

DEGRADATION CHARACTERISTICS OF VULCANIZED NATURAL RUBBER BY DIMETHYL ETHER THROUGH FILLER AND PLASTICIZER COMPOSITION VARIATIONS

Asep Handaya Saputra^{1*}, Johan¹, Tuti Indah Sari², Adi Cifriadi³, Dadi R. Maspanger³, Setijo Bismo¹

¹ *Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*

² *Department of Chemical Engineering, Faculty of Engineering, Sriwijaya University, Kampus Indralaya, Indralaya 30662, Indonesia*

³ *Indonesian Rubber Research Institute, Jl. Salak Bogor 16151, Indonesia*

(Received: November 2015 / Revised: March 2016 / Accepted: April 2016)

ABSTRACT

Dimethyl ether (DME) is a type of renewable energy that could replace the use of fossil fuel in Indonesia. Nevertheless, DME can cause degradation of rubber-based materials. Therefore, the performance of rubber that has been degraded by DME must be improved. This research study aims are to determine the degradation characteristics of modified vulcanized natural rubber in a DME environment. The effect of the filler (carbon black) and plasticizer (minarex-B) components of vulcanized natural rubber was examined. The vulcanized rubber samples were comprised of 10, 30, and 60 parts per hundred rubbers (phr) of filler and 0, 10 and 20 phr of plasticizer. The degradation of the mass and mechanical properties of the rubber were investigated. Degradation testing was conducted by immersing the samples inside a pressure vessel that was filled with the liquid phase of DME. The results indicate that the increasing of the filler composition reduces the impact of degradation, while the increasing of the plasticizer composition has the opposite effect. The plasticizer is needed to distribute the filler to all parts of the rubber. Consequently, a filler composition of 30 phr and a plasticizer composition of 10 phr provide a vulcanized natural rubber with optional protection against the degradation caused by DME. The characteristics of natural rubber, as measured by Fourier Transform Infra-Red Spectroscopy (FTIR) proved that DME does not damage the structure of the polymer chains, although DME may react with some ingredients in the rubber that have a similar polarity.

Keywords: Degradation; Dimethyl ether; Filler; Natural rubber; Plasticizer

1. INTRODUCTION

The fossil fuel reserves have been depleted in Indonesia. One type of alternative energy that is being developed is dimethyl ether (DME), which is being considered for the use as direct or mixed fuel in motor vehicles and also as a substitute for household liquefied petroleum gas (LPG) (PerMen-ESDM, 2013; Anggarani et al., 2014). As an alternative fuel, DME can be used to address energy security, energy conservation, and environmental concerns about the need for low carbon emissions (Thomas et al., Feng, 2014; Semelsberger et al., 2006). On the other hand, the value of the vapor pressure of DME is almost same with LPG, and DME can be handled as a liquid phase fuel when lightly pressurized (Park & Lee, 2014). The application of

*Corresponding author's email: sasep@che.ui.ac.id, Tel. +62-21-7863516, Fax. +62-21-7863515
Permalink/DOI: <http://dx.doi.org/10.14716/ijtech.v7i4.2587>

DME will be an important national energy security strategy due to the fact that Indonesia is rich in coal, natural gas and biomass, which can be used as raw materials to produce DME (Anggarani et al., 2014).

Rubber materials are often used in motor vehicles or gas canisters as a sealant to prevent fuel leakage (Chandrasekaran, 2009). However, rubber materials will be degraded in a DME environment. Rubber material degradation will decrease the performance of sealants, creating unsafe conditions (Wu et al., 2008; Haseeb et al., 2011). The state in which similar polarities exist between a solvent and a rubber material is known as “like dissolves like”. This mechanism governs rubber degradation. Furthermore, few studies have investigated rubber degradation caused by DME, so further research is needed.

Degradation of the mechanical properties of rubber after immersion in oil or solvent is caused by the permeation of the oil or solvent into the rubber. The permeation causes swelling or enlargement of the rubber’s volume and mass. Swelling occurs because the liquid’s molecules are diffused into the rubber (Wood-Adams, 2006) affecting the rubber’s solubility (Ebewele, 2000). In addition to the swelling, fluid permeation into the rubber can also cause shrinking or a decrease in volume and mass. This is caused by the fluids reacting to the components of the vulcanized rubber. Swelling or shrinking of volume and mass may cause a decrease in the rubber’s properties, including hardness, tensile strength, and tear strength.

During the natural rubber vulcanization process, the ingredients used to vulcanize rubber alter the mechanical properties of natural rubber. Filler is one of the ingredients used to vulcanize rubber that has an impact on the mechanical properties of natural rubber. Filler is reinforcement, which is used to strengthen the natural rubber that is vulcanized. Filler closes the space in the rubber’s macromolecules that is capable of reducing the diffusivity of liquids or gases that get into the network crosslink in the rubber (Mark et al., 2013). Plasticizer is one of the ingredients in vulcanized rubber that reinforces the rubber. Plasticizers are used in the rubber industry to meet two basic processing and compound requirements: to act as a processing additive or to act as a rubber extender and softener (Simpson, 2002).

This present study aimed to determine the characteristics of degradation caused by DME that occur in rubber materials, especially vulcanized natural rubber with different filler and plasticizer compositions. The degradation effect was observed by examining variations in the composition of the vulcanized natural rubber. In this experiment, mechanical characterizations, such as mass change, tensile strength, elongation at break, and hardness, were observed as well.

2. EXPERIMENT

2.1. Materials

Standard Indonesia Rubber type 10 (SIR10) was the raw material used in this study. All of the compound components consisted of natural rubber (SIR10), vulcanizer (sulfur), activator (stearic acid), activator (zinc oxide), accelerator (2-mercapto-benzothiazole/MBT), filler (carbon black N330), and plasticizer (minarex-B). All of the components were mixed in an open Berstorff roll mill with rotor speeds of 20 rpm and 28 rpm. After that, the rubber compound from each sample was vulcanized in a press molding machine at 150°C. The formulations of the vulcanized natural rubber are presented in Table 1.

2.2. Mechanical Property Measurements

Compression molded sheets from the press molding were used to measure tensile strength, elongation at break (fracture strain), and hardness. Each sample was cut into a dumbbell shape for the tensile test. The value of the tensile strength (MPa) and elongation at break (%) were measured using a LLOYD 2000R tensometer according to the ASTM D.412-06ae2 standard.

Hardness (Shore A) was measured using a durometer, according to the ASTM D.2240-05 standard.

Table 1 Formulation used in the preparation of the vulcanized natural rubber samples

Ingredients	Formulation (phr [*])
Natural rubber (SIR10)	100
Zinc oxide (ZnO)	5
Stearic acid	2
Carbon black	0 ; 30 ; 60
Minarex-B	0 ; 10 ; 20
2-mercaptobenzothiazole/MBT	1.8
Sulfur	2.4

* phr : part per hundred rubber

2.3. Mass Change Measurement

The vulcanized rubber samples were soaked in liquid phase DME in a pressurized vessel (volume: 1.3 L). The mass change of these samples was investigated after the samples had been soaked in DME for 7 days and then exposed to room temperature for 24 hours (Wu et al., 2008). The mass change is specified as a percentage (%), as shown in Equation 1 (Li & Zhou, 2008; Wu et al., 2008; Trakarnpruk & Porntangjitlikit, 2008; Abu-Abdeen & Elamer, 2010).

$$\text{The mass change (\%)} = \frac{m_f - m_i}{m_i} \times 100\% \quad (1)$$

where m_f (final mass) is the mass of the sample after it is soaked and m_i (initial mass) is the mass of the sample before it is soaked. The wet samples are the samples after they are soaked in DME and the dry samples are the samples after they are exposed to room temperature for 24 hours. The tensile strength, elongation at break, and hardness of the samples were tested after the change in the mass was measured.

2.4. Characterization of Spectrum and Morphology

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the spectrum of the vulcanized natural rubber. Toward that end, this study used a Nicolet iS5 FTIR spectrometer (Thermo Scientific) in the range of 500–4000 cm^{-1} . The samples were prepared using pyrolysis and the Soxhlet-extraction method. A scanning electron microscope (SEM) (model type ZEISS EVO 50) was used to observe the morphology of the vulcanized natural rubber before and after immersion in DME.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties and Mechanical Properties Changes

The mechanical properties are presented in Table 2. Figures 1–5 show the changes in the mechanical properties after the samples were soaked in liquid phase DME.

Table 2 Mechanical properties of the vulcanized natural rubber before immersion in liquid phase DME

Test	Plasticizer/Filler (phr)										
	0/0	0/10	0/30	0/60	10/10	10/30	10/60	20/10	20/30	20/60	
Tensile strength (MPa)	12.23	15.70	22.31	18.69	9.66	16.46	15.09	5.21	9.09	6.53	
Elongation at break (%)	750	680	670	460	680	670	510	660	500	480	
Hardness, Shore A	31	37	50	68	33	45	63	28	37	55	

Table 2 shows the tensile strength value of the samples with plasticizer and filler variations. The addition of plasticizer decreases the tensile strength. Moreover, the hardness increase with the addition of filler and decrease with the addition of plasticizer (Table 2). The addition of filler and plasticizer decreases the elongation at break.

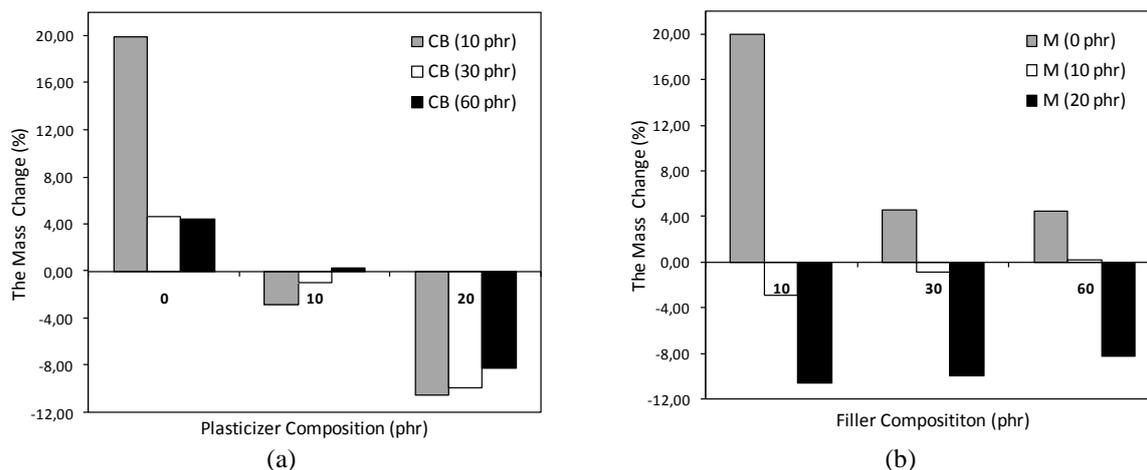


Figure 1 Mass changes for the wet samples (%)

Figure 1 shows the mass changes (%) after 7 days for the wet samples. The samples were measured using an analytical balance after they were taken directly from the vessel. Figure 1(a) shows that the value of the mass change was positive when the plasticizer loading was 0 phr. This result indicates that DME was absorbed into the rubber. However, when the plasticizer loading was increased to 10 phr, the value of the mass change was negative. The negative value of the mass change indicates that DME caused the rubber to shrink. This figure shows that increasing the plasticizer loading will cause an increase in the shrinking in the rubber. However, the absorption of DME in the rubber and the shrinking of rubber can be reduced in the presence of carbon black filler. When the carbon black filler loading increase, the absorption of DME and the shrinking of rubber decrease.

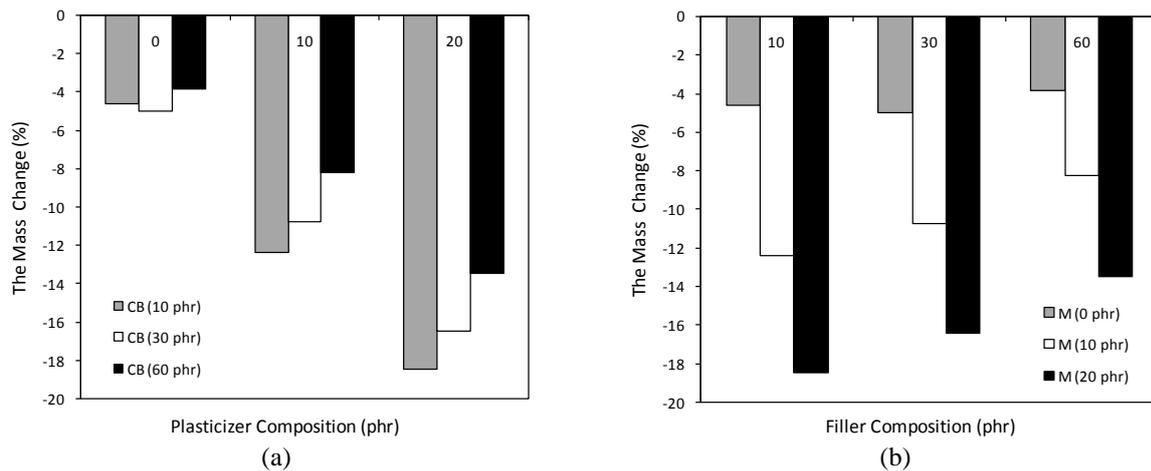


Figure 2 Mass changes for the dry samples (after 24 hours)

Figure 2 shows the mass changes (%) for the dry samples. The samples were measured using an analytical balance after the samples were aired for 24 hours at room temperature. As shown, the value of the mass change for all of the dry samples is negative. The results shown in Figure 2 (a) and (b) indicate that an increase of the plasticizer loading will increase the shrinking of the rubber. A similar outcome occurred for the wet samples (Figure 1).

The phenomenon, “like dissolves like”, caused DME to be absorbed into the network of the vulcanized natural rubber samples during immersion (Li & Zhou, 2008). The network in the samples was formed by cross-linking during the vulcanization process (Mark et al., 2013). This induces the increase in the percentage change in the mass of the vulcanized rubber. When liquid phase DME is absorbed in the network of rubber, a reaction occurs between the DME and some of the compounds in the vulcanized rubber. This causes a decrease in the mass.

Previous researchers, such as Mikhailova et al. (2009), investigated the increase of filler composition and found that it inhibited absorption and reaction in vulcanized rubber. Likewise, Muniandy et al. (2012) also found that carbon black filler loading resulted in a greater interaction between the rubber and the filler. The higher the extent of the interaction between the filler and the rubber matrix, the lower the swelling value (Muniandy et al., 2012; Ismail & Abdul Khalil, 2000).

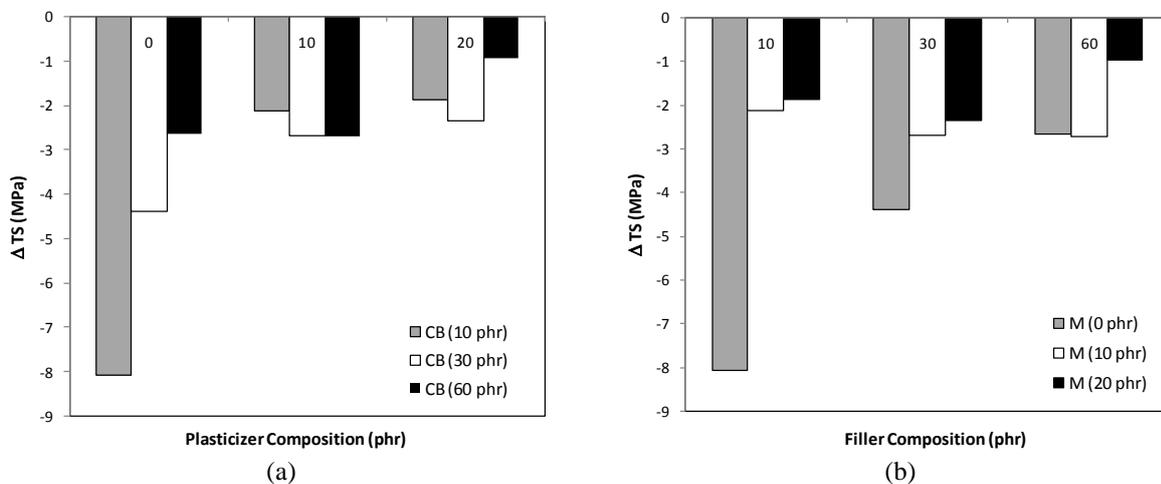


Figure 3 Tensile strength changes after the samples are soaked in DME

Figure 3 shows the tensile strength changes after the samples were soaked in DME. All of the samples have a negative value. This shows that the tensile strength of the sample decreases after

the rubber is soaked in DME. Figure 3 shows that plasticizer and filler loading will also result in the reduction of tensile strength.

The negative values of the tensile strength changes prove the existence of both degradations. According to Haseeb et al. (2011), the absorption of solvent in polymer followed by the extraction of ingredients out of rubber will weaken its polymer chain structures. Therefore, the tensile strength will decrease after the rubber is soaked.

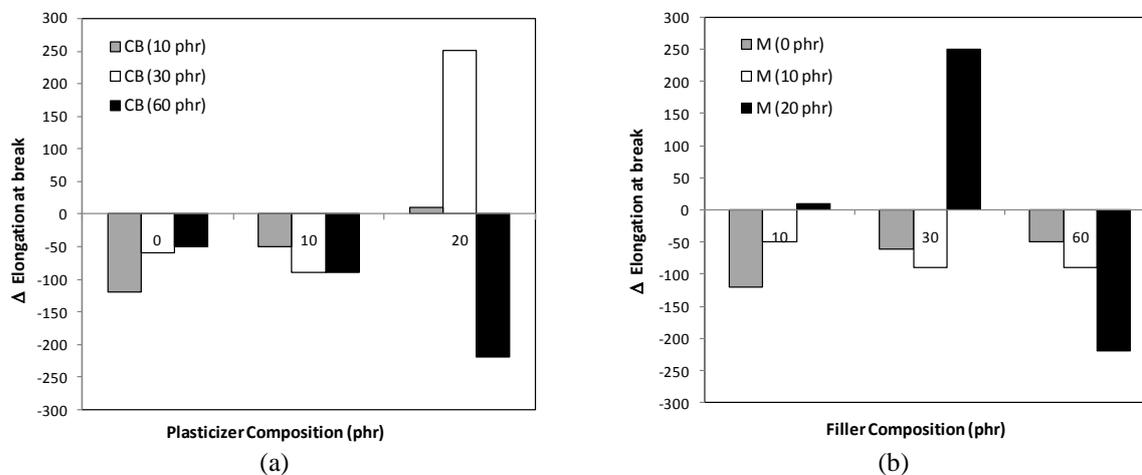


Figure 4 Changes in the elongation at break after the samples are soaked in DME

Figure 4 shows the changes in the elongation at break after the samples were soaked in liquid phase DME. This figure also shows that immersion in DME decrease the elongation at break. As seen in Figure 4(a), the elongation at break decrease with the addition of plasticizer. Based on Figure 4(a), Figure 4(b) indicates that the decrease of elongation at break also to decrease with the addition of filler.

Similar to the changes in tensile strength, the absorption of DME in rubber and the shrinking of rubber could weaken its structure. A weakness in the structure of rubber reduces its elasticity. The addition of filler decreases the elongation at break. Meanwhile, the addition of plasticizer decreases the magnitude of the elongation at break.

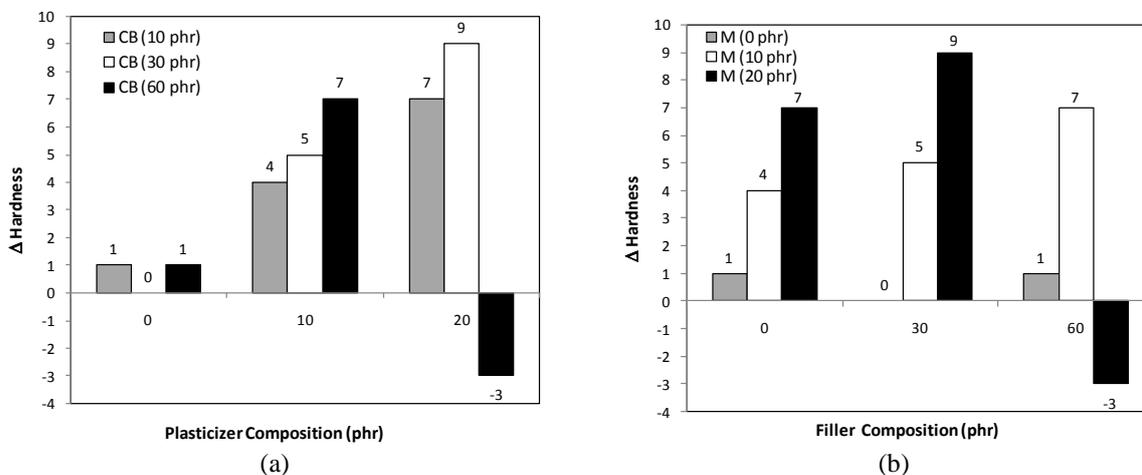


Figure 5 Changes in hardness: (a) variations in the plasticizer composition; (b) variations in the filler composition

Figure 5 shows that the hardness of the rubber changes after immersion in liquid phase DME. This result is different from the tensile strength and the elongation at break change results. The hardness value of the samples is greater after they are immersed in DME. Almost all of the samples have a positive hardness change value. When the plasticizer composition value stays the same, increasing the filler composition tends to increase the value of the hardness change. When the filler composition value stays the same, in general, the value of the hardness change increases. This outcome was also observed when the plasticizer composition was increased.

The hardness increase was caused by the presence of filler. During the immersion, plasticizer (minarex-B) maybe dissolved in DME due to the polarity interactions between these two components. However, filler (carbon black) may be inserted into the cavities in the rubber, thereby reducing the rubber's absorption capability. On the other hand, this condition will also improve the dominance of carbon black on the rubber's surface. Carbon black is used to improve the hardness of materials. Consequently, the hardness of almost all of the vulcanized natural rubber samples increased after immersion in liquid phase DME. Thus, the addition of filler increases the hardness change.

3.2. Spectrum of Vulcanized Natural Rubber

An analysis of the spectrum of vulcanized natural rubber that was not filled was performed using FTIR. As shown in Figure 6, there was no alteration in the polymer chain structure of the natural rubber after immersion in DME. This result indicates that DME did not react to the polymer chain, C-bond (C-C), double bond (C=C), or hydrogen bond (C-H) of the natural rubber.

This observation is different from the results shown in Figures 1–5. As demonstrated by the information presented in those figures, the degradation of the mechanical properties of vulcanized natural rubber was caused by DME. The results shown in Figure 6 prove that DME could not attack the polymer chain of natural rubber. This is consistent with the fact that natural rubber is non-polar and DME is a sufficient polar solvent. When natural rubber is immersed in DME, a reaction between DME and some of the ingredients in the vulcanized natural rubber can possibly occur.

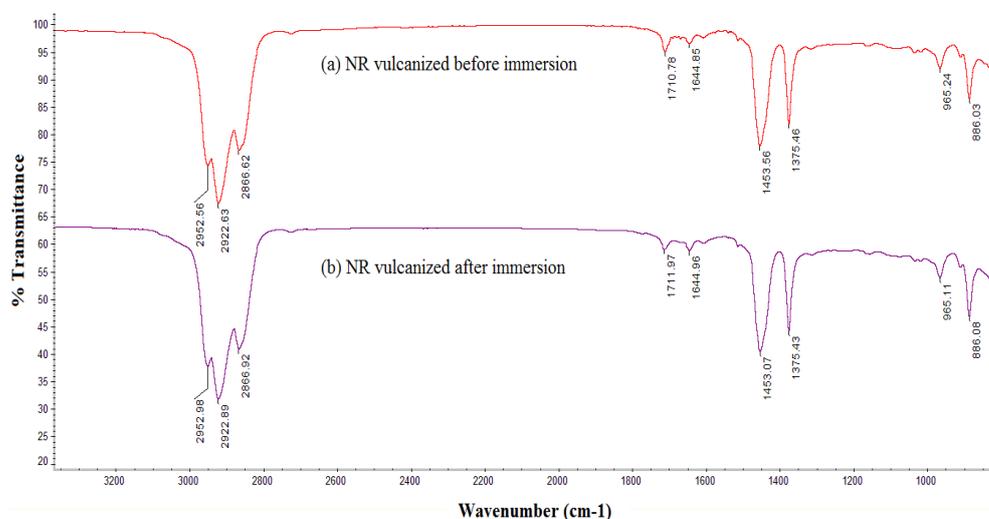


Figure 6 Spectrum of vulcanized natural rubber before and after immersion in DME

3.3. Surface Morphology

Figure 7 shows the Scanning Electron Micrograph (SEM) images of vulcanized natural rubber before and after immersion in DME. Figure 7a shows the SEM images of the vulcanized natural rubber without filler before immersion in DME. Figure 7b shows the vulcanized natural rubber

without filler after immersion in DME. Figure 7c shows the natural rubber with carbon black filler and plasticizer before immersion. Figure 7d shows the natural rubber with carbon black filler and plasticizer after immersion.

As seen in Figure 7d, the morphology shows that the addition of carbon black filler and plasticizer had a large shrinking effect on the structure of the vulcanized rubber. However, the structure of the vulcanized natural rubber without filler slightly shrunk. These results show that a significant level of interaction occurs between DME and the filler and plasticizer.

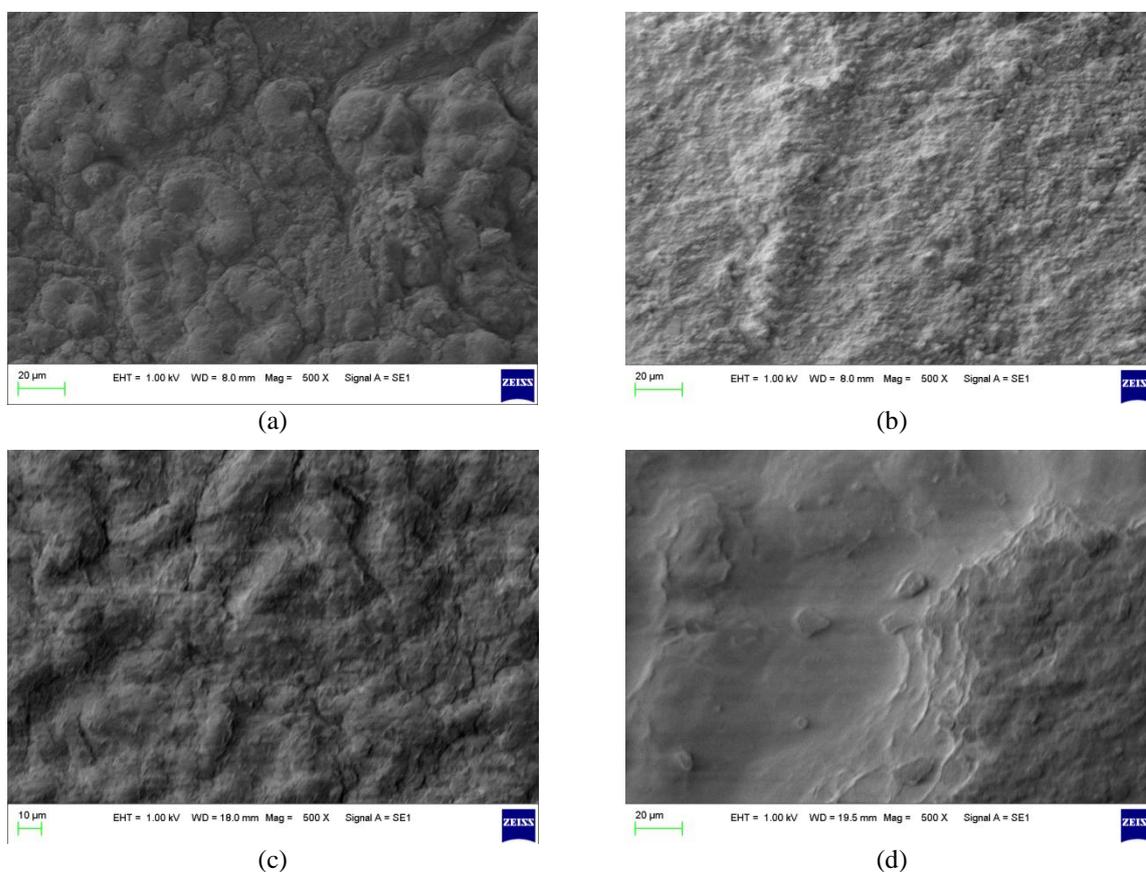


Figure 7 SEM images of the vulcanized natural rubber before and after immersion in DME

4. CONCLUSION

The following conclusions can be made for this study: (i) Absorption and reaction are the types of degradation that occur in vulcanized natural rubber in the presence of DME; (ii) The degradation of vulcanized natural rubber affects the mass change, the tensile strength, the elongation at break, as well as the hardness; (iii) The addition of filler composition decrease the degradation level, while the addition of plasticizer will make an severe degradation; (iv) The filler and plasticizer composition values that will best protect vulcanized natural rubber from degradation are 30 phr and 10 phr, respectively, and (v) The characteristics of natural rubber, as measured by FTIR, prove that DME does not damage the structure of its polymer chains. However, from the morphology, as observed by SEM, shows that the surface of the vulcanized natural rubber shrinks after immersion in DME.

5. ACKNOWLEDGEMENT

The author would like to express gratitude to The Indonesian Rubber Research Institute, Intensification of Process Laboratory of Chemical Engineering Department, Faculty of

Engineering Indonesia University, and to Kemenristekdikti RI for funding the study with a Competency Grant 2015.

6. REFERENCES

- Abu-Abdeen, M., Elamer, I., 2010. Mechanical and Swelling Properties of Thermoplastic Elastomer Blends. *Materials & Design*, Volume 31(2), pp. 808–815
- Anggarani, R., Wibowo, C.S., Rulianto, D., 2014. Application of Dimethyl Ether as LPG Substitution for Household Stove. *Energy Procedia*, Volume 47, pp. 227–234
- Chandrasekaran, C., 2009. *Rubber Seals for Fluid and Hydraulic Systems (1st Ed.)*. Elsevier Inc William Andrew
- Ebewele, R.O., 2000. *Polymer Science and Technology*. New York: CRC Press
- Haseeb, ASMA, Jun, T.S., Fazal, M.A., Masjuki, H.H., 2011. Degradation of Physical Properties of Different Elastomers upon Exposure to Palm Biodiesel. *Energy*, Volume 36(3), pp. 1814–1819
- Ismail, H., Abdul Khalil, H.P.S., 2000. The Effects of Partial Replacement of Oil Palm Wood Flour by Silica and Silane Coupling Agent on Properties of Natural Rubber Compounds. *Polymer Testing*, Volume 20(1), pp. 33–41
- Li, G.B., Zhou, L.B., 2008. Experimental Research on the Resistance of Rubber Materials to Dimethyl Ether. In: *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, Volume 222(6), pp. 975–978
- Mark, J.E., Erman, B., Roland, C.M., 2013. *The Science and Technology of Rubber Fourth Edition*. Boston: Academic Press
- Mikhailova, G.A., Baburina, V.A., Kalmykova, V.Ya, Deberdeev, R.Ya, Kutyrev, G.A., 2009. KR 08/02/16-Transl. serial no. 15983-Effect of Sorption-inactive Fillers on the Oil and Petrol Resistance of Siloxane Rubbers. *International Polymer Science and Technology*, Volume 36(4), p. T19
- Muniandy, K., Ismail, H., Othman, N., 2012. Effects of Partial Replacement of Rattan Powder by Commercial Fillers on the Properties of Natural Rubber Composites. *BioResources*, Volume 7(4), pp. 4640–4657
- Park, S.H., Lee, C.S., 2014. Applicability of Dimethyl Ether (DME) in a Compression Ignition Engine as an Alternative Fuel. *Energy Conversion and Management*, Volume 86, pp.848–863
- PerMen-ESDM, 2013. *Peraturan Menteri Energi dan Sumber Daya Mineral Republik Indonesia* Jakarta: Kementerian Energi dan Sumber Daya Meneral Available online at: [http://peraturan.bkpm.go.id/jdih/lampiran/PermenESDM 29 2013.pdf](http://peraturan.bkpm.go.id/jdih/lampiran/PermenESDM%2029%202013.pdf) (in Bahasa)
- Semelsberger, T.A., Borup, R.L., Greene, H. L., 2006. Dimethyl Ether (DME) as an Alternative Fuel. *Journal of Power Sources*, Volume 156(2), pp. 497–511
- Simpson, R.B., 2002. *Rubber Basics (1st Ed.)*. United Kingdom: Rapra Technology Limited
- Thomas, G., Feng, B., Veeraragavan, A., Cleary, M.J., Drinnan, N., 2014. Emissions from DME Combustion in Diesel Engines and their Implications on Meeting Future Emission Norms: A Review. *Fuel Processing Technology*, Volume 119, pp. 286–304
- Trakarnpruk, W., Porntangjitlikit, S., 2008. Palm Oil Biodiesel Synthesized with Potassium Loaded Calcined Hydrotalcite and Effect of Biodiesel Blend on Elastomer Properties. *Renewable Energy*, Volume 33(7), pp. 1558–1563
- Wood-Adams, P., 2006. Diffusion and Permeability in Polymers. Available online at: <http://users.encs.concordia.ca/~woodadam/GCH6101/Diffusion%20and%20permeability%20in%20polymers.pdf>
- Wu, N., Zhang, W., Huang, Z., 2008. Impact of Dimethyl Ether on Engine Seal Materials. *Frontiers of Energy and Power Engineering in China*, Volume 2(3), pp. 279–284