

X-Ray Diffraction and Morphology Studies of Sulfonated Polystyrene and Maleated Natural Rubber Blend with PE-g-MA as Compatibilised

Ahmad Nasir Pulungan^{1,3}, Basuki Wirjosentono², Eddiyanto^{2,3} and Sunit Hendrana⁴

¹Chemistry Postgraduate Study Programs, Universitas Sumatera Utara, Medan 20155, Indonesia

²Department of Chemistry, Universitas Negeri Medan, Jl. Willem Iskandar Psr. V Medan Estate 20371, Indonesia

³Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

⁴Research Centre for Chemistry Indonesian Institute of Sciences, Kompleks Puspitek 452, Serpong, Banten 15314, Indonesia

Keywords: Sulfonated Polystyrene, Maleated Natural Rubber, Blend, X-Ray Diffraction, Morphology.

Abstract: The preparation of blend of sulfonated polystyrene (sPS) and maleated natural rubber (MNR) using the Polyethylene-graft-maleicanhydride (PE-g-MA) as compatibilised has been done. The blending process was done in dilute solution in each polymer, followed a steam and casting process at particular temperatures. The composition of sPS and MNR was varied at 1:9; 2:8; 4:6 and 6:4 (w/w). The characterization of membrane blend of sPS-MNR/PE-g-MA properties was determined by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The data showed that the homogeneity and the crystallinity of membrane were affected by the composition and process condition. The XRD data show that the Membrane (sPS-MNR / PE-g-MA) with sPS: MNR ratio 2:8 produces diffraction patterns with higher intensity and SEM images showed that membrane has a better homogeneous surface morphology than the others.

1 INTRODUCTION

The formation of polymer blends generally aims to produce new materials with superior properties compared to each of the forming polymer materials (Jhons and Rao, 2019). This method is widely developed because of the low cost of processing and short processing time to produce new polymeric materials. The nature of the polymer blend is determined mainly by the compatibility of the polymer of the composition of the mixture, the process parameters and the desired application (Favis, BD, & Chalifoux, JP (1988). Polystyrene (PS) is included in the thermoplastic group with an extensive application, due to unique properties such as transparent, high chemical stability, ease of colouring and low cost (Ebewe, 2000), but the PS also has limitations such as its fragile nature, low heat deflection temperature and weak UV resistance (Ozden, 2004). However, currently sulfonated polystyrene (sPS) has been widely developed and used as an electrolyte polymer membrane as an alternative to the replacement of Nafion membrane

(Hendrana et al., 2016; Mulijani et al., 2014; Lee et al., 2008), because it has a price conductivity approaches Nafion. Therefore, the sPS membranes require other polymeric materials to improve their mechanical properties (elasticity).

Natural polymeric materials such as natural rubber (NR) exhibit the best physical properties with comprehensive industrial applications (Jhons and Rao, 2008; Sanguansap et al., 2004). NR has superior physical properties such as firmness, tensile strength and high elasticity, abrasion and tear resistance as well as good stickiness and are easy to grind (Arroyo et al., 2007; Peng et al., 2007 and Derouet et al., 2009). Therefore, these attracts many researchers to produce various products for industrial processes (Wirjosentono et al., 2018).

In this study, the sPS will be blended with the NR, with the aim to improve the mechanical properties (elasticity) of the membrane. Compatibility is improved by modifying the NR to form a maleated natural rubber (MNR) by grafting maleic anhydride (MA) into the NR structure. Nakason et al., (2004) studied grafting of MA onto natural rubber. The use of maleic anhydride (MA) as

a coupling agent increases the adhesion and interface properties of polymer composites (Cao et al., 2012; Machado, 2000). Ismail et al., (2002), Wirjosentono et al., (2008) and Wirjosentono et al., (2018) reported an increase in adhesion of composite Bamboo fibre with natural rubber; polypropylene with cyclic natural rubber; and Oil palm empty fruit bunch with polypropylene.

Preparation of polymer blend from the sPS and MNR with PE-g-MA as compatibilities is expected to produce a stable and homogeneous membrane blend product. Thus, the membrane can be applied as a proton exchange membrane. Therefore, it is essential to investigate the properties of the polymer blend. In this paper, an initial characterization of the sPS-MNR / PE-g-MA blend by X-ray (XRD) diffraction and scanning electron microscope (SEM) will be carried out.

2 MATERIALS AND METHODS

2.1 Materials

Sulfonated polystyrene (sPS) were prepared (Hendrana, 2013). High-ammonia concentrate natural rubber (HANR) latex DRC 60% is from PT IKN Medan-Indonesia. MNR were prepared according to Pulungan et al. (2017). PE-g-MA is from Aldrich (~0.5 wt. %). Methanol and toluene are p.a., grade and all use from Merck.

2.2 Preparation of Membrane Blend of sPS-MNR/PE-g-MA First Section

The blending process of sPS, MNR and PE-g-MA polymer materials has been carried out in a very dilute solution system, followed by a steam and casting process at particular temperatures. Comparison of sPS and MNR varied each: 1:90; 2:8; 4:6 and 6:4 (w/w) with the concentration of PE-g-MA is 3% (w/w). In the initial stages the sPS were dissolved in toluene: methanol with a ratio of 9:1 at 45°C and slowly stirred with a magnetic stirrer. The MNR and the PE-g-MA were also dissolved in toluene solvent and slowly stirred with a magnetic stirrer at 45°C. The PE-g-MA solution was added to the MNR solution, stirred until homogeneous. Furthermore, the sPS solution was added slowly and followed by the stirring process with a magnetic stirrer at 45°C for 8 hours. The resulting blend solution was cast and dried in an oven gear at 45°C for 24 hours. The membrane obtained was dried in a drying oven at 60°C for 8 hours.

2.3 Characterization of Membrane Blend of sPS-MNR/PE-g-MA

The initial characterization of membrane blend includes XRD analysis and morphology with SEM as follows:

2.3.1 X-Ray Diffraction Studies

The XRD patterns of the membrane were recorded with an X-ray diffractometer Shimadzu 6100, using Cu K α radiation, with a scanning rate of 2° min⁻¹ in a range from 7° to 70° (2 θ). The operating voltage and current of the tube kept at 40 kV and 30 mA respectively.

2.3.2 Morphology Analysis

SEM analysis was performed to investigate the morphology and homogeneity of the membrane blend. The SEM images were obtained from SEM of JSM-6510 LA. The surface of the membrane was coating with gold before being measured under the microscope.

3 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Studies

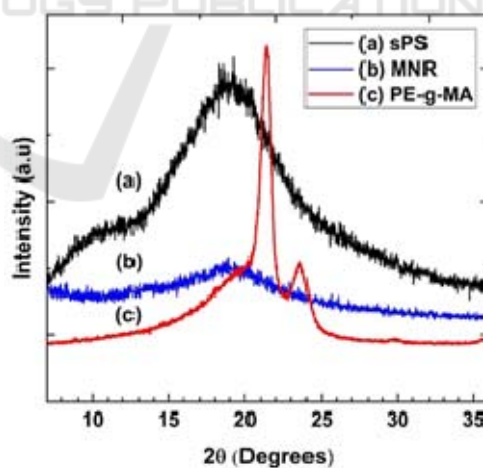


Figure 1: XRD diffractogram of (a) sPS, (b) MNR and (c) PE-G-MA.

The XRD diffractograms of sPS, MNR and PE-g-MA are depicted in Figure 1. The XRD diffractograms crystalline polymers produce sharp peaks, whereas amorphous polymers will produce widening peaks. Figure 1 (a) shows the crystalline

phase of PE-g-MA with a sharp peak intensity at 2θ around 21.5° . While the sPS diffractogram shows an amorphous phase with a peak widening at 2θ about 19.4° and the MNR shows a more amorphous phase than the sPS at 2θ around 19.4° . Martin et al. (2003) were reported that the sPS has amorphous properties because the pure PS polymer is initially amorphous. The sPS has a peak at 2θ around 19.8° and NR has a peak at 2θ around 19° (Jhon and Rao, 2008).

The XRD diffractogram in Figure 2 provides information about the structure of the polymer blend from the sPS-MNR/PE-g-MA. The figure shows the existence of a randomly mixed crystalline and amorphous state, which illustrates the combined characteristic peaks of MNR, sPS and PE-g-MA. The sPS-MNR/PE-g-MA membrane with the composition of sPS:MNR 2:8 produces the highest intensity of the main peaks. While the sPS-MNR/PE-g-MA membrane with the composition of sPS:MNR 4:6 and 6:4 shows a decrease in the intensity of the peak in the membrane. This shows that the ratio of the composition of the membrane blend gives an influence on the change in the crystallinity phase. With increasing content of sPS, the overall crystallinity of membrane blend decreases. In the polymer material, if the degree of crystallinity is getting smaller, the elasticity is getting bigger, this is caused by the branch chain that occurs, which causes the polymer material to be more elastic.

To investigate the effect of membrane composition, the interaction between the sPS and MNR on the membrane is observed based on the crystal size change approach. The X-ray diffraction scattering pattern can provide information about the configuration of the chain in crystallites, the estimated crystallite size and the comparison of the crystalline region with the amorphous region (degree of crystallinity) of the polymer material. Crystal size can be determined through the approach of the FWHM value (full width at half maximum) using the Debye-Scherrer equation (Kumar and Raji, 2011) as follows:

$$D = 0.9 \lambda / B \cos \theta \quad (1)$$

Where:

- D = Average Size Crystal
- λ = wavelength of XRD (0.15406 nm)
- θ = Braag Diffraction angle
- B = FWHM value in radian

The results of the calculation of the crystal size of each membrane are summarized in Table 1.

Table 1: The Average Size Crystal of membrane sPS-MNR/PE-g-MA.

	2θ ($^\circ$)	D (nm)
sPS:MNR (1:9)	19.49	1.49
	21.59	5.37
	23.97	4.82
sPS:MNR (2:8)	19.31	2.13
	21.49	6.97
	23.82	3.85
sPS:MNR (4:6)	19.37	1.54
	21.49	4.76
	23.82	5.12
sPS:MNR (6:4)	19.32	1.65
	21.63	5.46
	23.86	3.52

Based on the data in table 1, it can be seen that an increase in the sPS concentration to the sPS:MNR (2:8) increases the crystal grain size at 2θ around 19.4° but the crystal grain size gets smaller at the sPS:MNR ratio of 4:6 and 6:4. This is because in the sPS:MNR 2:8 the diffraction peak width is narrower so that the half peak width value (FWHM) is smaller, and the crystal grain size is increasing. However, at the sPS: MNR 4:6 and 6:4, the FWHM value is enlarge which shows that the width of the diffraction peak widened as well due to the increased concentration of sPS in the membrane. These data indicate that the effective interaction of the polymer blend is at the ratio of SPS: MNR 2:8 (w/w). The higher number of sPS actually disturbs the effectiveness of the interaction between sPS and MNR. This resulted in interactions that occurred between sPSS and NMR being dominated by sulfonate groups from sPS.

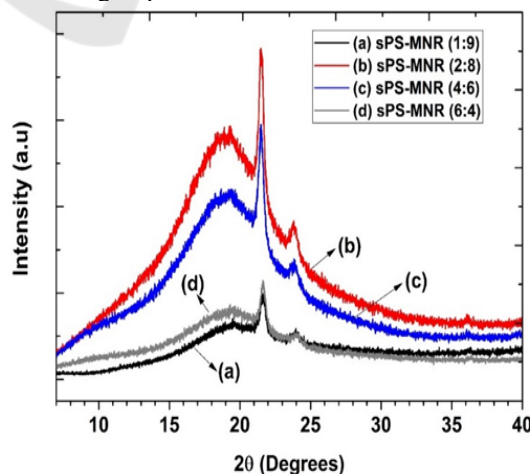


Figure 2: XRD diffractogram of sPS-MNR/PE-g-MA membrane with sPS: MNR composition: (a) 1: 9; (b) 2: 8; (c) 4: 6 and (d) 6: 4 (w/w) respectively.

3.2 Morphological Measurement using SEM

The surface morphology of each membrane is given in Figure 3.

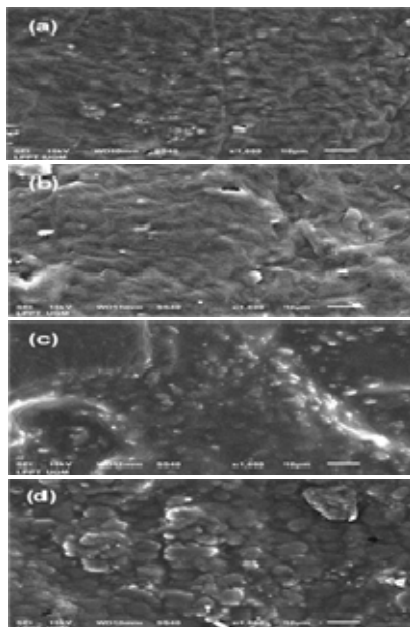


Figure 3: SEM images of sPS-MNR/PE-g-MA membrane with sPS: MNR composition ratio (a) 1: 9; (b) 2: 8; (c) 4: 6 and (d) 6: 4 (w/w).

In Figure 3, it can be seen that the sPS-MNR/PE-g-MA membrane with a sPS:MNR 2:8 composition ratio shows a more homogeneous surface compared to other membranes. In membranes with a composition ratio of sPS:MNR 2:8 produces a dense and homogeneous surface even though the presence of grainy components of the sPS is not completely dissolved with the MNR. This is due to the increase in adhesion between the sPS and MNR. While on membranes with a greater sPS composition ratio, i.e. on the sPS: MNR 4:6 and 6:4 membranes, it appears that the presence of grainy components from sPS forms larger sPS cluster groups as a result of the increasing number of sPS that are not completely dissolved with the MNR. From this data, information is obtained that the optimum blending composition is produced at the sPS:MNR ratio = 2:8 (w/w). This is due to the reduced adhesion force because the interactions that occur are dominated by sulfonate groups from sPS. Increased sPS concentrations do not provide better membrane compatibility. Concentration plays a role but not a high concentration of Sps.

4 CONCLUSIONS

Based on XRD data, membranes with the composition of sPS:MNR with ratio 2:8 produce the highest peak intensity diffractogram, as a result of the most effective interaction between sPS and MNR. This is also supported by SEM of the membrane surface with a more homogeneous surface morphology compared to that of the membrane surface with the composition of sPS: MNR 4:6; 6:4 and 1:9 respectively. The composition ratio plays a role to produce compatible sPS-MNR / PE-g-MA membrane.

ACKNOWLEDGEMENTS

The authors would like to thank University of Sumatera Utara and Universitas Negeri Medan for funding this work through research program of "Penelitian Disertasi Doktor tahun 2017", also to P2F LIPI, Chemistry Laboratory of The Department of Chemistry and Material Laboratory of The Department of physics, Universitas Negeri Medan for providing facilities of the work.

REFERENCES

- Arroyo, M., Lopez-Manchado, M. A., Valentin, J. L., and Carretero, J. 2007. Morphology/behaviour relationship of nanocomposites based on natural rubber/epoxidized natural rubber blends. *Composites science and technology*, 67(7), 1330-1339.
- Cao, X. V., Ismail, H., Rashid, A. A., Takeichi, T., and Vo-Huu, T. 2012. Maleated natural rubber as a coupling agent for recycled high density polyethylene/natural rubber/kenaf powder biocomposites. *Polymer-Plastics Technology and Engineering*, 51(9), 904-910.
- Derouet, D., Intharapat, P., Tran, Q. N., Gohier, F., and Nakason, C. 2009. Graft copolymers of natural rubber and poly (dimethyl (acryloyloxymethyl) phosphonate) (NR-g-PDMAMP) or poly (dimethyl (methacryloyloxyethyl) phosphonate) (NR-g-PDMMEP) from photopolymerization in latex medium. *European Polymer Journal*, 45(3), 820-836.
- Ebewele, R. O. 2000. *Polymer science and technology. CRC press.*
- Favis, B. D., and Chalifoux, J. P. 1988. Influence of composition on the morphology of polypropylene/polycarbonate blends. *Polymer*, 29(10), 1761-1767.
- Hendrana, S., Pudjiastuti, S., Chaldun, E. R., Widodo, H., Rochliadi, A., and Handono, M. A. 2016. Role of thickness and density on the ionic conductivity of fuel

- cell membrane prepared with supramolecular structure. In A. Rusydi, D. H. Wicaksono, T. Anggono, Y. Herbani, & F. Febriani (Eds.), *AIP Conference Proceedings*, 1711(1).
- Hendrana, S., Chaldun, E. R., Pudjiastuti, S., Rahayu, I., Natanael, C. L., Oktaverina, D., & Semboor, M. S. 2013. Heterogeneous Sulphonation of Polystyrene for Polymer Electrolyte Membrane Fuel Cell Application. *In Macromolecular Symposia*, 327(1), 80-84.
- Ismail, H., Edyham, M. R., and Wirjosentono, B. 2002. Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent. *Polymer testing*, 21(2), 139-144.
- Johns, J., and Rao, V. 2009. Thermal stability, morphology, and X-ray diffraction studies of dynamically vulcanized natural rubber/chitosan blends. *Journal of materials science*, 44(15), 4087-4094.
- Kumar, K. B., and Raji, P. 2011. Synthesis and characterization of nano zinc oxide by sol gel spin coating. *Recent research in science and technology*, 3(3).
- Lee, W., Kim, H., and Lee, H. 2008. Proton exchange membrane using partially sulfonated polystyrene-b-poly (dimethylsiloxane) for direct methanol fuel cell. *Journal of Membrane Science*, 320(1), 78-85.
- Machado, A.V., Van Duin, M. and Covas, J.A., 2000. Monitoring polyolefin modification along the axis of a twin-screw extruder. II. Maleic anhydride grafting. *Journal of Polymer Science part A: Polymer Chemistry*, 38(21), pp.3919-3932.
- Martins, C. R., Ruggeri, G., and De Paoli, M. A. 2003. Synthesis in pilot plant scale and physical properties of sulfonated polystyrene. *Journal of the Brazilian Chemical Society*, 14(5), 797-802.
- Mulijani, S., Dahlan, K., & Wulanawati, A. 2014. Sulfonated polystyrene copolymer: synthesis, characterization and its application of membrane for direct methanol fuel cell (DMFC). *Int J Mater, Mech Manuf*, 2, 36-40.
- Nakason, C., Kaesaman, A., and Supasanthitkul, P. (2004). The grafting of maleic anhydride onto natural rubber. *Polymer Testing*, 23(1), 35-41.
- Özden, G. Ü. L. S. Ü. M. 2004. Synthesis and Characterization of Polystyrene Clay Nanocomposites. *Chemical Engineering*.
- Peng, Z., Kong, L. X., Li, S. D., Chen, Y., and Huang, M. F. 2007. Self-assembled natural rubber/silica nanocomposites: its preparation and characterization. *Composites Science and Technology*, 67(15), 3130-3139.
- Pulungan, A. N., Wirjosentono, B., and Eddiyanto, S. H. Grafting Maleat Anhidrida Pada Lateks Karet Alam Dengan Inisiator Benzoil Peroksida. 2017. *Prosiding Seminar Hilirisasi Penelitian Untuk Kesejahteraan Masyarakat Lembaga Penelitian Universitas Negeri Medan*.
- Sanguansap, K., Suteewong, T., Saendee, P., Buranabunya, U., and Tangboriboonrat, P. 2005. Composite natural rubber based latex particles: a novel approach. *Polymer*, 46(4), 1373-1378.
- Suryanarayana, C., and Grant, N. 1998. A Practical Approach. *Plenum Press. New York*, 4, 513-515.
- Wirjosentono, B., Guritno, P., and Ismail, H. 2004. Oil palm empty fruit bunch filled polypropylene composites. *International Journal of Polymeric Materials*, 53(4), 295-306.
- Wirjosentono, B., Siregar, A. H., Nasution, T. I., Dalimunthe, K. Z., and Nasution, D. A. 2018. Compatibilization of cyclic natural rubber (resiprene-35) with polypropylene in the presence of oleic acid and benzoyl peroxide. *In Journal of Physics: Conference Series, IOP Publishing*, 1116(4).