

In this study, the composite membrane forming ability of chitosan (CS), polyvinyl alcohol (PVA) and graphene oxide were prepared. The graphene oxide was prepared from graphite powder. The graphite powder (GP) and prepared graphene oxide (GO) samples were characterized by the X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT IR) and Thermogravimetric- Differential thermal analysis (TG-DTA). The XRD pattern of graphite powder and exhibited a strong peak at 2θ of 26.4° corresponding to a basal spacing of d_{002} 0.336 nm and that of graphene oxide at 2θ of 9.79° corresponding to a basal spacing of d_{002} 0.901 nm. The composite membranes were prepared by 1.5 % (w/v) chitosan, 4 % (w/v) PVA and modified with variable loadings of graphene oxide (GO) ranging between 0.2 g to 0.5 g wt. percent. The criteria ratio was investigated using mechanical properties such as tensile strength, elongation at break and tear strength. According to the mechanical properties of composite membranes, CS-PVA-GO2, results revealed that the incorporation of graphene oxide into the CS-PVA polymer matrix lead to the improvement of tensile strength and percent of elongation of break. FT IR analysis, indicated that the characteristic absorption peak of CS-PVA-GO2 composite membrane confirmed the polymer blended with GO. SEM micrograph of CS-PVA-GO2 composite membrane exhibited homogeneous and smooth texture. TG-DTA analysis showed that CS-PVA-GO2 composite membrane exhibited the major thermal stability reflected in lower loss of weight with increasing temperature that led to the delay of decomposition.

Keywords: Graphene oxide, chitosan, polyvinyl alcohol, composite membrane

Introduction

Two-dimensional (2D) graphene oxide has a unique properties and wide range of applications, since the awarded of Nobel prize in physics for the discovering of graphene, it has large effect in the natural science communities. Nanocomposites of graphene due to the improvement in physical properties like electrical, thermal and mechanical as it compared with other nanocomposites and pure polymer. Graphene is an ideal nano filler for function composite due to exceptional properties likes, high surface area, along with its electrical, thermal and mechanical (Tagreed and Mustafa, 2015). GO can be easily dispersed in water; thus, hydrophilic polymer, or water-soluble polymers matrices for polymer/graphene nanocomposite, due to their dispersion properties. Polyvinyl alcohol (PVA) is a hydroxyl-rich, water-soluble, biocompatible and non-toxic polymer that is commonly used in fuel cells, drug delivery, coating material, and adhesives (Ye *et al.,* 2012).

Chitosan (CS) is the product of chitin deacetylation and contains a large quantity of hydrophilic groups (e.g., amino carboxyl groups). Thus, CS molecules are easily protonated. It has been widely used in medicine and has many excellent biological properties, such as biocompatibility, biodegradability and coagulation activity (Lu *et al.,* 2013). Not only does GO contain carboxyl and epoxy groups, it is also possible to insert small molecules or polymers between its layers. The surface anionic groups of GO are able to interact with the CS matrix via hydrogen bonding and electrostatic interactions, to achieve good dispersion (Yuan *et al.,* 2016). As the combination of properties of chitosan such as water binding capacity, fat binding capacity,

---

[1] PhD Candidate, Department of Chemistry, University of Yangon

[2] Dr, Lecturer, Department of Chemistry, West Yangon University

[3] Dr, Associate Professor, Department of Chemistry, Sittwe University

bioactivity, biodegradability, nontoxicity, biocompatibility and antifungal activity, chitosan and it modified analogs have shown many applications (Yang and Chiu, 2012).

Polyvinyl alcohol (PVA) is an inexpensive semi-crystalline polyhydroxy polymer, and has also excellent film-forming properties and a high density of reactive chemical functions (Feketefoldi *et al.,* 2016). The addition of graphene to polymeric matrices has been recently studied in which pristine CS and PVA, and hybrid CS:PVA membranes have been modified by means of the addition of graphene oxide (GO), providing an increase in tensile strength and at the glass transition temperature (Acurio *et al.,* 2017).

A vast number of studies have reported the incorporation of graphene oxide into biocompatible, eco-friendly and cheap polymers for instance, chitosan and polyvinyl alcohol in order to synthesize enhanced nanocomposite material for a wide number of applications (Jiang *et al.,* 2010). Membrane manufacture and performance are attracting great attention in academia and industry in a wide variety of industrial applications. The development of new membranes requires the materials has advanced for the last years, allowing the development of highly featured carbon nanostructures with properties that offer unexpected opportunities in many fields such as adsorption application (Garcia-Cruz *et al.,* 2016).

In this study, the composite membrane was prepared based from CS, PVA and doped with GO as a carbon filler. An intensive physicochemical characterization of this membrane was carried out by FT IR, SEM, TG-DTA and mechanical properties of these membranes were also studied.

Materials and Methods

Sample Collection

Chitosan, graphite powder, sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) were purchased from Academy Chemical shop (Yangon, Myanmar). Polyvinyl alcohol was purchased from First Prime Co. Ltd. Distilled water was used as the solvent in all analyses.

Preparation of Graphene Oxide from Graphite Powder

Graphene oxide (GO) was prepared starting with graphite powder by modified Hummer's Method (Shahriary and Athawale, 2014). Firstly, 3 g of graphite powder and 1.5 g of sodium nitrate and 69 mL of concentrated sulphuric acid were mixed under constant stirring for about 1 h in an ice bath. After stirring, 9 g of potassium permanganate was added gradually to the above mixture solution while keeping the rate of addition carefully controlled the reaction temperature below 20 °C to prevent overheating and explosion. At this state, the mixture solution was gradually becoming dark brown. The mixture was stirred at 35 °C for 12 h and then 1500 mL of deionized (DI) water was added under vigorous stirring. To ensure the completion of reaction of potassium permanganate, 15 mL of 30 % hydrogen peroxide was added to reduce the residual potassium permanganate. And then, dark brown coloured mixture solution gradually changed into bright yellow. Finally, the resulting mixture solution was washed by rinsing with 5 % (v/v) hydrochloric acid and then deionized (DI) water for several times until neutral pH. After centrifugation, the filtrate was dried in oven at 70 °C and graphene oxide (GO) was obtained as shown in Figure 1 (a) and (b).

(a) (b)

Figure 1 (a) Graphene oxide solution and (b) graphene oxide powder (GO)

Preparation of Chitosan (CS)-Polyvinyl Alcohol (PVA)-Graphene Oxide (GO)(CS-PVA-GO) Composite Membrane

CS-PVA-GO composite membrane were prepared from a blend of 1.5 wt. % of CS and 4 wt. % of PVA homogenous solution. Firstly, CS powder was added to the acidic aqueous solution (1 % (v/v) acetic acid) and stirred at room temperature for 12 h. Separately, PVA powder was added to distilled water and stirred at 70 °C for 2 h. Then, CS and PVA solution were filtered by vacuum filtration to remove impurities. The blend membrane was prepared with CS-PVA ratio of 50:50 (v/v %) by mixing the appropriate amounts of the single polymer solutions and stirring for 24 h. Then, a certain amount of GO (0.2, 0.3, 0.4, and 0.5 wt.%) was added into polymers mixture and stirred for three days until a brownish homogenous mixture was achieved. Finally, the CS-PVA-GO mixture solutions were kept for sufficient times to remove any bubble formation and were cast onto a cleaned and dried melamine plate at room temperature. The prepared CS-PVA-GO composite membranes were neutralized with 0.1M NaOH solution and the membranes were washed with water for several times and dried in air. All of the prepared CS-PVA-GO membranes (Figure 2) were kept under dry condition for further use.

(a) (b) (c) (d)

Figure 2 (a) CS-PVA-GO1 (b) CS-PVA-GO2 (c) CS-PVA-GO3 and (d) CS-PVA-GO4 composite membranes

CS-PVA-GO1 = 1.5 % CS - 4 % PVA – 0.2 % GO composite membrane
CS-PVA-GO2 = 1.5 % CS - 4 % PVA – 0.3 % GO composite membrane
CS-PVA-GO3 = 1.5 % CS - 4 % PVA – 0.4 % GO composite membrane
CS-PVA-GO3 = 1.5 % CS - 4 % PVA – 0.5 % GO composite membrane

Characterization of the Prepared Samples

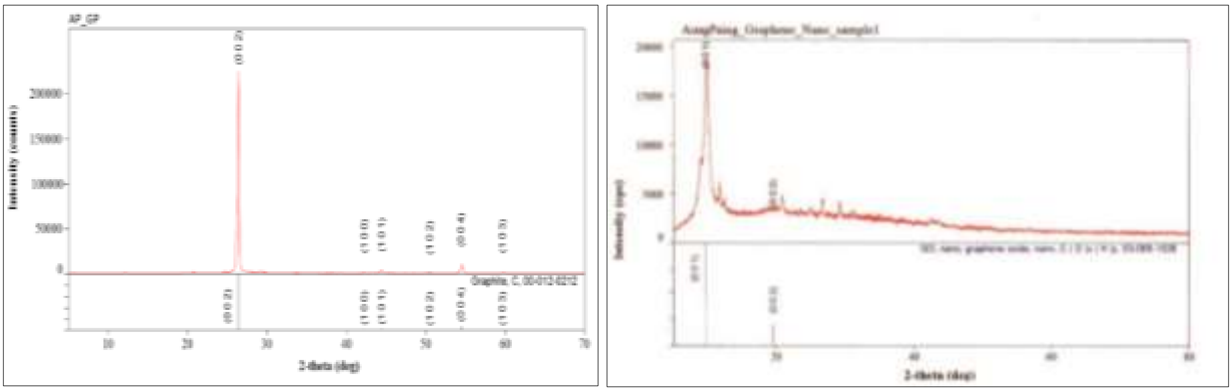
X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat. No 9240 J 101, Japan. Copper tube with nickel filter was used. The diffraction pattern was recorded in terms of 2θ in the range of 10-70 °. FT IR spectrum was recorded in the range of 4000-400 cm^{-1} by using 8400 SHIMADZU, Japan FT IR spectrophotometer. The scanning electron microscopy (SEM) images were recorded by using JSM-5610 Model SEM, JEOL-Ltd., Japan. Thermogravimetric and differential thermal analysis was carried out using (TG-DTA-BAHR-Thermoanalyse GmbH (Germany).

Results and Discussions

Characterization of Graphite Powder (GP) and Graphene Oxide (GO)

XRD analysis of graphite powder and graphene oxide

In XRD measurements, the peaks indicated with Miller indices in the graphite precursor were well matched with the standard graphite diffraction peaks. The smaller peaks are likely originated form impurities in the material. The X-ray diffraction profiles of GP and prepared GO samples are shown in Figure 3. The GP powder exhibited a strong and sharp peak at 2θ of 26.44° as shown in Figure 3 (a), indicating a higher ordered structure corresponding to a basal *d*-spacing d_{002} of 0.336 nm. The crystallite site calculated using the diffraction peak of (002) plane was 58.8 nm. Figure 3(b) shows the XRD pattern of GO which exhibited a strong peak with reflection at 2θ of 9.79° corresponding to a basal *d*-spacing d_{001} of 0.901 nm. The crystallite site of GO was 8.15 nm. This value is higher than interlayer spacing of prepared GO, due to the presence of oxygenated functional groups and intercalated water molecule. The addition of the oxygen-containing groups converted regions of the graphite to amorphous material, reducing the size of the crystalline regions.



(a) (b)

Figure 3 XRD diffractograms of (a) graphite powder (GP) and (b) prepared graphene oxide (GO)

FT IR analysis graphite powder and graphene oxide

The functional groups of GP and prepared GO were studied by Fourier Transform Infrared Spectrophotometer and the results are presented in Figure 4 and Table 1. From the FT IR data of GP, the band observed at 3703 cm^{-1} was attributed to O–H stretching group. The bands appeared at 2883 cm^{-1} and 1022 cm^{-1} were related to C–H stretching vibration and C–O–O stretching vibration, respectively. In FT IR spectrum of GO, the bands observed at 1716 cm^{-1} was due to C–O stretching group, that at 1626 cm^{-1} was due to the presence of C=O stretching group and the band at 1124 cm^{-1} was related to the C–OH stretching group present in prepared GO.

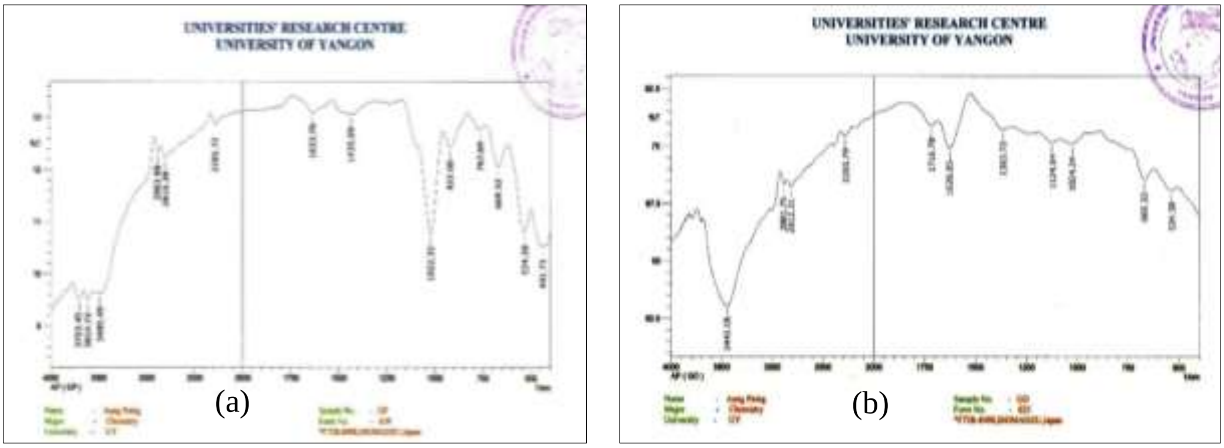


Figure 4 FT IR spectra of (a) graphite powder (GP) and (b) prepared graphene oxide (GO)

Table 1 FT IR Band Assignments for Graphite Powder (GP) and Prepared Graphene Oxide (GO)

Observed Wavenumber (cm^{-1})		**Literature* Wavenumber (cm^{-1})**	**Band Assignment**
GP	**GO**		
3703	3443	3700-3400	O – H stretching
2883	2881	2980-2850	C – H stretching
	1626	1665 - 1620	C = O stretching
	1363	1450 - 1350	C = C stretching
	1716	1870 - 1650	C – O stretching
	1124	1210 - 1120	C – OH stretching
1022	1024	1050 - 1000	C – O – O stretching
767		770 - 690	C – H bending
669	669	680 - 620	C - HO stretching

* Silverstein *et al*. (2003)

SEM analysis of graphite powder and graphene oxide

The SEM images show surface morphology of GP and prepared GO samples. It can be seen that the different surface morphology was observed. The GP particle showed plate like layer and the prepared GO particle showed both plate and nano-rod like surface morphology as shown in Figure 5.

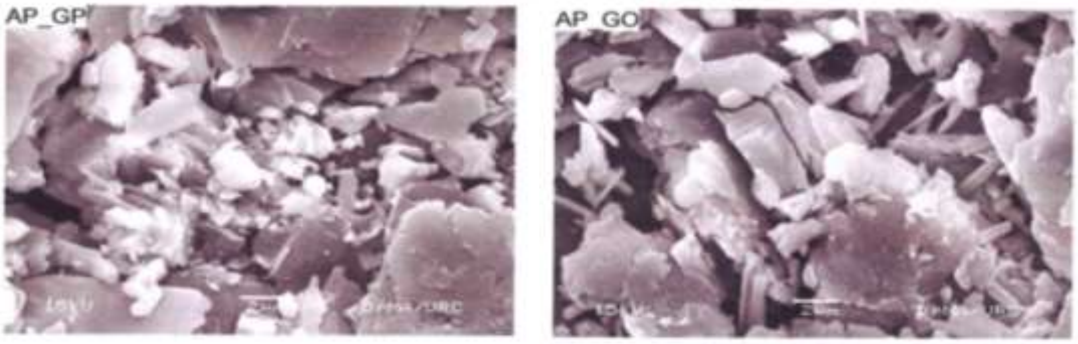


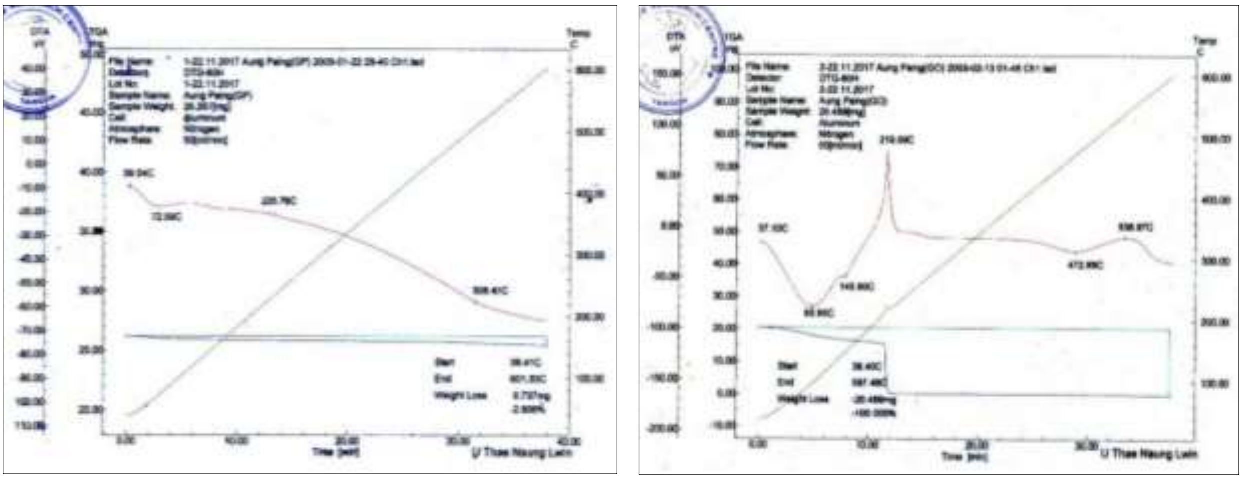
Figure 5 SEM images of (a) graphite powder (GP) and (b) prepared graphene oxide (GO)

TG-DTA analysis of graphite powder and graphene oxide

The TG-DTA thermogram of the GP is presented in Figure 5 (a). According to the TG-DTA thermogram profiles of GP, two steps of weight loss were observed. In the first step, the temperature range between 38 °C and 120 °C accompanied with 1.26 % weight loss was due to the removal of moisture and absorbed surface water. The weight loss approximately1.55 % was observed in the temperature range between 120 °C and 600 °C. In this state, the weight loss was due to the combustion of impurity compound.

The TG-DTA thermogram of the GO is presented in Figure 5 (b). Four steps or weight loss was occurred. In the first step, GO was decomposed (18.77 %) at 40 °C until 200 °C, showing the elimination of water molecule and unstable oxygen functional group.

In the second step, the decomposition was occurred at 200 °C until 430 °C (81.23 %). This decomposition was caused by elimination of more stable oxygen functional group as well as burning of ring carbon. Then, small endothermic and exothermic peaks occurred at 472 °C and 536 °C. The total weight loss was about 100.00%. The GP and prepared GO samples are thermally stable and decrease in weight loss when increasing temperature.



(a) (b)

Figure 6 TG-DTA thermograms of (a) graphite powder (GP) and (b) prepared graphene oxide (GO)

Physicomechanical Properties of Chitosan-Polyvinyl Alcohol-Graphene Oxide (CS-PVA-GO) Composite Membranes

The physicomechanical properties of CS-PVA-GO composite membranes are shown in Table 2 and Figure 7. The thicknesses of CS-PVA-GO composite membranes are approximately ~ 0.24 mm. The composite membranes were prepared from 1.5 wt. % of chitosan, 4 wt. % of polyvinyl alcohol and different weights of graphene oxide. In the concentration range of graphene oxide 0.2 g to 0.5 g, the tensile strength was found to increase to 17.3 MPa with graphene content up to 0.3 g for CS-PVA-GO2 composite membrane. Further increase in graphene oxide content to 0.4 g and 0.5 g, the temsile strength slightly decreased. The percent elongation at breaks slowly decreased with increase in graphene oxide content and the percent elongation value reached to 86 % when the graphene oxide content was 0.3 g. Thus, the maximum tensile strength and percent of elongation values are flexible in CS-PVA-GO2 composite membrane. Thus, CS-PVA-GO2 composite was selected for further investigation.

Table 2 Physicomechanical Properties of CS-PVA-GO Composite Membranes

CS-PVA-GO Composite Membranes (wt. %)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (kNm^{-1})
CS-PVA-GO1	13.8	104	64.7
CS-PVA-GO2	17.3	86	58.6
CS-PVA-GO3	16.7	66	39.7
CS-PVA-GO4	16.3	83	55.3

Membrane Thickness = ~ 0.24 mm

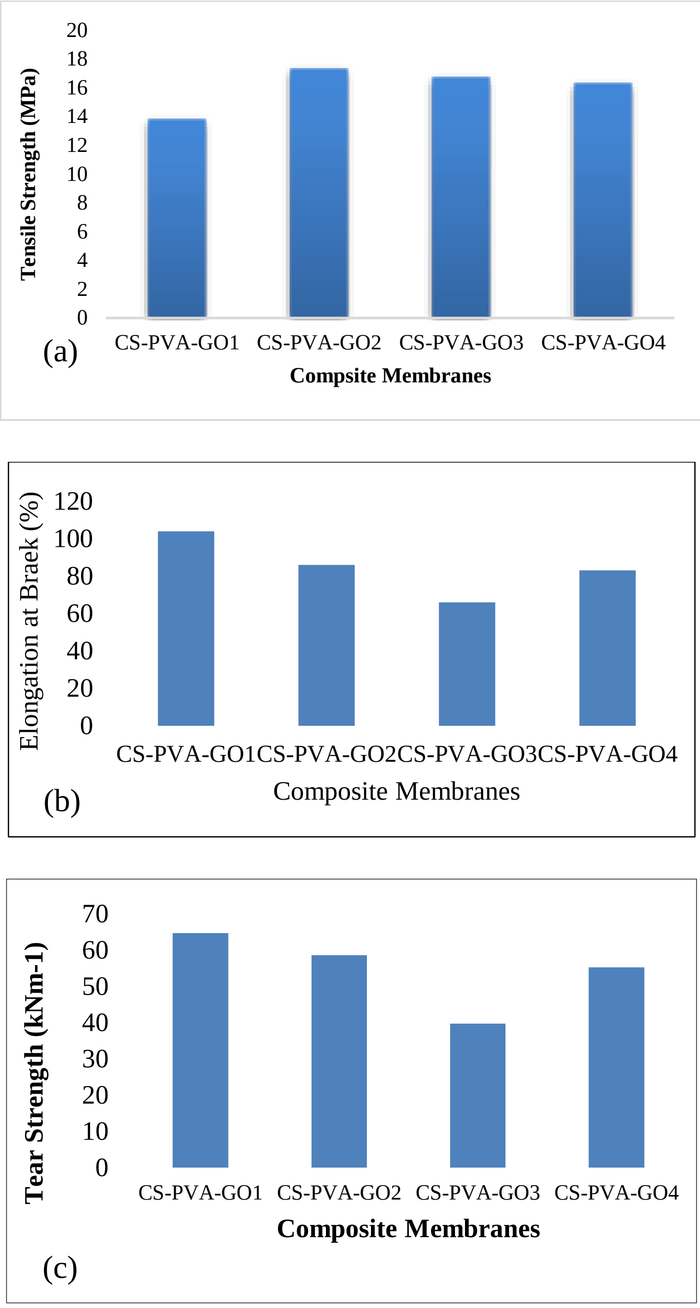


Figure 7 (a) Tensile strength (b) elongation at break and (c) tear strength of CS-PVA-GO composite membranes

Characterization of CS-PVA-GO2 Composite Membrane

FT IR analysis of CS-PVA-GO2 composite membrane

The chitosan and polyvinyl alcohol molecule are able to form hydrogen bonds. It is expected that some of the special interactions between different molecular groups influence the sample spectrum as shown in Figure 8 and Table 3. The band at 1075 cm^{-1} was related to C – O – C stretching groups. The peak at 1587 cm^{-1} was concerned with the symmetric deformation of – NH_2 resulting from ionization of primary amino groups in the acidic medium whereas the peak at 1419 cm^{-1} related to the C – N stretching vibration. The strong broad peak at 3461 cm^{-1} was caused by amine N – H symmetric vibration and – OH stretching vibration. When the addition of GO, the spectra did not show obvious changes.

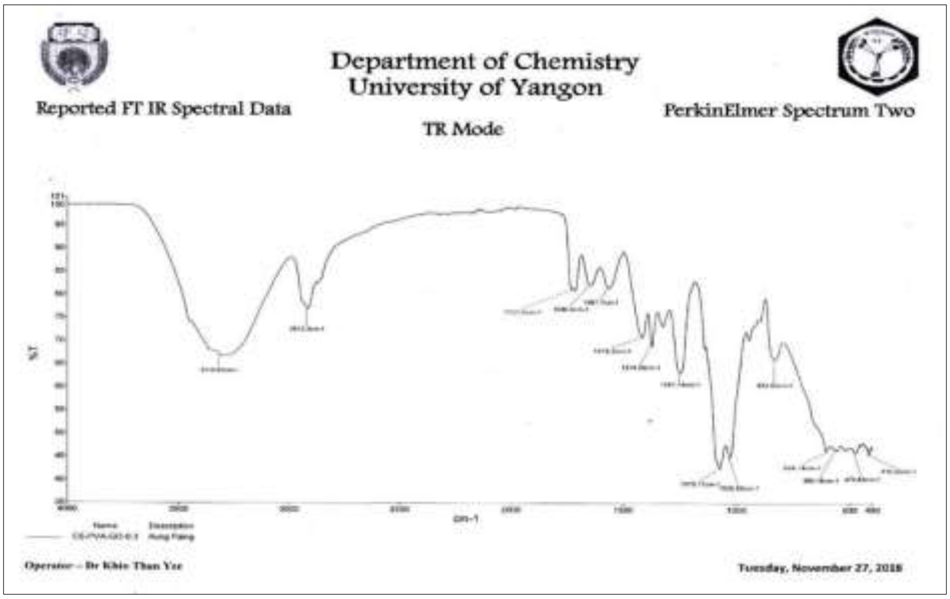


Figure 8 FT IR spectra of CS-PVA-GO2 composite membrane

Table 3 FT IR Band Assignment of CS-PVA-GO2 Composite Membrane

Observed Wavenumber (cm^{-1}) CS-PVA-GO2 Composite Membrane	*Literature Wavenumber (cm^{-1})	Band Assignment
3310	3400-3200	O – H stretching and N – H stretching
2913	2940-2915	C – H stretching of – CH_3 group
1731	1765-1725	C = O stretching
1646 1587	1650-1580	NH_2 deformation
1419	1420-1400	C – N stretching
1247	1285-1240	C – O Stretching
1075	1240-1070	C – O – C stretching

*Silverstein *et al*. (2003)

SEM analysis of CS-PVA-GO2 composite membrane

The scanning electron micrograph of CS-PVA-GO composite membrane is shown in Figure 9. From the SEM analysis, it was observed that the small loading of 0.3 wt. % of GO provides a homogenous surface where the GO sample were not distinguishable from the polymer membrane indicating that the dispersion step through stirring of GO in CS-PVA mixture ratio of (50:50 v/v) was sufficient upon membrane solution.

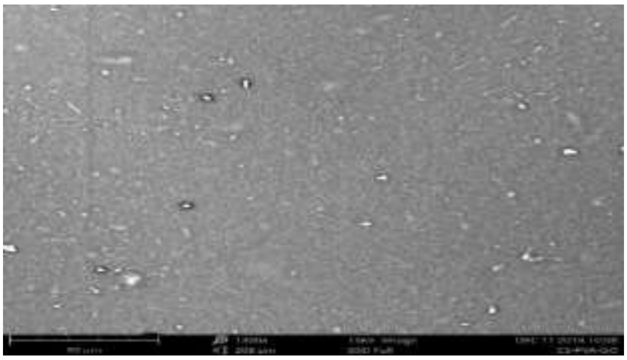


Figure 9 SEM micrograph of CS-PVA-GO2 composite membrane

TG-DTA analysis of CS-PVA-GO composite membrane

Thermal stability of prepared CS-PVA-GO2 composite membrane was investigated by TG-DTA analysis under nitrogen atmosphere and heating rate of 20 °C min^{-1} from 40 °C to 600 °C. The degradation peak value and weight loss of CS-PVA-GO2 composite membrane were presented in Figure 10. According to the TG-DTA thermogram of composite membrane, three steps of weight loss were observed. In the first step, the temperature range between 37 °C to 120 °C, the weight loss was 12.54 % which attributed to the release of the moisture preferentially absorbed by the polymer. The second weight loss started at 120 °C and 430 °C during which the polymer decomposition and elimination of the volatile products occurred. In the third step (from 430 °C to 600 °C) the weight loss about 25.73 % was actually observed due to the decomposition of the polymer matrix. According to the degradation results, the CS-PVA-GO2 composite membrane was found to retain its thermal stability.

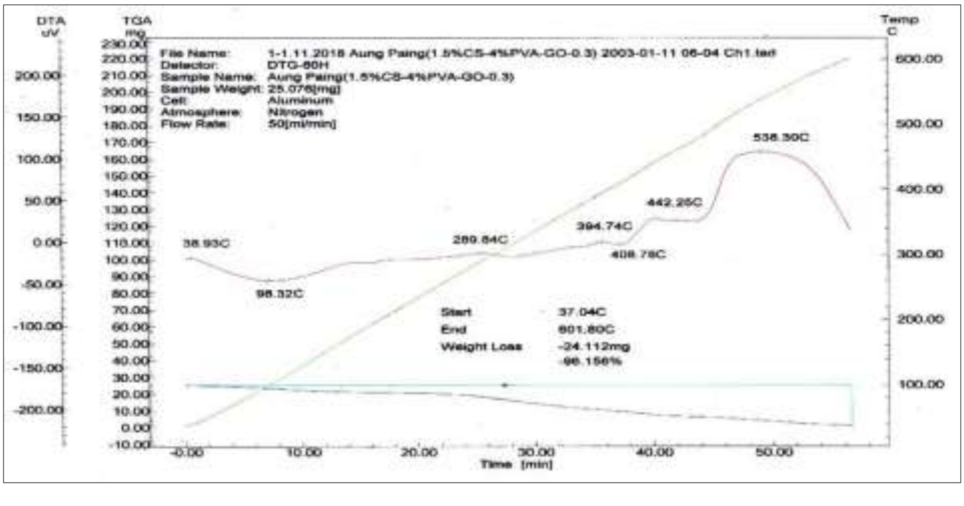


Figure 10 TG-DTA thermograms of CS-PVA-GO2 composite membrane

Conclusion

In this study, the graphene oxide was prepared by oxidizing graphite powder using modified Hummer's method. The XRD results demonstrated that the GP showed 2θ of 26.4° and the prepared GO showed 2θ of 9.79° with interlayer spacing equal to 0.901 nm. FT IR spectrum indicated that the graphite powder was oxidized and the oxygen atoms replaced into the graphite layers forming C=O, C–O and C–OH bonds in graphene oxide. SEM images showed that GP was found to be relatively the plate like layer and GO showed the mix plate and nano-rod like surface morphology. From the TG-DTA analysis, the total weight loss of GP was less than the prepared GO. The polymer composite membranes were prepared from chitosan, PVA and different weight percents of graphene oxide. According to the mechanical properties, CS-PVA-GO2 composite membrane was found to have optimum tensile strength and elongation at break. FT IR analysis showed that CS-PVA-GO2 composite membrane exists intermolecular interaction between CS, PVA and GO. From SEM analysis the surface morphology of CS-PVA-GO2 composite membrane exhibited homogenous nature and smooth surface texture. Thermal stability of CS-PVA-GO2 composite membrane was observed since the significant weight loss did not occur in the polymer matrix backbone.

Acknowledgement

The authors would like to express their profound gratitude to the Department of Higher Education, Ministry of Education, Yangon, Myanmar, for provision of opportunity to do this research and Myanmar Academy of Arts and Science for allowing to present this paper.

References

Acurio, E., Garcia-Cruz, L., Montiel, V. and Iniesta, J. (2017). "Preparation and Poly (Vinyl) Alcohol/Chitosan Hybrid Membranes Doped with Graphene Nanosheets". *J. Advance Mate. and Technol.*, vol. 1, pp. 9-19

Feketefoldi, B., Cermenek, B., Sprik, C., Schenk, A., Grimmer, C., Bodner, M., Koller, M., Ribitsch, V. and Hacker, V. (2016). "Chitosan-Based Anion Exchange Membranes for Direct Ethanol Fuel Cells". *J. Membra. Sci. Technol.,* vol 6 (1), pp. 1-9

Garcia-Cruz, L., Casado-Coterillo, C., Irabien, A. and Montiel, V. (2016). "High Performance of Alkaline Anion-Exchange Membrane Based on Chitosan/Poly (Vinyl) Alcohol Doped with Graphene Oxide for the Electrooxidation of Primary Alcohols". *J. Carbon Res.,* vol. 2 (10), pp. 1-19

Jiang, L., Shen, X. P., Wu, J. P. and Shenk, K. C. (2010). "Preparation and Characterization of Graphene/Poly (Vinyl Alcohol) Nanocomposites". *J. Appl. Polm. Sci.,* vol. 118, pp. 275-279

Lu, J. J., Feng, M. and Zhang, H. B. (2013). "Preparation and Adsorption of the Graphene Oxide/Chitosan Composite Films and Investigations on their Nanolinear Optical Limiting Effect". *Acta. Phys. Scn.,* vol. 62 (1), pp. 11-17

Shahriary, L. and Athawale, A. A. (2014), "Graphene Oxide Synthesized by Using Modified Hummers Approach". *International J. of Renewable Ener. and Envir. Eng.,* vol. 2 (1), pp. 58-63

Silverstein, R. M., Webster, F. X. and Kiemle, D. J. (2003). *Spectrometric Identification of Organic Compounds*. New York: 7th Edition, John Wiley and Sons, Inc. 216

Tagreed, M. A., and Mustafa, A. K. (2015). "Preparation and Characterization of Graphene/PMMA". *International J. of Adv Res. In Sci., Eng. and Tech.,* vol. 2 (10), pp. 902-909

Yang, J. Y. and Chiu, H.C. (2012). "Preparation and Characterization of Polyvinyl Alcohol/Chitosan Blend Membrane for Alkaline Direct Methanol Fuel Cells". *J. Membrane Sci.,* vol. 15, pp. 65-71

Ye, Y. S., Rick. J. and Hwang, B. J. (2012). "Water Soluble Polymers as Proton Exchange Membranes for Fuel Cells". *J. Polymers,* vol. *4* (2), pp. 913-963

Yuan, H., Meng, L. Y. and Park, S. J. (2016). "Synthesis and Application of Graphene/Chitosan Nanocomposites". *J. Carbon,* vol. 17 (1), pp. 11-17