

Dear **Dr. Tuti Indah Sari**

We have finished the review and made decision on your manuscript entitled [**DEPROTEINIZED NATURAL RUBBER GRAFTED WITH POLYACRYLONITRILE(PAN)/POLYSTYRENE(PS) AND ITS MECHANICAL PROPERTIES DEGRADATION BY DIMETHYL ETHER**] which was submitted to International Journal of Technology.

We have decided that your manuscript **Need to be Revised**

We also send you the review result from the reviewers. Here is the detail review result:

Notes from Editor:

Please revise according to reviewer's comment

Reviewer (1)

Introduction:

Appropriate

Methodology:

Requires improvement: grafting polymerization and emulsion polymerization? need explain. if there is no surfactant (SDS), it is called grafted polymerization. If there is surfactant (SDS) in the reaction, it called emulsion polymerization.

Methodology :

Have been revised.

Ada kekeliruan sedikit. Penulis menegaskan bahwa ini adalah proses polimerisasi emulsi dengan menggunakan SDS

Results and Discussion:

Figures: Labeling not clear English: Ambiguous (need improving)

Figure has been revised

In the Figure 3.. labeling elongation at break at 0/0 direvisi menjadi DPNR.

Mengenai data-data angka tidak ada perubahan karena benar-benar data real penelitian.

In the Figure 4...labeling di swelling → rasio menjadi ratio

In the Figure 5...labeling di shrinking → tambah ratio DPNR/M

In the Figure 6..benzene ring diubah gugus benzene—group of functional

Seragamkan the ratio or ratio ?

References:

clear

Other:

Abstract section: Requires modification and explain How authors synthesized grafted copolymer including initiator, solvent and temperature?

Abstract has been revised

Originality 3 (average)

Technical 3 (average)

Methodology 3 (average)

Readability 3 (average)

Practicability 3 (average)

Organization 3 (average)

Importance 3 (average)

Additional Comment:

Attachment File:

-

Reviewer (2)

Introduction:

good

Methodology:

good

Results and Discussion:

good. Have been revised accordingly

References:

good. Have been revised accordingly

Other:

Originality 4 (*above average*)

Technical 4 (*above average*)

Methodology 4 (*above average*)

Readability 3 (*average*)

Practicability 4 (*above average*)

Organization 4 (*above average*)

Importance 4 (*above average*)

Additional Comment:

Attachment File:

-

Please login into application <http://ijtech.eng.ui.ac.id/login> for more detail.

You must respond to this revise and resubmit request before **28 Sep 2019**, after which point we will presume that you have withdrawn your submission from International Journal of Technology (IJTech) Online System.

Yours sincerely,

Dr. Nyoman Suwartha
nsuwartha@eng.ui.ac.id

Managing Editor

International Journal of Technology (IJTech)

p-ISSN : 2086-9614

e-ISSN 2087-2100

<http://ijtech.eng.ui.ac.id/>

Ms ID #**R1-CE-1942**

Title : DEPROTEINIZED NATURAL RUBBER GRAFTED WITH
POLYACRYLONITRILE(PAN)/POLYSTIRENE(PS) AND ITS MECHANICAL PROPERTIES DEGRADATION BY
DIMETHYL ETHER

Author(s) : Tuti Indah Sari, Asep Handaya Saputra, Dadi R. Maspanger, Setijo Bismo

Dear Dr. Tuti Indah Sari:

This is a polite reminder that we recently requested a revision of your manuscript, which is now due on **[04 Oct 2019]**. If we do not receive your revision within that time, we will assume that you are not sending a revision and this constitutes your manuscript being inactivated.

If you need additional time to complete your revision, please informing us of the date you expect to submit it via email to ijtech@eng.ui.ac.id.

The additional time for Ms ID #R1-CE-1942

21 Mei jam 10.19

indah sari <ty_indahsari@yahoo.co.id>

Kepada: ijtech@eng.ui.ac.id <ijtech@eng.ui.ac.id>

Dear Dr. Nyoman Suwartha,

Managing Editor International Journal of Technology (IJTech),

I'd like to have your additional time to complete my revision of manuscript ID #R1-CE-1942 entitled [The Effect of Acrylonitrile and Styrene Composition on Reducing The Physical Properties Degradation of Natural Rubber by Dimethyl Ether] until 28 Mei 2019.

Thank you for taking the time to consider my request.

Best regards,

Dr. Tuti Indah Sari

Dear Dr. Nyoman Suwartha,

Managing Editor International Journal of Technology (IJTech),

I'd like to have your additional time to complete my revision of manuscript below until 10 October 2019.

Ms ID #**R1-CE-1942**

Title : DEPROTEINIZED NATURAL RUBBER GRAFTED WITH
POLYACRYLONITRILE(PAN)/POLYSTIRENE(PS) AND ITS MECHANICAL
PROPERTIES DEGRADATION BY DIMETHYL ETHER

Thank you for taking the time to consider my request.

Best regards,

Dr. Tuti Indah Sari

List of Changes

Manuscript: ID #R1-CE-1942

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Author(s) : Tuti Indah Sari, Asep Handaya Saputra, Dadi R. Maspanger, Setijo Bismo

Response and Revision made by Author(s)

Reviewer #1:

No	Comments	Revision/Changes
1	Introduction: Appropriate	-
2	Methodology: Requires improvement: grafting polymerization and emulsion polymerization? need explain. if there is no surfactant (SDS), it is called grafted polymerization. If there is surfactant (SDS) in the reaction, it called emulsion polymerization.	Have been revised in the methodology (highlight text) There is a mistake of the author. The author confirms that this is the process of emulsion polymerization using SDS
3	Results and Discussion: Figures: Labeling not clear English: Ambiguous (need improving)	The figures have been revised (highlight text) 1. Labeling in the Figure 1 have been revised 2. Labeling in the Figure 2 have been revised: ratio DPNR/M → the ratio of DPNR/M 3. Labeling in the Figure 3 have been revised: 0/0 → DPNR. ratio DPNR/M → the ratio of DPNR/M ratio AN/ST, %-w → the ratio of AN/ST, w/w 4. Labeling in the Figure 4 have been revised: The word “rstio” → ratio ratio DPNR/M → the ratio of DPNR/M The ratio of AN/ST, %-w → The ratio of AN/ST, w/w 5. Labeling in the Figure 5 have been revised: ratio DPNR/M → the ratio of DPNR/M dry measure → dry measurement

		<p>6. Labeling in the Figure 6 has been revised: Benzene ring → benzene group</p> <p>7. Labeling in the Figure 7 have been revised: ratio DPNR/M → the ratio of DPNR/M ratio AN/ST, %-w → the ratio of AN/ST, w/w the change → the deviation</p> <p>About the data in the figures, there is no change because they are actual research data.</p>
4	References: clear	-
5	Other: Abstract section: Requires modification and explain How authors synthesized grafted copolymer including initiator, solvent and temperature?	Abstract has been revised (highlight text)

DEPROTEINIZED NATURAL RUBBER GRAFTED WITH POLYACRYLONITRILE(PAN)/POLYSTYRENE(PS) AND ITS MECHANICAL PROPERTIES DEGRADATION BY DIMETHYL ETHER

ABSTRACT

Dimethyl ether (DME) is a clean fuel that has moderate polarity, swells easily, and dissolves organic compounds. It has the ability to attack some sealing materials and plastic components because of its low viscosity. The modification of deproteinized Natural Rubber with acrylonitrile and styrene monomers by emulsion copolymerization process to obtain DPNR-g-PAN/PS copolymers. The process uses a stirred reactor with conditions $T = 65^{\circ}\text{C}$, $P = 1 \text{ atm}$, initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and an emulsifier sodium dodecyl sulfate (SDS). The copolymer DPNR-g-PAN/PS can be used to seal storage for DME. It is expected to reduce the degradation of rubber due to the presence of the fuel. The parameters that were used in testing for the resistance include swelling, shrinking, Fourier Transform Infra-Red spectroscopy (FTIR) spectrum and the changes in the mechanical property after immersion. The results of this research revealed that the presence of acrylonitrile and styrene can increase the mechanical properties of DPNR. It also showed that an increase in the concentration of acrylonitrile decreased the swelling and increased the shrinking of rubber. However, the increase in the concentration of styrene was found to increase the swelling and decrease the shrinking of rubber. There was more degradation of the spectrum DPNR than the DPNR-g-PAN/PS after immersion. The surface morphology test which was carried out using a Scanning Electron Microscope (SEM) showed that DPNR-g-PAN/PS experienced a slight shrinking effect in its morphology while DPNR underwent a huge shrinking effect.

Keywords: acrylonitrile, deproteinized natural rubber; dimethyl ether, styrene

1. INTRODUCTION

Dimethyl ether (DME) is an alternative fuel with its own advantages such as higher oxygen content, higher cetane number than diesel oil, and low boiling point. It is also non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic (Semelsberger, et al., 2006; Arcoumanis, et al., 2008; Li & Zhou, 2008). However, its chemical properties are different from that of LPG which has moderate polarity and high gas permeability to organic compounds such as plastics and rubber, DME swells easily, and dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing materials and plastic components because of its low viscosity (Arcoumanis, et al., 2008). Previous studies made use of the immersion method through the use of swelling and mechanical properties as parameters to test for resistance in DME. According to research conducted by Li and Zhou (2008), immersion of rubber in a mixture of DME/diesel at 20/80-wt% was reported to produce a corroded rubber seal.

Furthermore, natural rubber grafted acrylonitrile and styrene has the potential to be used as a seal for the storage of DME. It has excellent properties such as good elasticity, high tensile strength, and best adhesion to metal. Polyacrylonitrile (PAN) is a non-solvent material with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (Mark, 2009). The presence of PAN in the mixture also increases its insolubility and resistance to organic solvents (Nataraj, et al., 2012). Styrene has also been observed to be a good co-monomer in the stability of the graft-copolymerization process (Angnanon et al., 2011; Prasassarakich, et al., 2001; Sari et al., 2015). According to studies conducted by Prasassarakich et al., the oil and solvent resistance of NR can be improved by graft copolymerization using acrylonitrile (Prasassarakich, et al., 2001). An increase in tensile strength and oil resistant was observed with an increase in the percentage of grafting efficiency of acrylonitrile monomer (Prukkaewkanjana, et al., 2014). The same thing was also reported by Angnanon et al. (2011).

The objective of this research was to obtain a copolymer DPNR-g-PAN/PS with high resistance to DME gas. This is important because resistance is the potency needed by natural rubber to survive the diffusion or corrosion caused by the DME. The copolymer is expected to reduce the degradation of rubber because of the action of the fuel according to simple research conducted by Sari et al. (2017). The characteristics of the copolymer were determined by Fourier Transform Infrared Spectroscopy (FTIR). The mechanical properties measured include tensile strength, elongation at break, and hardness while the resistance test parameters were swelling, shrinking and changes in mechanical properties after immersion. Surface morphology test was also performed through the use of a Scanning Electron Microscope (SEM) analysis.

2. METHODS

2.1. Materials

The materials used include a natural rubber latex with a high level of stabilized ammonia containing about 59–60% of Dry Rubber Content (DRC) from South Sumatera, Indonesia. Acrylonitrile (AN \geq 99%) and styrene monomer (ST \geq 99%) were purchased from Sigma–Aldrich (SGP). The emulsifier sodium dodecyl sulfate (SDS~90%), urea, potassium persulfate ($K_2S_2O_8 \geq$ 99%), N,N-dimethylformamide (DMF) and methyl ethyl ketone (MEK) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was purchased from PT. Trijaya Gasesindo (INA). Zinc oxide (ZnO), stearic acid, 2-mercaptobenzothiazole/MBT, and sulfur were used in the production of vulcanized rubber. Dimethyl ether was purchased from PT. Bumi Tangerang, Banten (INA) while DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate et al., 2008; Suksawad et al., 2011).

2.2. Preparation of copolymer DPNR-g-PAN/PS

This was conducted in a 1.3 L reactor glass equipped with hot plate, magnetic stirrer, and nitrogen gas inlet. The DPNR, SDS (0.67 w/w % of rubber), and distilled water were first charged into a reactor glass with the use of $K_2S_2O_8$ an initiator having 1 wt% of total monomer (Sahoo, 2019), and the reaction was conducted for 6 hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer and it was synthesized using emulsion polymerization methods with a ratio of DPNR to Monomer (M) at (65/35); (70/30); (75/25) w/w, and 95/5; 92/8; 90/10; 80/20 w/w for AN/ST. For the purpose of calculating the percentage Grafting Efficiency (GE) as shown in equation (1), the free DPNR, PAN, and PS-free homopolymer were removed using Soxhlet extraction with petroleum ether, N,N-dimethylformamide, and methyl ethyl ketone respectively. GE is a parameter that is influenced by reaction variables such as DPNR/M ratio and AN/ST ratio.

$$\%GE = \frac{\text{weight of copolymer DPNR-g-PAN/PS}}{\text{weight of dry coagulan}} \times 100 \quad (1)$$

2.3. Characterization

Tensile strength (MPa) and elongation at break (%) were measured using TENSOMETER LLOYD 2000R according to ASTM D.412-06ae2 standard. Hardness (Shore A) was measured using durometer and adequate steps were taken to ensure that it complied with ASTM D.2240-05 standard. The Fourier Transform Infrared spectroscopy (FTIR) spectra of the DPNR and DPNR-g-PAN/PS were recorded in solid state using a Nicolet iS5 spectrometer (Thermo Scientific) between 500 and 4000 cm^{-1} . The preparation of the samples was done using pyrolysis and Soxhlet-extraction method and scanning electron microscope (SEM) model type ZEISS EVO 50 was used to analyze the surface morphology of DPNR and DPNR-g-PAN/PS before and after the immersion.

2.4. Swelling and Shrinking Test

The rubber to be vulcanized were immersed in DME liquid phase in a 1.3L pressure vessel. The change in the mass of these samples was investigated after the samples had been immersed for several days and exposed to the atmosphere for 24 hours (Wu et al., 2008). The swelling was measured in percentage (%) as shown in equation (2) (Li & Zhou, 2008; Hinchiranan et al., 2013).

$$\text{Swelling/Shrinking}(\%) = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sample before immersion while M_2 is the mass after. The samples are referred to as wet samples after they have been immersed and called dry samples after being exposed to the atmosphere for 24 hours.

3. RESULTS AND DISCUSSION

3.1. Grafting Characteristics

Grafting characteristics of copolymer showed the formation of DPNR-g-PAN/PS to consist of FTIR spectrum, Grafting Efficiency (GE), and mechanical properties. Figure 1(a) shows a comparison between the FTIR spectrum of DPNR (2) and the grafted copolymers (1) such that $C\equiv N$ group as shown at wave number 2,242.75 cm^{-1} , indicated PAN grafted on natural rubber chain while the presence of benzene groups as shown at wave number 705.16 cm^{-1} indicated PS grafted on natural rubber. The spectrum in Figure 1(a) based on previous research by Sari et al. (2017). The nitrile group ($C\equiv N$) could be indicated at wave numbers 2,240 – 2,260 cm^{-1} , (Smith, 1979) and at wave

number $2,242\text{ cm}^{-1}$ (Nacimient et al., 2012). In the previous work, (Luo, et.al 2012) reported in a functional group the benzene ring at the wave number $\sim 700\text{ cm}^{-1}$ and $\sim 760\text{ cm}^{-1}$, respectively. Figure 1(b) shows FTIR spectrum DPNR-g-PAN/PS is based on variations in the composition of AN/ST.

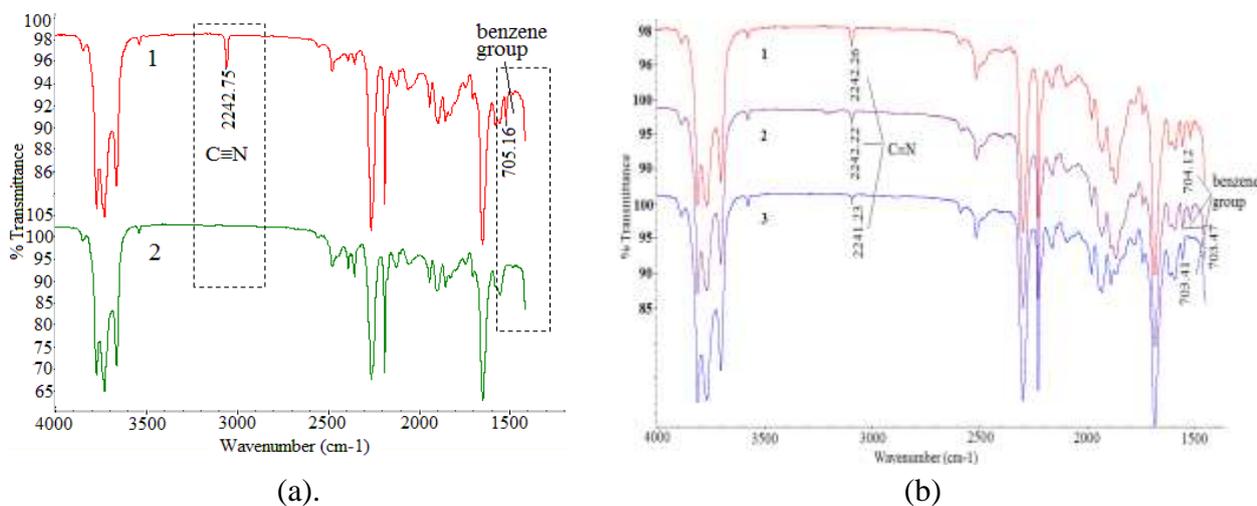


Figure 1 (a). Spectrum FTIR: 1.DPNR; 2.and DPNR-g-PAN/PS (b). Spectrum FTIR DPNR-g-PAN/PS with variation composition of AN/ST; 1. AN/ST 95/5; 2. AN/ST 90/10; AN/ST 80/20

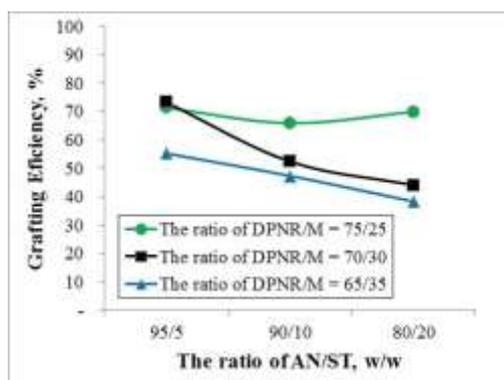


Figure 2 Grafting Efficiency (GE) with the ratio of DPNR/M and AN/ST

Figure 2 shows the effect of DPNR/M ratio on GE and it can be discovered from the graph that the decreasing ratio of DPNR/M and AN/ST decrease the percentage of GE. This indicates immiscibility between AN and ST molecule. It is, therefore, possible that the grafting copolymerization occurs only on the surface of the latex particles. It was also found that the continuous addition of both of total monomers AN and ST does not increase the percentage of GE, however, most free polymers were formed (Wongthong et al., 2013).

3.2. Mechanical Properties of Vulcanized DPNR and DPNR-g-PAN/PS

The mechanical properties of the vulcanized copolymers were represented by Tensile Strength (TS), elongation at break (EB) and hardness. Figure 3a shows that the value of TS in DPNR-g-PAN/PS copolymers is higher than DPNR's and that increasing concentration of the total monomer increases the value of TS. However, PAN and PS, as a free polymer, can also function as a filler to reinforce the mixture, thus, increasing the value of TS. This value is inversely proportional to the value of EB that decreases with PAN polymer and PS. Therefore, the decreased value of EB is not particularly significant. It can be concluded from these results that the presence of PAN and PS as a free polymer makes vulcanized rubber slightly rigid because they cover most of its pores.

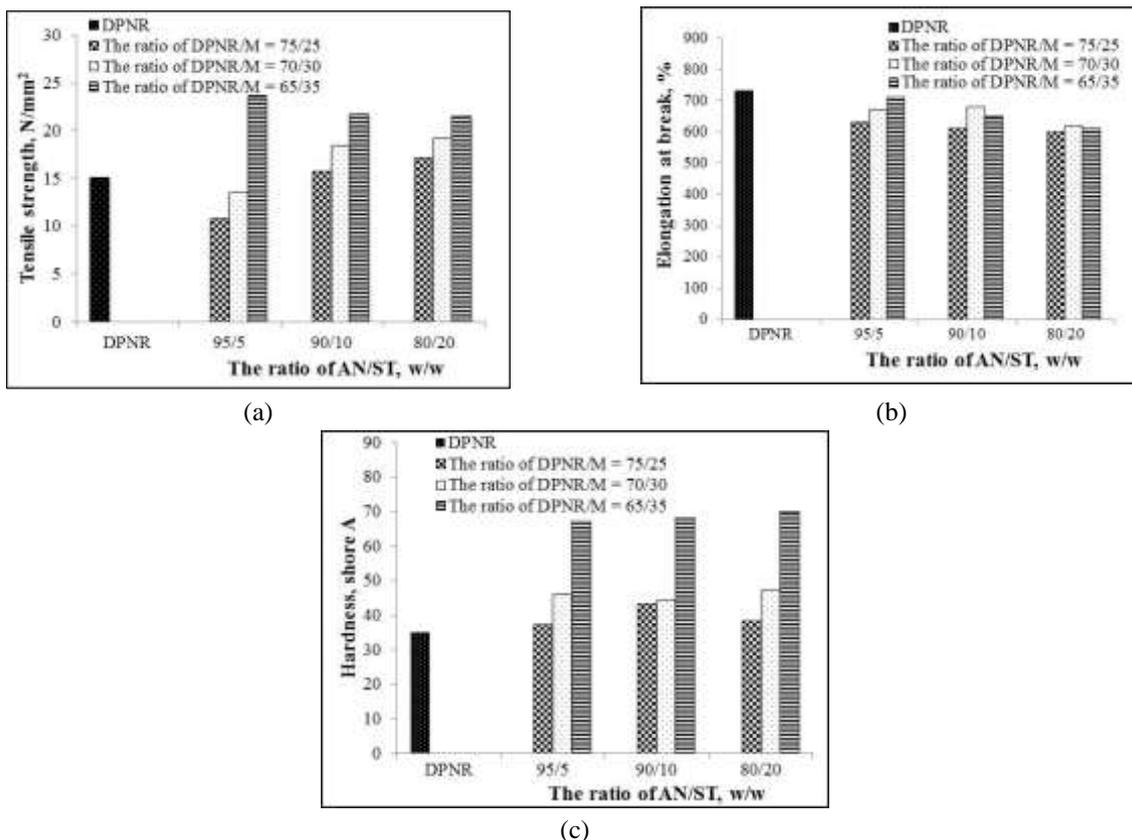


Figure 3 The influence of monomer concentration AN/ST on: a. tensile strength; b. elongation at break; c. hardness of vulcanized DPNR-g-PAN/PS

The mechanical properties of grafted vulcanized rubber are influenced by the properties of the grafted polymers. The hardness of the polymer affects the flexibility of the rubber material, and the same applies to the types and molecular weight of the polymers (Mark et al., 2013). Polyacrylonitrile (PAN), a fiber polymer, is hard and has high molecular weight while Polystyrene (PS), a plastic polymer, is softer. Grafting of the PAN onto a natural rubber can increase its TS and hardness (George et al., 2007; Prukkaewkanjana et al., 2014). Figure 3a shows that decreasing concentration of AN increases TS value while Figure 3b reveals that the value of EB decreases with an increase in ST concentration.

Several previous studies have discussed the process of grafting AN onto natural rubber. A study by Angnanon et al. reported that NR-g-AN/ST functioned as a compatibility material in the process of blending natural rubber with NBR (Angnanon et al., 2011). In this research, the presence of copolymer grafting increased the value of TS, but its variation did not significantly affect the value of the vulcanized TS. Another research conducted by George stated that an increase in the concentration of AN in the copolymerization process increases the value of TS and decreases the value of EB (George et al., 2007). Similarly, a study carried out by Prukkaewkanjana et al., revealed that the TS of DPNR-graft-PAN increased along with increasing efficiency of grafting acrylonitrile. In addition, DPNR-graft-PAN has a dipole-dipole interaction between its nitrile groups. Therefore, a decrease in the content of PAN in rubber increases the rigidity of the graft copolymer (Prukkaewkanjana et al., 2014). The use of PAN and PS as either grafted or free polymers in vulcanized rubber improve hardness. Figure 3c shows that an increase in the concentration of total monomer increases the value of hardness.

3.3. Swelling and Shrinking Test on DPNR and DPNR-g-PAN/PS in DME

The change in the mass of wet sample measured indicates swelling in DPNR and DPNR-g-PAN/PS as shown in Figure 4a. The figure also shows that the decrease in swelling of DPNR-g-PAN/PS occurs in all concentration ratio of AN/ST when compared with DPNR and that the increasing concentration of styrene increases swelling. The ratio DPNR/M 65/35 and ratio AN/ST 95/5 with the lowest swelling at 23.14%. Figure 4b shows the change of mass for the dry sample measured after 24 hours. This figure indicates that there is a decrease in mass after immersion for 7 days. However, the opposite of swelling, the increasing concentration of ST will be smaller decreasing of mass in copolymer rubber.

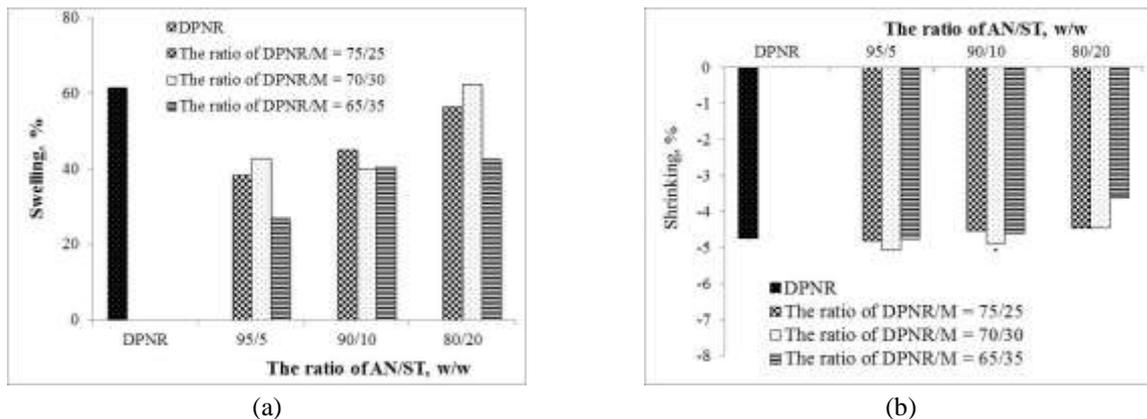


Figure 4 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME 168 hours at (a). Wet sample measured (b). Dry sample measured

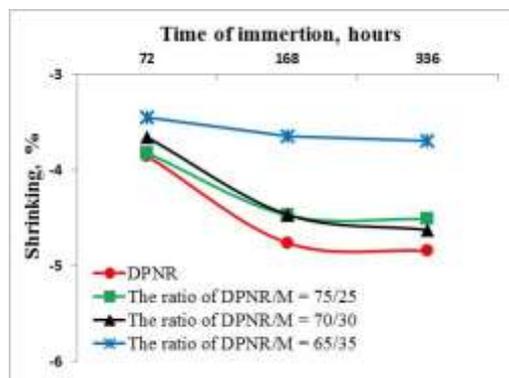


Figure 5 The mass degradation of DPNR-g-PAN/PS after immersion in DME (dry measurement) at the ratio of AN/ST = 80/20

Figure 5 shows that all DPNR and DPNR-g-PAN/PS samples lost mass. This means that increased concentration of ST decreases the loss of mass. The lowest was recorded to be (-3.64%) at AN/ST ratio of 80/20 and DPNR/M ratio of 65/35. The smallest decreasing of mass in Figure 5 can be attached to the presence of polyacrylonitrile and polystyrene-free in it more than in other AN/ST ratios. This phenomenon of free polymers acts as filler for the crosslinked rubber. As shown by Saputra, et al., this shows that increased loading in rubber filler decreases mass loss (Saputra et al., 2016). Previous researchers such as Mikhailova et al. (2009) investigated the increase in filler composition and found that it inhibited absorption and reaction in vulcanized rubber. Likewise, Muniandy et al. (2012) also found that filler loading resulted in greater interaction between the rubber and the filler. Therefore, the higher the level of interaction between the filler and the rubber matrix the lower the swelling value. The shrinking of mass as shown in Figure 5 reveals the degradation caused by the DME to the vulcanized rubber.

Chemical and Physical Properties After Immersion

Figure 6 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. At DPNR spectrum after immersion, group C=C double bonds were lost at wave number 1576.59 cm^{-1} . The bond might have broken and changed into C-C at wave number between $1000\text{-}700\text{ cm}^{-1}$ and C-H at 669.35 cm^{-1} . This can be as a result of its interaction with DME. In Figure 6c and 6d, a comparison of the DPNR-g-PAN/PS spectrum was done before and after immersion. It was discovered that they had a little broken C=C double bonds, changed C≡N group from wave number 2242.57 cm^{-1} to 2242.27 cm^{-1} , and functional group of benzene ring from wave number 703.95 cm^{-1} to 702.72 cm^{-1} . This is probably caused by the interaction of DME with PAN, PS, and DPNR as a free polymer. The comparison shows that DPNR degraded more than DPNR-g-PAN/PS.

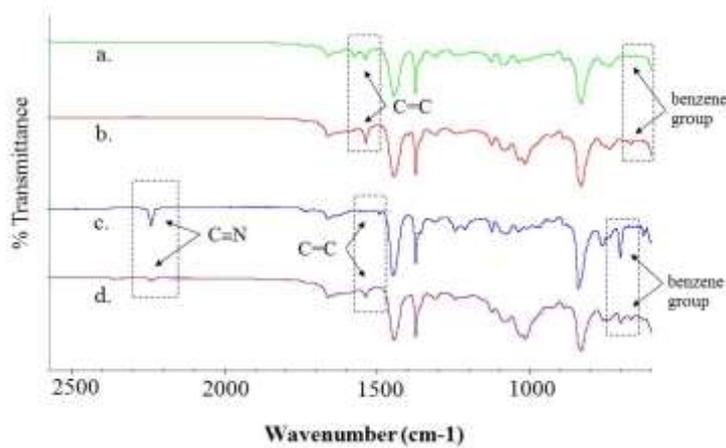
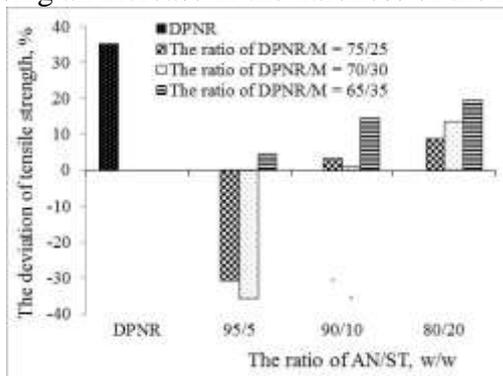
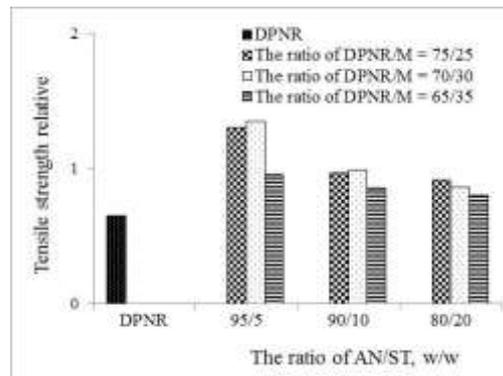


Figure 6 The spectrum FTIR of (a). DPNR before immersion; (b) DPNR after immersion; (c) DPNR-g-PAN/PS before immersion; (d) DPNR-g-PAN/PS after immersion

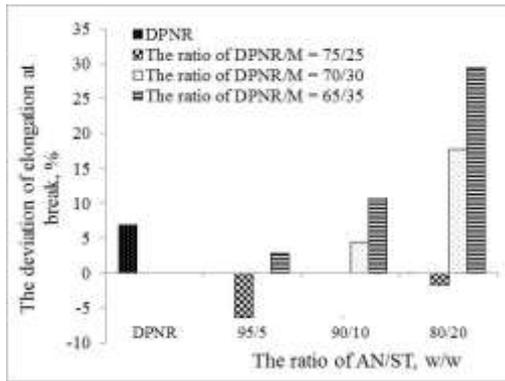
The deviation in Tensile Strength (TS) is as shown in Figure 7a. It was observed from the FTIR spectrum in the figure that the breaking of double bond C=C to C-C and C-H can also reduce the strength and elasticity of the rubber. Therefore, TS and EB as shown in Figure 7a and 7c generally decrease. Figure 7b shows that the tensile strength of DPNR-g-PAN/PS is generally higher than that of DPNR except for AN/ST 80/20 ratio. It can be concluded that the relatively high tensile strength of the dispersed DPNR is surrounded by the polyacrylonitrile phase which makes it function as an oil-resistant compound and this restrained its swelling. However, in the ratio of AN/ST = 80/20, polyacrylonitrile activities were covered by polystyrene, which increases shrinking and then decreases tensile strength relative value. Figure 7d shows that the hardness values increased after immersion and that the occurrence of swelling and shrinking caused a reduction in some of the material contained in the rubber. Therefore, sol fraction decreased and rubber becomes denser causing an increase in the hardness of the material.



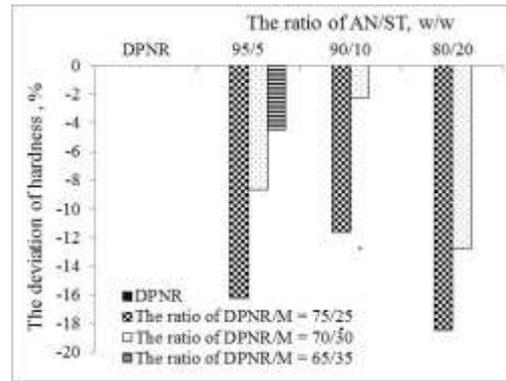
(a)



(b)

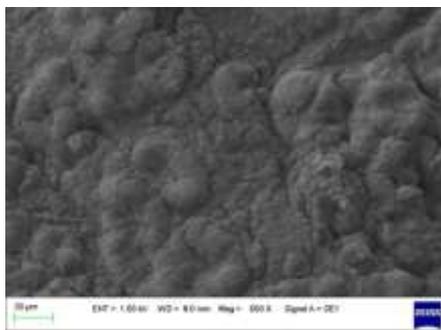


(c)

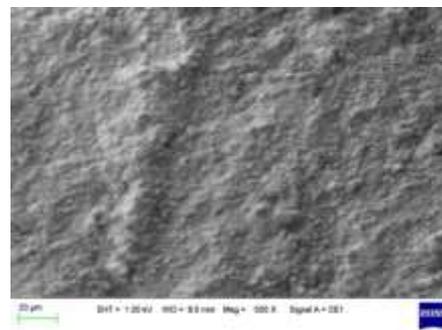


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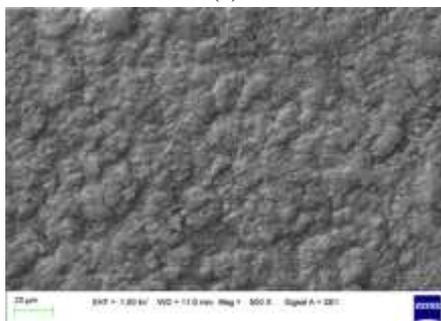
Figure 7 The deviation of: (a. tensile strength; b. tensile strength relative; c. elongation at break; d. hardness); after immersion in DME



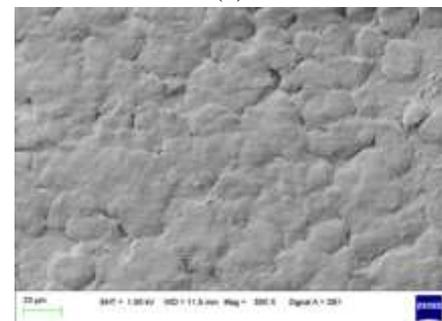
(a)



(b)



(c)



(d)

Figure 8 The surface morphology of DPNR and DPNR-g-PAN/PS by SEM analysis before and after immersion in DME: (a) vulcanized DPNR before immersion; (b) vulcanized DPNR after immersion; (c) vulcanized DPNR-g-PAN/PS before immersion; (d) DPNR-g-PAN/PS after immersion

Analysis of the surface morphology through the use of ZEISS EVO 50 scanning electron microscope (SEM) was conducted at 500 times magnification to characterize the degradation behavior of DPNR and DPNR-g-PAN/PS before and after immersion in DME. Figure 8a and 8b show a difference between the morphology of DPNR. Figure 8b shows that the erosion of the material (shrinking) is as a result of the absorption and desorption of DME into the rubber network. This can be attributed to a possible reaction between DME and some ingredients during its absorption in the rubber. The same thing happens in Figure 8c and 8d. In Figure 8d, shrinking resulted in morphological changes that were not seen in Figure 8c. The surface in it is smooth, flat and sallow in color. The whole figure reveals that DPNR-g-PAN/PS morphology experienced a slight shrinking effect while that of DPNR undergone a huge one. In compare to SEM result in Saputra et al. 2018, concluded that acrylonitrile content on rubber can prevent DME diffusion.

4. CONCLUSION

The research was focused on the production and resistance test of copolymer DPNR-g-PAN/PS in DME with the influence of acrylonitrile and styrene monomer. It was found that the presence of acrylonitrile and styrene increased the mechanical properties of DPNR and DPNR-g-PAN/PS and that increase in the concentration of acrylonitrile decreases rubber swelling and increases its shrinking. However, increased concentration of styrene was discovered to result in the opposite reaction for the rubber. Another finding of the research is that the FTIR spectrum of DPNR degraded more than DPNR-g-PAN/PS spectrum and that the DPNR-g-PAN/PS morphology experienced a slight shrinking effect while that of DPNR undergone a huge one.

5. ACKNOWLEDGMENT

The authors express gratitude to the Research Laboratory of Chemical Engineering FT-UI and Rubber Research Center Bogor for their support in this research.

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DEPROTEINIZED NATURAL RUBBER GRAFTED WITH POLYACRYLONITRILE (PAN)/POLYSTYRENE (PS) AND ITS MECHANICAL PROPERTIES DEGRADATION BY DIMETHYL ETHER

ABSTRACT

Dimethyl ether (DME) is a clean fuel that has moderate polarity, swells easily, and dissolves organic compounds. It has the ability to attack some sealing materials and plastic components because of its low viscosity. The modification of deproteinized natural rubber with acrylonitrile (AN) monomer and styrene (ST) monomers by an emulsion copolymerization process to obtain DPNR-g-PAN/PS copolymers. This process uses a stirred reactor with conditions $T = 65^{\circ}\text{C}$, $P = 1$ atm, initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and an emulsifier sodium dodecyl sulfate (SDS). The copolymer DPNR-g-PAN/PS can be used to seal storage for DME. It is expected to reduce the degradation of rubber due to the presence of the fuel. The parameters that were used in testing for the resistance of DPNR included swelling, shrinking, Fourier Transform Infrared spectroscopy (FTIR) spectrum, and the changes in the mechanical properties of DPNR after immersion. The results of this research revealed that the presence of AN and ST can increase the mechanical properties of DPNR. They also showed that an increase in the concentration of AN decreased the swelling and increased the shrinking of rubber. However, the increase in the concentration of ST was found to increase the swelling and decrease the shrinking of rubber. After immersion, there was more degradation of the spectrum DPNR showed more evidence of degradation than the DPNR-g-PAN/PS after immersion. The surface morphology test, which was carried out with a Scanning Electron Microscope (SEM), showed that DPNR-g-PAN/PS experienced a slight shrinking effect in its morphology while DPNR underwent a huge shrinking effect.

Keywords: Acrylonitrile; Deproteinized natural rubber; Dimethyl ether; Styrene

1. INTRODUCTION

Dimethyl ether (DME) is an alternative fuel with several advantages, such as higher oxygen content, a higher cetane number than diesel oil, and a low boiling point. It is also non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic (Semelsberger, et al., 2006; Arcoumanis, et al., 2008; Li & Zhou, 2008). However, its chemical properties are different from those of LPG, which has moderate polarity and high gas permeability to organic compounds such as plastics and rubber; DME swells easily; and dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing materials and plastic components because of its low viscosity (Arcoumanis, et al., 2008). Previous studies have made use of the immersion method through the use of swelling and mechanical properties as parameters to test for resistance in DME. According to research conducted by Li and Zhou (2008), immersion of rubber in a mixture of DME/diesel at 20/80 wt% was reported to produce a corroded rubber seal.

Furthermore, natural rubber grafted with acrylonitrile (AN) and styrene (ST) has the potential to be used as a seal for the storage of DME. It has excellent properties such as good elasticity, high tensile strength (TS), and good adhesion to metal. Polyacrylonitrile (PAN) is a non-solvent material with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (Mark, 2009). The presence of PAN in the mixture also increases its insolubility and resistance to organic solvents (Nataraj, et al., 2012). Styrene has also been observed to be a good co-monomer for the stability of the graft-copolymerization process (Angnanon et al., 2011; Prasassarakich, et

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al., 2001; Sari et al., 2015). According to studies conducted by Prasassarakich et al. (2001), the oil and solvent resistance of NR can be improved by graft copolymerization using ANaerylonitrile (Prasassarakich, et al., 2001). An increase in TStensile strength and oil resistant ~~were~~ observed with an increase in the ~~percentage~~ percentage of grafting efficiency (GE) of ANaerylonitrile monomer (Prukkaewkanjana, et al., 2014); ~~these results. The same thing were~~ also reported by Angnanon et al. (2011).

The objective of the ~~present study is research~~ was to obtain a copolymer DPNR-g-PAN/PS with a high resistance to DME gas. This is important because resistance is the potency needed by natural rubber to survive the diffusion or corrosion caused by the DME. According to research conducted by Sari et al. (2017), ~~(The copolymer is expected to reduce the degradation of rubber because of the action of the fuel) according to simple research conducted by Sari et al. (2017)~~. The characteristics of the copolymer were determined ~~using~~ by Fourier ~~(T)ransform i(n)frared s(pectroscopy~~ (FTIR). The mechanical properties measured included ~~TStensile strength~~, elongation at break (EB), and hardness, while the resistance test parameters ~~included were~~ swelling, shrinking, and changes in mechanical properties after immersion. A ~~s~~Surface morphology test was also performed ~~through the using~~ of a ~~s~~Scanning ~~e~~lectron ~~m~~icroscope (SEM) analysis.

2. METHODS

2.1. Materials

The materials used ~~in the present study~~ included ~~a~~ natural rubber latex with a high level of stabilized ammonia containing ~~approximately~~ about 59–60% of ~~d~~ry ~~r~~ubber ~~c~~ontent (DRC) from South Sumatera, Indonesia. ~~Acrylonitrile~~ (AN monomer ($\geq 99\%$) and ~~ST~~styrene monomer ($\geq 99\%$) were purchased from Sigma–Aldrich (SGP). The emulsifier ~~sodium dodecyl sulfate~~ (SDS ($\sim 90\%$), urea, ~~potassium persulfate~~ ($\text{K}_2\text{S}_2\text{O}_8$ ($\geq 99\%$), N,N-dimethylformamide (DMF), and methyl ethyl ketone (MEK) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was purchased from PT: Trijaya Gasesindo (INA). Zinc oxide (ZnO), stearic acid, 2-mercaptobenzothiazole/MBT, and sulfur were used in the production of vulcanized rubber. ~~DME~~ ~~methyl ether~~ was purchased from PT: Bumi Tangerang, Banten (INA), while DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate et al., 2008; Suksawad et al., 2011).

2.2. Preparation of ~~C~~opolymer DPNR-g-PAN/PS

~~This~~ was conducted in a 1.3 L reactor glass equipped with a hot plate, a magnetic stirrer, and a nitrogen gas inlet. The DPNR, SDS (0.67 w/w-% of rubber), and distilled water were first charged into a reactor glass with the use of $\text{K}_2\text{S}_2\text{O}_8$ an initiator ~~with having~~ 1 wt% of total monomers (Sahoo, 2019). ~~Then, and~~ the reaction ~~was~~ conducted for ~~six~~ 6 hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer, and it was synthesized using emulsion polymerization methods with a ~~ratio of~~ DPNR to ~~m~~onomer ~~ratio~~ (M) of at (65/35); (70/30); (75/25) w/w, and 95/5; 92/8; 90/10; 80/20 w/w for AN/ST. For the purpose of calculating the ~~percentage Grafting Efficiency (GE)~~ as shown in equation (1), the free DPNR, PAN, and PS-free homopolymer were removed using Soxhlet extraction with petroleum ether, ~~DMF~~ ~~N~~ dimethylformamide, and ~~MEK~~ ~~methyl ethyl ketone~~ respectively. GE is a parameter that is influenced by reaction variables such as DPNR/M ratio and AN/ST ratio.

$$\%GE = \frac{\text{weight of copolymer DPNR-g-PAN/PS}}{\text{weight of dry coagulan}} \times 100 \quad (1)$$

2.3. Characterization

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The ~~T~~Tensile strength (MPa) and ~~E~~Elongation at break (%) were measured using a ~~Tensometer~~ENSOMETER LLOYD 2000R according to the ASTM D.412-06ae2 standard. Hardness (Shore A) was measured using a durometer, and adequate steps were taken to ensure that ~~this measurement~~ complied with the ASTM D.2240-05 standard. The ~~Fourier Transform Infrared spectroscopy (FTIR)~~ spectra of the DPNR and DPNR-g-PAN/PS were recorded in solid state using a Nicolet iS5 spectrometer (Thermo Scientific) between 500 and 4000 cm⁻¹. ~~The preparation of the sample preparation~~ was ~~completed~~done using pyrolysis and the Soxhlet-extraction method, and ~~an scanning electron microscope (SEM)~~ (model type ZEISS EVO 50) was used to analyze the surface morphology of DPNR and DPNR-g-PAN/PS before and after ~~the~~immersion.

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2.4. Swelling and Shrinking Test

The rubber to be vulcanized ~~was~~immersed in ~~liquid-phase DME~~liquid phase in a 1.3 L pressure vessel. The changes in the masses of these samples ~~were~~investigated after the samples had been immersed for several days and exposed to the atmosphere for 24 hours (Wu et al., 2008). ~~The swelling~~ was measured ~~as a~~ percentage (%), as shown in equation (2) (Li & Zhou, 2008; Hinchiranan et al., 2013).

$$\text{Swelling/Shrinking(\%)} = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sample before immersion ~~and~~while M_2 is the mass after ~~immersion~~. The samples ~~were~~referred to as wet samples after they ~~had~~been immersed and ~~were~~called dry samples after being exposed to the atmosphere for 24 hours.

3. RESULTS AND DISCUSSION

3.1. Grafting Characteristics

~~The~~ Grafting characteristics of ~~the~~ copolymer showed the formation of DPNR-g-PAN/PS, ~~to~~ consisting of ~~its~~ FTIR spectrum, ~~Grafting Efficiency (GE)~~, and mechanical properties. Figure 1(a) shows a comparison between the FTIR spectrum of DPNR (2) and ~~that of~~ the grafted copolymers (1); ~~thesuch that~~ C≡N group ~~as~~ shown at wave number 2,242.75 cm⁻¹; indicated PAN grafted on a natural rubber chain, while the presence of benzene groups ~~as~~ shown at wave number 705.16 cm⁻¹ indicated PS grafted on natural rubber. The spectrum ~~shown~~ in Figure 1(a) ~~is~~ based on previous research by Sari et al. (2017). ~~A~~The nitrile group (C≡N) could be indicated at wave numbers 2,240–2,260 cm⁻¹; (Smith, 1979) and at wave number 2,242 cm⁻¹ (Nacimiento et al., 2012). In ~~at~~the previous ~~study work~~, (Luo, et al. (2012) reported in a functional group the benzene ring at the wave number ~700 cm⁻¹ and ~760 cm⁻¹, respectively. Figure 1(b) shows ~~that the~~ FTIR spectrum of DPNR-g-PAN/PS is based on variations in the composition of AN/ST.

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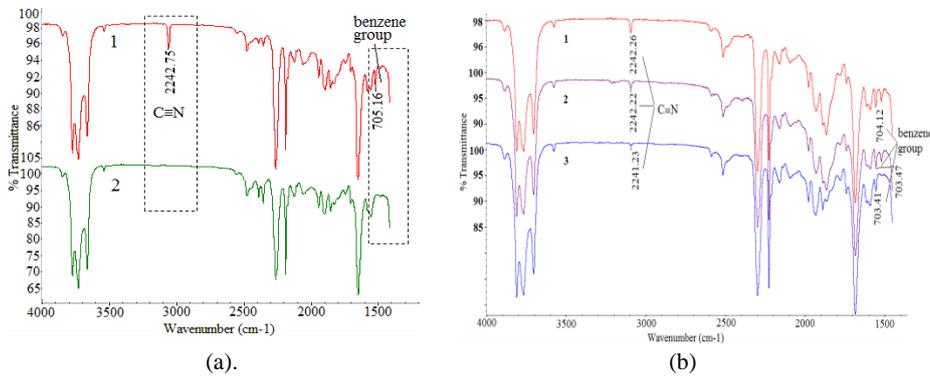


Figure 1 (a)- Spectrum FTIR: 1. DPNR; and 2. DPNR-g-PAN/PS (b)- Spectrum FTIR of DPNR-g-PAN/PS with variation composition of AN/ST; 1. AN/ST 95/5; 2. AN/ST 90/10; and 3. AN/ST 80/20

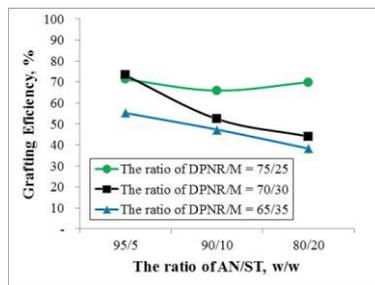


Figure 2 Grafting Efficiency (GE) with the ratios of DPNR/M and AN/ST

Figure 2 shows the effect of the DPNR/M ratio on GE, and showing it can be discovered from the graph that the decreasing ratio of DPNR/M and AN/ST ratios decrease the percentage of GE. This indicates immiscibility between the AN and ST molecules. It is, therefore, it is possible that the grafting copolymerization occurs only on the surface of the latex particles. It was also found that the continuous addition of both of total monomers AN and ST does not increase the percentage of GE; however, most free polymers were formed (Wongthong et al., 2013).

3.2. Mechanical Properties of Vulcanized DPNR and DPNR-g-PAN/PS

The mechanical properties of the vulcanized copolymers were represented by Tensile Strength (TS), elongation at break (EB), and hardness. Figure 3a shows that the value of TS was higher in DPNR-g-PAN/PS copolymers is higher than in DPNR-s and that increasing concentration of the total monomers increases the value of TS. However, PAN and polystyrene (PS), as a free polymers, can also function as a fillers to reinforce the mixture, thus, increasing the value of TS. This value is inversely proportional to the value of EB, which that decreases with PAN polymer and PS. Therefore, the decreased value of EB was not particularly significant. It can be concluded from these results that the presence of PAN and PS as a free polymers makes vulcanized rubber slightly rigid because they cover most of its pores.

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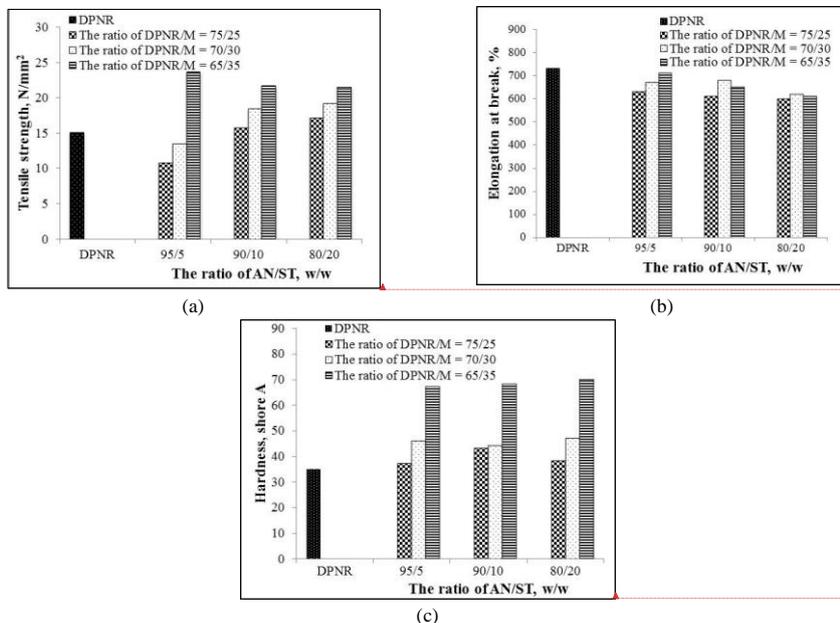


Figure 3 The influence of ~~monomer concentration~~ AN/ST ~~monomer concentration~~ on: a. tensile strength, b. elongation at break, and; c. hardness of vulcanized DPNR-g-PAN/PS

The mechanical properties of grafted vulcanized rubber are influenced by the properties of the grafted polymers. The hardness of the polymer affects the flexibility of the rubber material, and this ~~concept also same~~ applies to the types and molecular weights of the polymers (Mark et al., 2013). ~~Polyacrylonitrile (PAN)~~, a fiber polymer, is hard and has a high molecular weight, while ~~Polystyrene (PS)~~, a plastic polymer, is softer. Grafting ~~of the~~ PAN onto a natural rubber can increase ~~its the rubber's~~ TS and hardness (George et al., 2007; Prukkaewkanjana et al., 2014). Figure 3a shows that decreasing AN concentration ~~of AN~~ increases TS, ~~value~~ while Figure 3b reveals that ~~the value of~~ EB decreases with an increase in ST concentration.

Several previous studies have discussed the process of grafting AN onto natural rubber. ~~For example, a~~ study by Angnanon et al. (2011) reported that NR-g-AN/ST functioned as a compatibility material in the process of blending natural rubber with NBR (~~Angnanon et al., 2011~~). In ~~this research~~, the presence of copolymer grafting increased the ~~value of~~ TS, but ~~its~~ variation did not significantly affect ~~the value of~~ the vulcanized TS. Another ~~study research~~ conducted by George et al. (2007), stated that an increase in the concentration of AN in the copolymerization process increases the ~~value of~~ TS and decreases the ~~value of~~ EB (~~George et al., 2007~~). Similarly, a study carried out by Prukkaewkanjana et al. revealed that the TS of DPNR-graft-PAN increased along with increasing ~~ly efficient AN grafting~~ ~~of grafting acrylonitrile~~. In addition, DPNR-graft-PAN has a dipole-dipole interaction between its nitrile groups. Therefore, a decrease in the ~~content of~~ PAN ~~content of~~ rubber increases the rigidity of the graft copolymer (Prukkaewkanjana et al., 2014). The use of PAN and PS as either grafted or free polymers in vulcanized rubber improves hardness. Figure 3c shows that an increase in the concentration of total monomers ~~increases the value of~~ hardness.

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3.3. Swelling and Shrinking Test on DPNR and DPNR-g-PAN/PS in DME

The change in the mass of the wet sample indicated swelling in DPNR and DPNR-g-PAN/PS, as shown in Figure 4a. This figure also shows that the decrease in the swelling of DPNR-g-PAN/PS occurred in all AN/ST concentration ratios, when compared with DPNR, and that the increasing concentration of ST increased swelling. The DPNR/M 65/35 ratio and the AN/ST 95/5 ratio had the least swelling at 23.14%. Figure 4b shows the change in the mass of the dry sample after 24 hours. This figure indicates that the mass decreased after seven days of immersion. However, the opposite of swelling, the increasing concentration of ST will be smaller decreasing of mass in copolymer rubber.

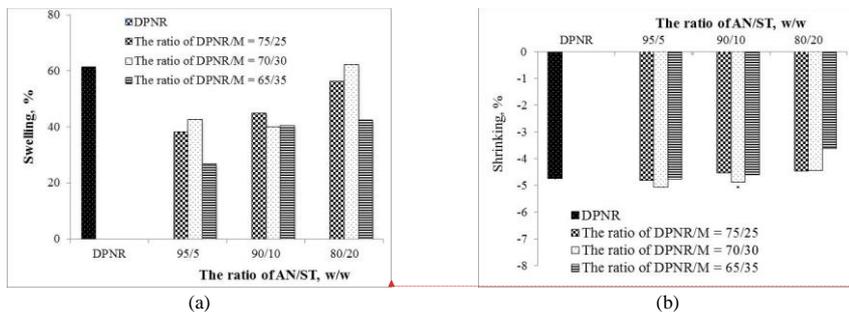


Figure 4 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME for 168 hours: (a) wet sample measured; (b) dry sample measured

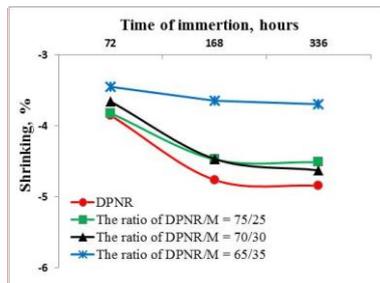


Figure 5 The mass degradation of DPNR-g-PAN/PS after immersion in DME (dry measurement) at the AN/ST ratio of AN/ST = 80/20

Figure 5 shows that all DPNR and DPNR-g-PAN/PS samples lost some mass. This means that increasing STed concentration of ST decreases the loss of mass. The lowest mass was recorded to be (-3.64%) was recorded at an AN/ST ratio of 80/20 and a DPNR/M ratio of 65/35. The smallest decreasing inof mass shown in Figure 5 couldan be attached to the presence of more free PANpolyacrylonitrile and PSpolystyrene free in it more than in other AN/ST ratios. This phenomenon of free polymers providesacts as filler for the crosslinked rubber. As shown by Saputra; et al. (2016), this shows that increased loading in rubber filler decreases the loss of mass loss (Saputra et al., 2016). Previous researchers, such as Mikhailova et al. (2009), have investigated the increase in filler composition and found that it inhibiteded absorption and reaction in vulcanized rubber. Likewise, Muniandy et al. (2012) also found that filler loading resultseed in greater interaction between the rubber and the filler. Therefore, atthe higher the-level of interaction between

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the filler and the rubber matrix corresponds to a lower the swelling value. The shrinking of mass, as shown in Figure 5, reveals the vulcanized rubber degradation caused by the DME to the vulcanized rubber.

Chemical and Physical Properties After Immersion

Figure 6 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. At the DPNR spectrum after immersion, group C=C double bonds were lost at wave number 1576.59 cm⁻¹. These bonds might have been broken, and changed into C-C at a wave number between 1000 cm⁻¹ and 700 cm⁻¹, and changed into C-H at 669.35 cm⁻¹. This could have been as a result of its interaction with DME. In Figures 6c and 6d depict, a comparison of the DPNR-g-PAN/PS spectrum was done before and after immersion. It was discovered that they had a little broken C=C double bonds, changed C≡N group from wave number 2242.57 cm⁻¹ to wave number 2242.27 cm⁻¹, and a functional group of benzene ring from wave number 703.95 cm⁻¹ to wave number 702.72 cm⁻¹. This was probably caused by the interaction of DME with PAN, PS, and DPNR as a free polymer. The comparison shows that DPNR degraded more than DPNR-g-PAN/PS.

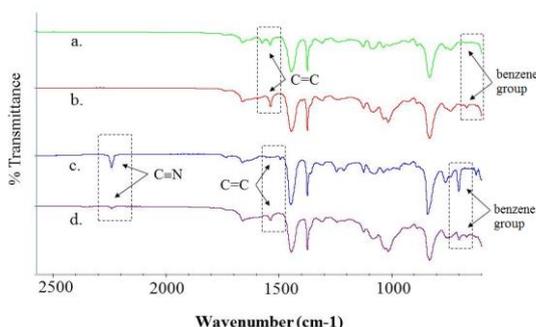


Figure 6 The spectrum FTIR spectrum of (a)- DPNR before immersion, (b) DPNR after immersion, (c) DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

The deviation in Tensile Strength (TS) is as shown in Figure 7a. It was observed from the FTIR spectrum in this figure showed that the breaking of double bond C=C double bonds to C-C and C-H can also reduce the strength and elasticity of the rubber. Therefore, TS and EB as shown in Figure 7a and 7e generally decrease, as shown in Figures 7a and 7c. Figure 7b shows that the Tensile strength of DPNR-g-PAN/PS was generally higher than that of DPNR except for the AN/ST 80/20 ratio. It can be concluded that the relatively high Tensile strength of the dispersed DPNR was surrounded by the PANpolyacrylonitrile phase, which makes it function as an oil-resistant compound and therefore is restrained its swelling. However, in the ratio of AN/ST = 80/20 ratio, the PANpolyacrylonitrile activities were covered by PSpolystyrene, which increases shrinking and then decreased the relative s-Tensile strength relative value. Figure 7d shows that the hardness values increased after immersion and that the occurrence of swelling and shrinking caused a reduction in some of the material contained in the rubber. Therefore, the sol fraction decreased and the rubber becomes denser, causing an increase in the hardness of the material.

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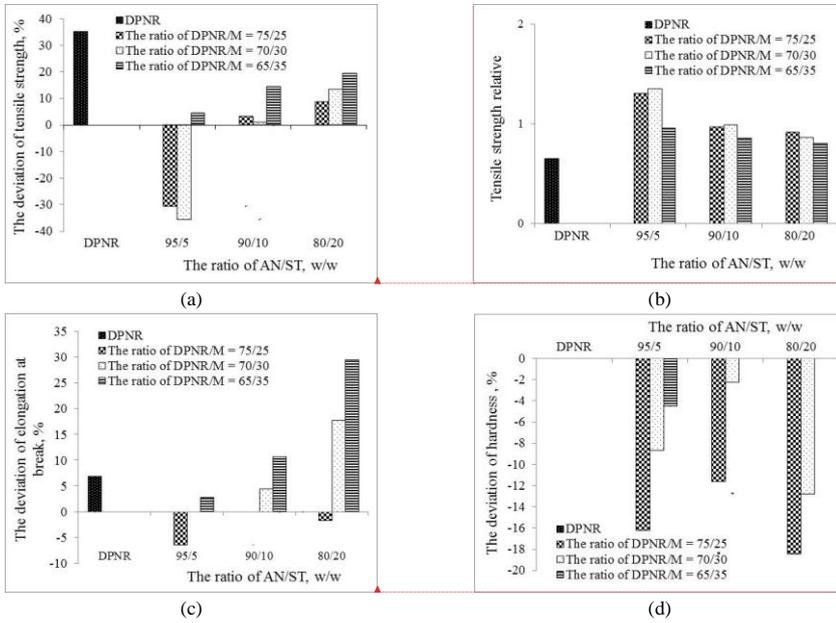


Figure 7 The deviation of: (a)- tensile strength, (b)- relative tensile strength, (c)- elongation at break, and (d)- hardness- after immersion in DME

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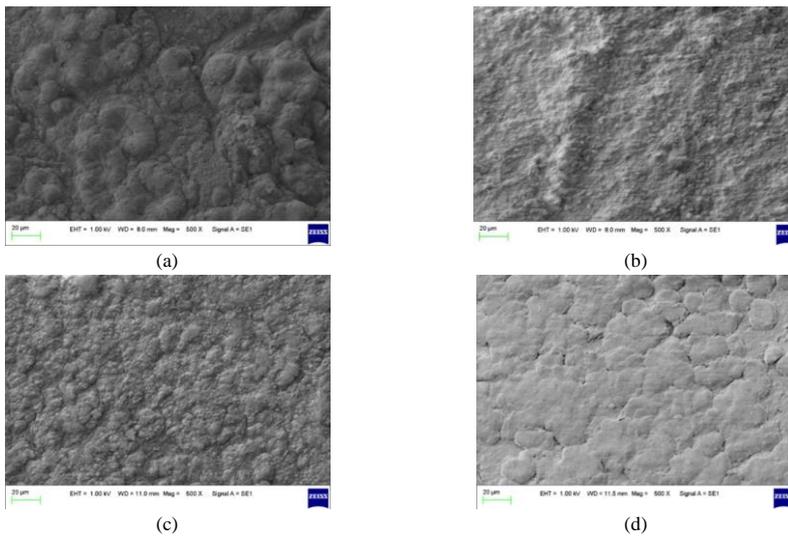


Figure 8 The surface morphology of DPNR and DPNR-g-PAN/PS as shown by SEM analysis before and after immersion in DME: (a) vulcanized DPNR before immersion, (b) vulcanized DPNR after immersion, (c) vulcanized DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

~~A s~~Analysis of the surface morphology ~~analysis was conducted with~~through the use of a ZEISS EVO 50 ~~scanning electron microscope (SEM) was conducted~~ at 500 times magnification to characterize the degradation behavior of DPNR and DPNR-g-PAN/PS before and after immersion in DME. Figures 8a and 8b show a difference ~~between the morphology of DPNR.~~ Figure 8b shows that the erosion of the material (shrinking) ~~was~~as a result of the absorption and desorption of DME into the rubber network. This can be attributed to a possible reaction between DME and ~~some ingredients~~ during its absorption ~~into~~ the rubber. ~~This same phenomenon is also shown~~thing happens in Figures 8c and 8d. In Figure 8d, shrinking resulted in morphological changes that ~~can~~were not be seen in Figure 8c. The surface ~~of~~it ~~was~~smooth, flat, and sallow in color. ~~The whole figure reveals that~~ the morphology of DPNR-g-PAN/PS ~~morphology~~ experienced a slight shrinking effect while that of DPNR ~~under~~wentgone a ~~large~~huge shrinking effect~~one~~. In a ~~comparisone to~~ SEM ~~analysis,~~result in Saputra et al. (2018); concluded that ~~the~~ ANaerylonitrile content of ~~a~~ rubber can prevent DME diffusion.

4. CONCLUSION

The ~~present study~~research ~~was~~ focused on the production and resistance testing of ~~copolymer~~ DPNR-g-PAN/PS in DME with the influence of ANaerylonitrile monomer and STstyrene monomer. It was found that the presence of ANaerylonitrile and STstyrene ~~increase~~d the mechanical properties of DPNR and DPNR-g-PAN/PS. ~~It was also found~~and that ~~an~~ increase in the concentration of ANaerylonitrile ~~decrease~~s rubber swelling and ~~increase~~s rubber ~~its~~ shrinking. However, increased ~~concentration of ST~~ concentrationstyrene was ~~found~~discovered to result in the opposite reaction ~~for the rubber.~~ ~~It was also found.~~Another finding of the research is that the FTIR spectrum of DPNR degraded more than ~~that of~~ DPNR-g-PAN/PS spectrum and that the ~~morphology of~~ DPNR-g-PAN/PS ~~morphology~~ experienced a slight shrinking effect while that of DPNR ~~under~~wentgone a ~~large~~huge shrinking effect~~one~~.

5. ACKNOWLEDGMENT

The authors ~~wish to~~ express ~~their~~ gratitude to the Research Laboratory of Chemical Engineering FT-UI and ~~the~~ Rubber Research Center Bogor for their support in this research.

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DEPROTEINIZED NATURAL RUBBER GRAFTED WITH POLYACRYLONITRILE (PAN)/POLYSTYRENE (PS) AND ITS MECHANICAL PROPERTIES DEGRADATION BY DIMETHYL ETHER

ABSTRACT

Dimethyl ether (DME) is a clean fuel that has moderate polarity, swells easily, and dissolves organic compounds. It has the ability to attack some sealing materials and plastic components because of its low viscosity. The modification of deproteinized natural rubber with acrylonitrile (AN) monomer and styrene (ST) monomer by an emulsion copolymerization process to obtain DPNR-g-PAN/PS copolymers. This process uses a stirred reactor with $T = 65^{\circ}\text{C}$, $P = 1$ atm, initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and an emulsifier sodium dodecyl sulfate (SDS). The copolymer DPNR-g-PAN/PS can be used to seal storage for DME. It is expected to reduce the degradation of rubber due to the presence of the fuel. The parameters that were used in testing for the resistance of DPNR included swelling, shrinking, Fourier transform infra-red spectroscopy (FTIR) spectrum, and changes in the mechanical properties of DPNR after immersion. The results of this research revealed that the presence of AN and ST can increase the mechanical properties of DPNR. They also showed that an increase in the concentration of AN decreased the swelling and increased the shrinking of rubber. However, an increase in the concentration of ST was found to increase the swelling and decrease the shrinking of rubber. After immersion, the spectrum DPNR showed more evidence of degradation than the DPNR-g-PAN/PS. The surface morphology test, which was carried out with a scanning electron microscope (SEM), showed that DPNR-g-PAN/PS experienced a slight shrinking effect in its morphology while DPNR underwent a huge shrinking effect.

Keywords: Acrylonitrile; Deproteinized natural rubber; Dimethyl ether; Styrene

1. INTRODUCTION

Dimethyl ether (DME) is an alternative fuel with several advantages, such as higher oxygen content, a higher cetane number than diesel oil, and a low boiling point. It is also non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic (Semelsberger et al., 2006; Arcoumanis et al., 2008; Li & Zhou, 2008). However, its chemical properties are different from those of LPG, which has moderate polarity and high gas permeability to organic compounds such as plastics and rubber; DME swells easily and dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing materials and plastic components because of its low viscosity (Arcoumanis et al., 2008). Previous studies have made use of the immersion method through the use of swelling and mechanical properties as parameters to test for resistance in DME. According to research conducted by Li and Zhou (2008), immersion of rubber in a mixture of DME/diesel at 20/80 wt% produces a corroded rubber seal.

Furthermore, natural rubber grafted with acrylonitrile (AN) and styrene (ST) has the potential to be used as a seal for the storage of DME. It has excellent properties such as good elasticity, high tensile strength (TS), and good adhesion to metal. Polyacrylonitrile (PAN) is a non-solvent material with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (Mark, 2009). The presence of PAN in the mixture increases its insolubility and resistance to organic solvents (Nataraj et al., 2012). ST has also been observed to be a good co-monomer for the stability of the graft-copolymerization process (Angnanon et al., 2011; Prasassarakich et al., 2001; Sari et al., 2015). According to studies conducted by Prasassarakich et al. (2001), the oil and solvent resistance

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of NR can be improved by graft copolymerization using AN. Increases in TS and oil resistant were observed with an increase in the percentage grafting efficiency (GE) of AN monomer (Pruksaewkanjana et al., 2014); these results were also reported by Angnanon et al. (2011).

The objective of the present study was to obtain a copolymer DPNR-g-PAN/PS with a high resistance to DME gas. This is important because resistance is the potency needed by natural rubber to survive the diffusion or corrosion caused by the DME. According to research conducted by Sari et al. (2017), the copolymer is expected to reduce the degradation of rubber because of the action of the fuel. The characteristics of the copolymer were determined using Fourier transform infrared spectroscopy (FTIR). The mechanical properties measured included TS, elongation at break (EB), and hardness, while the resistance test parameters included swelling, shrinking, and changes in mechanical properties after immersion. A surface morphology test was also performed using a scanning electron microscope (SEM) analysis.

2. METHODS

2.1. Materials

The materials used in the present study included natural rubber latex with a high level of stabilized ammonia containing approximately 59–60% dry rubber content (DRC) from South Sumatera, Indonesia. AN monomer ($\geq 99\%$) and ST monomer ($\geq 99\%$) were purchased from Sigma–Aldrich (SGP). The emulsifier SDS ($\sim 90\%$), urea, $K_2S_2O_8$ ($\geq 99\%$), N,N-dimethylformamide (DMF), and methyl ethyl ketone (MEK) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was purchased from PT Trijaya Gasesindo (INA). Zinc oxide (ZnO), stearic acid, 2-mercaptobenzothiazole/MBT, and sulfur were used in the production of vulcanized rubber. DME was purchased from PT Bumi Tangerang, Banten (INA), while DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate et al., 2008; Suksawad et al., 2011).

2.2. Preparation of Copolymer DPNR-g-PAN/PS

This was conducted in a 1.3 L reactor glass equipped with a hot plate, a magnetic stirrer, and a nitrogen gas inlet. The DPNR, SDS (0.67 w/w% rubber), and distilled water were first charged into a reactor glass with the use of $K_2S_2O_8$, an initiator with 1 wt% total monomers (Sahoo, 2019). Then, the reaction was conducted for six hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer, and it was synthesized using emulsion polymerization methods with a DPNR to monomer ratio of (65/35); (70/30); (75/25) w/w, and 95/5; 92/8; 90/10; 80/20 w/w for AN/ST. For the purpose of calculating the GE, as shown in equation (1), the free DPNR, PAN, and PS-free homopolymer were removed using Soxhlet extraction with petroleum ether, DMF, and MEK, respectively. GE is a parameter that is influenced by reaction variables such as DPNR/M ratio and AN/ST ratio.

$$\%GE = \frac{\text{weight of copolymer DPNR-g-PAN/PS}}{\text{weight of dry coagulan}} \times 100 \quad (1)$$

2.3. Characterization

The TS (MPa) and EB (%) were measured using a Tensometer LLOYD 2000R according to the ASTM D.412-06ae2 standard. Hardness (Shore A) was measured using a durometer, and adequate steps were taken to ensure that this measurement complied with the ASTM D.2240-05 standard. The FTIR spectra of the DPNR and DPNR-g-PAN/PS were recorded in solid states using a Nicolet iS5 spectrometer (Thermo Scientific) between 500 and 4000 cm^{-1} . Sample preparation was

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completed using pyrolysis and the Soxhlet-extraction method, and an SEM (model type ZEISS EVO 50) was used to analyze the surface morphology of DPNR and DPNR-g-PAN/PS before and after immersion.

2.4. Swelling and Shrinking Test

The rubber to be vulcanized was immersed in liquid-phase DME in a 1.3 L pressure vessel. The changes in the masses of these samples were investigated after the samples had been immersed for several days and exposed to the atmosphere for 24 hours (Wu et al., 2008). Swelling was measured as a percentage (%), as shown in equation (2) (Li & Zhou, 2008; Hinchiranan et al., 2013).

$$\text{Swelling/Shrinking(\%)} = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sample before immersion and M_2 is the mass after immersion. The samples were referred to as wet samples after they had been immersed and were called dry samples after being exposed to the atmosphere for 24 hours.

3. RESULTS AND DISCUSSION

3.1. Grafting Characteristics

The grafting characteristics of the copolymer showed the formation of DPNR-g-PAN/PS, consisting of its FTIR spectrum, GE, and mechanical properties. Figure 1(a) shows a comparison between the FTIR spectrum of DPNR (2) and that of the grafted copolymers (1); the C≡N group shown at wave number 2,242.75 cm⁻¹ indicated PAN grafted on a natural rubber chain, while the presence of benzene groups shown at wave number 705.16 cm⁻¹ indicated PS grafted on natural rubber. The spectrum shown in Figure 1(a) is based on previous research by Sari et al. (2017). A nitrile group (C≡N) could be indicated at wave numbers 2,240–2,260 cm⁻¹ (Smith, 1979) and at wave number 2,242 cm⁻¹ (Nacimiento et al., 2012). In a previous study, Luo et al. (2012) reported in a functional group the benzene ring at the wave number ~700 cm⁻¹ and ~760 cm⁻¹, respectively. Figure 1(b) shows that the FTIR spectrum of DPNR-g-PAN/PS is based on variations in the composition of AN/ST.

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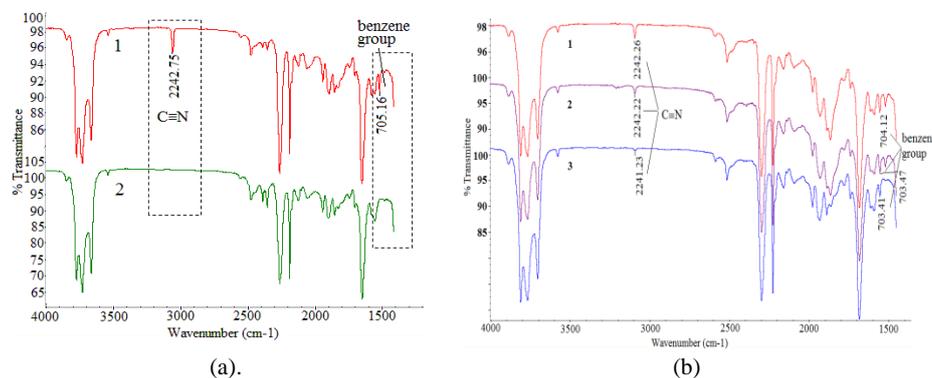


Figure 1 (a) Spectrum FTIR: 1. DPNR; and 2. DPNR-g-PAN/PS (b) Spectrum FTIR of DPNR-g-PAN/PS with variation composition of AN/ST: 1. AN/ST 95/5; 2. AN/ST 90/10; and 3. AN/ST 80/20

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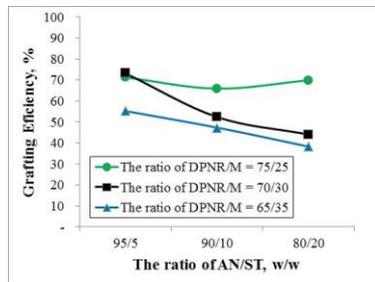


Figure 2 Grafting efficiency (GE) with the ratios of DPNR/M and AN/ST

Figure 2 shows the effect of the DPNR/M ratio on GE, showing that decreasing DPNR/M and AN/ST ratios decrease the percentage of GE. This indicates immiscibility between the AN and ST molecules. Therefore, it is possible that grafting copolymerization occurs only on the surfaces of latex particles. It was also found that the continuous addition of both of total monomers AN and ST does not increase the percentage of GE; however, most free polymers were formed (Wongthong et al., 2013).

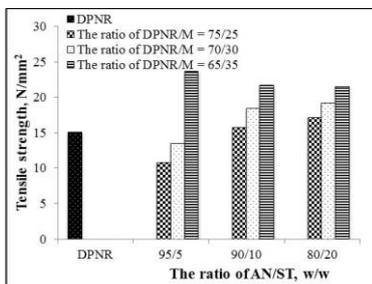
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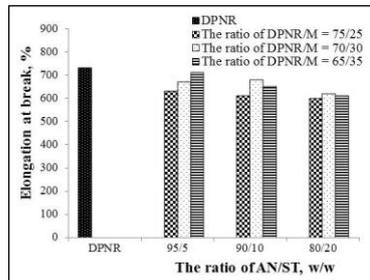
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3.2. Mechanical Properties of Vulcanized DPNR and DPNR-g-PAN/PS

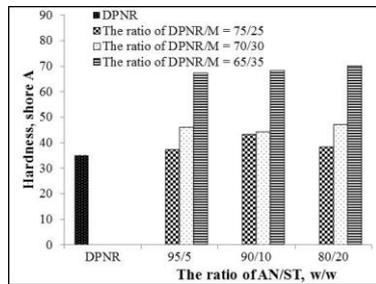
The mechanical properties of the vulcanized copolymers were represented by TS, EB, and hardness. Figure 3a shows that TS was higher in DPNR-g-PAN/PS copolymers than in DPNR and that increasing concentration of the total monomers increased the TS. However, PAN and polystyrene (PS), as free polymers, can also function as fillers to reinforce the mixture, thus increasing the TS. TS is inversely proportional to EB, which decreases with PAN and PS. Therefore, the decreased value of EB was not particularly significant. It can be concluded from these results that the presence of PAN and PS as free polymers makes vulcanized rubber slightly rigid because they cover most of its pores.



(a)



(b)



(c)

Figure 3 The influence of AN/ST monomer concentration on: a. tensile strength, b. elongation at break, and c. hardness of vulcanized DPNR-g-PAN/PS

The mechanical properties of grafted, vulcanized rubber are influenced by the properties of the grafted polymers. The hardness of the polymer affects the flexibility of the rubber material, and this concept also applies to the types and molecular weights of the polymers (Mark et al., 2013). PAN, a fiber polymer, is hard and has a high molecular weight, while PS, a plastic polymer, is softer. Grafting PAN onto a natural rubber can increase the rubber's TS and hardness (George et al., 2007; Prukkaewkanjana et al., 2014). Figure 3a shows that decreasing AN concentration increases TS, while Figure 3b reveals that EB decreases with an increase in ST concentration.

Several previous studies have discussed the process of grafting AN onto natural rubber. For example, a study by Angnanon et al. (2011) reported that NR-g-AN/ST functioned as a compatibility material in the process of blending natural rubber with NBR. In this research, the presence of copolymer grafting increased the TS, but its variation did not significantly affect the vulcanized TS. Another study, conducted by George et al. (2007), stated that an increase in the concentration of AN in the copolymerization process increases the TS and decreases the EB. Similarly, a study carried out by Prukkaewkanjana et al. revealed that the TS of DPNR-graft-PAN increased along with increasingly efficient AN grafting. In addition, DPNR-graft-PAN has a dipole-dipole interaction between its nitrile groups. Therefore, a decrease in the PAN content of rubber increases the rigidity of the graft copolymer (Prukkaewkanjana et al., 2014). The use of PAN and PS as either grafted or free polymers in vulcanized rubber improves hardness. Figure 3c shows that an increase in the concentration of total monomers increases hardness.

3.3. Swelling and Shrinking Test on DPNR and DPNR-g-PAN/PS in DME

The change in the mass of the wet sample indicated swelling in DPNR and DPNR-g-PAN/PS, as shown in Figure 4a. This figure also shows that the decrease in the swelling of DPNR-g-PAN/PS occurred in all AN/ST concentration ratios, when compared with DPNR, and that the increasing concentration of ST increased swelling. The DPNR/M 65/35 ratio and the AN/ST 95/5 ratio had the least swelling at 23.14%. Figure 4b shows the change in the mass of the dry sample after 24 hours. This figure indicates that the mass decreased after seven days of immersion. However, the opposite of swelling, the increasing concentration of ST will be smaller decreasing of mass in copolymer rubber.

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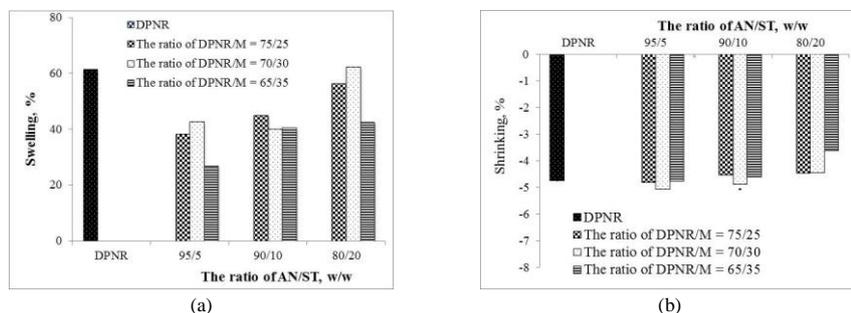


Figure 4 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME for 168 hours; (a) wet sample; (b) dry sample

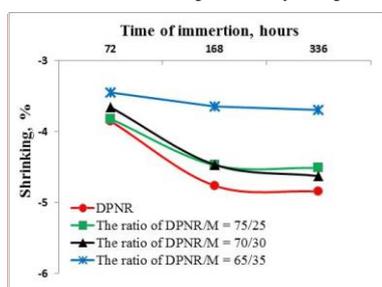


Figure 5 The mass degradation of DPNR-g-PAN/PS after immersion in DME (dry measurement) at an AN/ST ratio of 80/20

Figure 5 shows that all DPNR and DPNR-g-PAN/PS samples lost some mass. This means that increasing ST concentration decreases the loss of mass. The lowest mass (-3.64%) was recorded at an AN/ST ratio of 80/20 and a DPNR/M ratio of 65/35. The smallest decrease in mass shown in Figure 5 could be attributed to the presence of more free PAN and PS than in other AN/ST ratios. This phenomenon of free polymers provides filler for the crosslinked rubber. As shown by Saputra et al. (2016), increased loading in rubber filler decreases the loss of mass. Previous researchers, such as Mikhailova et al. (2009), have investigated the increase in filler composition and found that it inhibits absorption and reaction in vulcanized rubber. Likewise, Muniandy et al. (2012) found that filler loading results in greater interaction between the rubber and the filler. Therefore, a higher level of interaction between the filler and the rubber matrix corresponds to a lower swelling value. The shrinking of mass, as shown in Figure 5, reveals the vulcanized rubber degradation caused by DME.

Chemical and Physical Properties After Immersion

Figure 6 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. At the DPNR spectrum after immersion, group C=C double bonds were lost at wave number 1576.59 cm^{-1} . These bonds might have been broken, changed into C-C at a wave number between 1000 cm^{-1} and 700 cm^{-1} , and changed into C-H at 669.35 cm^{-1} . This could have been a result of interaction with DME. Figures 6c and 6d depict a comparison of the DPNR-g-PAN/PS spectrum before and after immersion. It was discovered that they had a little broken C=C double bonds, changed C≡N group from wave number 2242.57 cm^{-1} to wave number 2242.27 cm^{-1} , and a functional group of benzene ring from wave number 703.95 cm^{-1} to wave number 702.72 cm^{-1} . This

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was probably caused by the interaction of DME with PAN, PS, and DPNR as a free polymer. The comparison shows that DPNR degraded more than DPNR-g-PAN/PS.

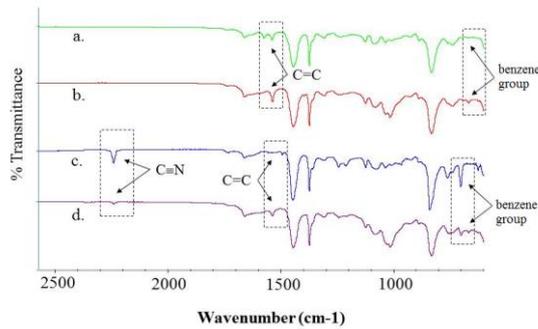
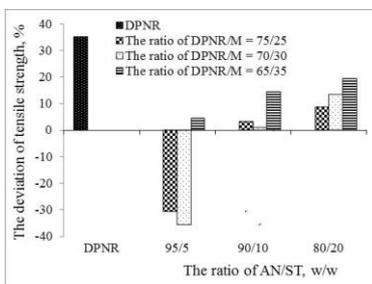


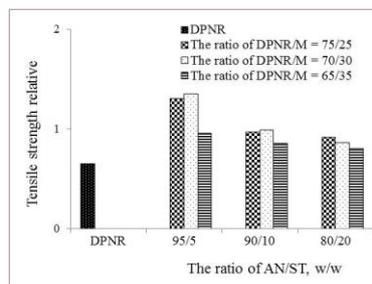
Figure 6 The FTIR spectrum of (a) DPNR before immersion, (b) DPNR after immersion, (c) DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

The deviation in TS is as shown in Figure 7a. The FTIR spectrum in this figure showed that the breaking of C=C double bonds to C-C and C-H can also reduce the strength and elasticity of the rubber. Therefore, TS and EB generally decrease, as shown in Figures 7a and 7c. Figure 7b shows that the TS of DPNR-g-PAN/PS was generally higher than that of DPNR except for the AN/ST 80/20 ratio. It can be concluded that the relatively high TS of the dispersed DPNR was surrounded by the PAN phase, which made it function as an oil-resistant compound and therefore restrained its swelling. However, in the AN/ST 80/20 ratio, the PAN activities were covered by PS, which increased shrinking and then decreased the relative TS. Figure 7d shows that hardness increased after immersion and that the occurrence of swelling and shrinking caused a reduction in some of the material contained in the rubber. Therefore, the sol fraction decreased and the rubber became denser, causing an increase in the hardness of the material.

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(a)



(b)

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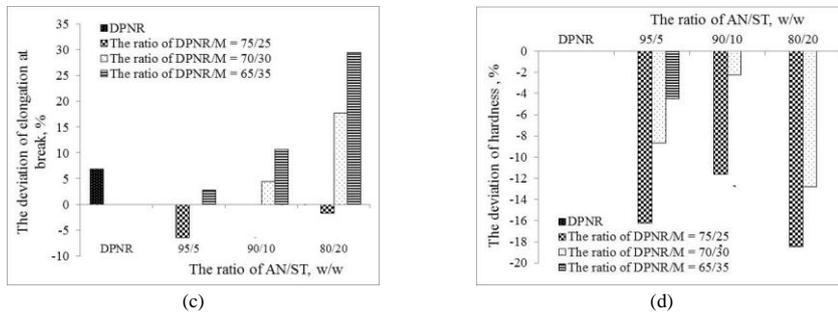


Figure 7 The deviation of (a) tensile strength, (b) relative tensile strength, (c) elongation at break, and (d) hardness after immersion in DME

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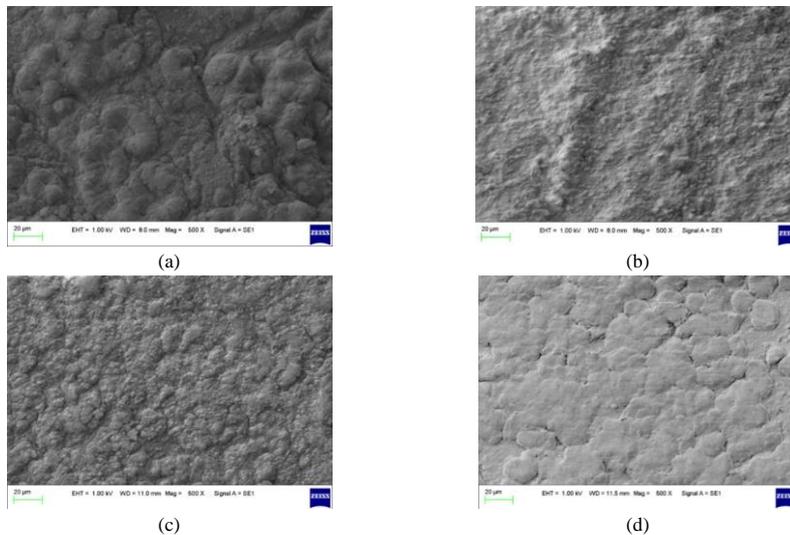


Figure 8 The surface morphology of DPNR and DPNR-g-PAN/PS as shown by SEM analysis before and after immersion in DME: (a) vulcanized DPNR before immersion, (b) vulcanized DPNR after immersion, (c) vulcanized DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

A surface morphology analysis was conducted with a ZEISS EVO 50 SEM at 500 times magnification to characterize the degradation behavior of DPNR and DPNR-g-PAN/PS before and after immersion in DME. Figures 8a and 8b show a difference between the morphology of DPNR. Figure 8b shows that the erosion of the material (shrinking) was a result of the absorption and desorption of DME into the rubber network. This can be attributed to a possible reaction between DME and some ingredients during its absorption into the rubber. This phenomenon is also shown in Figures 8c and 8d. In Figure 8d, shrinking resulted in morphological changes that cannot be seen in Figure 8c. The surface of it was smooth, flat, and sallow in color. The whole figure reveals that the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR

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underwent a large shrinking effect. In a comparison SEM analysis, Saputra et al. (2018) concluded that the AN content of rubber can prevent DME diffusion.

4. CONCLUSION

The present study focused on the production and resistance testing of copolymer DPNR-g-PAN/PS in DME with the influence of AN monomer and ST monomer. It was found that the presence of AN and ST increases the mechanical properties of DPNR and DPNR-g-PAN/PS. It was also found that an increase in the concentration of AN decreases rubber swelling and increases rubber shrinking. However, increased ST concentration was found to result in the opposite reaction. It was also found that the FTIR spectrum of DPNR degraded more than that of DPNR-g-PAN/PS spectrum and that the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR underwent a large shrinking effect.

5. ACKNOWLEDGMENT

The authors wish to express their gratitude to the Research Laboratory of Chemical Engineering FT-UI and the Rubber Research Center Bogor for their support in this research.

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DEPROTEINIZED NATURAL RUBBER GRAFTED WITH POLYACRYLONITRILE (PAN)/POLYSTYRENE (PS) AND DEGRADATION OF ITS MECHANICAL PROPERTIES BY DIMETHYL ETHER

Tuti Indah Sari¹, Asep Handaya Saputra², Setijo Bismo², Dadi R. Maspanger³

¹Department of Chemical Engineering, Faculty of Engineering, Sriwijaya University, Kampus Indralaya, Indralaya 30662, Indonesia

²Department of Chemical Engineering, Faculty of Engineering, Indonesia University, Kampus Baru UI Depok, Depok 16424, Indonesia

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

ABSTRACT

Dimethyl ether (DME) is a clean fuel that has moderate polarity, swells easily, and dissolves organic compounds. It has the ability to attack some sealing materials and plastic components because of its low viscosity. The modification of deproteinized natural rubber with acrylonitrile (AN) monomer and styrene (ST) monomer by an emulsion copolymerization process can be used to obtain DPNR-g-PAN/PS copolymers. This process uses a stirred reactor with $T = 65^{\circ}\text{C}$, $P = 1$ atm, initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and an emulsifier sodium dodecyl sulfate (SDS). The copolymer DPNR-g-PAN/PS can be used to seal storage for DME because it is expected to reduce the degradation of rubber due to the presence of DME. The parameters that were used in testing for the resistance of DPNR included swelling, shrinking, the infrared spectrum obtained through Fourier transform infra-red spectroscopy (FTIR), and changes in the mechanical properties of DPNR after immersion. The results of this research revealed that the presence of AN and ST can improve the mechanical properties of DPNR. They also showed that an increase in the concentration of AN decreased the swelling and increased the shrinking of rubber. However, an increase in the concentration of ST was found to increase the swelling and decrease the shrinking of rubber. From the results of the FTIR spectrum, DPNR was indicated to be more degraded compared to DPNR-g-PAN/PS after immersion with DME. The surface morphology test, which was carried out with a scanning electron microscope (SEM), showed that DPNR-g-PAN/PS experienced a slight shrinking effect in its morphology while DPNR underwent a huge shrinking effect.

Keywords: Acrylonitrile, Deproteinized natural rubber, Dimethyl ether, Styrene

1. INTRODUCTION

Dimethyl ether (DME) is an alternative fuel with several advantages over other fuels, such as higher oxygen content, a higher cetane number than diesel oil, and a low boiling point. It is also non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic (Semelsberger et al., 2006; Arcoumanis et al., 2008; Li & Zhou, 2008). However, its chemical properties are different from those of LPG, which has moderate polarity and high gas permeability to organic compounds such as plastics and rubber; DME swells easily and dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing materials and plastic components because of its low viscosity (Arcoumanis et al., 2008). Previous studies have made use of the immersion method through the use of swelling and mechanical properties as parameters to test for resistance in DME (Li and Zhou, 2008; Wu et al., 2008; Sari et al., 2017; Saputra et al., 2016 & 2018). According to research conducted by Li and Zhou (2008), immersion of rubber in a mixture of DME/diesel at 20/80 w/w produces a corroded rubber seal.

Furthermore, natural rubber grafted with acrylonitrile (AN) and styrene (ST) has the potential to be used as a seal for the storage of DME. It has excellent properties such as good elasticity, high tensile strength (TS), and good adhesion to metal. Polyacrylonitrile (PAN) is a non-solvent material with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (Mark, 2009). The presence of PAN could increase its insolubility and resistance to organic solvents (Nataraj et al., 2012). ST has also been observed to be a good co-monomer for the stability of the graft-copolymerization process (Angnanon et al., 2011; Prasassarakich et al., 2001; Sari et al., 2015). According to studies conducted by Prasassarakich et al. (2001), the oil and solvent resistance of **Natural Rubber** can be improved by graft copolymerization using AN. Increases in TS and **oil resistance** were observed with an increase in the percentage grafting efficiency (GE) of AN monomer (Prukkaewkanjana et al., 2014); these results were also reported by Angnanon et al. (2011).

The objective of the present study was to obtain **a copolymer of DPNR-g-PAN/PS** with a high resistance to DME gas. This is important because resistance is the potency needed by natural rubber to survive the diffusion or corrosion caused by the DME. According to research conducted by Sari et al. (2017), the copolymer is expected to reduce the degradation of rubber because of the action of **DME**. The characteristics of the copolymer were determined using Fourier transform infrared spectroscopy (FTIR). The mechanical properties measured included TS, elongation at break (EB), and hardness, while the resistance test parameters included swelling, shrinking, and changes in mechanical properties after immersion. A surface morphology test was also performed using a scanning electron microscope (SEM) analysis.

2. METHODS

2.1. Materials

The materials used in the present study included natural rubber latex with a high level of stabilized ammonia containing **about** 59–60% dry rubber content (DRC) from South Sumatera, Indonesia. AN monomer ($\geq 99\%$) and ST monomer ($\geq 99\%$) were purchased from Sigma–Aldrich (SGP). The emulsifier SDS ($\sim 90\%$), urea, $K_2S_2O_8$ ($\geq 99\%$), N,N-dimethylformamide (DMF), and methyl ethyl ketone (MEK) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was purchased from PT Trijaya Gasesindo (INA). Zinc oxide (ZnO), stearic acid, 2-mercaptobenzothiazole/MBT, and sulfur were used in the production of vulcanized rubber. **Dimethyl ether (DME)** was purchased from PT Bumi Tangerang, Banten (INA), while DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate et al., 2008; Suksawad et al., 2011).

2.2. Preparation of Copolymer DPNR-g-PAN/PS

This study was conducted in a 1.3 L reactor glass equipped with a hot plate, a magnetic stirrer, and a nitrogen gas inlet. The DPNR, SDS (0.67 w/w% rubber), and distilled water were first charged into a reactor glass with the use of $K_2S_2O_8$, an initiator with 1 wt% total monomers (Sahoo, 2019). Then, the reaction was continued for 6 hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer, and it was synthesized using emulsion polymerization methods with a ratio of DPNR/Monomer are 65/35, 70/30, 75/25 w/w, **and a ratio of AN/ST are 95/5, 92/8, 90/10, 80/20 w/w**. For the purpose of calculating the GE, as shown in equation (1), the free DPNR, PAN, and PS-free homopolymer were removed using Soxhlet extraction with petroleum ether, DMF, and MEK, respectively. GE is a parameter that is influenced by reaction variables such as DPNR/M ratio and AN/ST ratio.

$$\%GE = \frac{\text{weight of copolymer DPNR-g-PAN/PS}}{\text{weight of dry coagulan}} \times 100 \quad (1)$$

2.3. Characterization

The TS (MPa) and EB (%) were measured using a Tensometer LLOYD 2000R according to the ASTM D.412-06ae2 standard. Hardness (Shore A) was measured using a durometer, and adequate steps were taken to ensure that this measurement complied with the ASTM D.2240-05 standard. The FTIR spectra of the DPNR and DPNR-g-PAN/PS were recorded in solid states using a Nicolet iS5 spectrometer (Thermo Scientific) between 500 and 4000 cm^{-1} . The scanning electron microscope (SEM) model type ZEISS EVO 50 was used to analyze the surface morphology of DPNR and DPNR-g-PAN/PS before and after immersion.

2.4. Swelling and Shrinking Test

The rubber to be vulcanized was immersed in liquid-phase DME in a 1.3 L pressure vessel. The changes in the masses of these samples were investigated after the samples had been immersed for several days and exposed to the atmosphere for 24 hours (Wu et al., 2008). Swelling was measured as a percentage (%), as shown in equation (2) (Li & Zhou, 2008; Hinchiranan et al., 2013).

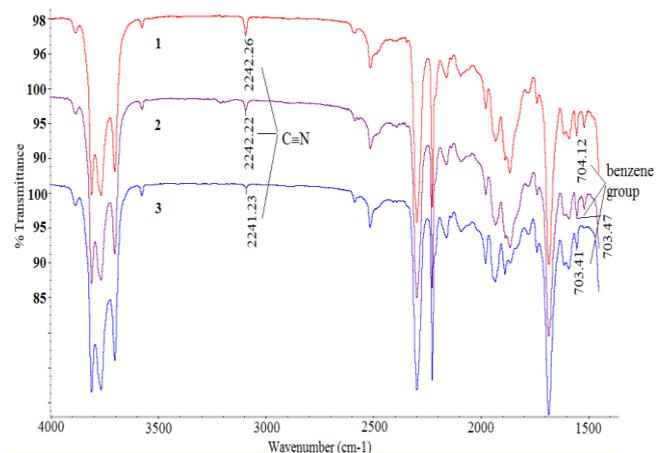
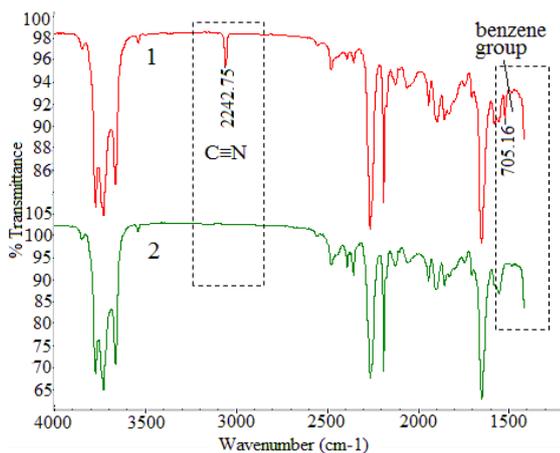
$$\text{Swelling/Shrinking(\%)} = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sample before immersion and M_2 is the mass after immersion. The samples were referred to as wet samples after they had been immersed and were called dry samples after being exposed to the atmosphere for 24 hours.

3. RESULTS AND DISCUSSION

3.1. Grafting Characteristics

The grafting characteristics of the DPNR-g-PAN/PS are shown by FTIR spectrum, GE, and mechanical properties. Figure 1(a) shows a comparison between the FTIR spectrum of DPNR (2) and that of the grafted copolymers (1); the $\text{C}\equiv\text{N}$ group shown at wave number 2,242.75 cm^{-1} indicated PAN grafted on a natural rubber chain, while the presence of benzene groups shown at wave number 705.16 cm^{-1} indicated PS grafted on natural rubber. The spectrum shown in Figure 1(a) is based on previous research by Sari et al. (2017). A nitrile group ($\text{C}\equiv\text{N}$) could be indicated at wave numbers 2,240–2,260 cm^{-1} (Smith, 1979) and at wave number 2,242 cm^{-1} (Nacimientto et al., 2012). In a previous study, Luo et al. (2012) reported that a functional group the benzene ring at the wave number 701 and 760 cm^{-1} . Figure 1 (b) shows the FTIR spectrum can evidence that AN and ST are grafted onto DPNR to form DPNR-g-PAN/PS, however the effect of varying composition AN/ST can not clearly observed.



(a). (b)
Figure 1 (a) FTIR spectrum of: 1). DPNR; 2). DPNR-g-PAN/PS

(b) FTIR spectrum of DPNR-g-PAN/PS with varying composition of AN/ST: 1). 95/5; 2). 90/10; 3). 80/20

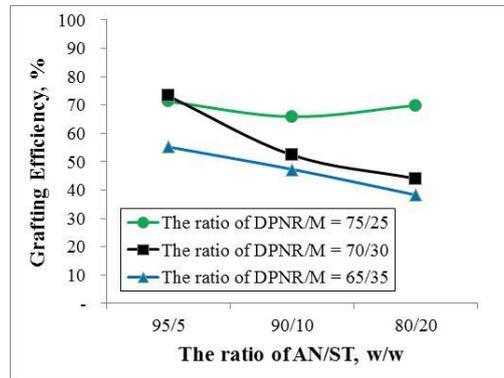
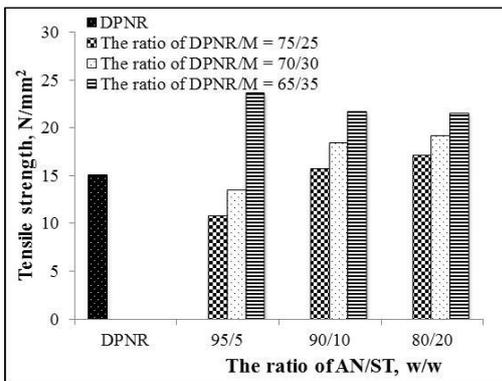


Figure 2 Grafting efficiency (GE) with the ratios of DPNR/M and AN/ST

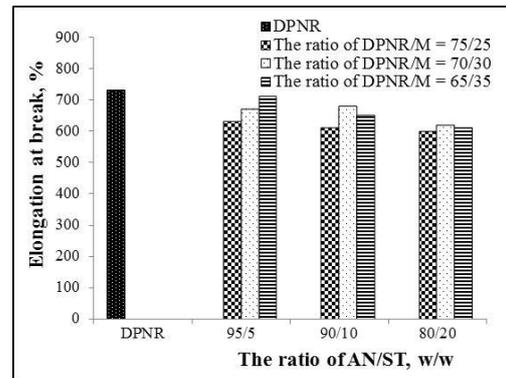
Figure 2 observes the effect of the DPNR/M ratio on GE. It shows that decreasing the composition of DPNR in the ratio DPNR/M will be decreasing percentage of GE. Similarly, the decreasing the composition of AN in the ratio of AN/ST decrease the percentage of GE. This indicates immiscibility between the AN and ST molecules. Therefore, it is possible that grafting copolymerization occurs only on the surfaces of latex particles. It was also found that the continuous addition of monomers AN and ST does not increase the percentage of GE; however, most free polymers were formed (Wongthong et al., 2013).

3.2. Mechanical Properties of Vulcanized DPNR and DPNR-g-PAN/PS

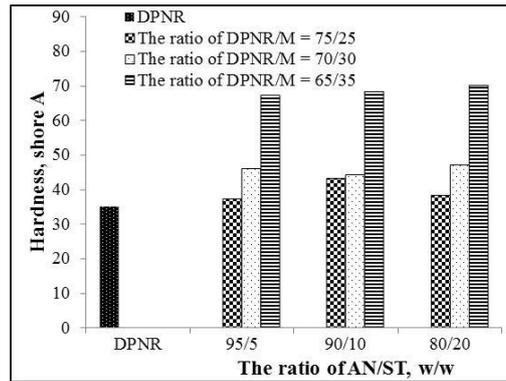
The mechanical properties of the vulcanized copolymers were represented by TS, EB, and hardness. Figure 3a shows that TS was higher in DPNR-g-PAN/PS copolymers than in DPNR and that increasing concentration of the total monomers increased the TS. However, PAN and polystyrene (PS), as free polymers, can also function as fillers to reinforce the mixture, thus increasing the TS. TS is inversely proportional to EB, which decreases with PAN and PS. Therefore, the decreased value of EB was not particularly significant. It can be concluded from these results that the presence of PAN and PS as free polymers makes vulcanized rubber slightly rigid because they cover most of its pores.



(a)



(b)



(c)

Figure 3 The influence of AN/ST monomer concentration on: a. tensile strength, b. elongation at break, and c. hardness of vulcanized DPNR-g-PAN/PS

The mechanical properties of grafted, vulcanized rubber are influenced by the properties of the grafted polymers. The hardness of the polymer affects the flexibility of the rubber material, and this concept also applies to the types and molecular weights of the polymers (Mark et al., 2013). PAN, a fiber polymer, is hard and has a high molecular weight, while PS, a plastic polymer, is softer. Grafting PAN onto a natural rubber can increase the rubber's TS and hardness (George et al., 2007; Prukkaewkanjana et al., 2014). Figure 3a shows that decreasing AN concentration increases TS, while Figure 3b reveals that EB decreases with an increase in ST concentration.

Several previous studies have discussed the process of grafting AN onto natural rubber. For example, a study by Angnanon et al. (2011) reported that NR-g-AN/ST functioned as a compatibility material in the process of blending natural rubber with NBR. In Figure 3, the presence of copolymer grafting increased the TS, but the varying composition of AN/ST did not significantly affect the vulcanized TS. Another study, conducted by George et al. (2007), stated that an increase in the concentration of AN in the copolymerization process increases the TS and decreases the EB. Similarly, a study carried out by Prukkaewkanjana et al. revealed that the TS of DPNR-graft-PAN increased along with increasingly efficient AN grafting. In addition, DPNR-graft-PAN has a dipole-dipole interaction between its nitrile groups. Therefore, a decrease in the PAN content of rubber increases the rigidity of the graft copolymer (Prukkaewkanjana et al., 2014). The use of PAN and PS as either grafted or free polymers in vulcanized rubber improves hardness. Figure 3c shows that an increase in the concentration of total monomers increases hardness.

3.3. Swelling and Shrinking Test on DPNR and DPNR-g-PAN/PS in DME

The change in the mass of the wet sample indicated swelling in DPNR and DPNR-g-PAN/PS, as shown in Figure 4a. This figure also shows that the decrease in the swelling of DPNR-g-PAN/PS occurred in all AN/ST concentration ratios, as opposed to that of DPNR, and that the increasing concentration of ST increased swelling. The lowest swelling 23.14% is attained at the ratio of DPNR/M = 65/35 with the composition of the monomer AN/ST = 95/5. Figure 4b shows the change in the mass of the dry sample after 24 hours. This figure indicates that the mass decreased after seven days of immersion in DME. The Figures 4a and 4b show that the ratio DPNR/M = 65/35 attains the lowest percentage of swelling and shrinking. However, the lowest percent swelling was attained with the composition of AN / ST = 95/5, while the lowest percent of shrinking was attained at the composition of AN/ST = 80/20. This condition requires the advance optimization of the AN/ST composition for swelling and shrinking test.

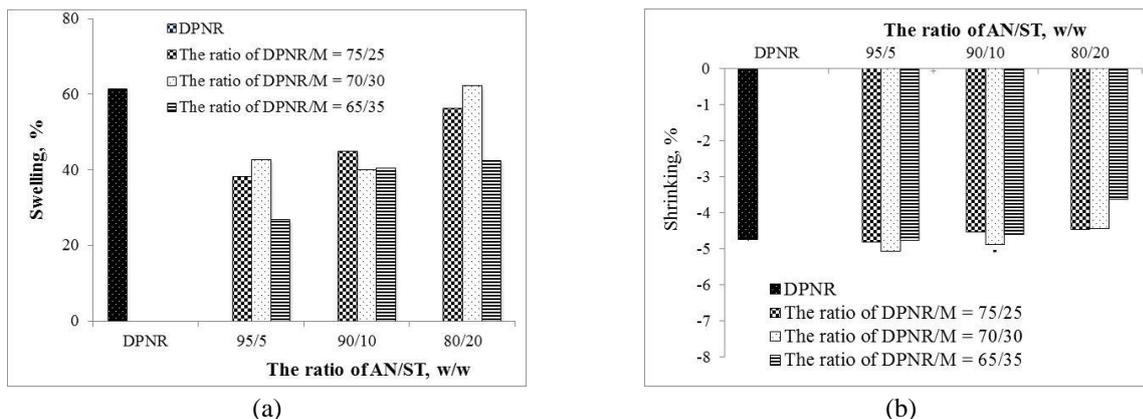


Figure 4 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME for 168 hours; (a) wet sample; (b) dry sample

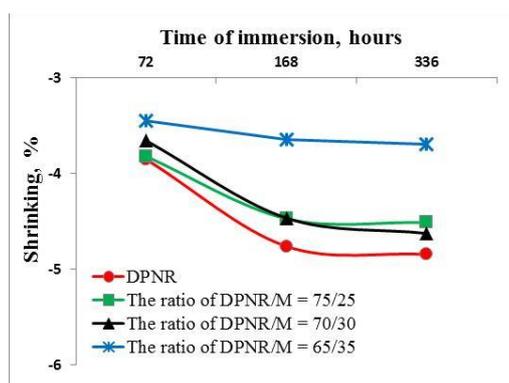


Figure 5 The mass degradation of DPNR-g-PAN/PS after immersion in DME (dry measurement) at an AN/ST ratio of 80/20

Figure 5 shows that all DPNR and DPNR-g-PAN/PS samples lost some mass. This means that increasing ST concentration decreases the loss of mass. The lowest mass (-3.64%) was recorded at an AN/ST ratio of 80/20 and a DPNR/M ratio of 65/35. The smallest decrease in mass shown in Figure 5 could be attributed to the presence of PAN and PS as a free homopolymer. At the ratio DPNR/M = 65/35, PAN and PS homopolymer formation is more than other ratios. This phenomenon of free polymers provides filler for the crosslinked rubber. As shown by Saputra et al. (2016), increased loading in rubber filler decreases the loss of mass. Previous researchers, such as Mikhailova et al. (2009), have investigated the increase in filler composition and found that it inhibits absorption and reaction in vulcanized rubber. Likewise, Muniandy et al. (2012) found that filler loading results in greater interaction between the rubber and the filler. Therefore, a higher level of interaction between the filler and the rubber matrix corresponds to a lower swelling value. The shrinking of mass, as shown in Figure 5, reveals the vulcanized rubber degradation caused by DME.

Chemical and Physical Properties After Immersion

Figure 6 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. In the DPNR spectrum after immersion, group C=C double bonds were lost at wave number 1576.59 cm^{-1} . These bonds might have been broken, changed into C-C at a wave number between 1000 cm^{-1} and 700 cm^{-1} , and changed into C-H at 669.35 cm^{-1} . This could have been a result of interaction with DME. Figures 6c and 6d depict a comparison of the DPNR-g-PAN/PS spectrum before and after immersion. It was discovered that the spectrums Figure 6c and 6d had slightly broken C=C double bonds, the changed of C≡N group from wave number 2242.57 cm^{-1} to wave number 2242.27 cm^{-1} , and a benzene ring functional group from wave number 703.95 cm^{-1} to wave

number 702.72 cm^{-1} . This was probably caused by the interaction of DME with PAN, PS, and DPNR as a free polymer. The comparison shows that DPNR degraded more than DPNR-g-PAN/PS.

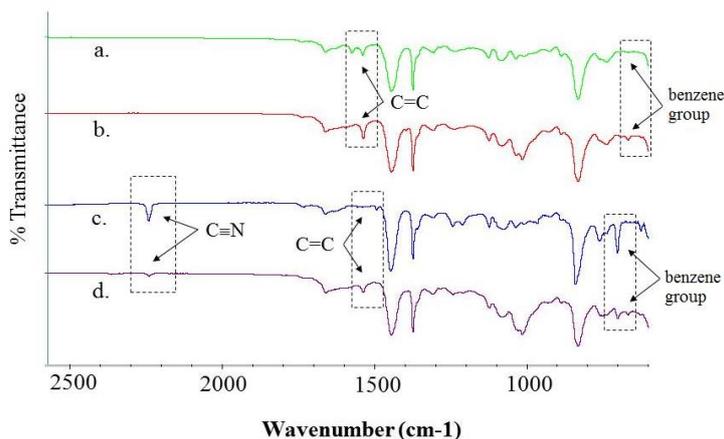
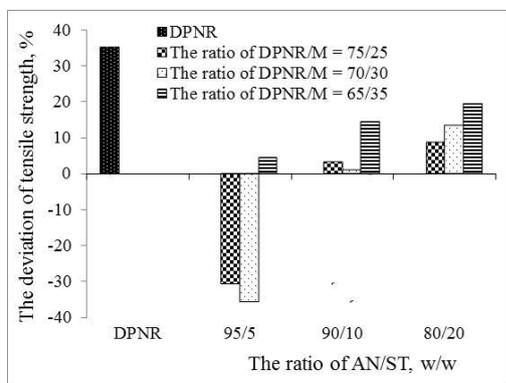
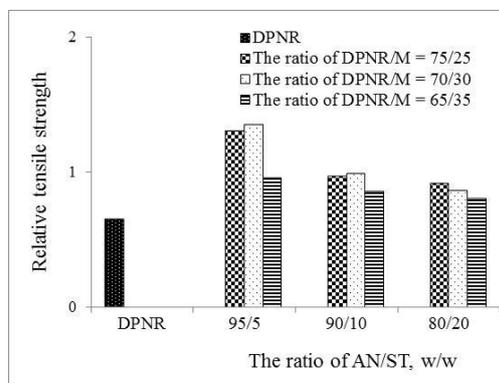


Figure 6 The FTIR spectrum of (a) DPNR before immersion, (b) DPNR after immersion, (c) DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

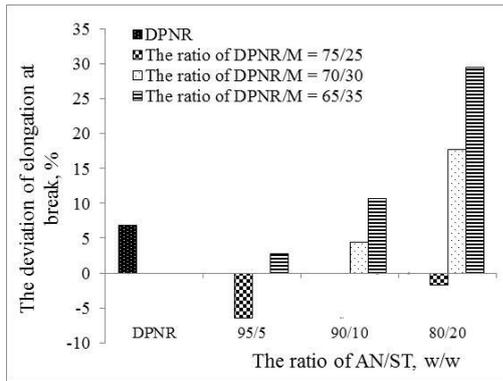
The deviation in TS is as shown in Figure 7a. The FTIR spectrum in this figure showed that the breaking of C=C double bonds to C-C and C-H can also reduce the strength and elasticity of the rubber. Therefore, TS and EB generally decrease, as shown in Figures 7a and 7c. Figure 7b shows that the TS of DPNR-g-PAN/PS was generally higher than that of DPNR except for the AN/ST 80/20 ratio. It can be concluded that the relatively high TS of the dispersed DPNR was surrounded by the PAN phase, which made it function as an oil-resistant compound and therefore restrained its swelling. However, in the ratio AN/ST = 80/20, there more PS than other ratio, therefore the resistance to swelling decreases. This causes an increase in swelling and decreases relative TS. Figure 7d shows that hardness increased after immersion and that the occurrence of swelling and shrinking caused a reduction in some of the material contained in the rubber. Therefore, the sol fraction decreased and the rubber became denser, causing an increase in the hardness of the material.



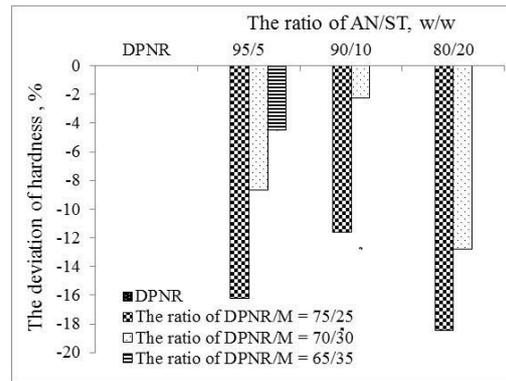
(a)



(b)

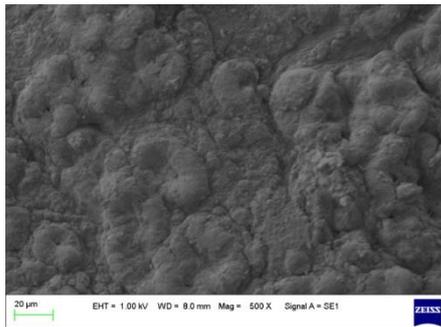


(c)

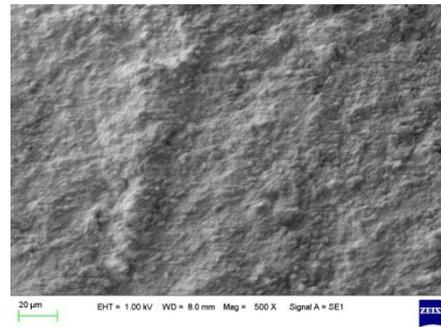


(d)

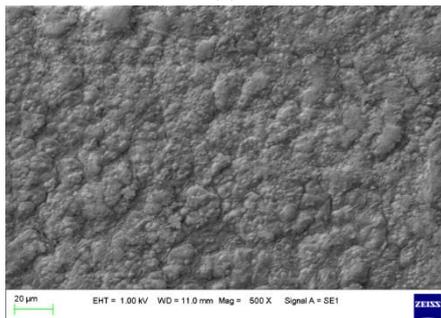
Figure 7 The deviation of mechanical properties after immersion in DME (a) tensile strength; (b) relative tensile strength; (c) elongation at break; (d) hardness



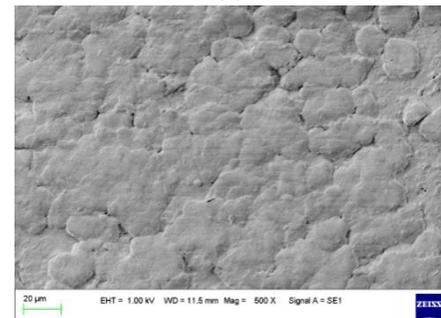
(a)



(b)



(c)



(d)

Figure 8 The surface morphology of DPNR and DPNR-g-PAN/PS as shown by SEM analysis before and after immersion in DME: (a) vulcanized DPNR before immersion, (b) vulcanized DPNR after immersion, (c) vulcanized DPNR-g-PAN/PS before immersion, and (d) DPNR-g-PAN/PS after immersion

A surface morphology analysis was measured with SEM model type ZEISS EVO 50 at 500 times magnification to characterize the degradation behavior of DPNR and DPNR-g-PAN/PS before and after immersion in DME. Figures 8a and 8b show a difference between the surface morphology of vulcanized DPNR. Figure 8b shows that the erosion of the material (shrinking) was a result of the absorption and desorption of DME into the rubber network. This can be attributed to a possible reaction between DME and some ingredients like as ZnO, stearic acid, MBT or sulfur during its absorption into the rubber. This phenomenon is also shown in Figures 8c and 8d. In Figure 8d, shrinking resulted in morphological changes that cannot be seen in Figure 8c. The surface of Figure 8d was smooth, flat, and sallow in color. The Figures 8a, b, c and d reveals that the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR underwent a huge shrinking effect. In a comparison SEM analysis, Saputra et al. (2018) concluded that the filler can

prevent DME diffusion. As a matter of fact, the PAN and PS can act as a filler that can prevent DME diffusion.

4. CONCLUSION

The present study focused on the production and resistance testing of a DPNR-g-PAN/PS copolymer in DME with the influence of AN monomer and ST monomer. The presence of AN and ST increases the mechanical properties of DPNR and DPNR-g-PAN/PS. It was found that the lowest percent swelling was attained with the highest of composition of AN, while the lowest percent of shrinking was attained at the highest of composition of ST. This condition requires the advance optimization of the AN/ST composition for swelling and shrinking test. The FTIR spectrum of DPNR degraded more than that of DPNR-g-PAN/PS spectrum and the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR underwent a huge shrinking effect.

5. ACKNOWLEDGMENT

The authors wish to express their gratitude to the Research Laboratory of Chemical Engineering FT-UI and the Rubber Research Center Bogor for their support in this research.

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Deproteinized Natural Rubber Grafted with Polyacrylonitrile (PAN)/Polystyrene (PS) and Degradation of its Mechanical Properties by Dimethyl Ether

Tuti Indah Sari^{1*}, Asep Handaya Saputra², Setijo Bismo², Dadi R. Maspanger³

¹Department of Chemical Engineering, Faculty of Engineering, Sriwijaya University, Kampus Indralaya, Indralaya 30662, Indonesia

²Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

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

Abstract. Dimethyl ether (DME) is a clean fuel that has moderate polarity, swells easily, and dissolves organic compounds. It has the ability to attack some sealing materials and plastic components because of its low viscosity. The modification of deproteinized natural rubber with acrylonitrile (AN) monomer and styrene (ST) monomer by an emulsion copolymerization process can be used to obtain DPNR-g-PAN/PS copolymers. This process uses a stirred reactor with $T = 65^{\circ}\text{C}$, $P = 1 \text{ atm}$, initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and an emulsifier sodium dodecyl sulfate (SDS). The copolymer DPNR-g-PAN/PS can be used to seal storage for DME because it is expected to reduce the degradation of rubber due to the presence of DME. The parameters that were used in testing for the resistance of DPNR included swelling, shrinking, the infrared spectrum obtained through Fourier transform infra-red spectroscopy (FTIR), and changes in the mechanical properties of DPNR after immersion. The results of this research revealed that the presence of AN and ST can improve the mechanical properties of DPNR. They also showed that an increase in the concentration of AN decreased the swelling and increased the shrinking of rubber. However, an increase in the concentration of ST was found to increase the swelling and decrease the shrinking of rubber. From the results of the FTIR spectrum, DPNR was indicated to be more degraded compared to DPNR-g-PAN/PS after immersion with DME. The surface morphology test, which was carried out with a scanning electron microscope (SEM), showed that DPNR-g-PAN/PS experienced a slight shrinking effect in its morphology while DPNR underwent a huge shrinking effect.

Keywords: Acrylonitrile; Deproteinized natural rubber; Dimethyl ether; Styrene

1. Introduction

Dimethyl ether (DME) is an alternative fuel with several advantages over other fuels, such as higher oxygen content, a higher cetane number than diesel oil, and a low boiling point. It is also non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic (Semelsberger et al., 2006; Arcoumanis et al., 2008; Li and Zhou, 2008). However, its chemical properties are different from those of LPG, which has moderate polarity and high gas permeability to organic compounds such as plastics and rubber; DME swells easily and dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing

*Corresponding author's email: ty_indahsari@yahoo.co.id; tutiindahsari@ft.unsri.ac.id;
Tel.: +6281282466080 doi: 10.14716/ijtech.v11i1.1942

dissolves organic compounds (Nishimoto, 2011). It can also attack some sealing materials and plastic components because of its low viscosity (Arcoumanis et al., 2008). Previous studies have made use of the immersion method through the use of swelling and mechanical properties as parameters to test for resistance in DME (Li and Zhou, 2008; Wu et al., 2008; Saputra et al., 2016; Sari et al., 2017; Saputra et al., 2018). According to research conducted by Li and Zhou (2008), immersion of rubber in a mixture of DME/diesel at 20/80 w/w produces a corroded rubber seal.

Furthermore, natural rubber grafted with acrylonitrile (AN) and styrene (ST) has the potential to be used as a seal for the storage of DME. It has excellent properties such as good elasticity, high tensile strength (TS), and good adhesion to metal. Polyacrylonitrile (PAN) is a non-solvent material with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (Mark, 2009). The presence of PAN could increase its insolubility and resistance to organic solvents (Nataraj et al., 2012). ST has also been observed to be a good co-monomer for the stability of the graft-copolymerization process (Prasassarakich et al., 2001; Angnanon et al., 2011; Sari et al., 2015). According to studies conducted by Prasassarakich et al. (2001), the oil and solvent resistance of Natural Rubber can be improved by graft copolymerization using AN. Increases in TS and oil resistance were observed with an increase in the percentage grafting efficiency (GE) of AN monomer (Prukkaewkanjana et al., 2014); these results were also reported by Angnanon et al. (2011).

The objective of the present study was to obtain a copolymer of DPNR-g-PAN/PS with a high resistance to DME gas. This is important because resistance is the potency needed by natural rubber to survive the diffusion or corrosion caused by the DME. According to research conducted by Sari et al. (2017), the copolymer is expected to reduce the degradation of rubber because of the action of DME. The characteristics of the copolymer were determined using Fourier transform infrared spectroscopy (FTIR). The mechanical properties measured included TS, elongation at break (EB), and hardness, while the resistance test parameters included swelling, shrinking, and changes in mechanical properties after immersion. A surface morphology test was also performed using a scanning electron microscope (SEM) analysis.

2. Methods

2.1. Materials

The materials used in the present study included natural rubber latex with a high level of stabilized ammonia containing about 59–60% dry rubber content (DRC) from South Sumatera, Indonesia. AN monomer ($\geq 99\%$) and ST monomer ($\geq 99\%$) were purchased from Sigma–Aldrich (SGP). The emulsifier SDS ($\sim 90\%$), urea, $K_2S_2O_8$ ($\geq 99\%$), N,N-dimethylformamide (DMF), and methyl ethyl ketone (MEK) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was purchased from PT Trijaya Gasesindo (INA). Zinc oxide (ZnO), stearic acid, 2-mercaptobenzothiazole/MBT, and sulfur were used in the production of vulcanized rubber. Dimethyl ether (DME) was purchased from PT Bumi Tangerang, Banten (INA), while DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate et al., 2008; Suksawad et al., 2011).

2.2. Preparation of Copolymer DPNR-g-PAN/PS

This study was conducted in a 1.3 L reactor glass equipped with a hot plate, a magnetic stirrer, and a nitrogen gas inlet. The DPNR, SDS (0.67 w/w% rubber), and distilled water were first charged into a reactor glass with the use of $K_2S_2O_8$, an initiator

with 1 wt% total monomers (Sahoo, 2019). Then, the reaction was continued for 6 hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer, and it was synthesized using emulsion polymerization methods with a ratio of DPNR/Monomer are 65/35, 70/30, 75/25 w/w, and a ratio of AN/ST are 95/5, 92/8, 90/10, 80/20 w/w. For the purpose of calculating the GE, as shown in Equation 1, the free DPNR, PAN, and PS-free homopolymer were removed using Soxhlet extraction with petroleum ether, DMF, and MEK, respectively. GE is a parameter that is influenced by reaction variables such as DPNR/M ratio and AN/ST ratio.

$$\%GE = \frac{\text{weight of copolymer DPNR-g-PAN/PS}}{\text{weight of dry coagulan}} \times 100 \quad (1)$$

2.3. Characterization

The TS (MPa) and EB (%) were measured using a Tensometer LLOYD 2000R according to the ASTM D.412-06ae2 standard. Hardness (Shore A) was measured using a durometer, and adequate steps were taken to ensure that this measurement complied with the ASTM D.2240-05 standard. The FTIR spectra of the DPNR and DPNR-g-PAN/PS were recorded in solid states using a Nicolet iS5 spectrometer (Thermo Scientific) between 500 and 4000 cm^{-1} . The scanning electron microscope (SEM) model type ZEISS EVO 50 was used to analyze the surface morphology of DPNR and DPNR-g-PAN/PS before and after immersion.

2.4. Swelling and Shrinking Test

The rubber to be vulcanized was immersed in liquid-phase DME in a 1.3 L pressure vessel. The changes in the masses of these samples were investigated after the samples had been immersed for several days and exposed to the atmosphere for 24 hours (Wu et al., 2008). Swelling was measured as a percentage (%), as shown in Equation 2 (Li and Zhou, 2008; Hinchiranan et al., 2013).

$$\text{Swelling/Shrinking}(\%) = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sample before immersion and M_2 is the mass after immersion. The samples were referred to as wet samples after they had been immersed and were called dry samples after being exposed to the atmosphere for 24 hours.

3. Results and Discussion

3.1. Grafting Characteristics

The grafting characteristics of the DPNR-g-PAN/PS are shown by FTIR spectrum, GE, and mechanical properties. Figure 1a shows a comparison between the FTIR spectrum of DPNR (2) and that of the grafted copolymers (1); the $\text{C}\equiv\text{N}$ group shown at wave number 2,242.75 cm^{-1} indicated PAN grafted on a natural rubber chain, while the presence of benzene groups shown at wave number 705.16 cm^{-1} indicated PS grafted on natural rubber. The spectrum shown in Figure 1a is based on previous research by Sari et al. (2017). A nitrile group ($\text{C}\equiv\text{N}$) could be indicated at wave numbers 2,240–2,260 cm^{-1} (Smith, 1979) and at wave number 2,242 cm^{-1} (Nacimiento et al., 2012). In a previous study, Luo and Wu (2012) reported that a functional group the benzene ring at the wave number 701 and 760 cm^{-1} . Figure 1b shows the FTIR spectrum can evidence that AN and ST are grafted onto DPNR to form DPNR-g-PAN/PS, however the effect of varying composition AN/ST can not clearly observed.

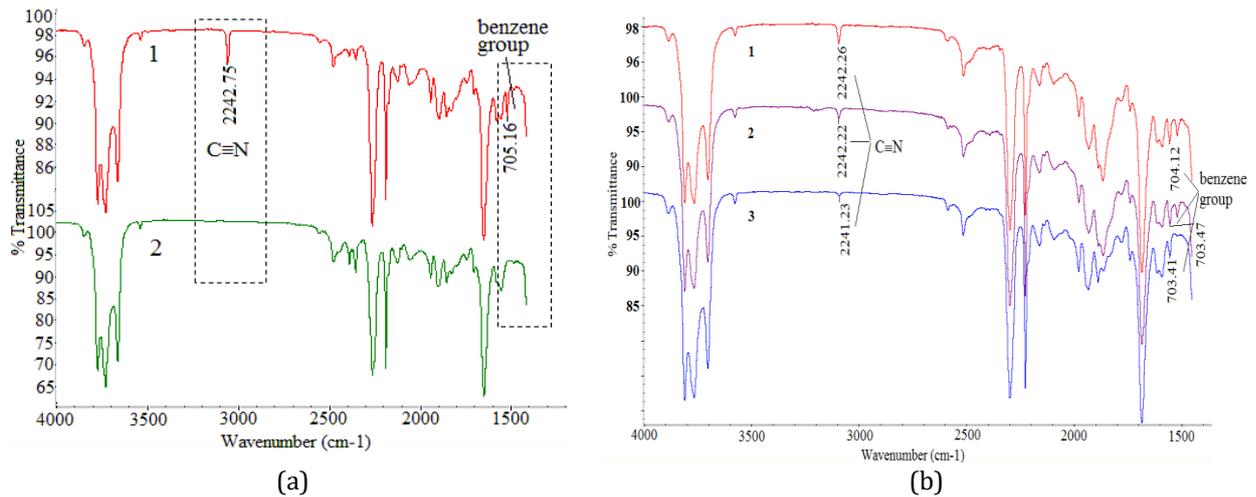


Figure 1 (a) FTIR spectrum of: (1) DPNR; (2) DPNR-g-PAN/PS. (b) FTIR spectrum of DPNR-g-PAN/PS with varying composition of AN/ST: (1) 95/5; (2) 90/10; (3) 80/20

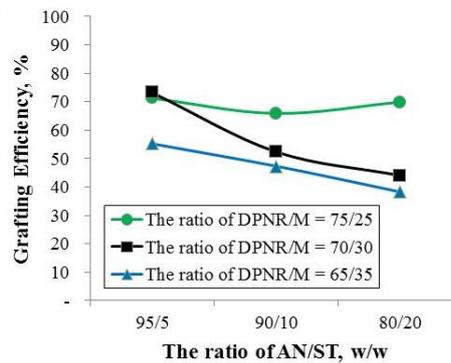


Figure 2 Grafting efficiency (GE) with the ratios of DPNR/M and AN/ST

Figure 2 observes the effect of the DPNR/M ratio on GE. It shows that decreasing the composition of DPNR in the ratio DPNR/M will be decreasing percentage of GE. Similarly, the decreasing the composition of AN in the ratio of AN/ST decrease the percentage of GE. This indicates immiscibility between the AN and ST molecules. Therefore, it is possible that grafting copolymerization occurs only on the surfaces of latex particles. It was also found that the continuous addition of monomers AN and ST does not increase the percentage of GE; however, most free polymers were formed (Wongthong et al., 2013).

3.2. Mechanical Properties of Vulcanized DPNR and DPNR-g-PAN/PS

The mechanical properties of the vulcanized copolymers were represented by TS, EB, and hardness. Figure 3a shows that TS was higher in DPNR-g-PAN/PS copolymers than in DPNR and that increasing concentration of the total monomers increased the TS. However, PAN and polystyrene (PS), as free polymers, can also function as fillers to reinforce the mixture, thus increasing the TS. TS is inversely proportional to EB, which decreases with PAN and PS. Therefore, the decreased value of EB was not particularly significant. It can be concluded from these results that the presence of PAN and PS as free polymers makes vulcanized rubber slightly rigid because they cover most of its pores.

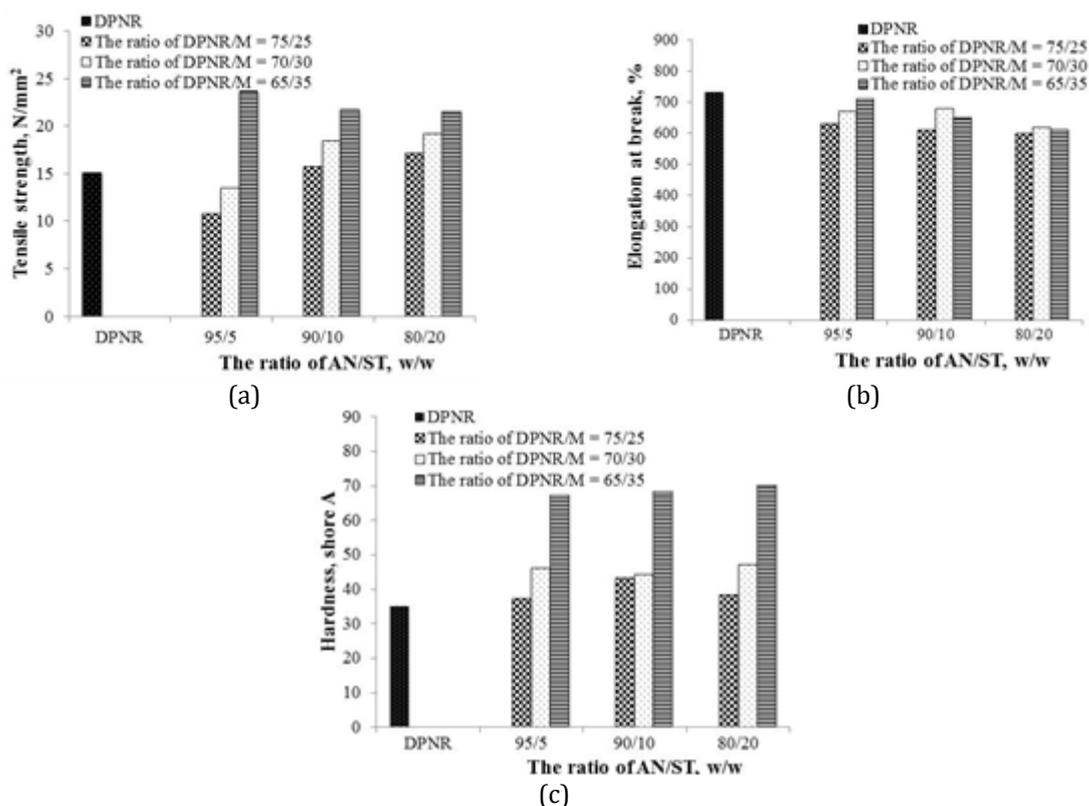


Figure 3 The influence of AN/ST monomer concentration on: (a) tensile strength; (b) elongation at break; and (c) hardness of vulcanized DPNR-g-PAN/PS

The mechanical properties of grafted, vulcanized rubber are influenced by the properties of the grafted polymers. The hardness of the polymer affects the flexibility of the rubber material, and this concept also applies to the types and molecular weights of the polymers (Mark et al., 2013). PAN, a fiber polymer, is hard and has a high molecular weight, while PS, a plastic polymer, is softer. Grafting PAN onto a natural rubber can increase the rubber's TS and hardness (George et al., 2007; Prukkaewkanjana et al., 2014). Figure 3a shows that decreasing AN concentration increases TS, while Figure 3b reveals that EB decreases with an increase in ST concentration.

Several previous studies have discussed the process of grafting AN onto natural rubber. For example, a study by Angnanon et al. (2011) reported that NR-g-AN/ST functioned as a compatibility material in the process of blending natural rubber with NBR. In Figure 3, the presence of copolymer grafting increased the TS, but the varying composition of AN/ST did not significantly affect the vulcanized TS. Another study, conducted by George et al. (2007), stated that an increase in the concentration of AN in the copolymerization process increases the TS and decreases the EB. Similarly, a study carried out by Prukkaewkanjana et al. (2014) revealed that the TS of DPNR-graft-PAN increased along with increasingly efficient AN grafting. In addition, DPNR-graft-PAN has a dipole-dipole interaction between its nitrile groups. Therefore, a decrease in the PAN content of rubber increases the rigidity of the graft copolymer (Prukkaewkanjana et al., 2014). The use of PAN and PS as either grafted or free polymers in vulcanized rubber improves hardness. Figure 3c shows that an increase in the concentration of total monomers increases hardness.

3.3. Swelling and Shrinking Test on DPNR and DPNR-g-PAN/PS in DME

The change in the mass of the wet sample indicated swelling in DPNR and DPNR-g-PAN/PS, as shown in Figure 4a. This figure also shows that the decrease in the swelling of DPNR-g-PAN/PS occurred in all AN/ST concentration ratios, as opposed to that of DPNR, and that the increasing concentration of ST increased swelling. The lowest swelling 23.14% is attained at the ratio of DPNR/M = 65/35 with the composition of the monomer AN/ST = 95/5. Figure 4b shows the change in the mass of the dry sample after 24 hours. This figure indicates that the mass decreased after seven days of immersion in DME. The Figures 4a and 4b show that the ratio DPNR/M = 65/35 attains the lowest percentage of swelling and shrinking. However, the lowest percent swelling was attained with the composition of AN/ST = 95/5, while the lowest percent of shrinking was attained at the composition of AN/ST = 80/20. This condition requires the advance optimization of the AN/ST composition for swelling and shrinking test.

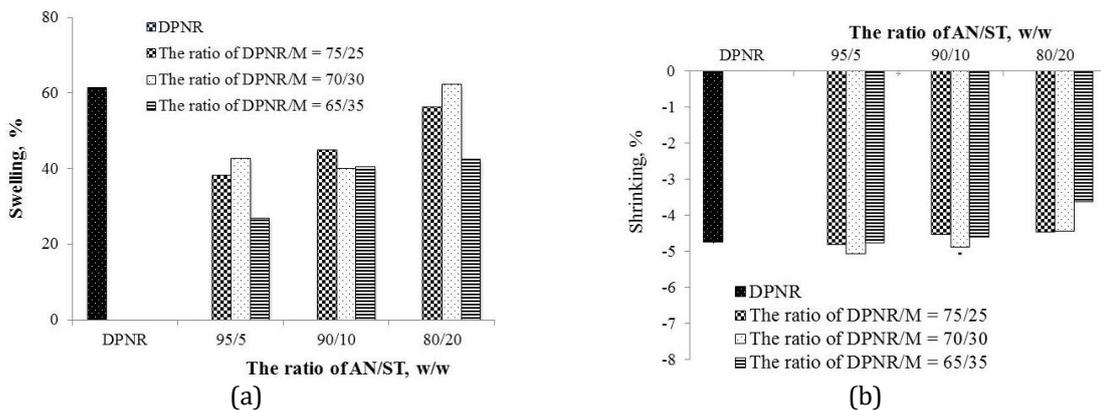


Figure 4 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME for 168 hours: (a) wet sample; (b) dry sample

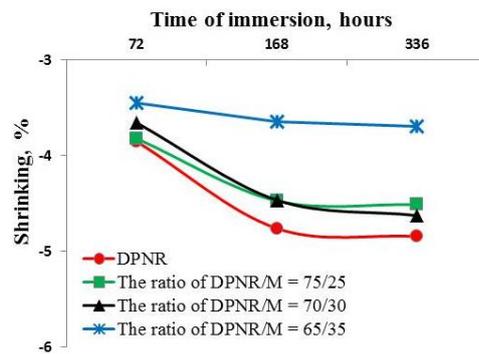


Figure 5 The mass degradation of DPNR-g-PAN/PS after immersion in DME (dry measurement) at an AN/ST ratio of 80/20

Figure 5 shows that all DPNR and DPNR-g-PAN/PS samples lost some mass. This means that increasing ST concentration decreases the loss of mass. The lowest mass (-3.64%) was recorded at an AN/ST ratio of 80/20 and a DPNR/M ratio of 65/35. The smallest decrease in mass shown in Figure 5 could be attributed to the presence of PAN and PS as a free homopolymer. At the ratio DPNR/M = 65/35, PAN and PS homopolymer formation is more than other ratios. This phenomenon of free polymers provides filler for the crosslinked rubber. As shown by Saputra et al. (2016), increased loading in rubber filler decreases the loss of mass. Previous researchers, such as Mikhailova et al. (2009),

have investigated the increase in filler composition and found that it inhibits absorption and reaction in vulcanized rubber. Likewise, [Muniandy et al. \(2012\)](#) found that filler loading results in greater interaction between the rubber and the filler. Therefore, a higher level of interaction between the filler and the rubber matrix corresponds to a lower swelling value. The shrinking of mass, as shown in Figure 5, reveals the vulcanized rubber degradation caused by DME.

3.4. Chemical and Physical Properties After Immersion

Figure 6 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. In the DPNR spectrum after immersion, group C=C double bonds were lost at wave number 1576.59 cm^{-1} . These bonds might have been broken, changed into C-C at a wave number between 1000 cm^{-1} and 700 cm^{-1} , and changed into C-H at 669.35 cm^{-1} . This could have been a result of interaction with DME. Figures 6c and 6d depict a comparison of the DPNR-g-PAN/PS spectrum before and after immersion. It was discovered that the spectrums Figures 6c and 6d had slightly broken C=C double bonds, the changed of C≡N group from wave number 2242.57 cm^{-1} to wave number 2242.27 cm^{-1} , and a benzene ring functional group from wave number 703.95 cm^{-1} to wave number 702.72 cm^{-1} . This was probably caused by the interaction of DME with PAN, PS, and DPNR as a free polymer. The comparison shows that DPNR degraded more than DPNR-g-PAN/PS.

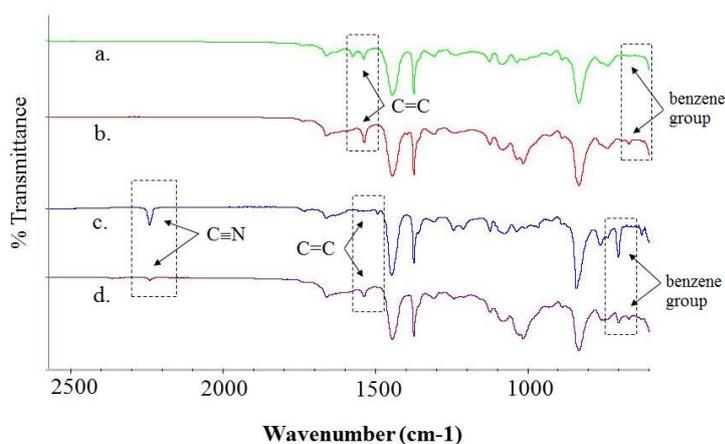


Figure 6 The FTIR spectrum of: (a) DPNR before immersion; (b) DPNR after immersion; (c) DPNR-g-PAN/PS before immersion; and (d) DPNR-g-PAN/PS after immersion

The deviation in TS is as shown in Figure 7a. The FTIR spectrum in this figure showed that the breaking of C=C double bonds to C-C and C-H can also reduce the strength and elasticity of the rubber. Therefore, TS and EB generally decrease, as shown in Figures 7a and 7c. Figure 7b shows that the TS of DPNR-g-PAN/PS was generally higher than that of DPNR except for the AN/ST 80/20 ratio. It can be concluded that the relatively high TS of the dispersed DPNR was surrounded by the PAN phase, which made it function as an oil-resistant compound and therefore restrained its swelling. However, in the ratio AN/ST = 80/20, there more PS than other ratio, therefore the resistance to swelling decreases. This causes an increase in swelling and decreases relative TS. Figure 7d shows that hardness increased after immersion and that the occurrence of swelling and shrinking caused a reduction in some of the material contained in the rubber. Therefore, the sol fraction decreased and the rubber became denser, causing an increase in the hardness of the material.

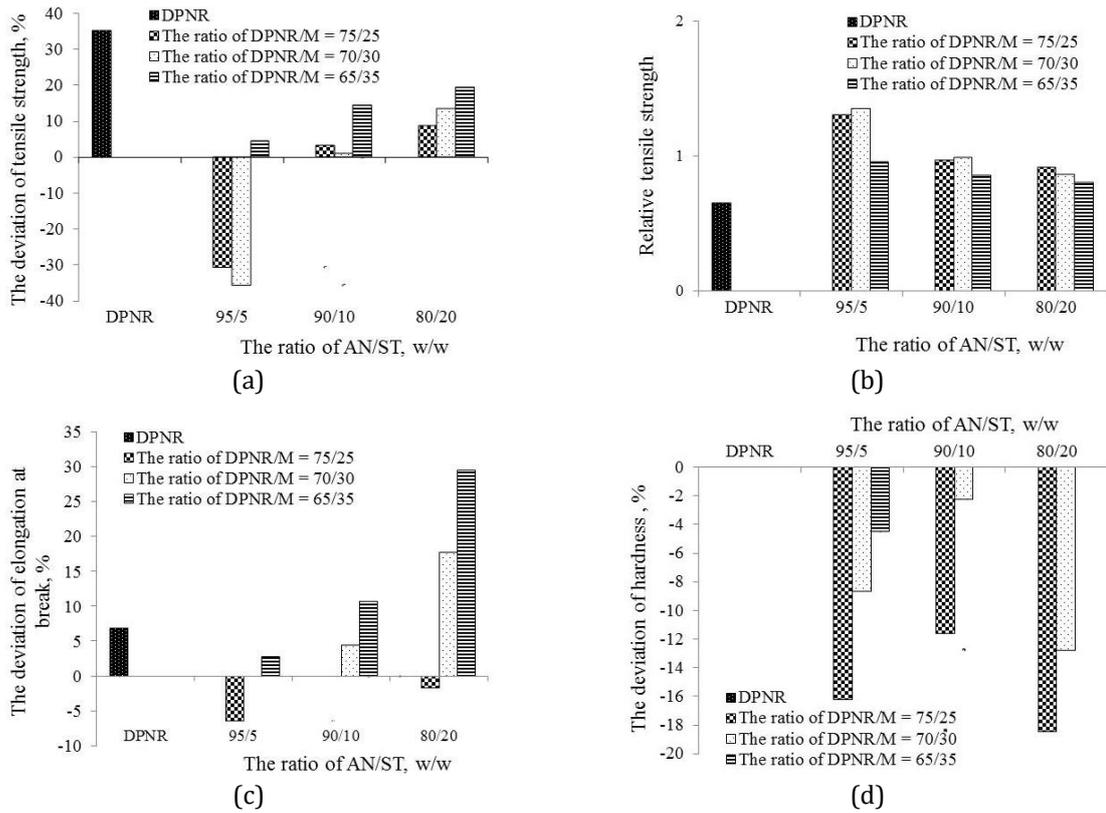


Figure 7 The deviation of mechanical properties after immersion in DME: (a) tensile strength; (b) relative tensile strength; (c) elongation at break; (d) hardness

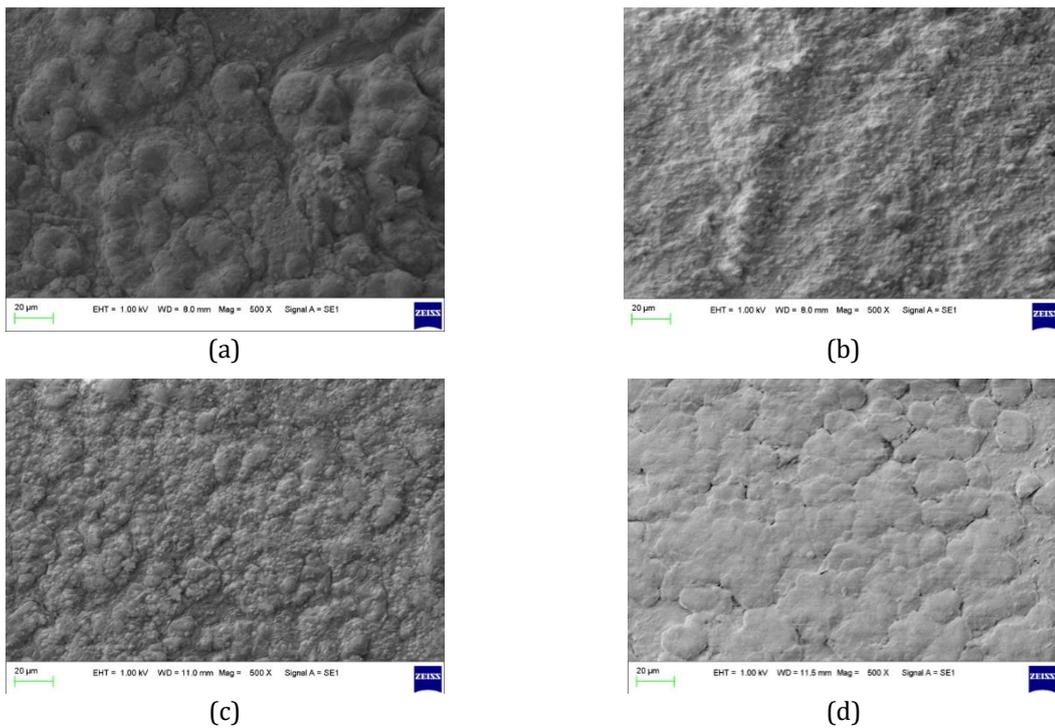


Figure 8 The surface morphology of DPNR and DPNR-g-PAN/PS as shown by SEM analysis before and after immersion in DME: (a) vulcanized DPNR before immersion; (b) vulcanized DPNR after

A surface morphology analysis was measured with SEM model type ZEISS EVO 50 at 500 times magnification to characterize the degradation behavior of DPNR and DPNR-g-

PAN/PS before and after immersion in DME. Figures 8a and 8b show a difference between the surface morphology of vulcanized DPNR. Figure 8b shows that the erosion of the material (shrinking) was a result of the absorption and desorption of DME into the rubber network. This can be attributed to a possible reaction between DME and some ingredients like as ZnO, stearic acid, MBT or sulfur during its absorption into the rubber. This phenomenon is also shown in Figures 8c and 8d. In Figure 8d, shrinking resulted in morphological changes that cannot be seen in Figure 8c. The surface of Figure 8d was smooth, flat, and sallow in color. The Figures 8a, 8b, 8c and 8d reveals that the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR underwent a huge shrinking effect. In a comparison SEM analysis, [Saputra et al. \(2018\)](#) concluded that the filler can prevent DME diffusion. As a matter of fact, the PAN and PS can act as a filler thats can prevent DME diffusion.

4. Conclusions

The present study focused on the production and resistance testing of a DPNR-g-PAN/PS copolymer in DME with the influence of AN monomer and ST monomer. The presence of AN and ST increases the mechanical properties of DPNR and DPNR-g-PAN/PS. It was found that the lowest percent swelling was attain with the highest of composition of AN, while the lowest percent of shrinking was attain at the highest of composition of ST. This condition requires the advance optimization of the AN/ST composition for swelling and shrinking test. The FTIR spectrum of DPNR degraded more than that of DPNR-g-PAN/PS spectrum and the morphology of DPNR-g-PAN/PS experienced a slight shrinking effect while that of DPNR underwent a huge shrinking effect.

Acknowledgments

The authors wish to express their gratitude to the Research Laboratory of Chemical Engineering FT-UI and the Rubber Research Center Bogor for their support in this research.

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